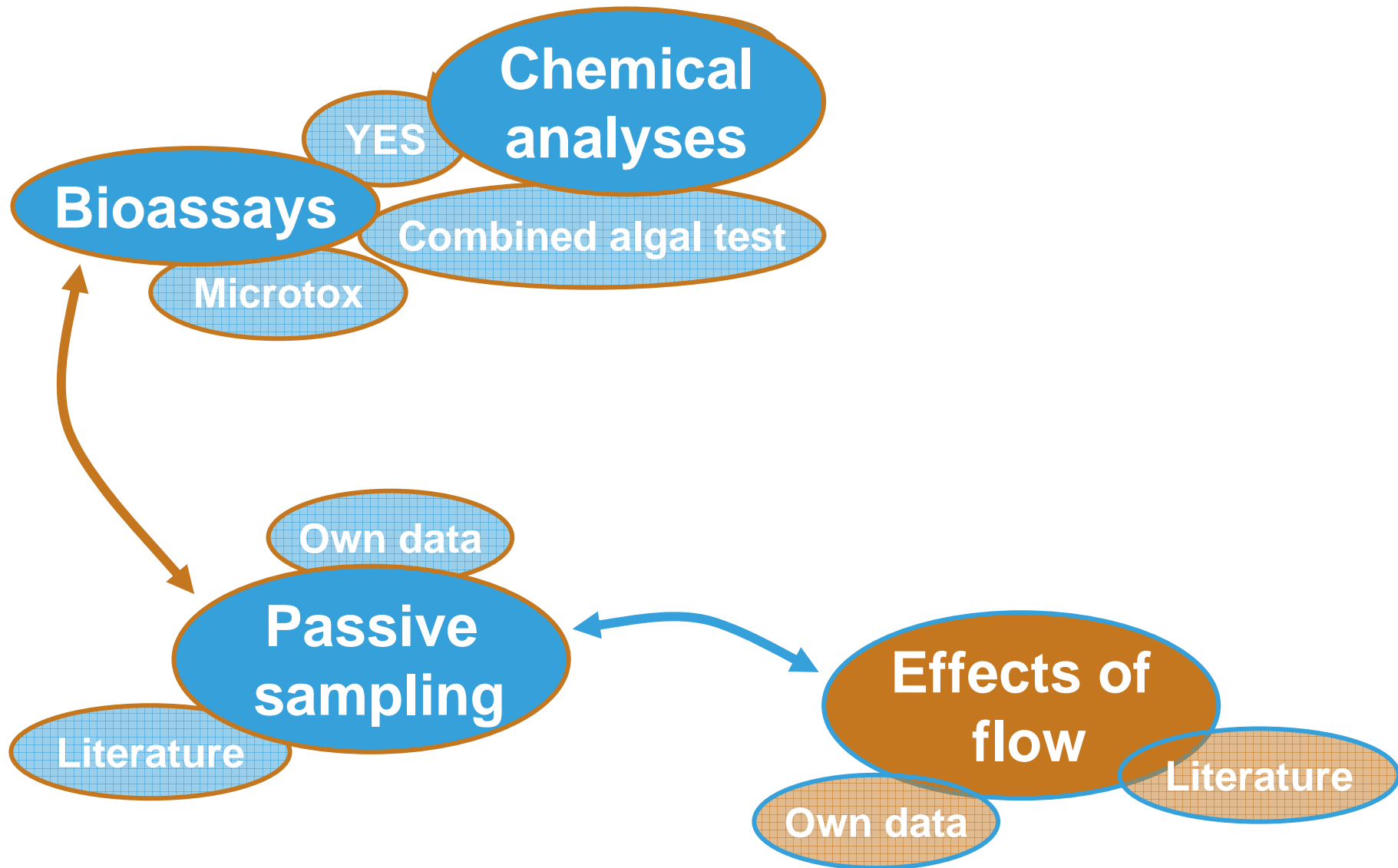


Combining passive sampling with bioassays

Evaluating effects of flow under environmental conditions

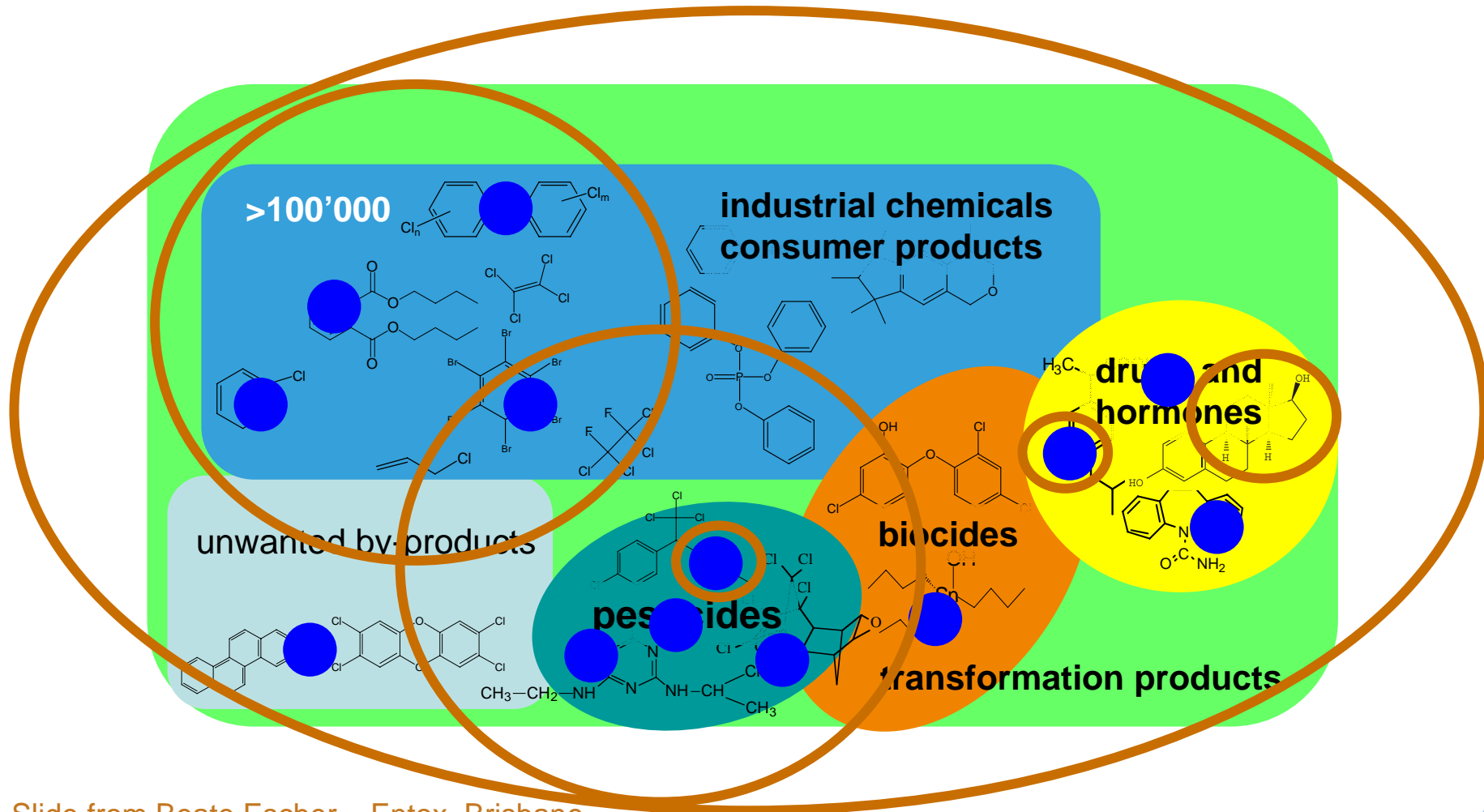
Contents



A rationale for bioassays

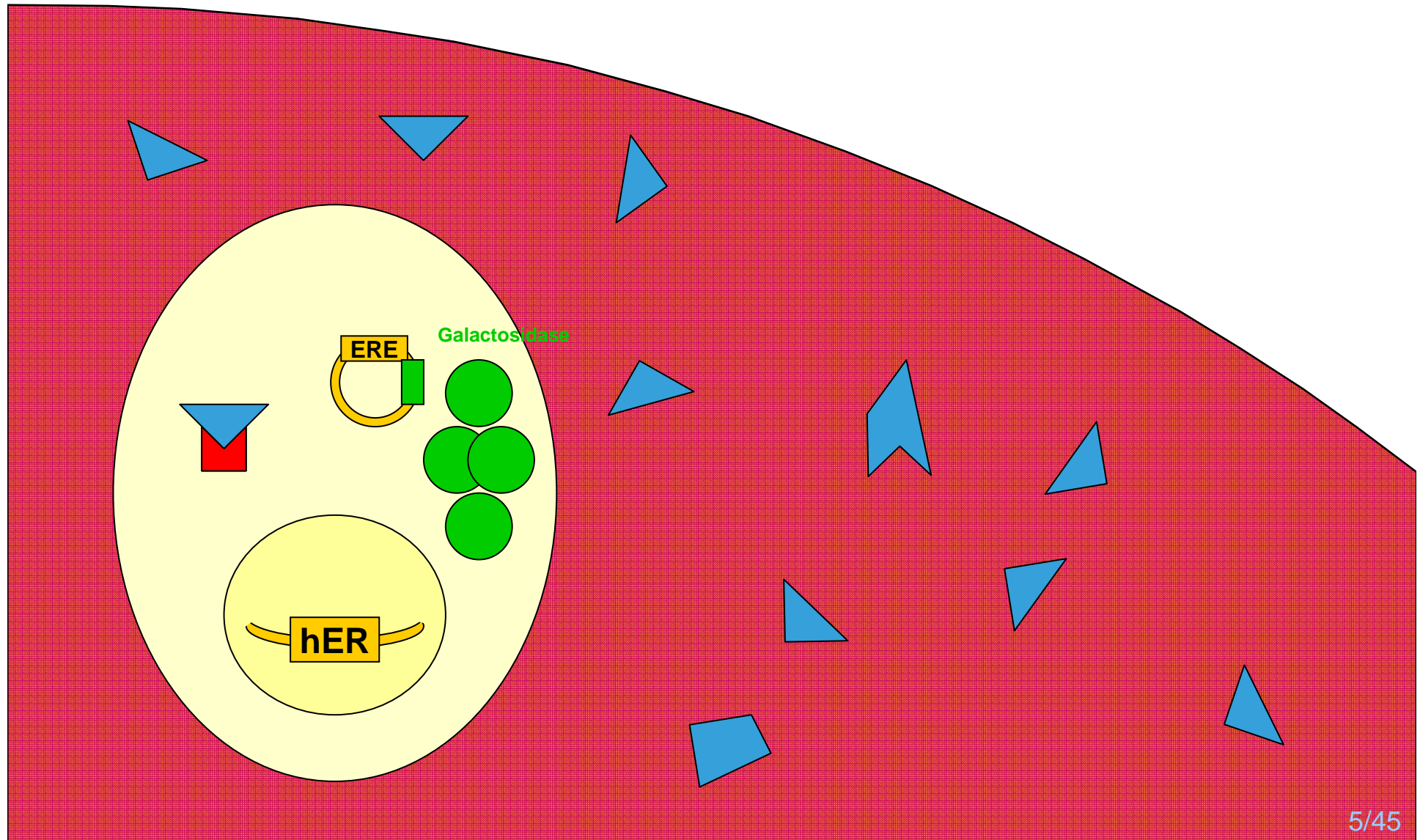
● Chemical analysis

● Biological analysis



Yeast estrogen screen

Routledge and Sumpter, 1996 ET&C 15

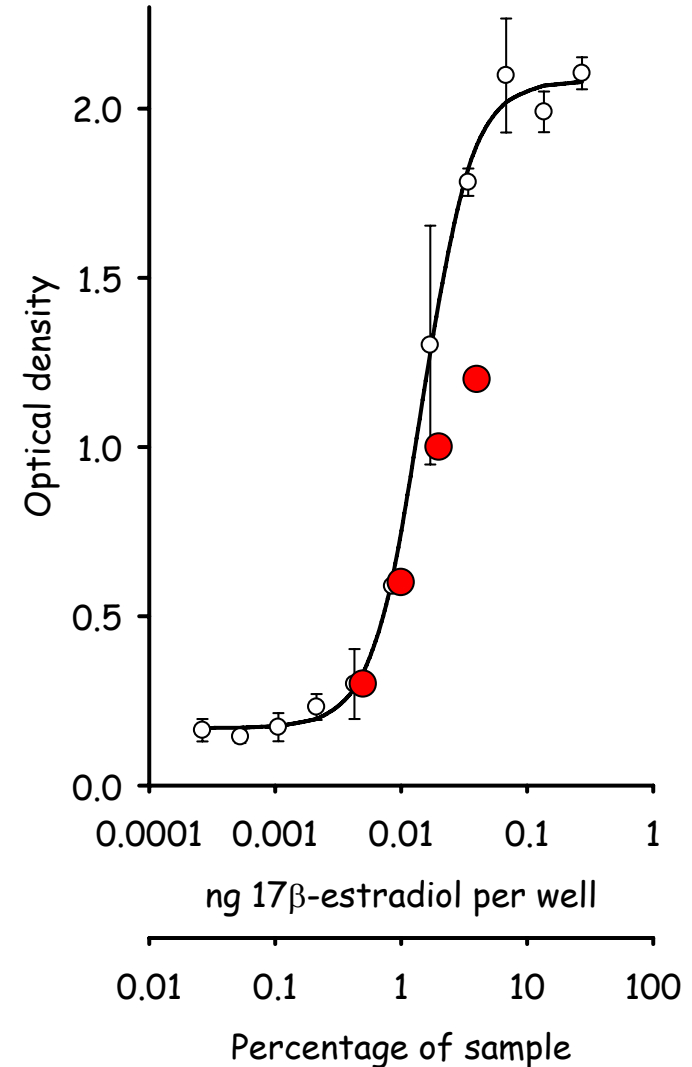
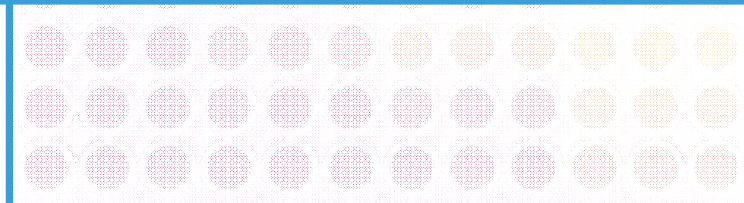


Toxicity equivalents

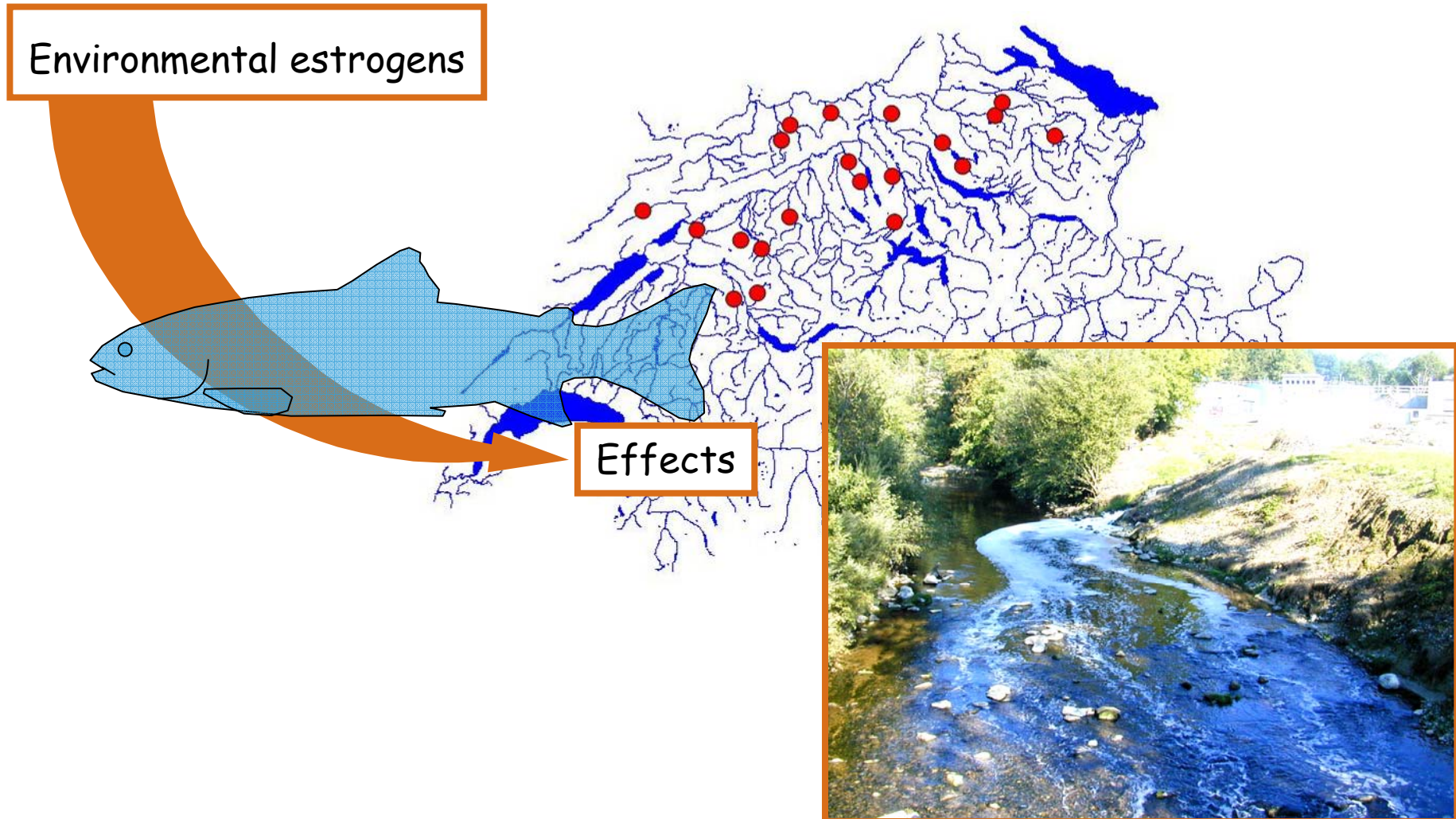
Data evaluation along:
“toxicity equivalent concentrations”



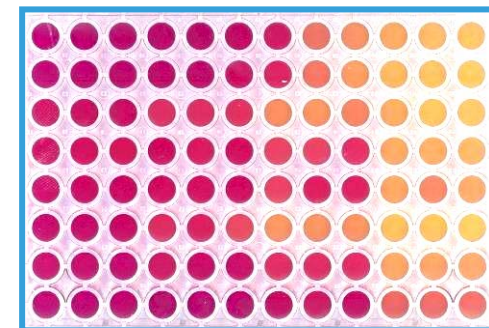
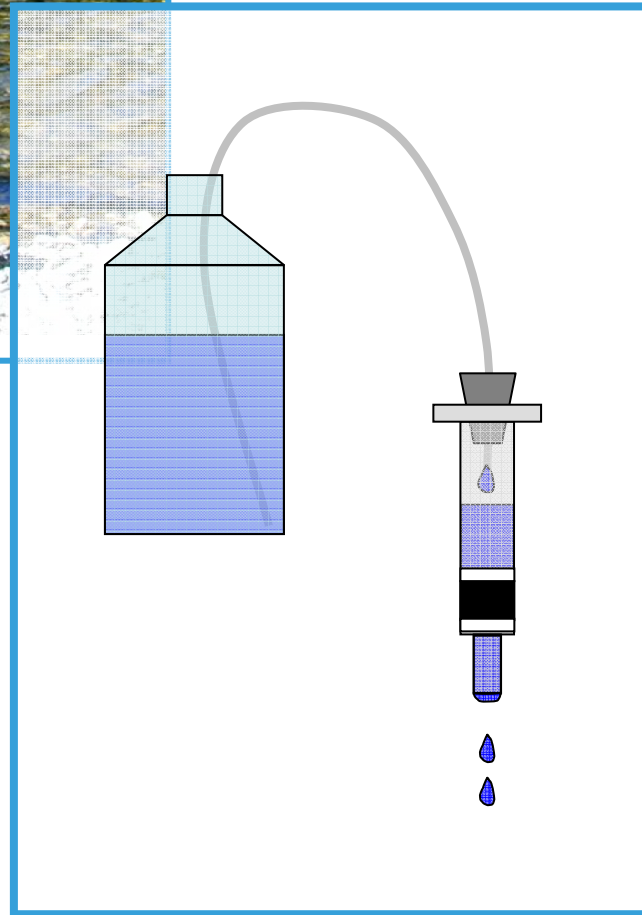
EEQ: 17β-estradiol equivalents



From grab sampling to passive sampling



From grab sampling to passive sampling



From grab sampling to passive sampling

“Estrogens in Swiss rivers and effluents - sampling matters” Vermeirssen et al. (2008) Chimia 62

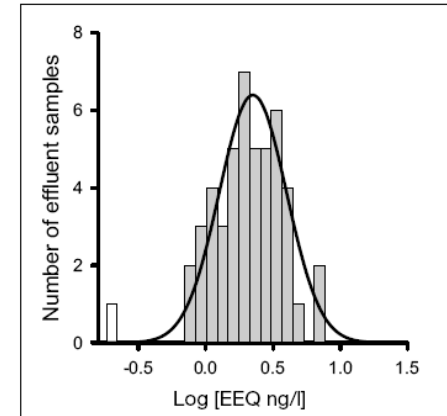
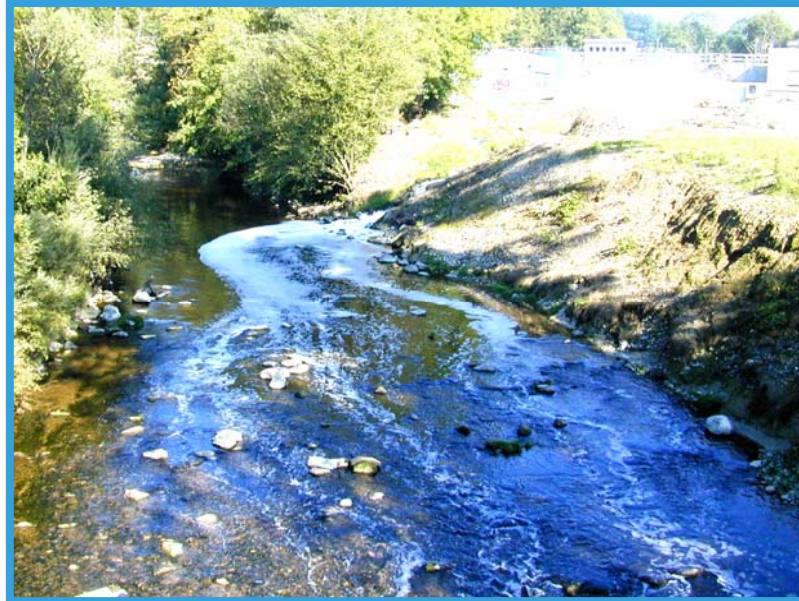


Fig. 4. Histogram of effluent estrogenic activity (EEQ). The normal distribution plot was fitted to 47 data (grey); one EEQ (open bar) was excluded.^[20]

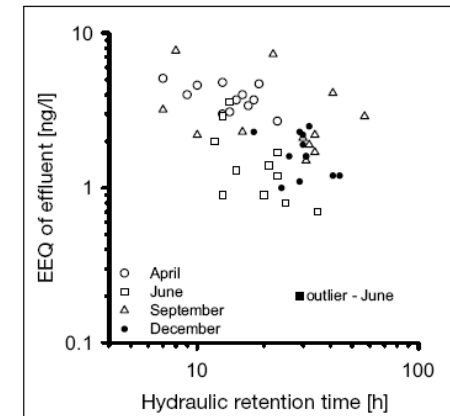


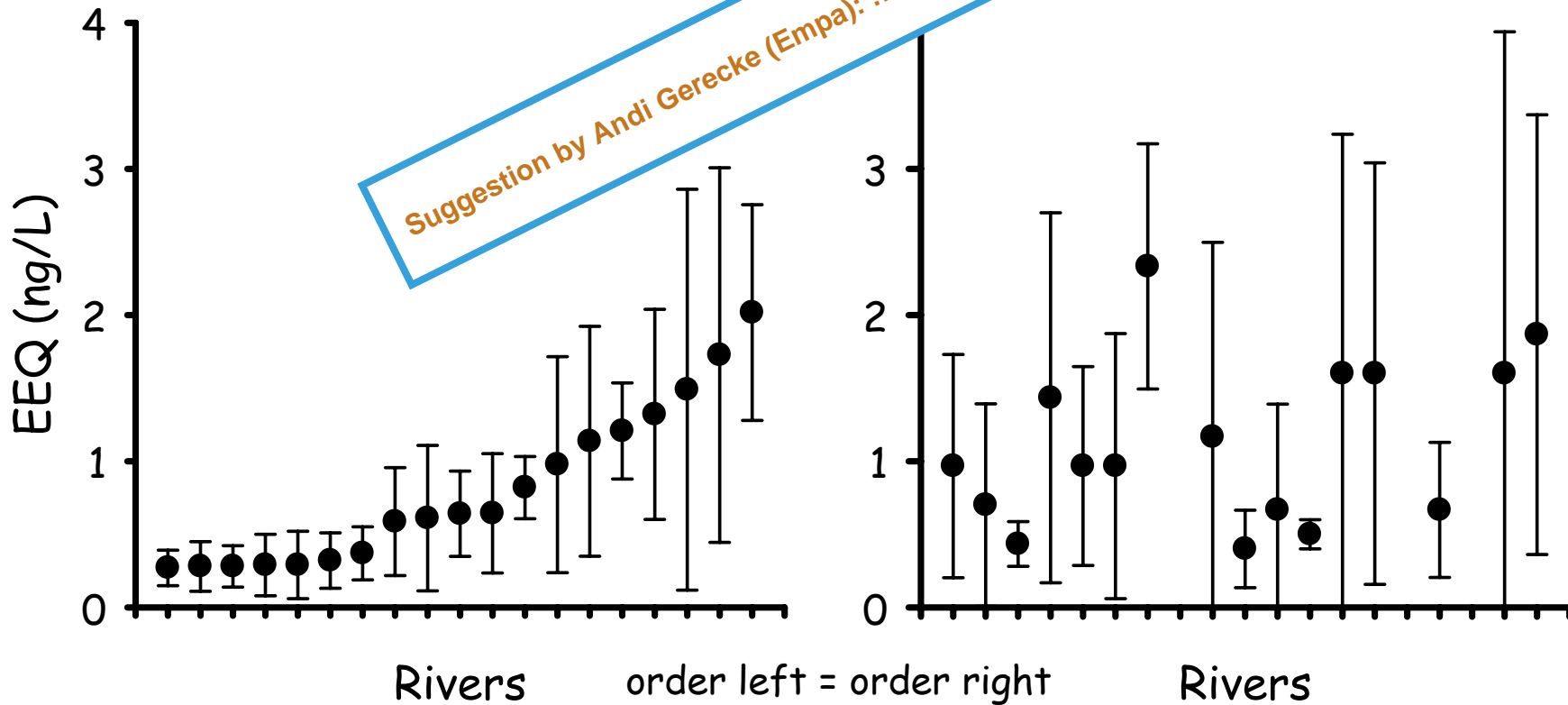
Fig. 5. Relationship between the hydraulic retention time (HRT) and the estrogenic activity (EEQ) of effluent over four 12-day sampling periods. The association between HRT and EEQ was negative in all but one sampling period (small filled circles).^[20]

From grab sampling to passive sampling



n = 3

Suggestion by Andi Gerecke (Empa): ...passive sampling ...artificial fish



Nov 2003: passive sampling and bioassays



Chemosphere 54 (2004) 1217–1224

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Purification of triolein for use in semipermeable membrane devices (SPMDs)

J.A. Lebo ^{a,*}, F.V. Almeida ^b, W.L. Cranor ^a, J.D. Petty ^a, J.N. Huckins ^a,
A. Rastall ^c, D.A. Alvarez ^a, B.B. Mogensen ^d, B.T. Johnson ^a

CHEMOSPHERE

Chemosphere 54 (2004) 695–705

www.elsevier.com/locate/chemosphere

A holistic passive integrative sampling approach for assessing the presence and potential impacts of waterborne environmental contaminants

J.D. Petty ^{a,*}, J.N. Huckins ^a, D.A. Alvarez ^a, W.G. Brumbaugh ^a,
W.L. Cranor ^a, R.W. Gale ^a, A.C. Rastall ^b, T.L. Jones-Lepp ^c,
T.J. Leiker ^d, C.E. Rostad ^d, E.T. Furlong ^d

Petty et al. (2004) Chemosphere 54

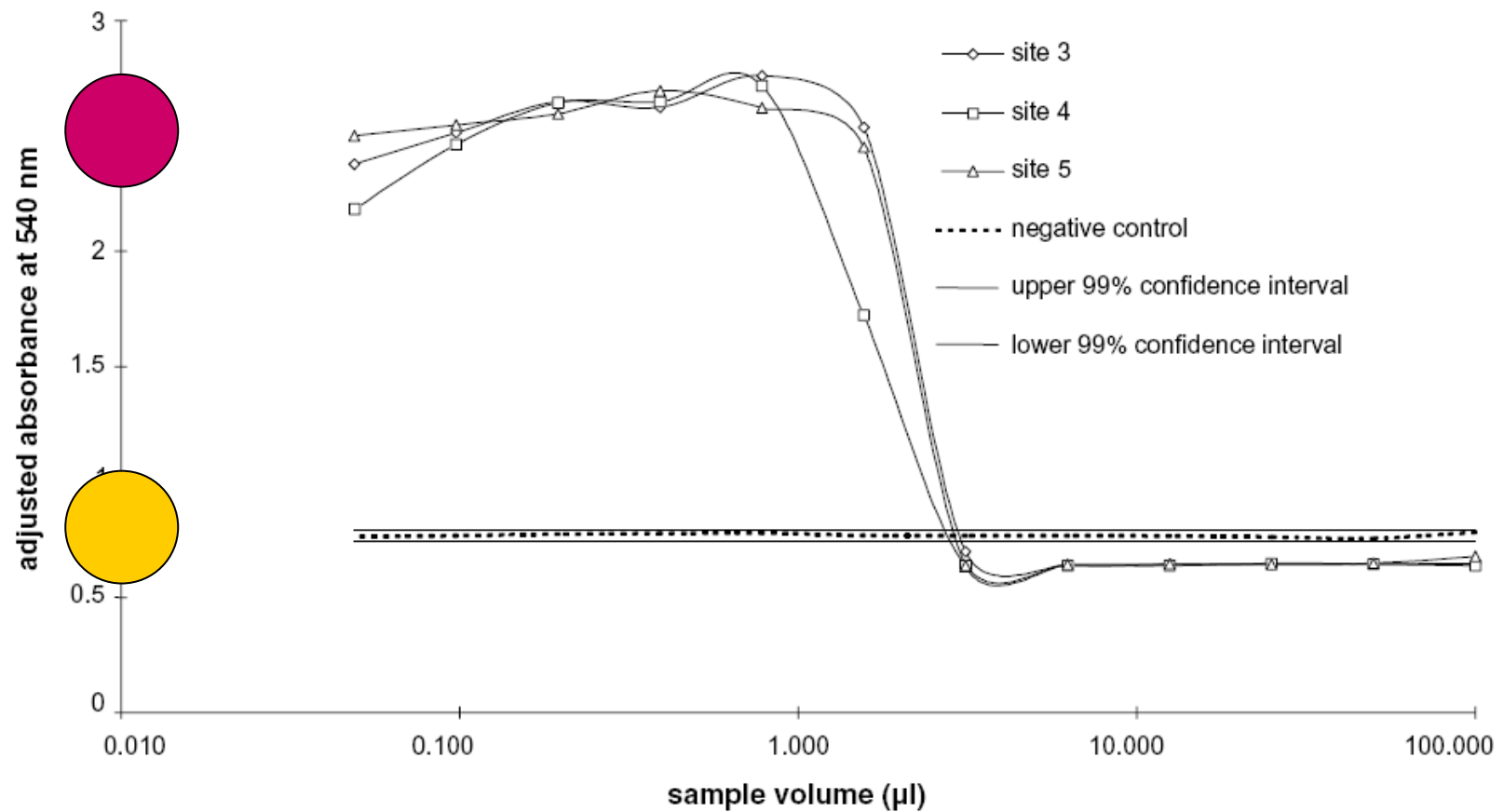
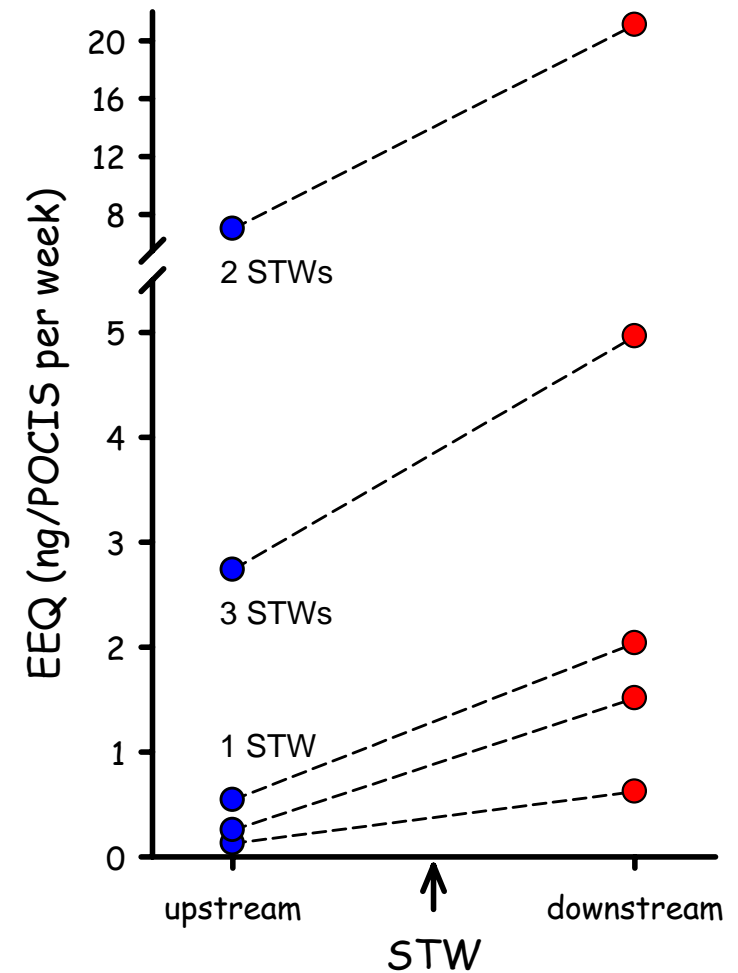
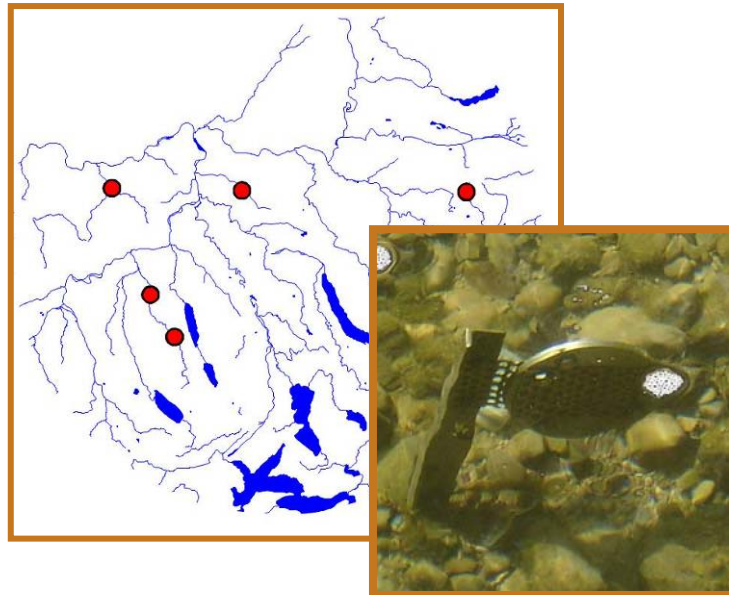


Fig. 2. Results of the YES assay performed on POCIS extracts.

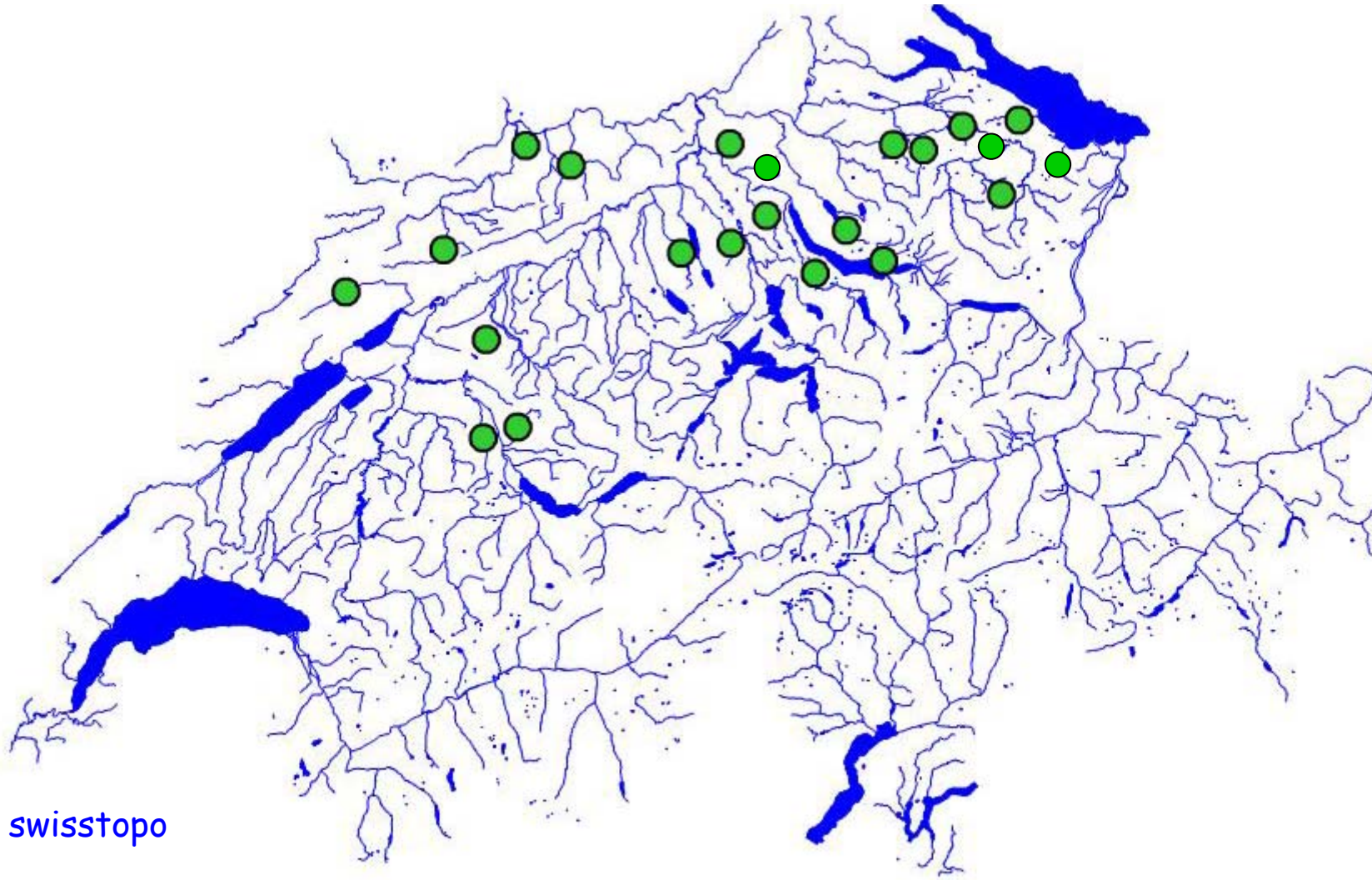
POCIS feasibility test

Vermeirssen et al. 2005 ES&T 39/ 2008 Chimia 62

- Do POCIS see the effluent?
- Do POCIS data correlate with repeated grab sampling data?
- Do POCIS compare to bioaccumulation?
- Do bioassay data relate to LC/MS/MS?



Further evaluation of POCIS – EPSA



© swisstopo

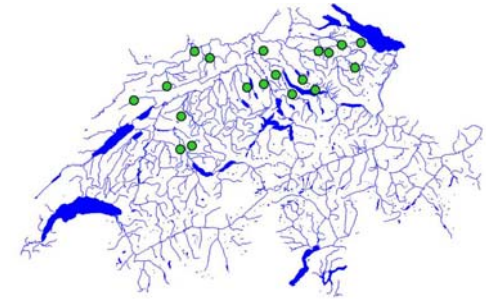
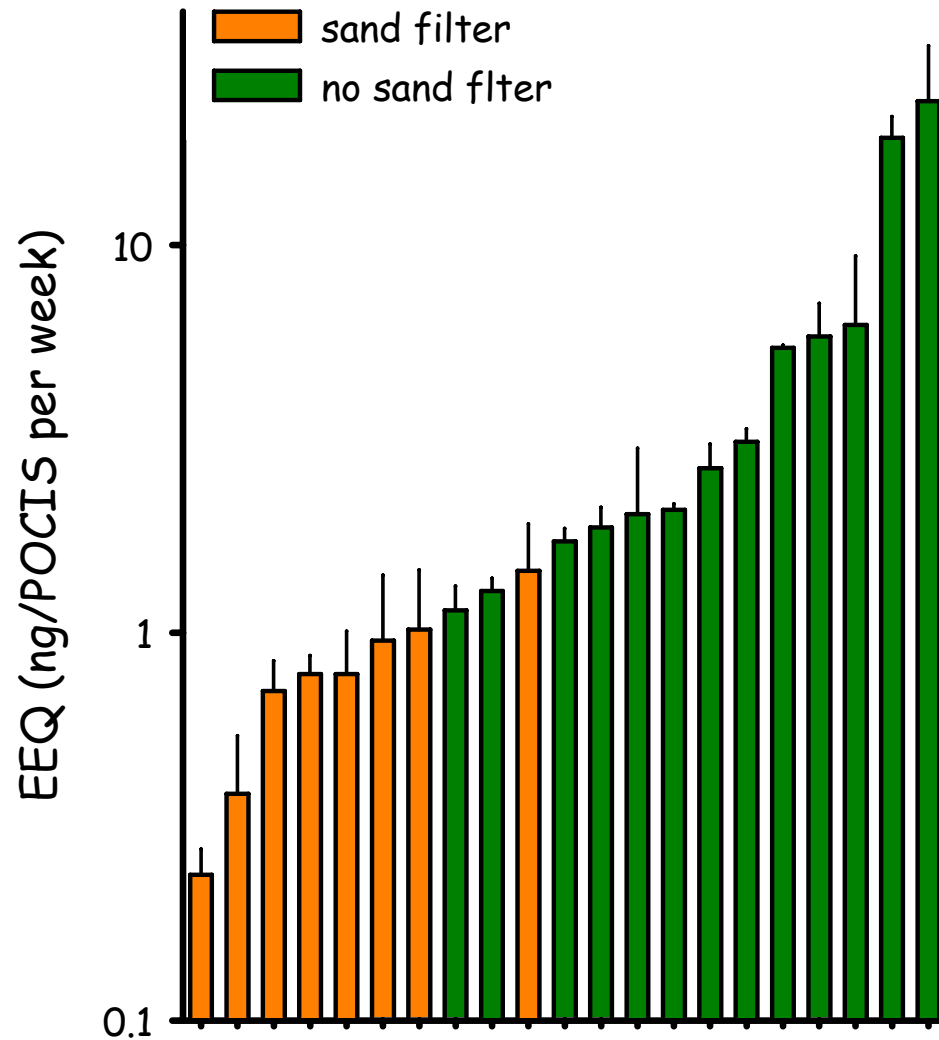
Deployment in effluents (and rivers)



EPSA – results: YES

POCIS in effluent for 5 weeks

Vermeirssen et al. (2008) *Chimia* 62





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Science of the Total Environment 367 (2006) 616–630

Science of the
Total Environment

An International Journal for Scientific Research
into the Environment and its Relationship with Humankind

www.elsevier.com/locate/scitotenv

Contamination of headwater streams in the United Kingdom by oestrogenic hormones from livestock farms

P. Matthiessen^{a,*}, D. Arnold^b, A.C. Johnson^c, T.J. Pepper^b,
T.G. Pottinger^a, K.G.T. Pulman^a

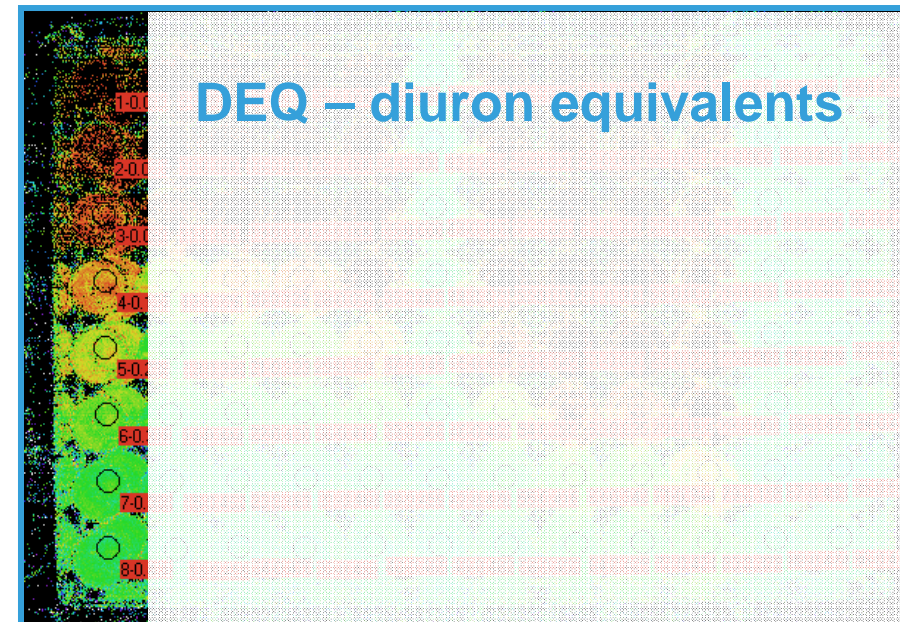
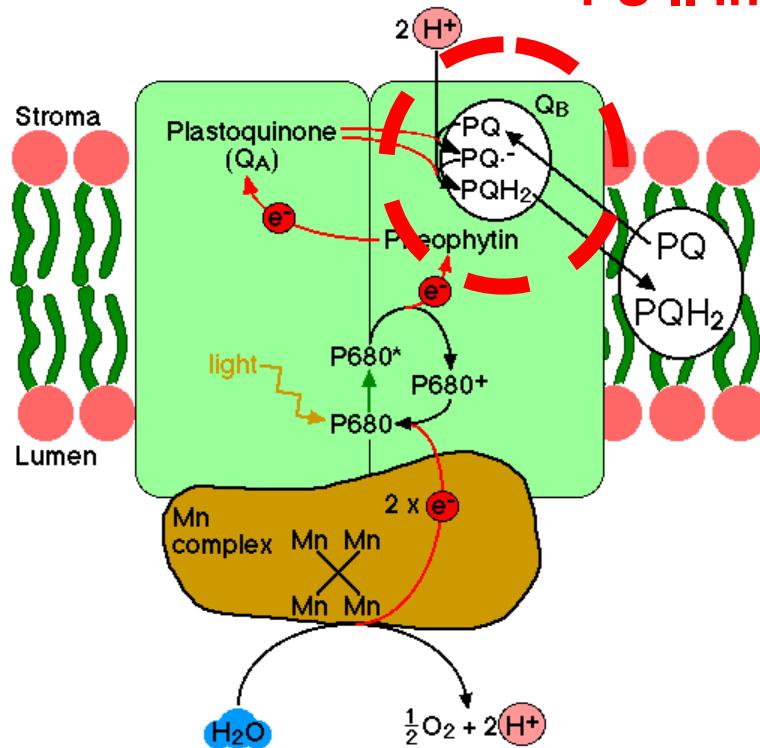
- Calibration of the POCIS
- LC/MS/MS
- YES
- Link between biological and chemical analysis

Combined algal test

Escher et al. 2008 J. Environ. Monit. 10

Photosystem II

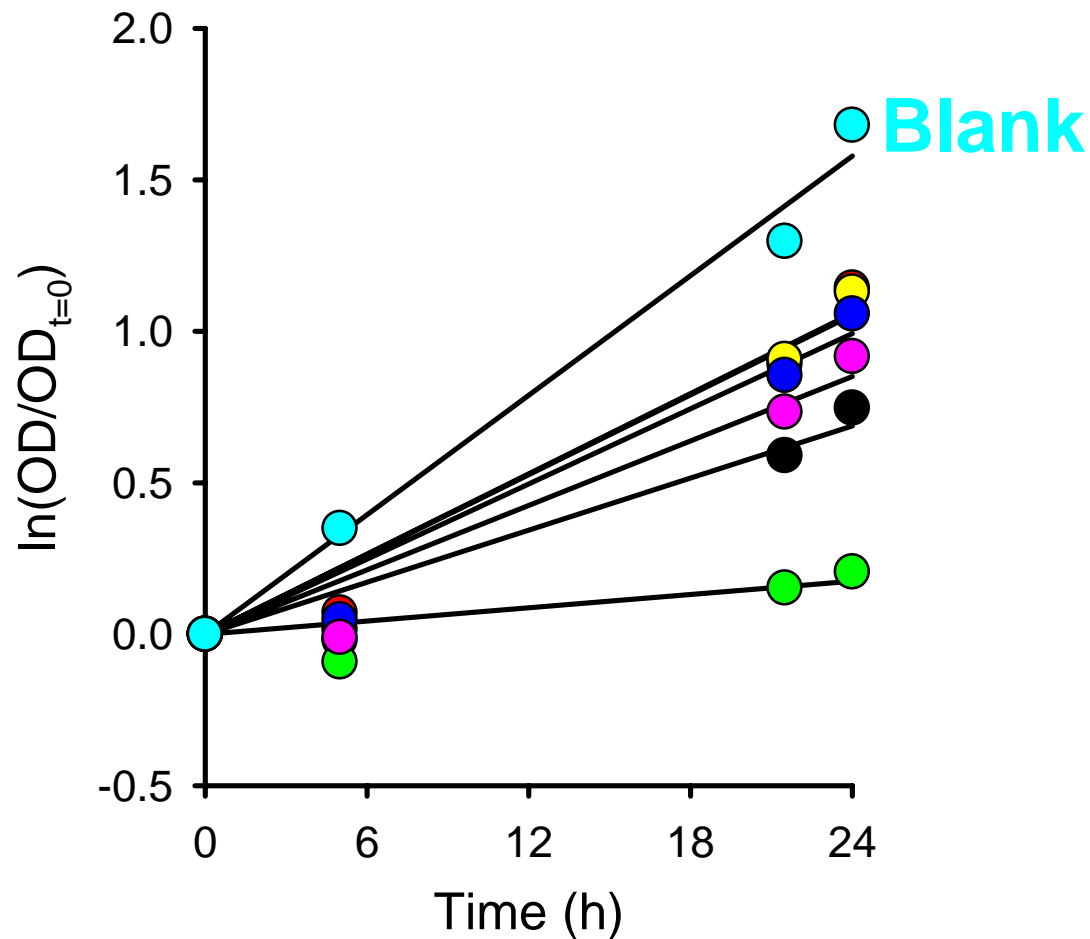
PS-II inhibitors, e.g. diuron



Combined algal test – inhibition of algal growth

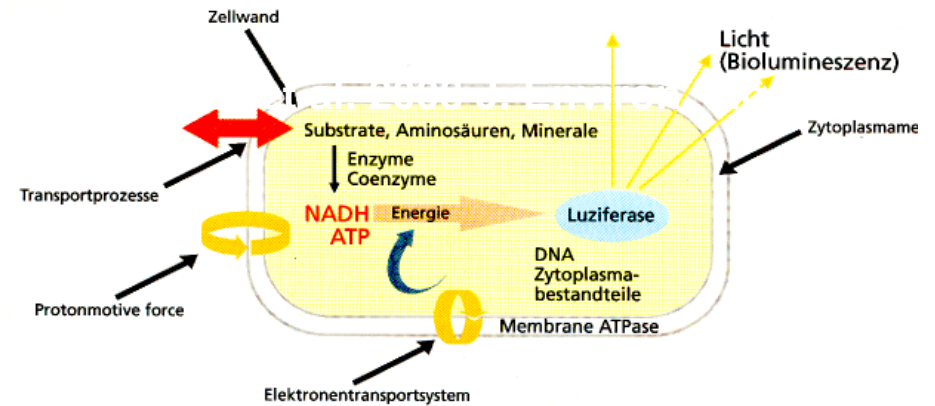
Escher et al. 2008 J. Environ. Monit. 10

Output: TEQ – toxicity equivalent concentration

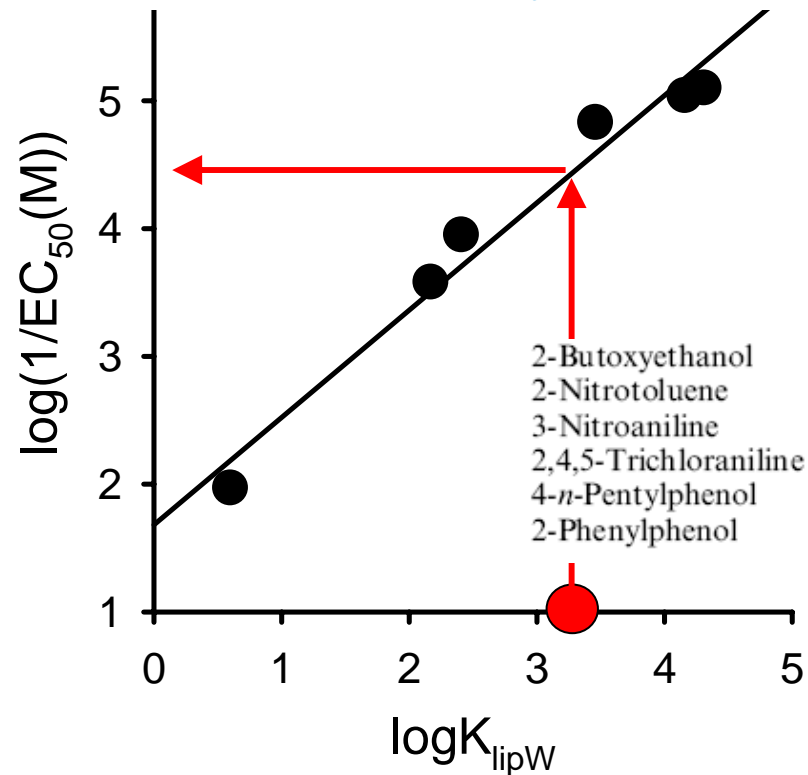


Bacterial bioluminescence

Escher et al. 2008 J. Environ. Monit. 10



QSAR:
quantitative structure-activity relationship



Output: TEQ

Virtual toxicant: $\log K_{OW} = 3$

$\log K_{lipW} = 3.2$

$EC_{50} = 4.1 \times 10^{-5} \text{ M}$

MW = 300

POCIS: 21 effluents – 3 bioassays

Vermeirssen et al. (in preparation): Micropollutants in effluent-exposed passive samplers – linking toxicity in algal and bacterial assays with chemical analysis

Estrogens

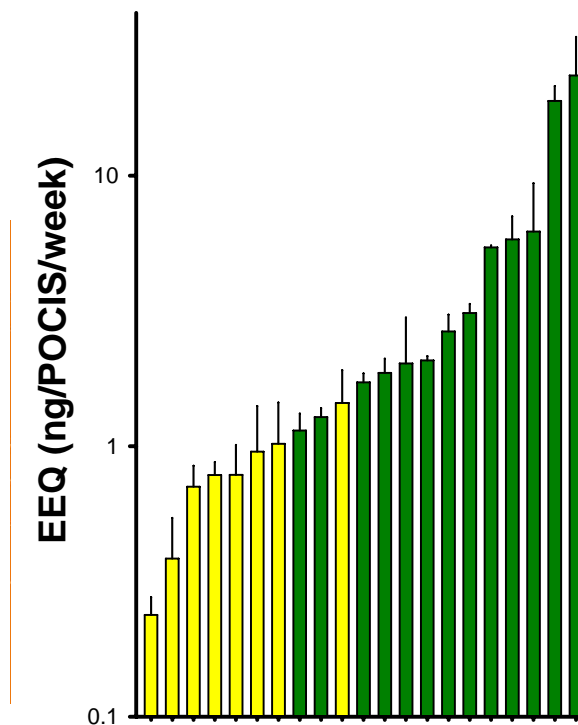
100-fold

PS-II inhibition

160-fold

Non-specific

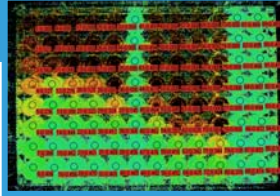
11-fold



DEQ (µg/POCIS)

TEQ (mg/POCIS)

Linking bioassays with chemical analyses



Diuron equivalents (µg/POCIS)

ng x

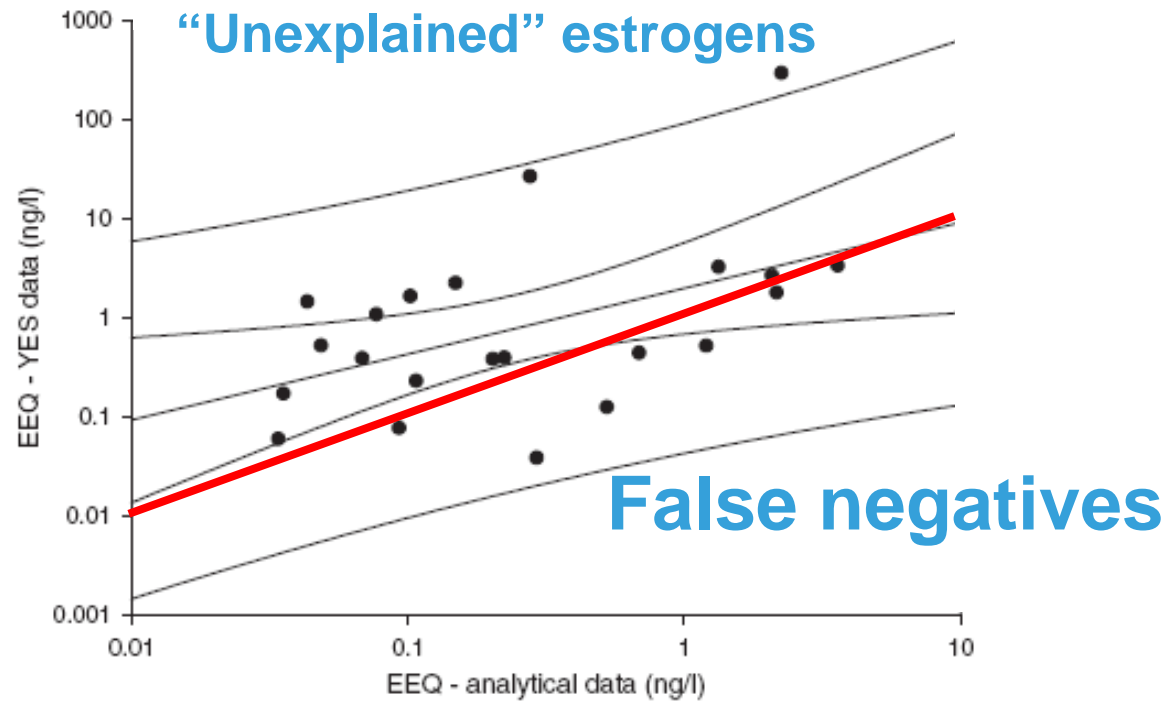
Relative potencies

Diuron	=	1.00
Terbutryn	=	0.78
Isoproturon	=	0.16
Atrazine	=	0.11
Irgarol	=	2.51
Terbutylazine	=	0.46

sum of herbicides

Calculated diuron equivalents (µg/POCIS)

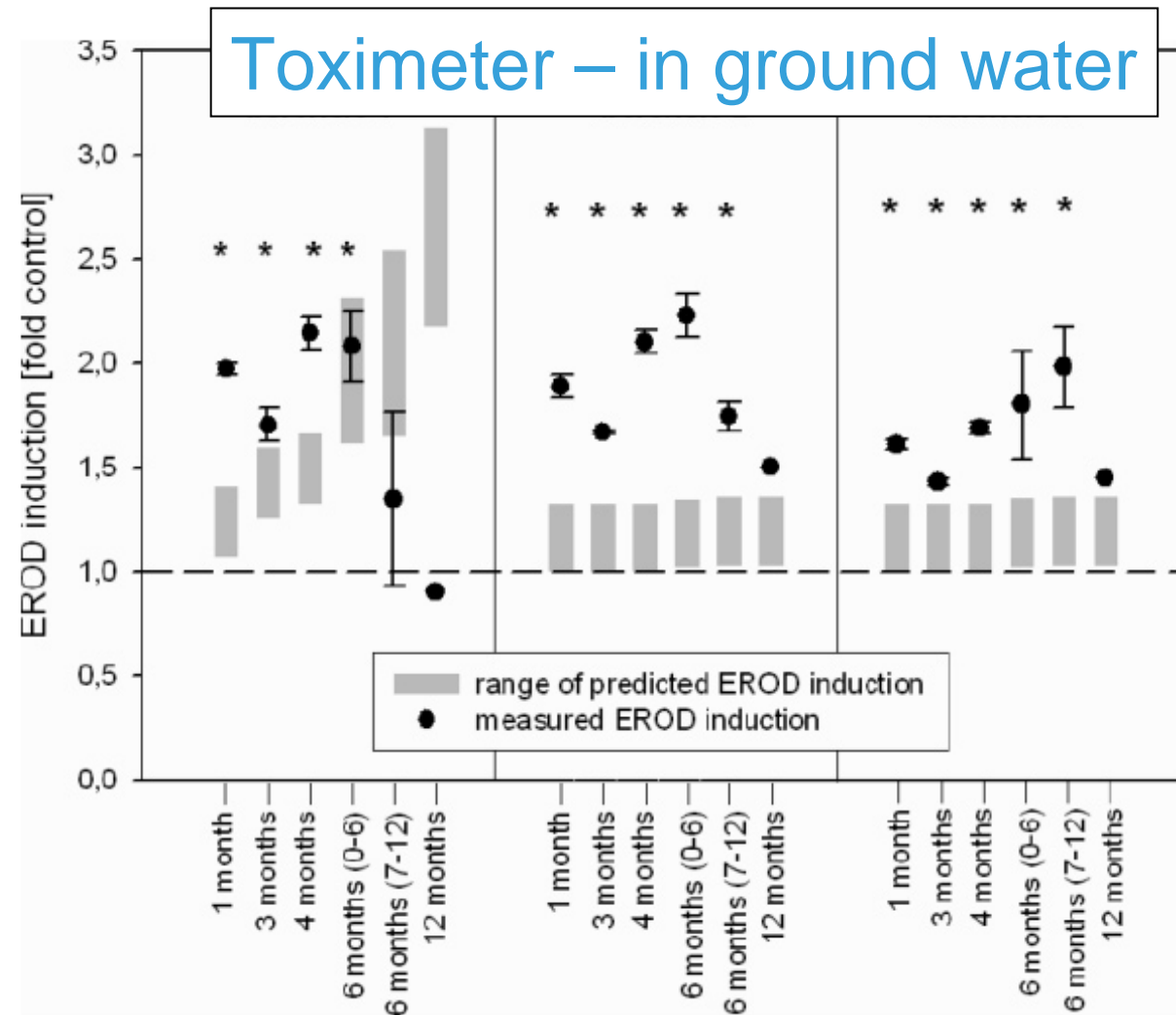
Bioassays and chemical analyses – other examples



Bioassays and chemical analyses – other examples

Bopp et al. 2007 ES&T 41

Rastall et al. 2004 ESPR 11: on SPMDs, EROD, YES, AMES test



Passive sampling and flow rate

$$Sh = k_f \frac{L}{D_{AB}} = 0.664 \cdot Re^{0.5} \cdot Sc^{1/3} \quad (k_f, L)$$

$$k_u = k_b K \quad Re = \frac{L v \rho}{\mu} \quad (v, \rho, \mu)$$

Stephens et al. 2005 ES&T 39

Flow rate

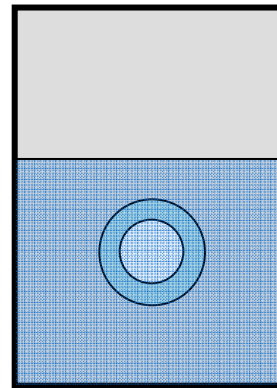
“Channel trials”



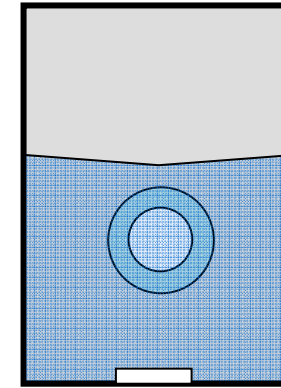
Matrix:
effluent
river water

Effects of flow: basic set-up

Alvarez et al. 2004 ETC 23



No stirring

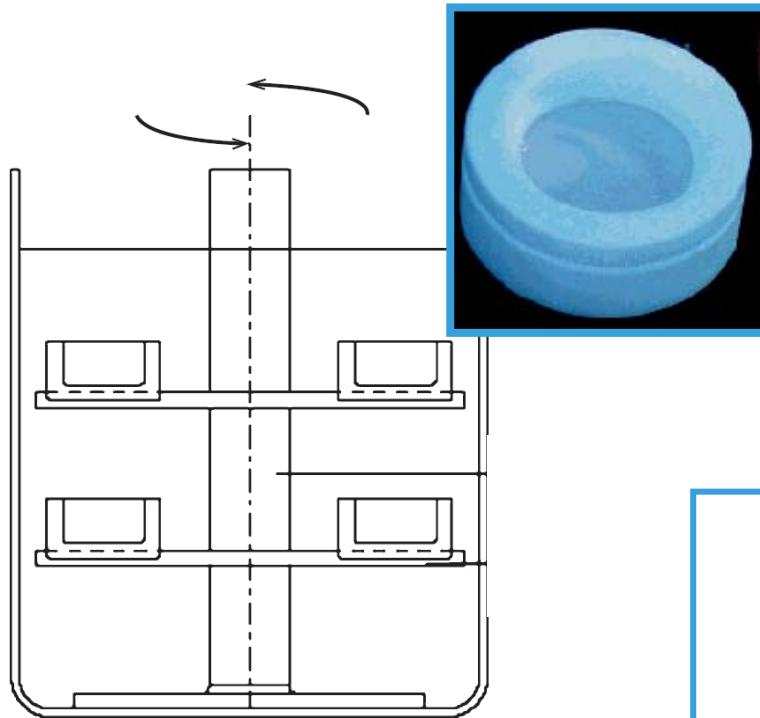


Stirring

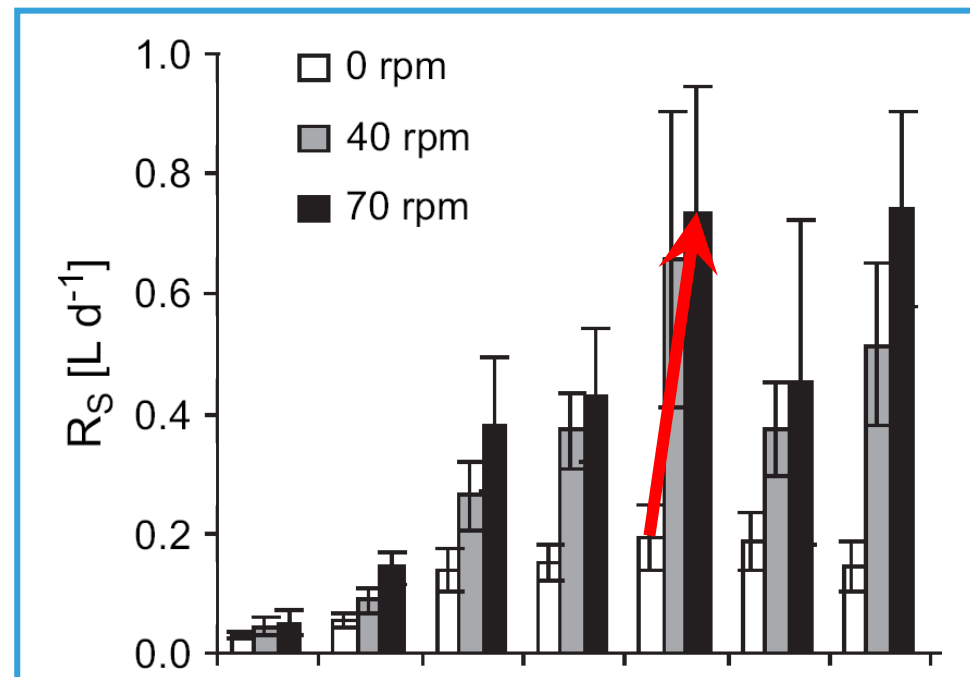
Analyte	R_S from quiescent renewals (L/d)	R_S from turbulent renewals (L/d)
Diuron	0.005 (0.002)	0.045 (0.016)
Isoproturon	0.015 (0.003)	0.086 (0.008)
Azithromycin	0.021 (0.006)	0.120 (0.075)
Fluoxetine	0.012 (0.007)	0.086 (0.023)
Levothyroxine	0.009 (0.008)	0.053 (0.028)
Omeprazole	0.007 (0.004)	0.030 (0.008)

Rotating samplers

Vrana et al. 2006 Environ. Pollut. 142



Microcosm running at 2 to 50 cm/s
Mazzella et al. 2008 Chemosphere 73



SPMDs and effects of flow rate

Fig 3.6 from “The SPMD book”: Huckins, Petty and Booij (2006)

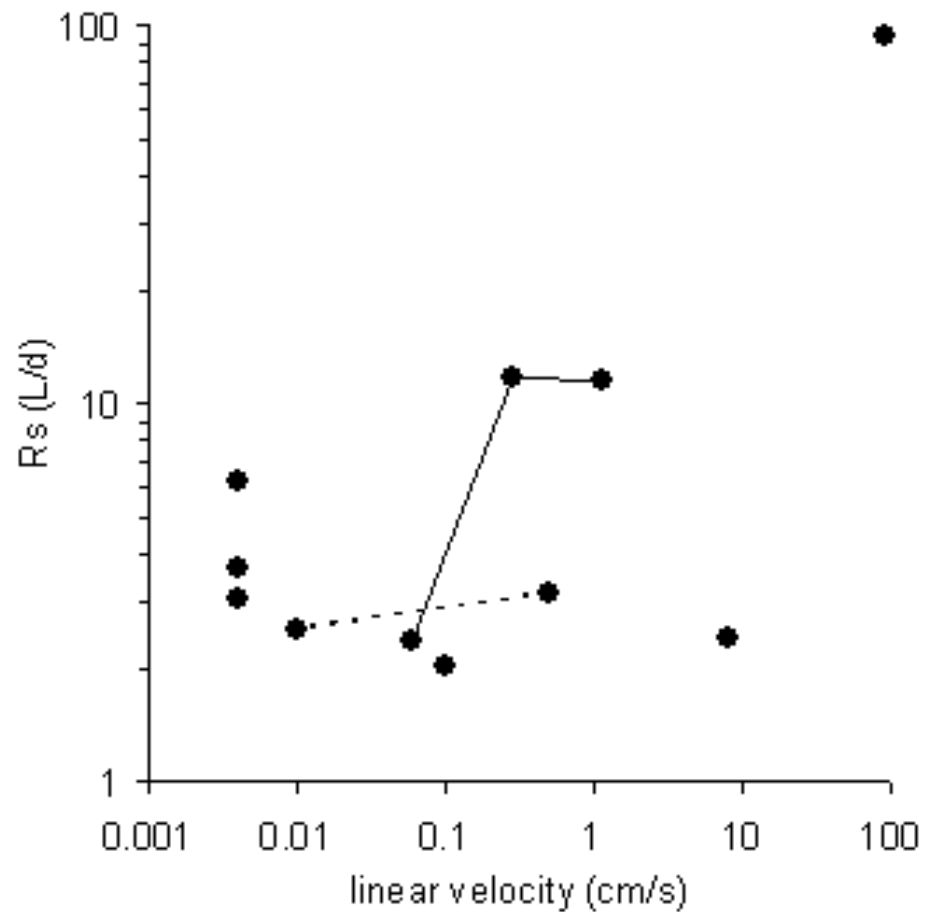
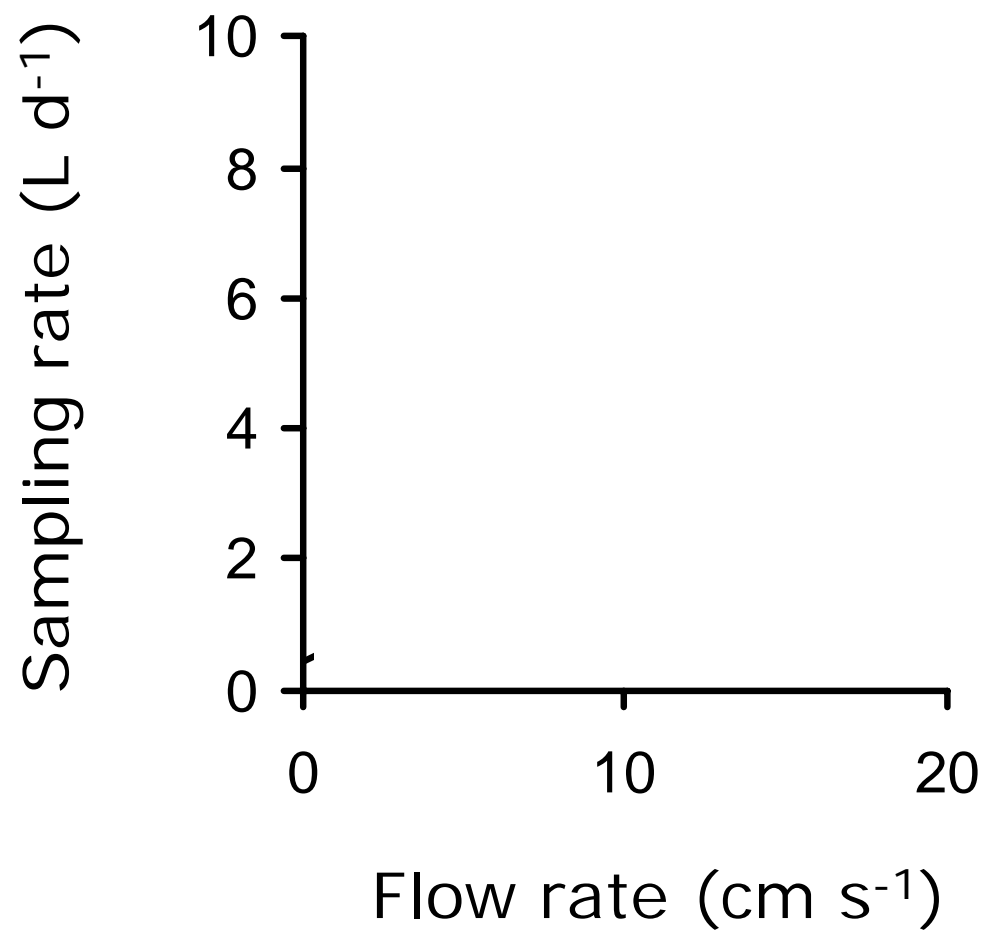


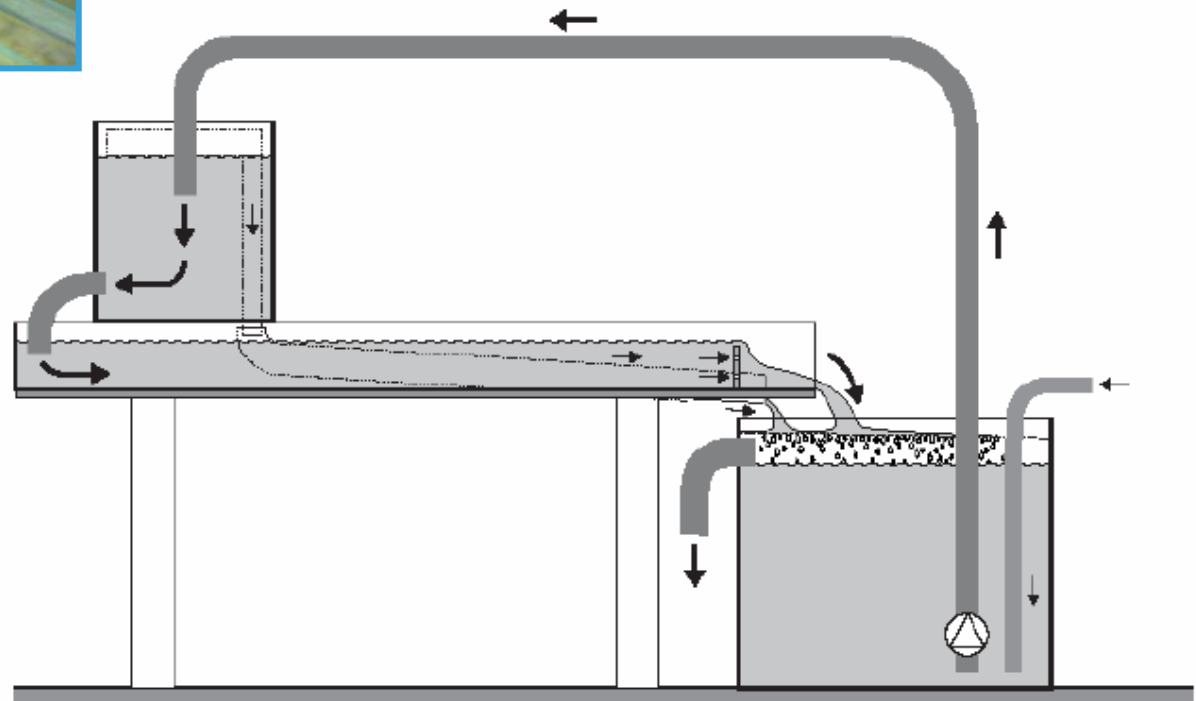
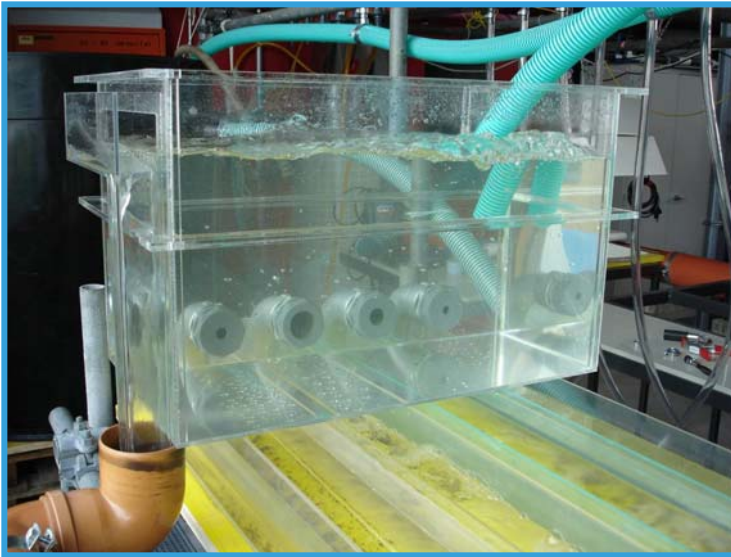


Figure provided by: Kees Booij
Royal Netherlands Institute for Sea Research



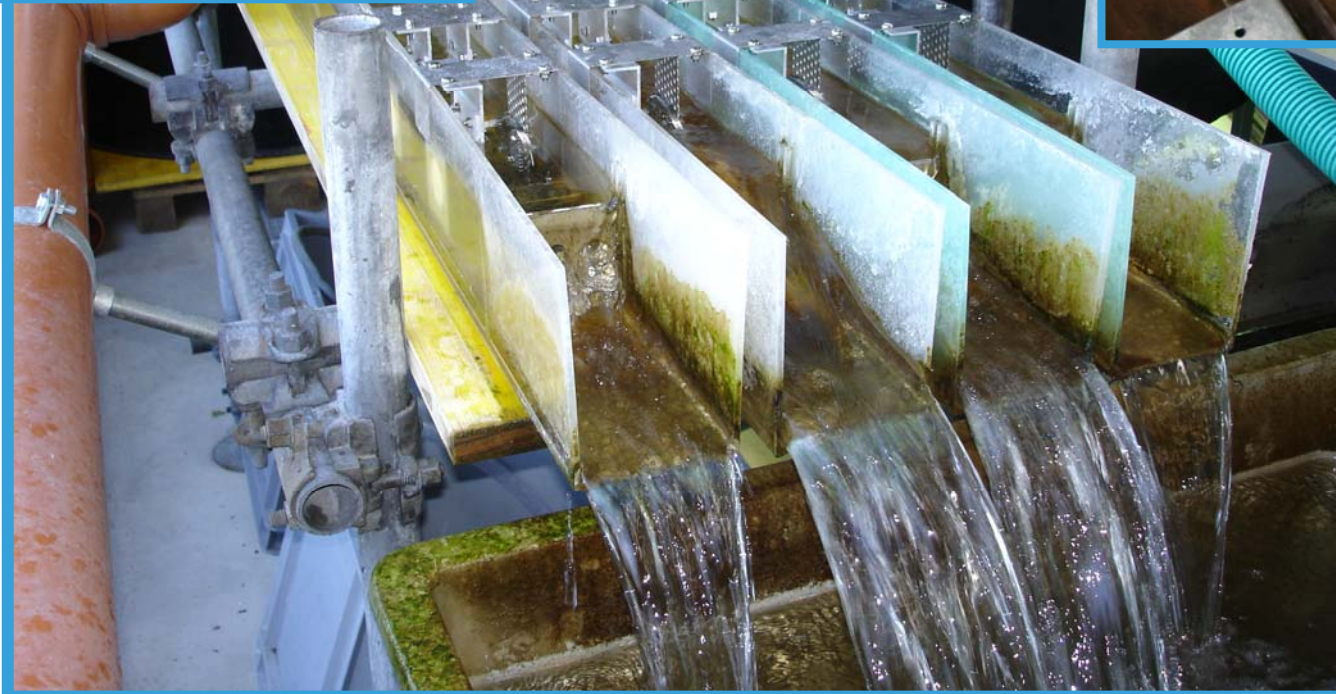
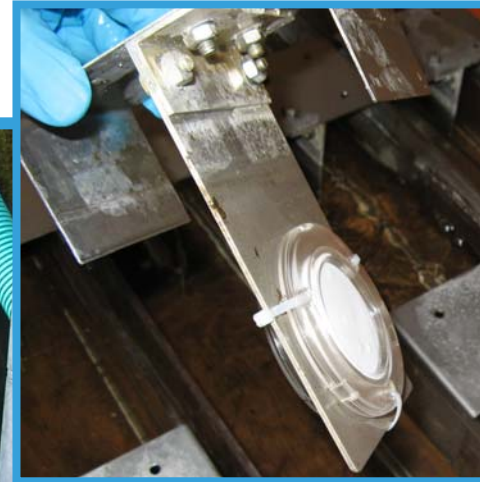
Channel system set-up

Vermeirssen et al. 2008 J. Environ. Monit. 10



Environmental conditions

Vermeirssen et al. 2008 J. Environ. Monit. 10



Channel system running with effluent

Vermeirssen et al. 2008 J. Environ. Monit. 10

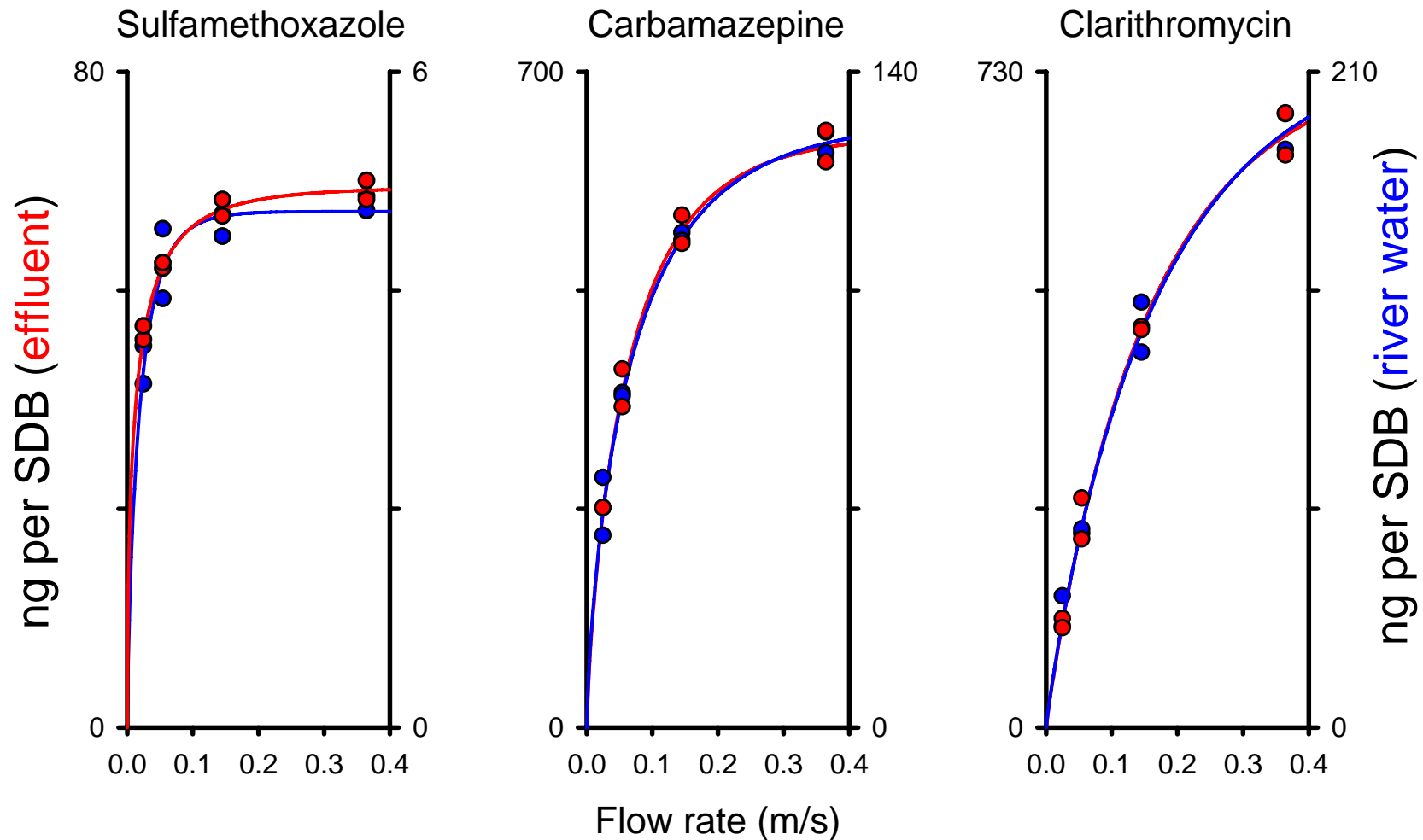


Three pharmaceuticals in two matrices

Empore SDB-RPS disks

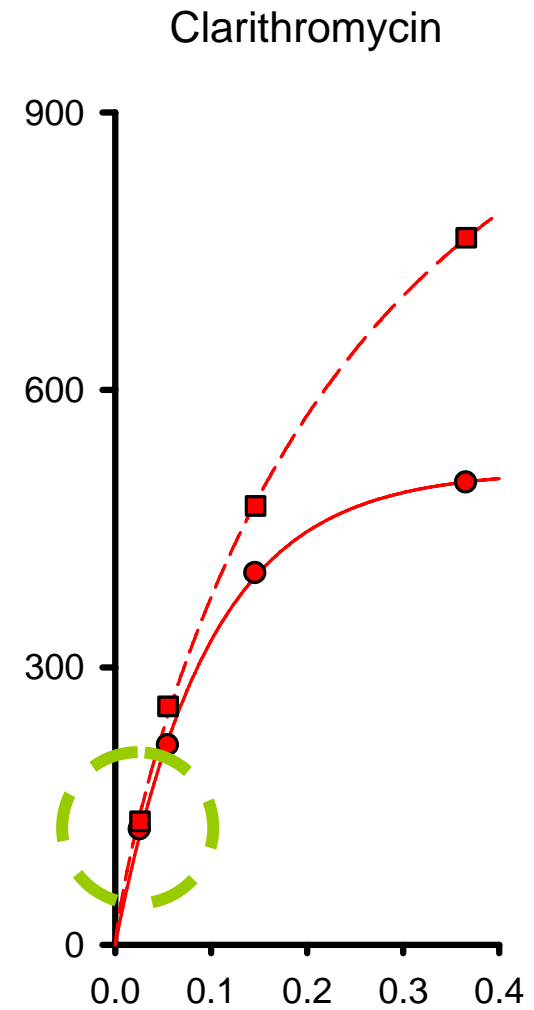
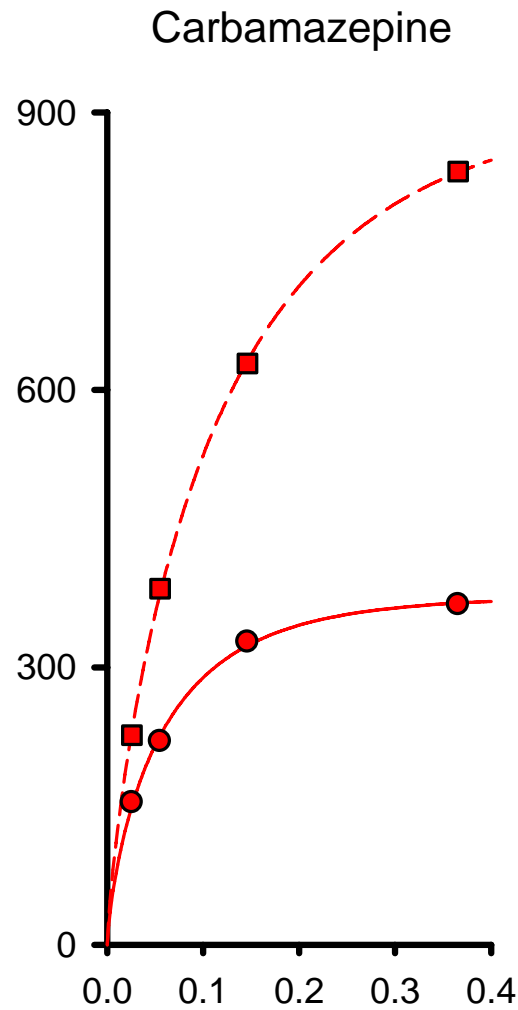
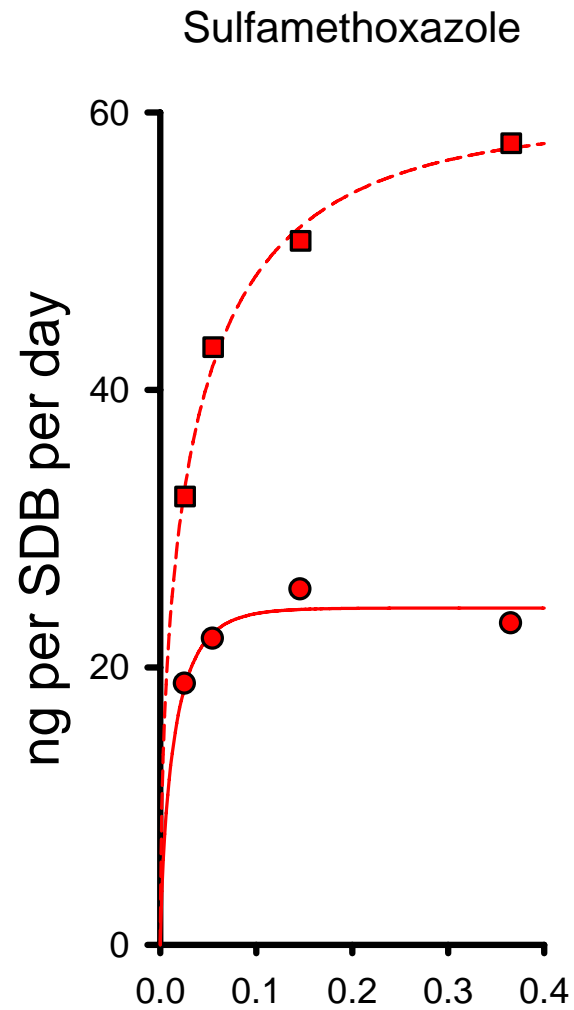
Vermeirssen et al. 2008 J. Environ. Monit. 10

Salinity: Togola & Budzinski 2007 AC 79



Three pharmaceuticals; overlapping exposure slots

Vermeirssen et al. 2008 J. Environ. Monit. 10

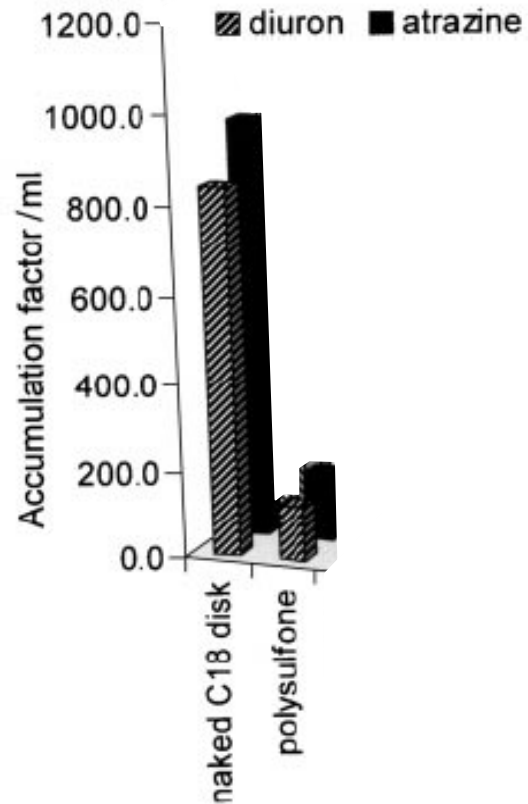


Extending the integrative sampling window

Cover the Empore disk
with a **membrane**

Explore Empore **SDB-XC**

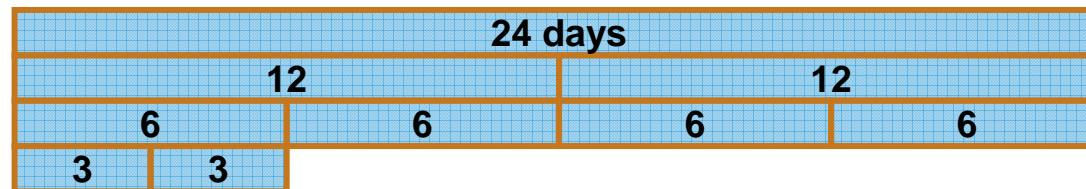
Gunold et al. 2008 Env. Pollut. 155
Approximate linear uptake for 12 days



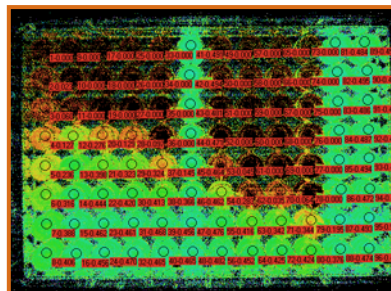
Kingston et al. 2000 J. Env. Monit. 2 Figure 2
see also Tran et al. 2007 ET&C 26

Three experiments

1. 5 day flow rate trials with **SDB-RPS** and **SDB-RPS-PES** (polyethersulfone)
2. 5 day flow rate trials with **SDB-RPS** and **SDB-XC**
3. overlapping sampling blocks with all three configurations at 0.1 m/s

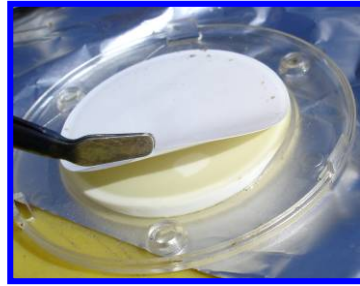
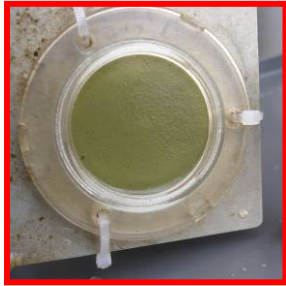


Combined bioanalysis and chemical analysis

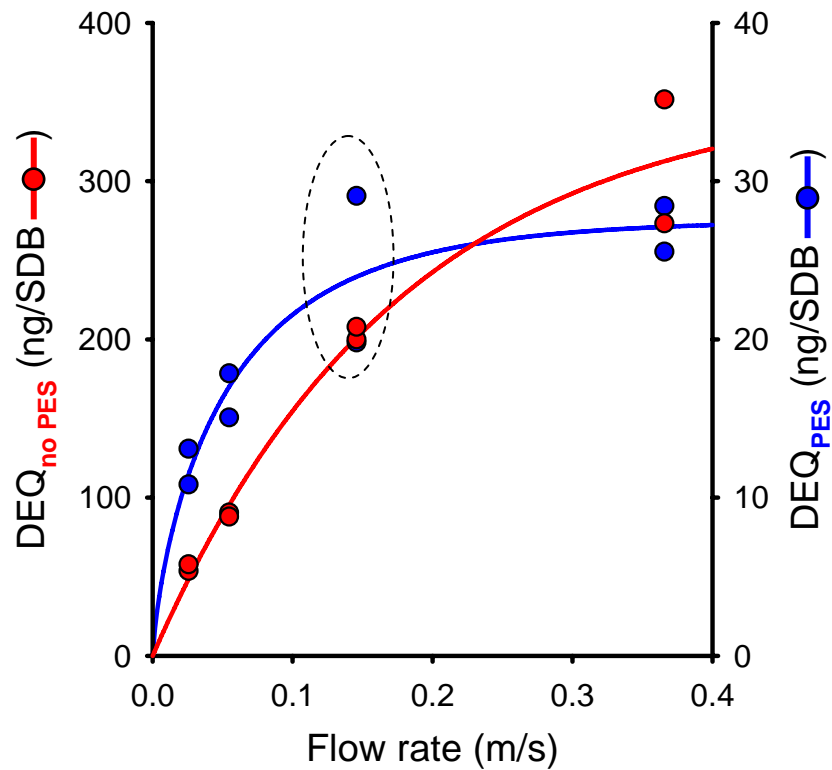


Adding a PES membrane

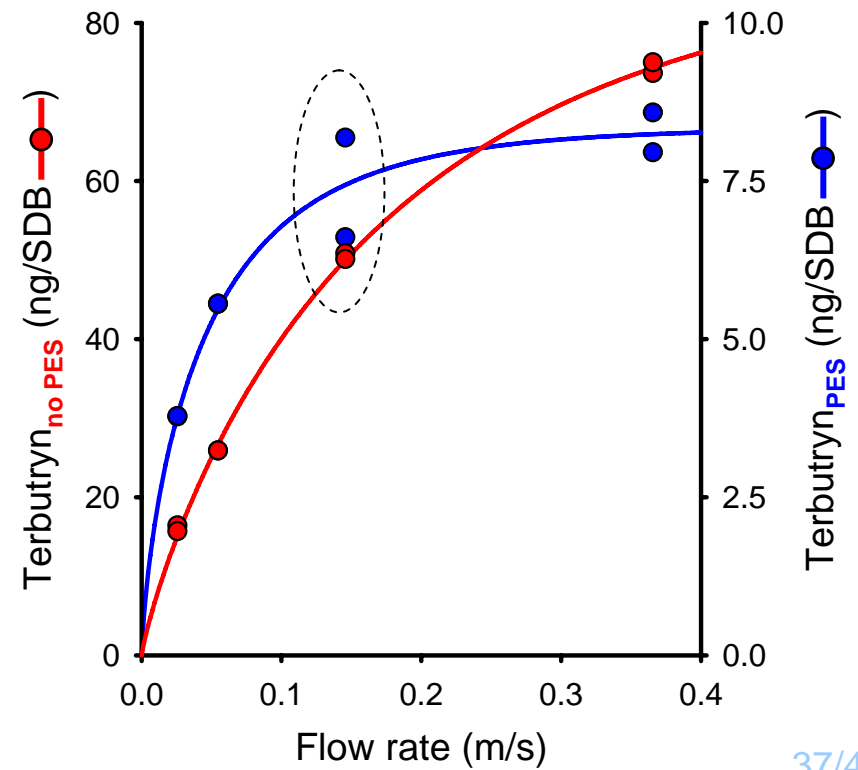
Vermeirssen et al. 2008 Wat. Res. 43



Diuron equivalents

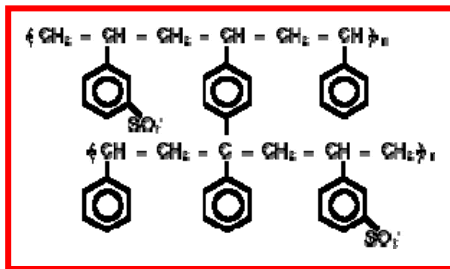


Terbutryn



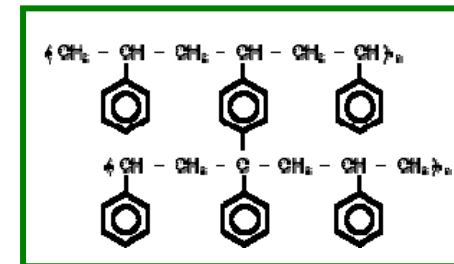
Comparing RPS and XC

Vermeirssen et al. 2008 Wat. Res. 43



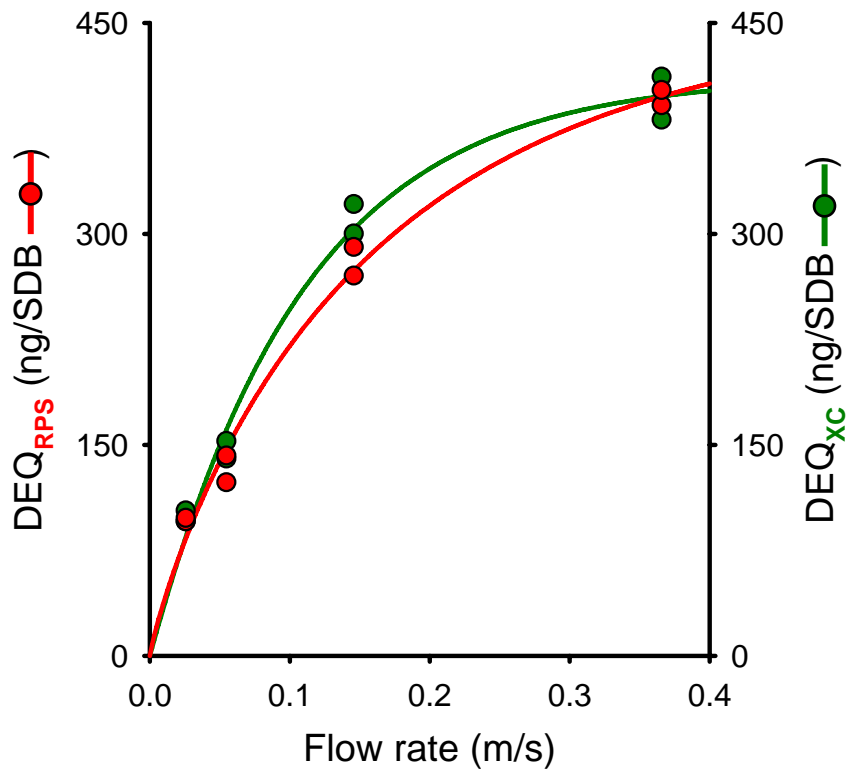
RPS

sulfonic acid groups

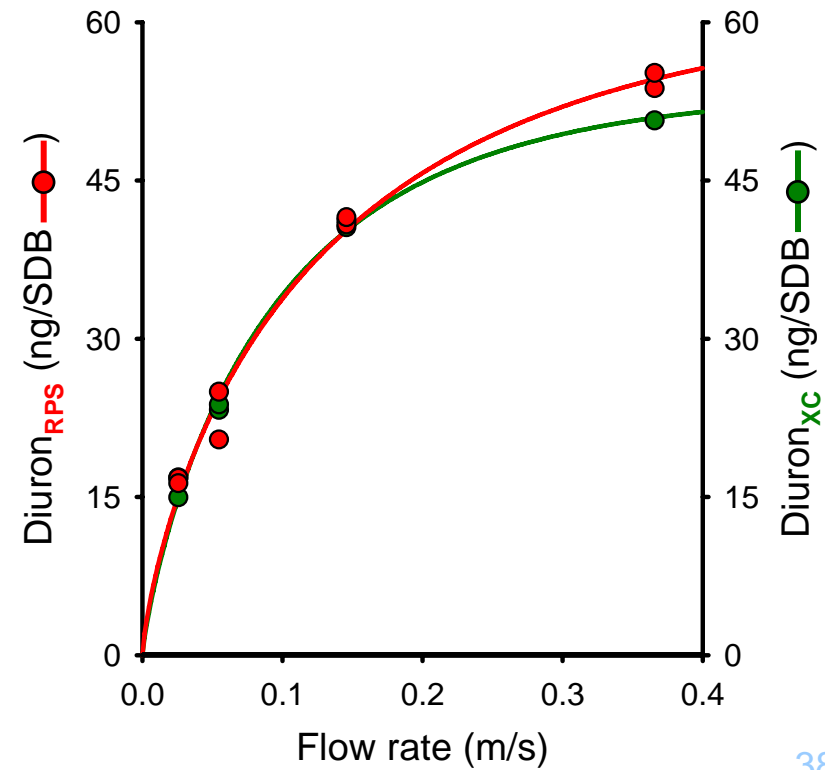


XC

Diuron equivalents

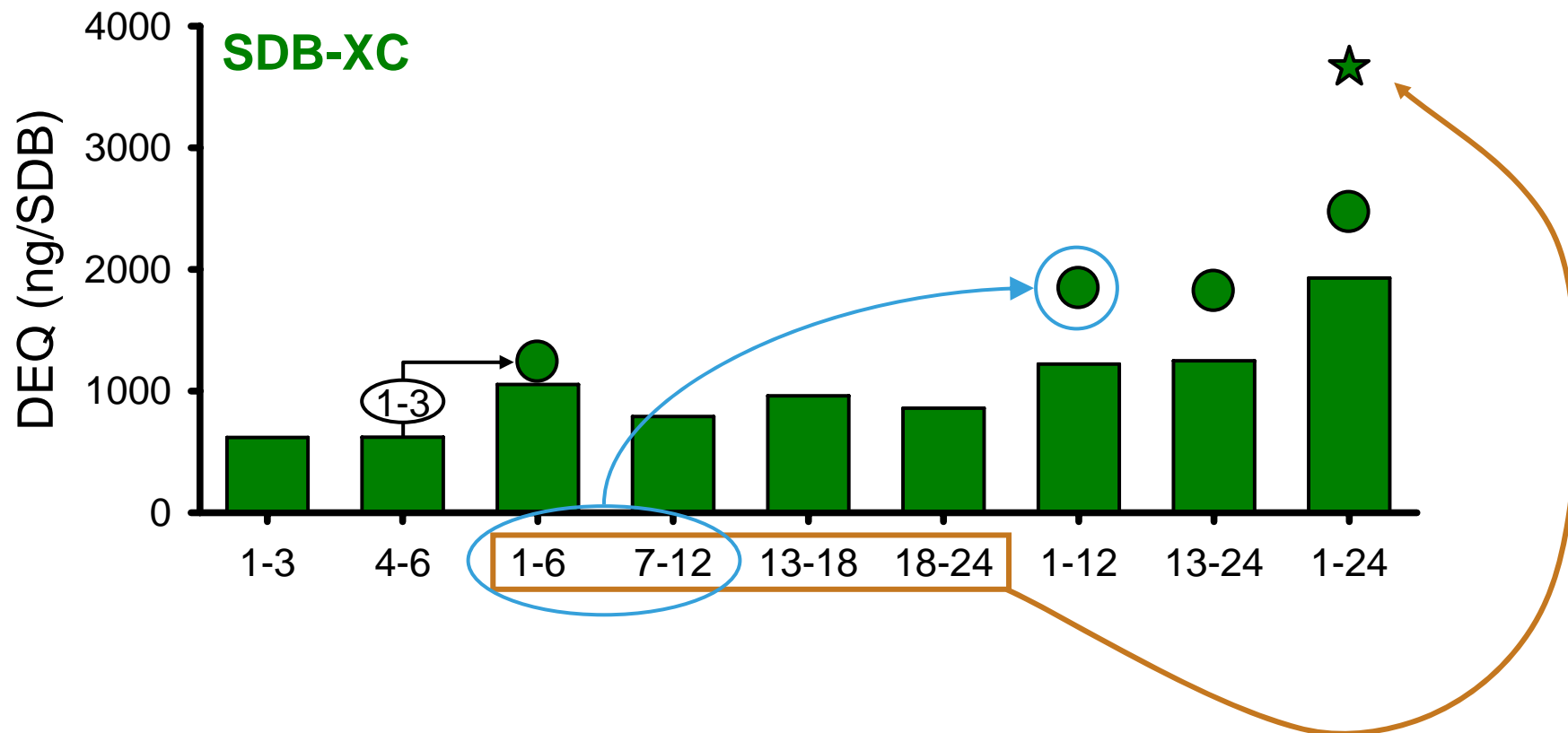


Diuron



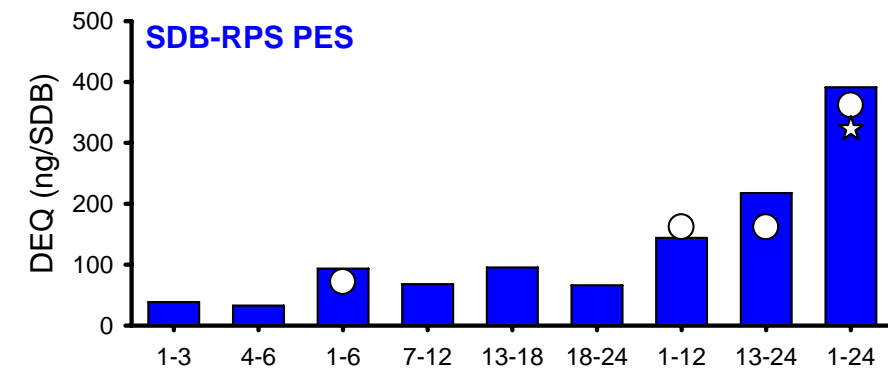
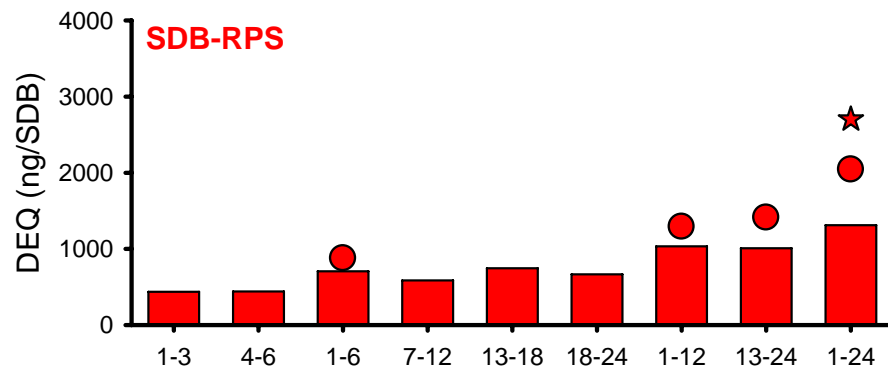
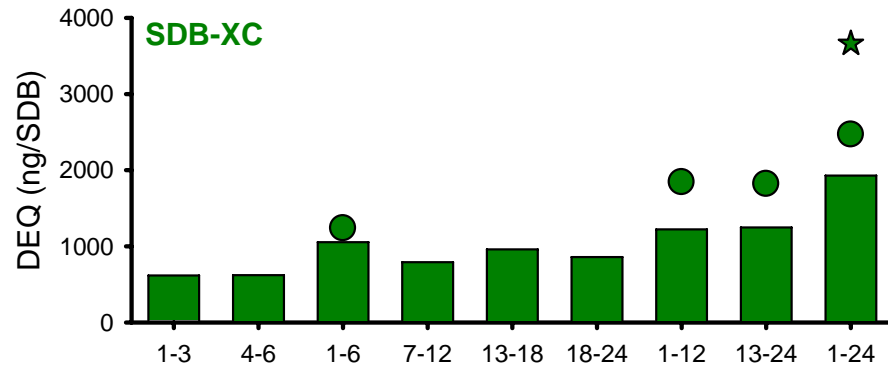
Duration of integrative period

Vermeirssen et al. 2008 Wat. Res. 43

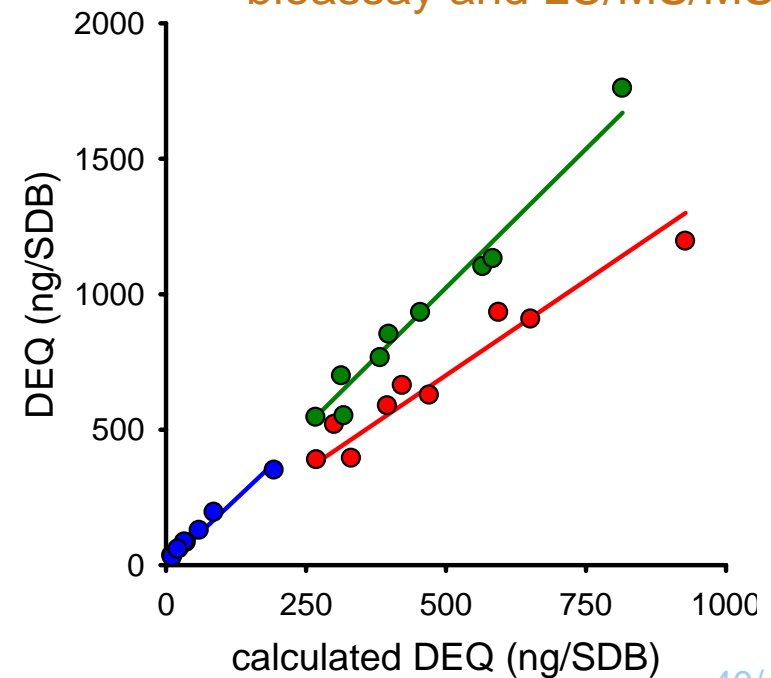


Three Chemcatcher configurations – 24 days

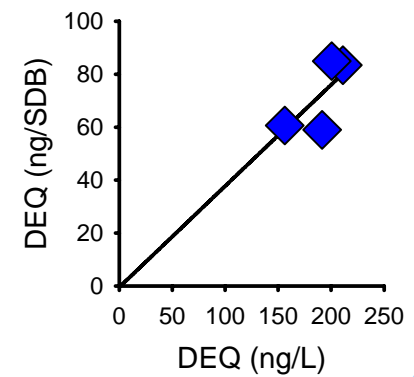
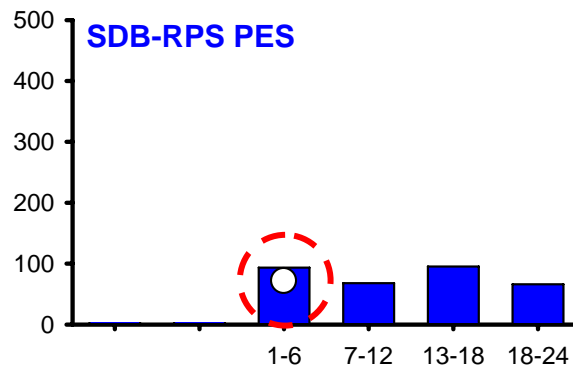
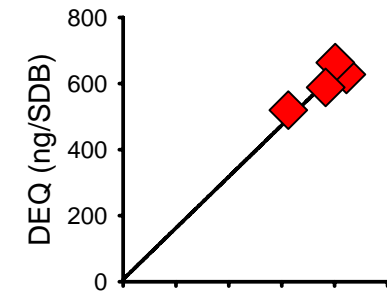
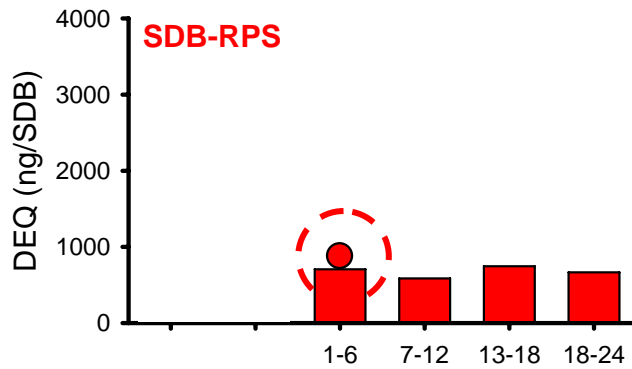
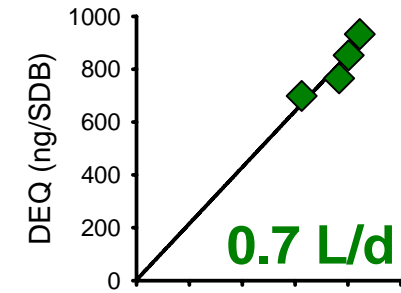
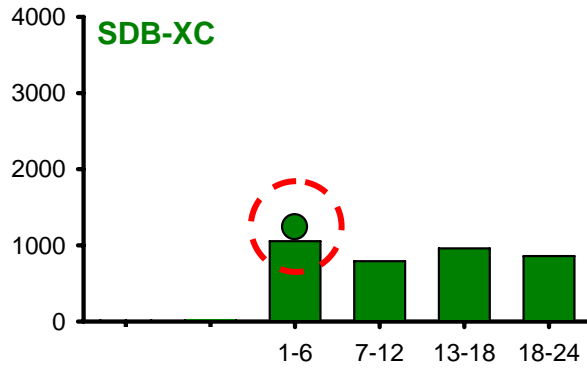
Vermeirssen et al. 2008 Wat. Res. 43



Again, a good association between bioassay and LC/MS/MS



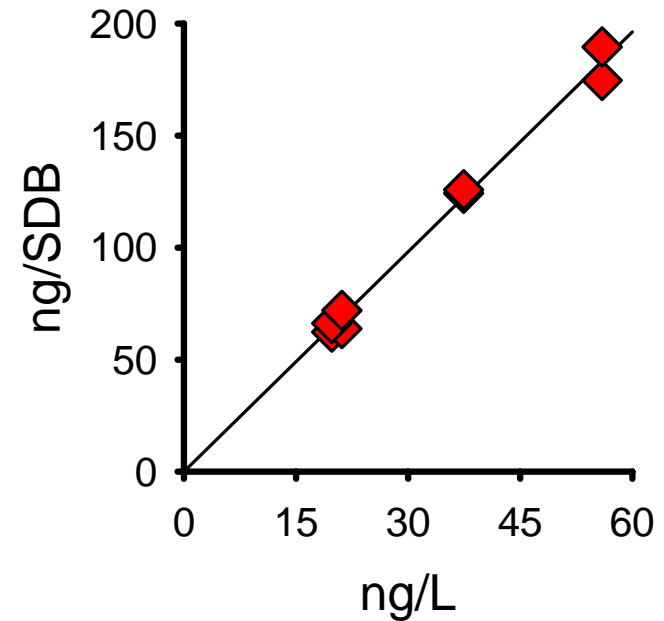
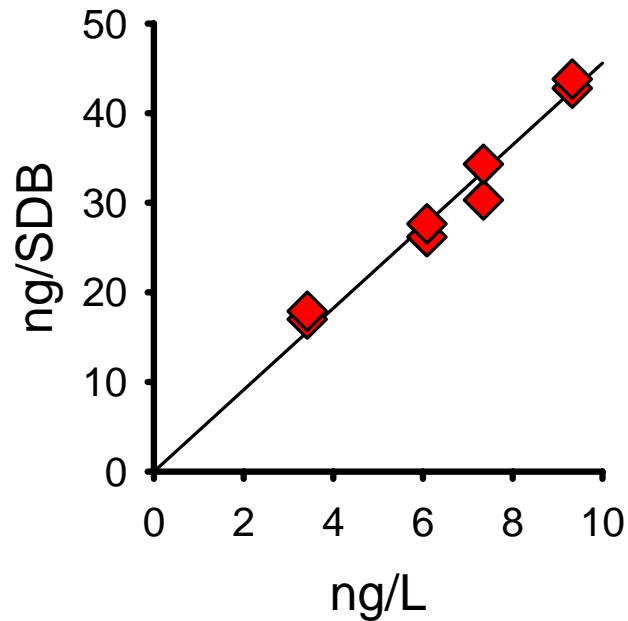
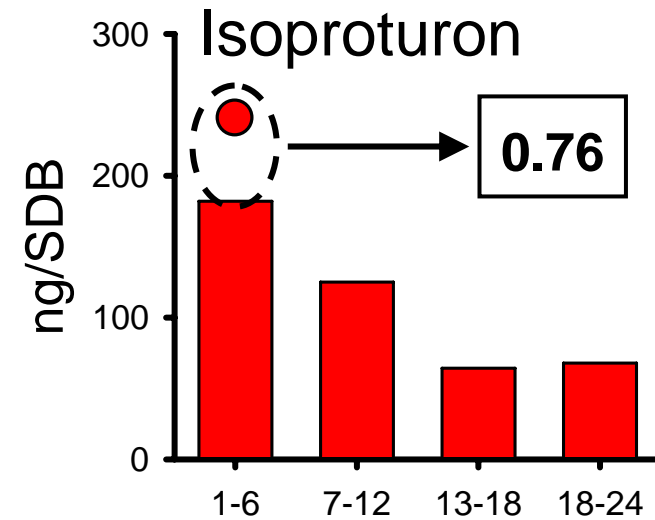
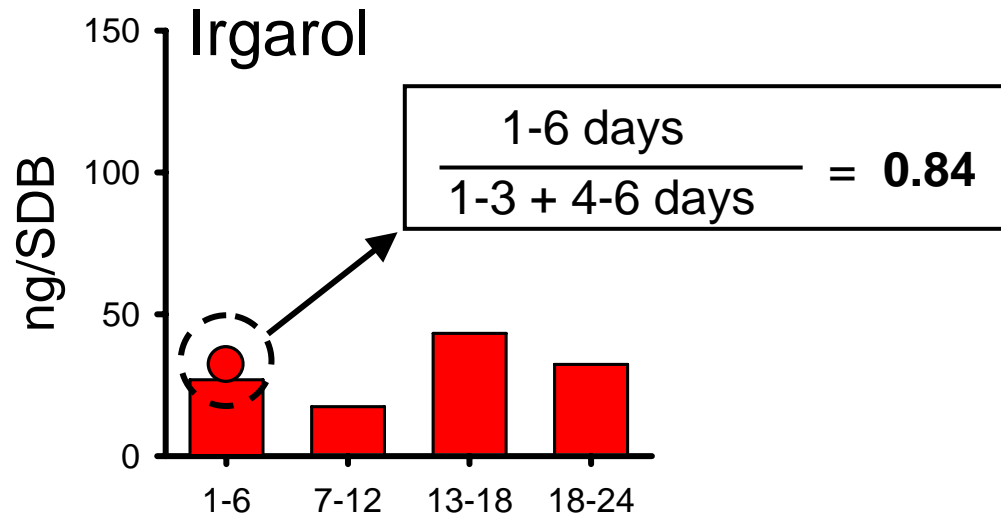
Estimating sampling rates



4 times a 6 day water sample

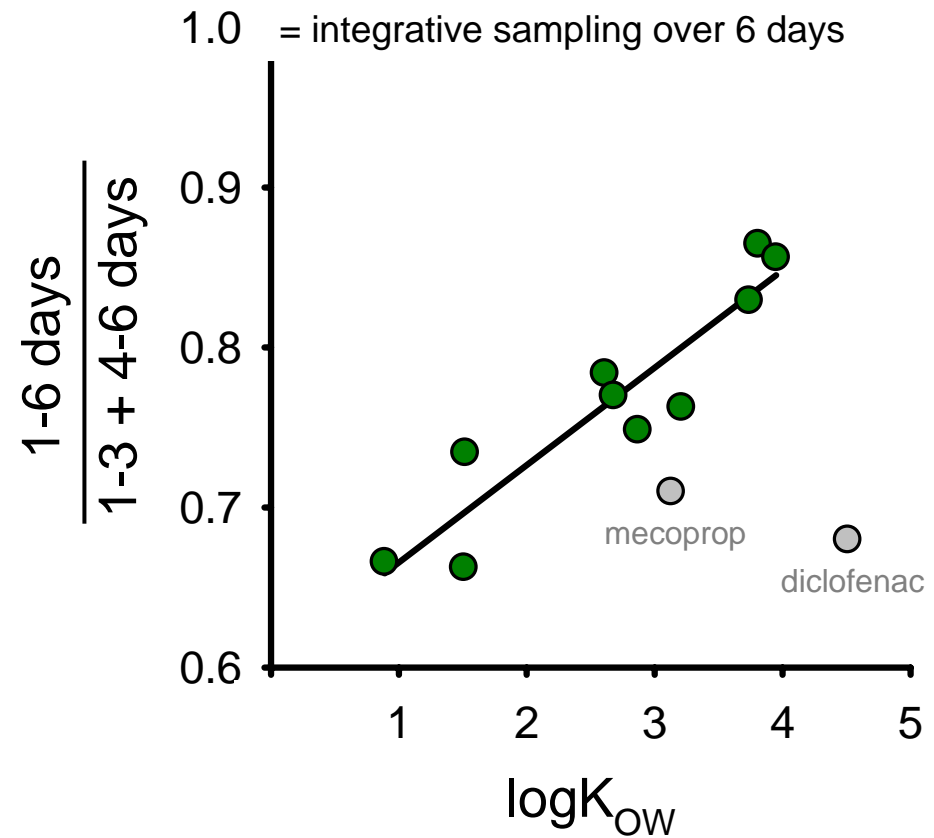
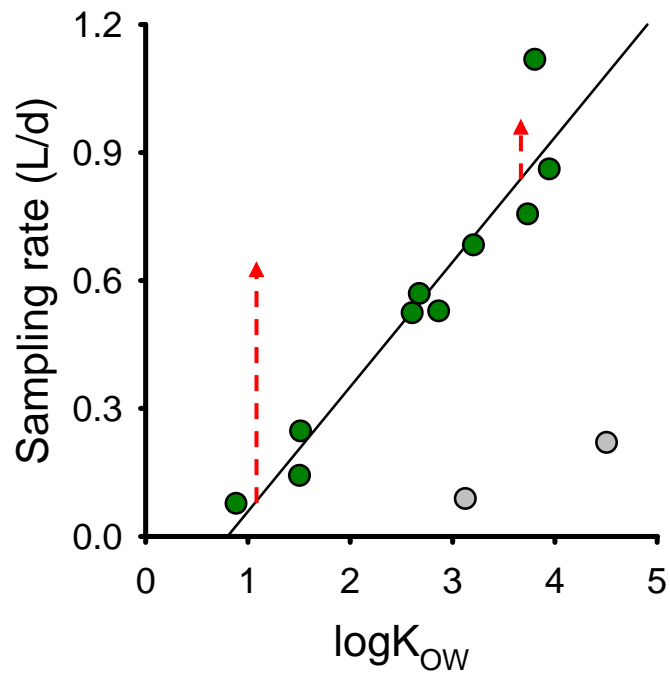
An integrative ratio

Vermeirssen et al. 2008 Wat. Res. 43

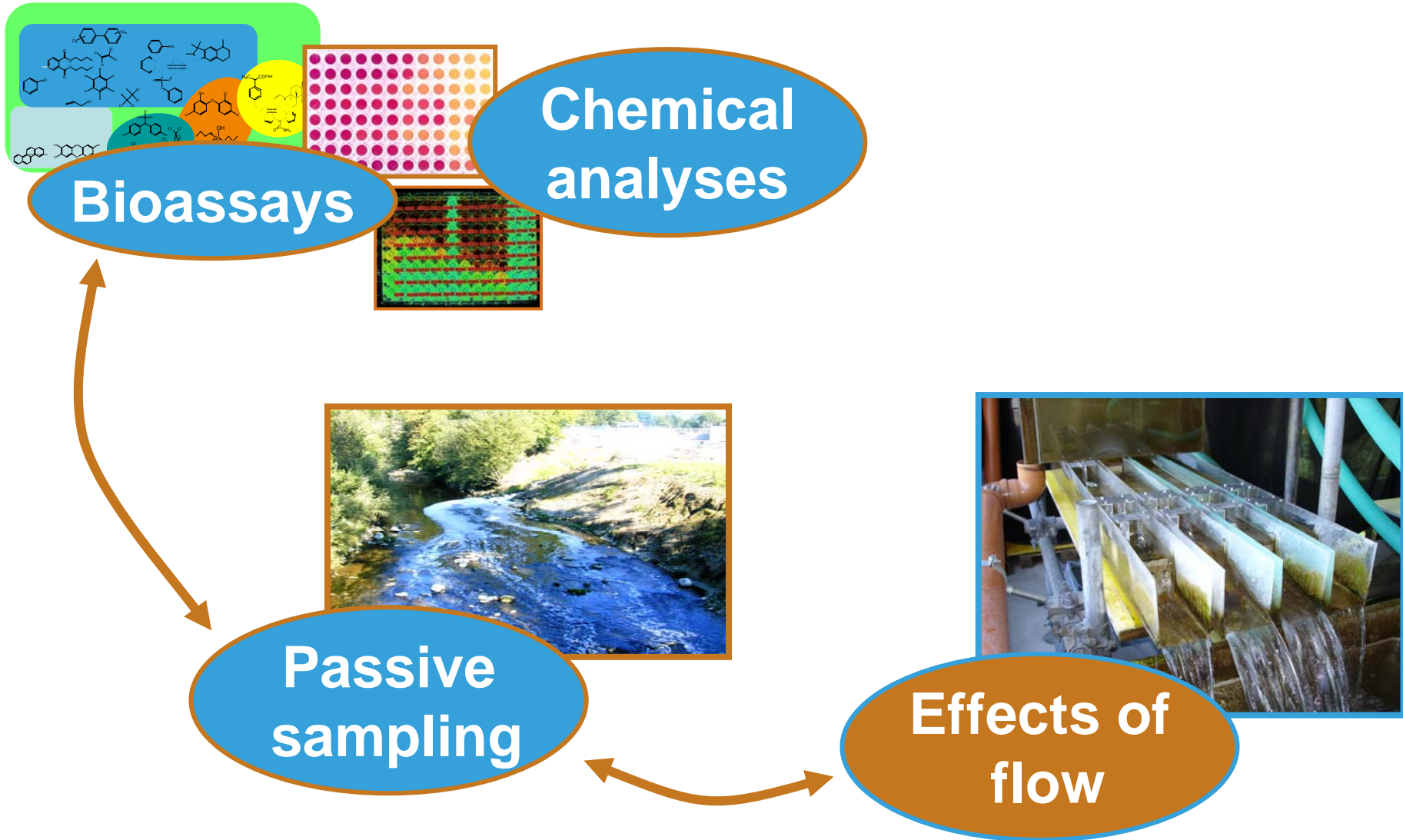


Sampling properties and logK_{OW}

Vermeirssen et al. 2008 Wat. Res. 43



Summary



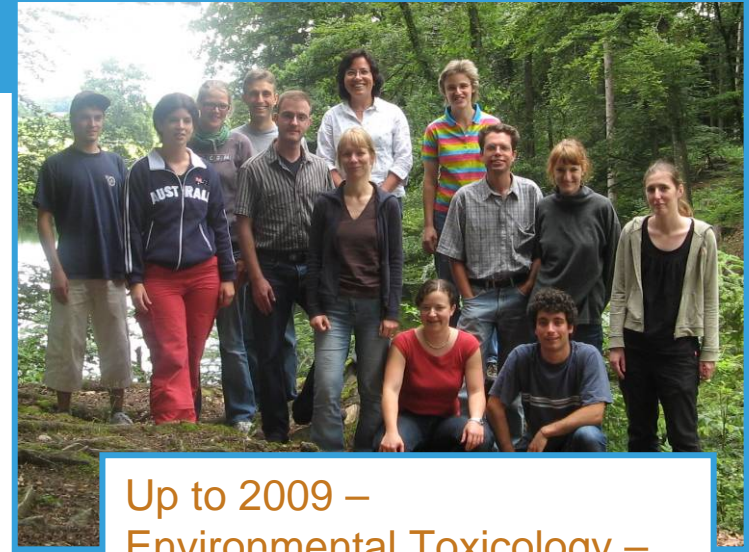
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Up to 2009 –
Environmental Toxicology –
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Since January 2009 –
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Juliane Hollender

Thank you for your
attention!

