



# Passive methods for sampling and in situ extraction of emerging contaminants - *challenges and opportunities*

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# Passive sampling

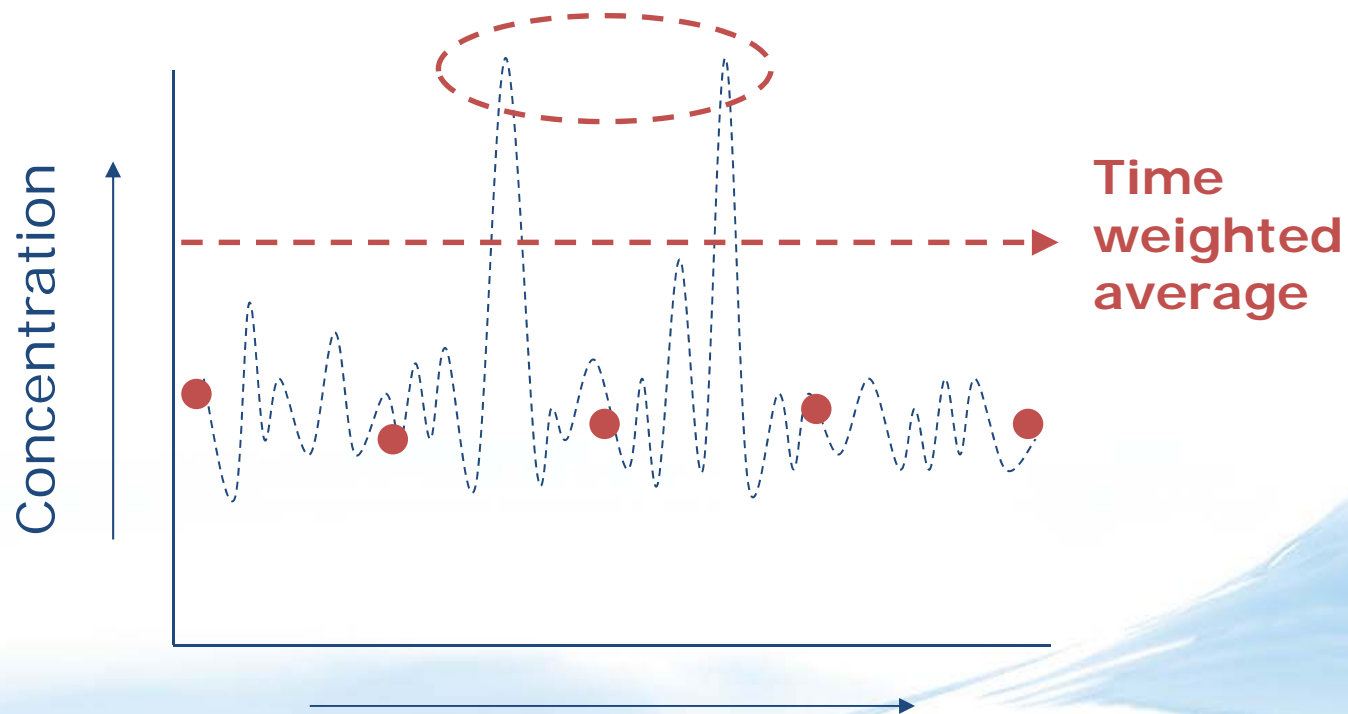
## *-Definition*

- *"Passive sampling is the deployment of a device to accumulate target chemicals over a certain period of time, where collection and extraction occurs entirely without the aid of external energy" (Huckins 2006)*
- The need for measurement of chemical compounds in the aquatic environment
- Traditionally achieved by taking 'grab' samples, using bottles and extracting/analysing in the laboratory
- Instead a passive sampler is exposed in the environment and left there for a fixed period of time during which it continues to accumulate (and extract) chemicals, before collection and elution/analysis

# Passive sampling

## -Why?

- Representativeness - spot water samples reflect residue composition only at the moment of sampling and may fail to detect or overestimate episodic contamination
  - *Passive samplers (PSDs) are typically left to accumulate contaminants for periods of several weeks, unlike spot samples*
- Detection problems - standard techniques often fail to detect low, but ecologically relevant, levels of contaminants, (e.g. TBT, EQS 0.2 ng L<sup>-1</sup>)
  - *New substance WFD EQS values e.g. 17β-estradiol (E2, 0.4 ng L<sup>-1</sup>) 17α-ethinylestradiol (EE2, 0.035 ng L<sup>-1</sup>)*
  - *The sampling rate concept (R<sub>s</sub> L d<sup>-1</sup>)*
  - *Hydrophobic compounds R<sub>s</sub> typically 2-20 L d<sup>-1</sup>, (<600 L)*



# Types of sampler

- DGT based samplers
  - Metals
  - Phosphate
  - Gel based polar sampler?
- Hydrophobic samplers
  - SPMDs
  - LDPE
  - Silicone
  - POM
  - Chemcatcher
- Polar passive samplers
  - POCIS
  - Chemcatcher
  - Naked disc samplers
  - Silicone (POM?)
- Micro methods
  - SPME etc.
- Others
  - Ceramic dosimeter
  - Many more

Focus here «polar samplers» and integrative sampling

# Differences between *polymers* - *not necc' interchangeable for emerging*

STN	«Unique detections»	
	SIL	LDPE
1	246	82
2	617	186
3	615	32
4	352	77
5	199	105
6	286	75
Blank	21	15

- 6 week deployment in polluted river (Alna, Oslo)
- Silicone and LDPE samplers
- Identical surface area, exposure system and conditions (silicone higher volume)
- No. of defined peaks in chromatogram (GC-ToF-MS)
- Ca. 15 organophosphorus flame retardents found in silicone, only one identified in LDPE
- Silicone samplers have been shown to accumulate a wide range of medium polar compounds such as pharmaceuticals, pesticides

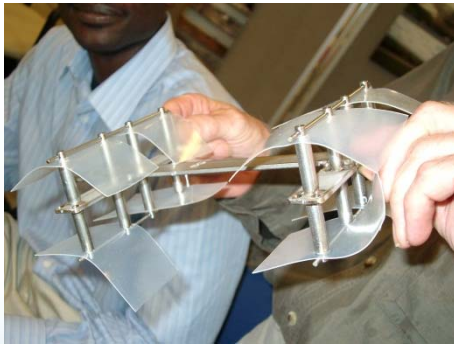


Photo: F smedes

# Methods for polar compounds

## - Polar Organic Chemical Integrative Sampler (POCIS)

- Various sorbent between two polyethersulphone membranes (0.1 $\mu$ m pore size)
- Polar- moderately hydrophobic organic chemicals with  $\log K_{ow} < 3.5$  are accumulated
- Been used successfully to measure over 300 compounds including various; hormones, pharmaceuticals, pesticides and industrial chemicals
- Sampling rates dependent on exposure conditions and compound properties



*Photo: Chris Harman*

# POCIS calibration methods

- Calibration is required to gain  $R_s$  and allow time integrated  $C_w$  estimation
- **Static renewal**
  - Small volume exposures with periodically renewed exposure solution
- **Static depletion**
  - Small volume exposures no renewal, first order model fitted to water concentration changes, positive control issues
- **Flow through**
  - Large volume constant flow of fortified exposure solution. More resource intensive, no positive control issues
- ***In situ***
  - calibration at measurement site, resource intensive but likely to provide more accurate sampling rates

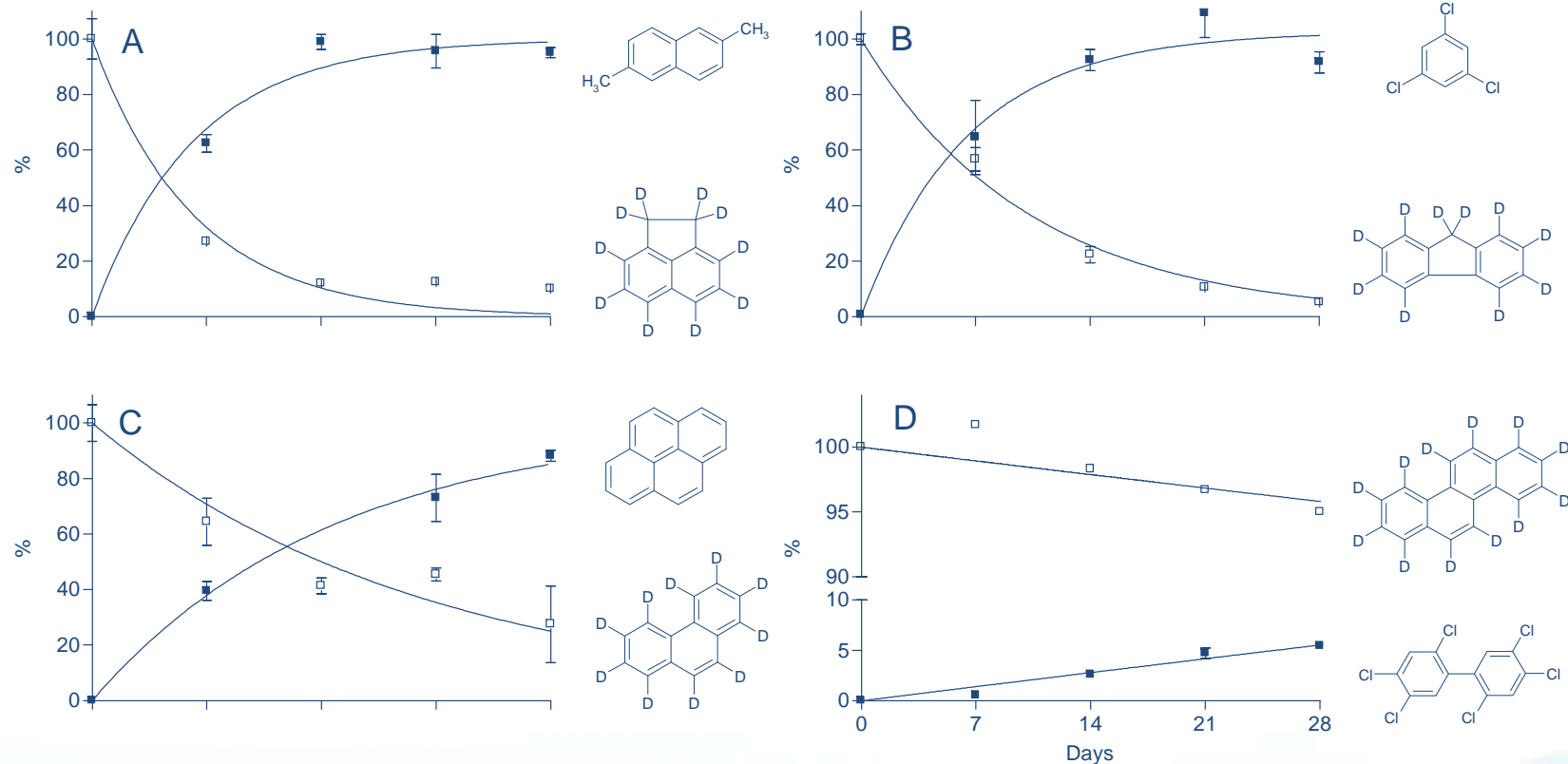
# The POCIS Problem 1

*- Lack of exposure correction method*



# The solution

- for hydrophobic samplers (LDPE, Silicon, SPMD)



The PRC approach allows adjustment for the effects of exposure specific factors on uptake (Booij et al., 1998; Huckins et al., 2002)

Various models may be used to correct for the effects of compound specific factors on uptake (Booij et al., 2007)

# PRC Summary

- Inter-site comparisons are hampered by differences in exposure conditions (flow, temperature, bio-fouling)
- PRCs are always useful - how much water have we extracted?
  - identify equilibrium
  - check for inter-site differences in  $R_s$  / normalise amounts
  - calculate water concentrations ( $C_w$ )
- But there are limitations

# Hydrophobic sampler correction methods (PRCs) for polar samplers?

Adsorption versus Absorption



## Problem 2: Lack of uptake model

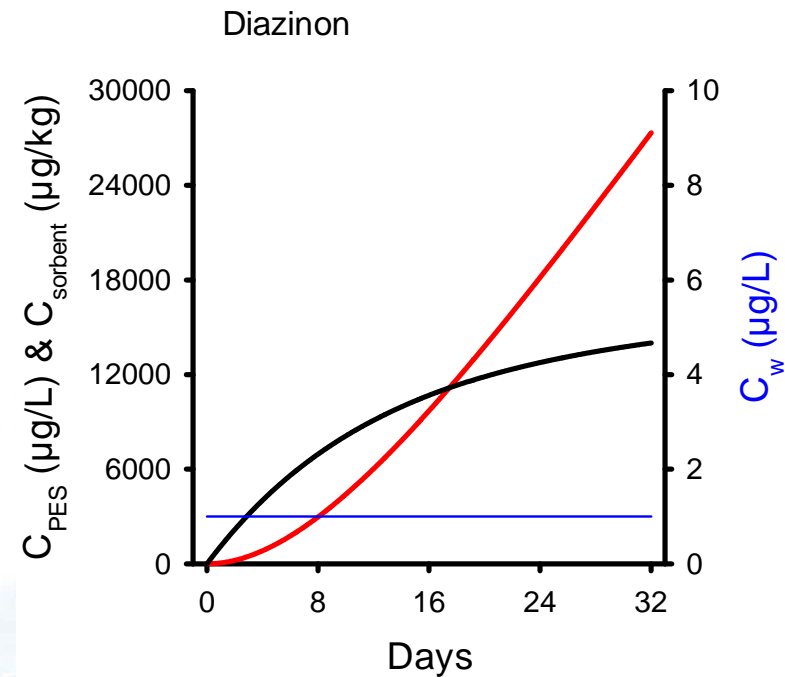
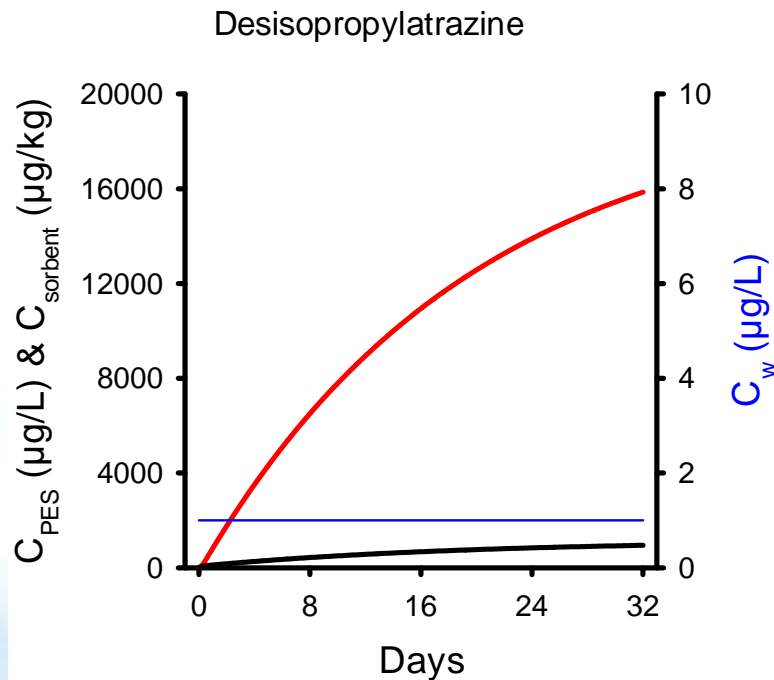
- Published sampling rates ( $R_s$ ) for POCIS for various chemical groups
- Results dependent on the type of calibration more than the type of chemicals, high  $R_s$  = calibration method artifact?
- «Guessing» as accurate as taking an *unadjusted* sampling rate from the literature for estimating  $C_w$
- Median  $R_s$  0.19 L d<sup>-1</sup> (turb)
- Harman et al. *Submitted*



# Model that describes POCIS

-Based on Gale 1998 for SPMDs

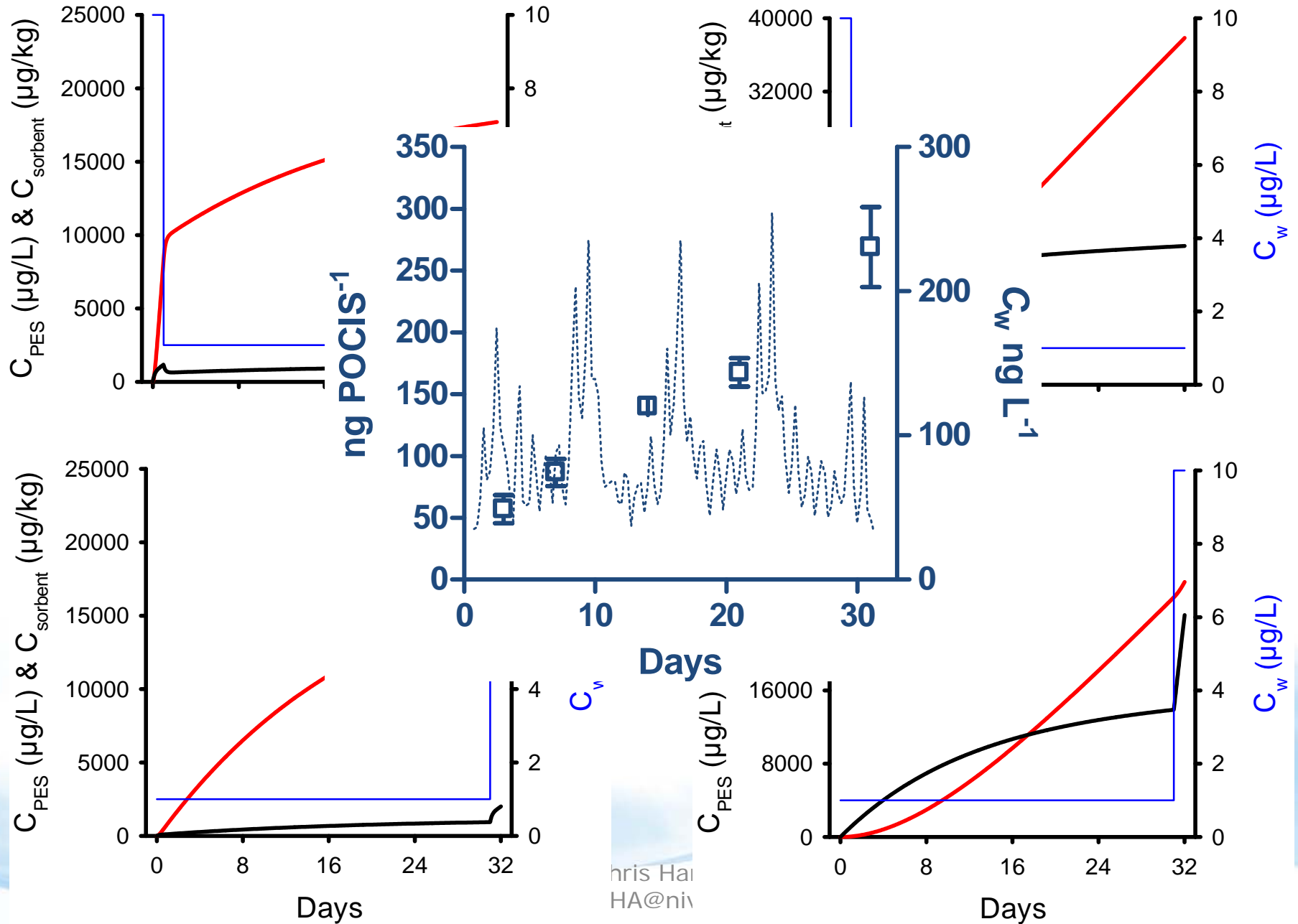
Importance of membrane interactions, simple scenario:  $C_w = 1 \mu\text{g/L}$



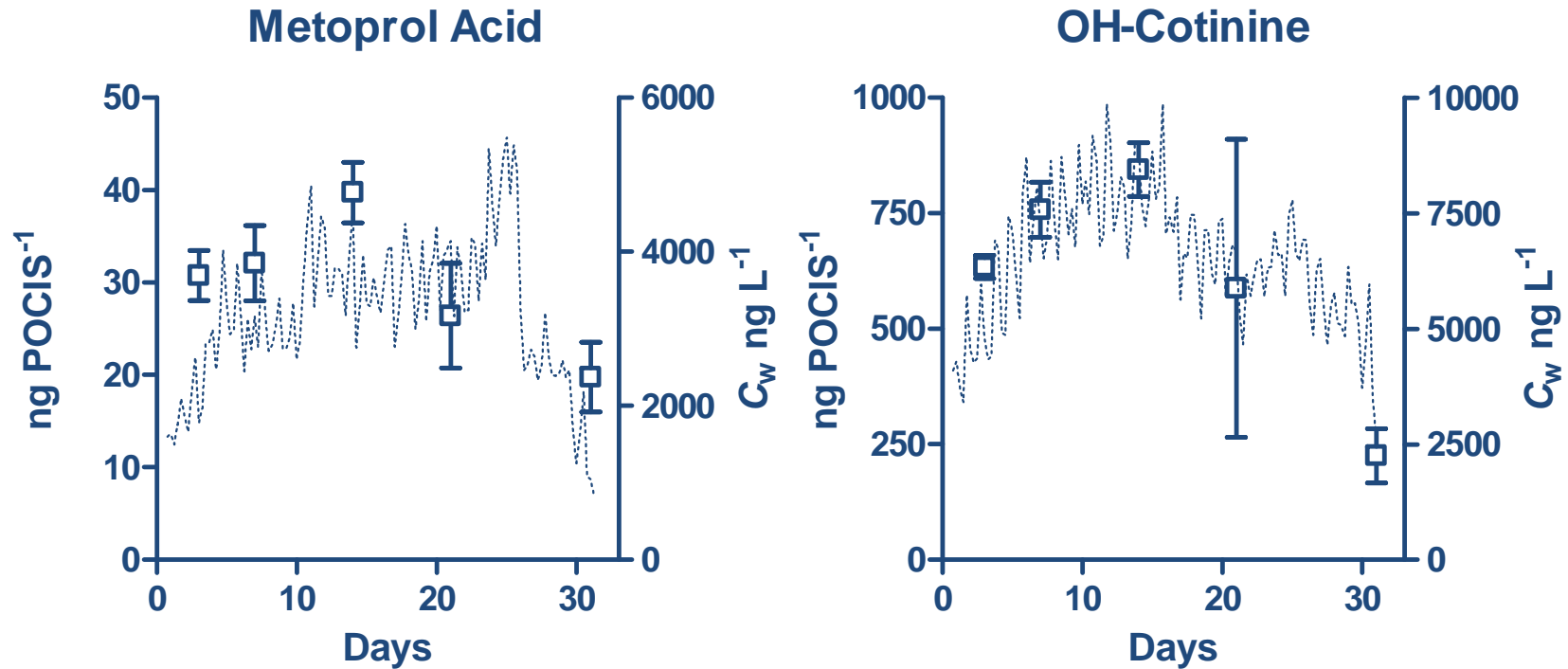
# Model - integration of peak scenarios

Desisopropylatrazine

Diazinon



# Competitive sorption?



- Rapidly equilibrating compounds (Short integrative phase) Isotropic exchange?
- Competitive sorption?
- Consequence for PRC approach in POCIS
- Harman et al. 2011a;b



# Identifying trends

*- Use of antihistamine in relation to pollen count*

# Towards quantitative data?

## *year-long integrative measurement*

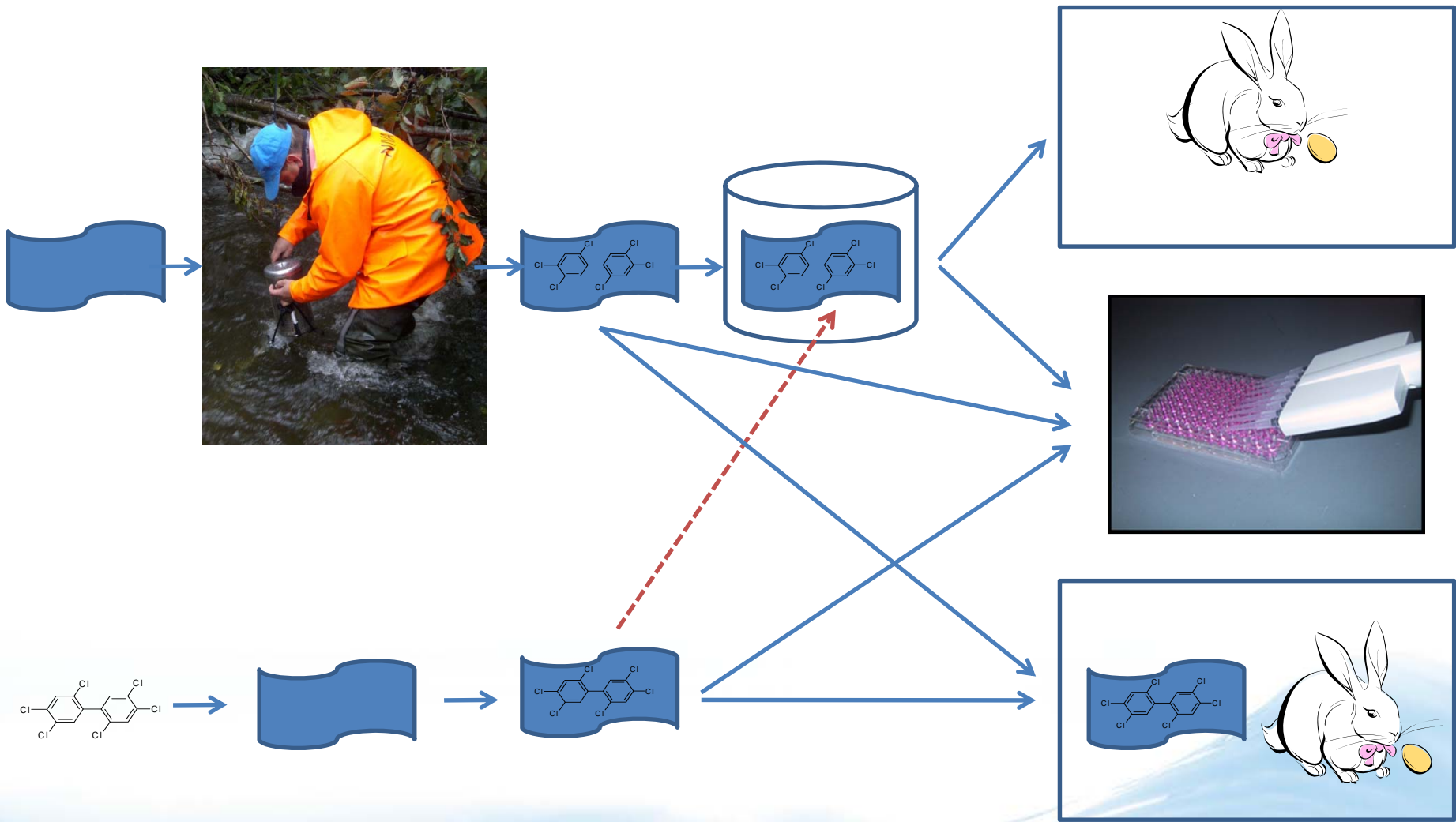
- Flux of cetirizine through the STW calculated using POCIS estimated, time integrated water concentrations (after *in situ* calibration)
- Yearly DDD (daily designated dose), 10 mg d<sup>-1</sup>, 50% excreted as parent compound (Pfizer, 2006)
- Public Health Institute registered 5.5 million sold DDD in 2010 (pop. adj.), POCIS derived estimate ca. 6 million
- Can we determine population response/exposure to environmental events/contaminants by passive methods
  - Not feasible using bottle or autosampling
- Likely requires *in situ* calibration?

# POCIS for exposure screening

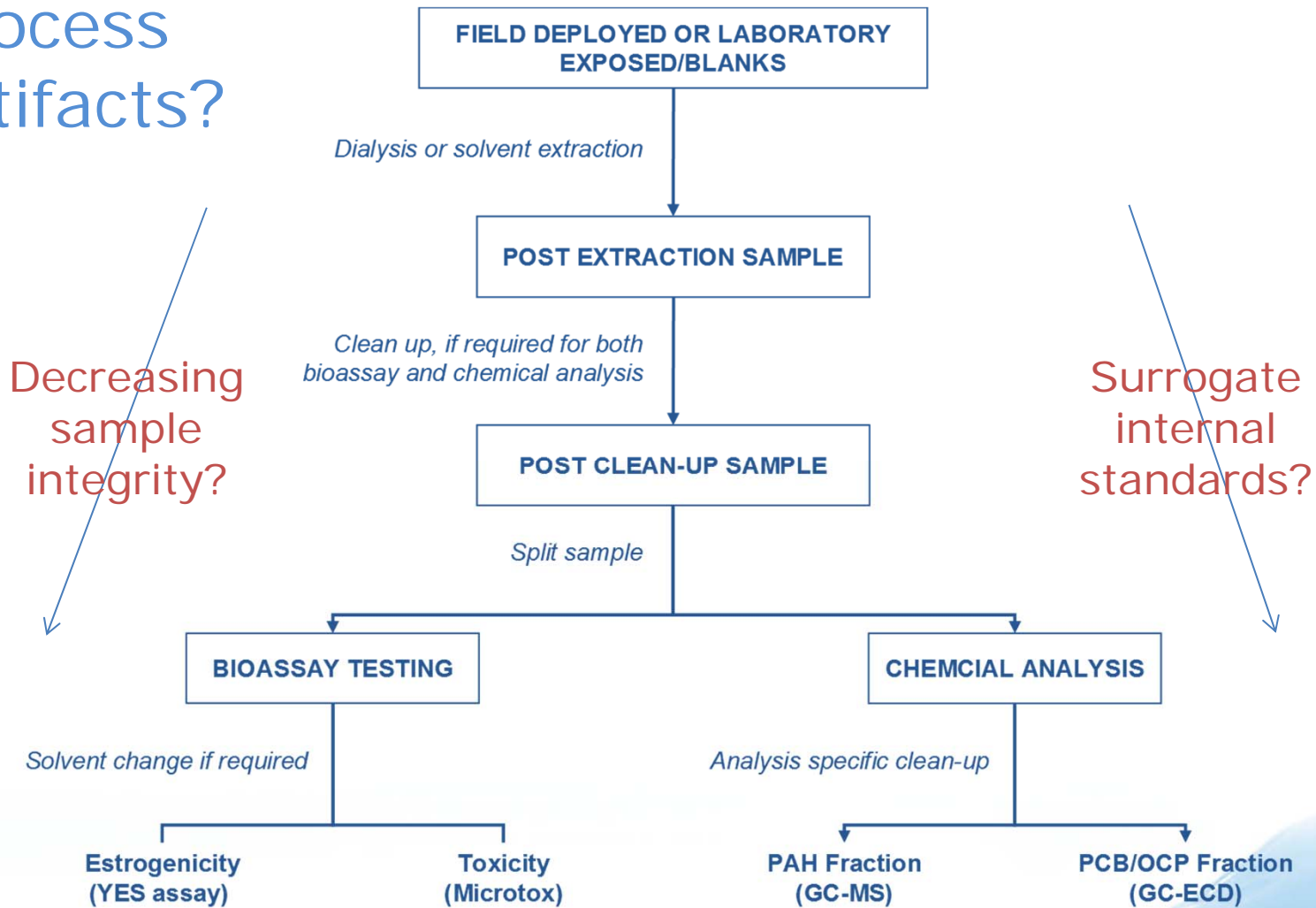
*naphthenic acids in offshore discharges*

# Possibilities

- *Passive sampling for ecotoxicology*



# Process artifacts?



After Alvarez et al, 2007, *Comp. Ana. Chem.*

# PS for regulatory monitoring?

## EU Water Framework Directive monitoring:

- Surveillance monitoring
- Operational and investigative monitoring

## More specifically:

- Testing for compliance with EQS?
  - Resolve  $C_{Wfree}$  for  $C_{Wtotal}$
- Monitoring long-term trends in contaminant levels
- Measurements of transboundary fluxes
- Sources tracking/spatial distribution
- Linking exposure and effects
- Contaminant speciation
- Support to more common monitoring methods (bottle sampling and biomonitoring)

# Regulatory monitoring

## *-recent steps forward*

2006	BSI PAS 61:2006	Passive sampling for priority pollutants in surface waters
2007	ISO 17402:2008	Measurement of contaminant bioavailability in soils and sediments*
2009	WFD CMA Guidance 19	PSDs mentioned as «complementary» tools for chemical quality monitoring of water
2010	WFD CMA Guidance 25	Listed in the guidance for sediment and biota monitoring
2010	Norman Network position paper	PSDs for screening for emerging substances and contaminants
2011	ISO 5667-23:2011	Passive sampling in surface waters
2011	PSD for WFD workshop	Deltares, position paper coming (?)

# Regulatory monitoring

## *-PS interlaboratory comparisons*

2005	SWIFT-WFD project	Tank calibration and field exposure of 7 types of PSDs for polar/nonpolar substances and metals
2006-2007	PSTS water/sed (ICES)	12 laboratories
2009-2011	Eclipse project	Tank calibration and field exposure of 5 types of PSDs for nonpolar substances
2010	Aquaref intercomparison	Field exposures involving 25 laboratories, polar and nonpolar substances
2011	Norman Network intercomparison	Intercomparison of PSDs for emerging substances



# Summary and way forward (POCIS)

- POCIS is a useful investigative monitoring tool but results are currently semi-quantitative
- Exposure correction method and uptake model lacking
- New thinking required for polar samplers - not fitting hydrophobic sampling theory
- Emerging hydrophobic or medium polar compounds may be sampled by existing samplers LDPE and (especially) silicone rubber
  - PRC approach available
- PS can generate environmentally relevant extracts for ecotoxicology testing
- For POCIS start by thinking about your targets and sorbents
  - “SPE method development” and consider membrane effects (PES/other)
- Consider calibration conditions in relation to environmental exposure conditions
  - *In situ* calibrations