



NORMAN Interlaboratory study (ILS) on
passive sampling of emerging pollutants
Study results:
pharmaceuticals and polar pesticides

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STUDY REALISATION

Pre-screening for presence of contaminants: Pharmaceuticals



Sampler: POCIS; 18.6.-2.7.2010; 18.6.-2.7.2010

Analysed by: University of Bordeaux1

pg/sampler

	Blank POCIS - 1 ng	Blank POCIS - 2 ng	Blank POCIS - 3 ng	Exposed POCIS 1 ng	Exposed POCIS 2 ng	Exposed POCIS 3 ng
Aspirine	0.00	0.00	0.00	14.66	2.79	27.08
Ibuprofene	0.00	0.00	0.00	58.84	60.37	0.00
Naproxene	0.00	0.00	0.00	201.64	197.48	238.96
Gemfibrozil	0.00	0.00	0.00	8.90	0.77	0.79
Ketoprofene	0.00	0.00	0.00	249.07	214.96	245.95
Diclofenac	0.37	0.00	0.00	487.09	547.69	533.99
Paracetamol	0.00	0.00	0.00	0.00	0.00	0.00
Théophylline	1.89	2.18	1.25	25.31	9.95	13.30
Cafeine	9.13	8.94	5.57	21.25	10.54	22.97
Terbutaline	0.86	0.81	0.95	0.00	2.10	1.52
Carbamazépine	0.19	0.09	0.03	447.08	466.47	453.73
Salbutamol	0.02	0.03	0.03	9.30	0.76	0.87
Nordiazepam	0.00	0.00	0.00	23.55	17.67	16.55
Clenbuterol	0.00	0.00	0.00	0.00	0.00	0.00
Amitriptiline	0.00	0.00	0.00	21.53	10.63	9.53
Doxepine	0.00	0.00	0.00	2.48	0.39	0.34
Imipramine	0.01	0.00	0.00	4.57	0.17	0.17
Diazepam	0.06	0.03	0.02	10.11	5.37	4.66
Alprazolam	0.00	0.00	0.00	25.84	7.17	6.15
Fluoxetine	0.00	0.00	0.00	0.11	2.75	2.47
Bromazepam	0.00	0.00	0.00	24.06	10.03	7.82

Pre-screening for presence of contaminants: Polar pesticides



Sampler: POCIS; 18.6.-2.7.2010; 18.6.-2.7.2010

Analysed by: Irstea Bordeaux

ng/POCIS	Blank 1	Blank 2	BRNO 1	BRNO 2
Acetochlore	<LOQ	<LOQ	5	5
Alachlore	<LOQ	<LOQ	0	0
Atrazine	<LOQ	<LOQ	29	13
Azoxystrobine	<LOQ	<LOQ	<LOQ	<LOQ
Carbaryl	<LOQ	<LOQ	25	25
Carbendazime	<LOQ	<LOQ	30	27
Carbofuran	<LOQ	<LOQ	<LOQ	<LOQ
Carbofuran-3-hydroxy	<LOQ	<LOQ	0	0
Chlorfenvinphos	<LOQ	<LOQ	<LOQ	<LOQ
Chlorpyrifos	<LOQ	<LOQ	0	0
Chlortoluron	<LOQ	<LOQ	<LOQ	<LOQ
DCPMU	<LOQ	<LOQ	<LOQ	<LOQ
DCPU	<LOQ	<LOQ	26	23
DEA	<LOQ	<LOQ	40	36
DET	<LOQ	<LOQ	17	16
DIA	<LOQ	<LOQ	<LOQ	<LOQ
Dimethoate	<LOQ	<LOQ	0	0
Dimetomorph	<LOQ	<LOQ	5	5
Diuron	<LOQ	<LOQ	122	151
Hexazinone	<LOQ	<LOQ	<LOQ	<LOQ
IPPMU	<LOQ	<LOQ	<LOQ	<LOQ
IPPU	<LOQ	<LOQ	0	0
Irgarol	<LOQ	<LOQ	0	0
Isoproturon	<LOQ	<LOQ	5	5
Linuron	<LOQ	<LOQ	<LOQ	<LOQ
Metazachlore	<LOQ	<LOQ	<LOQ	<LOQ
Methomyl	<LOQ	<LOQ	0	0
Metolachlore	<LOQ	<LOQ	87	78
Metoxuron	<LOQ	<LOQ	0	0
Pyrimicarb	<LOQ	<LOQ	15	18
Simazine	<LOQ	<LOQ	13	11
Terbutylazine	<LOQ	<LOQ	136	127
Thiodicarb	<LOQ	<LOQ	0	0

Pre-screening for presence of contaminants: Polar pesticides + pharmaceuticals

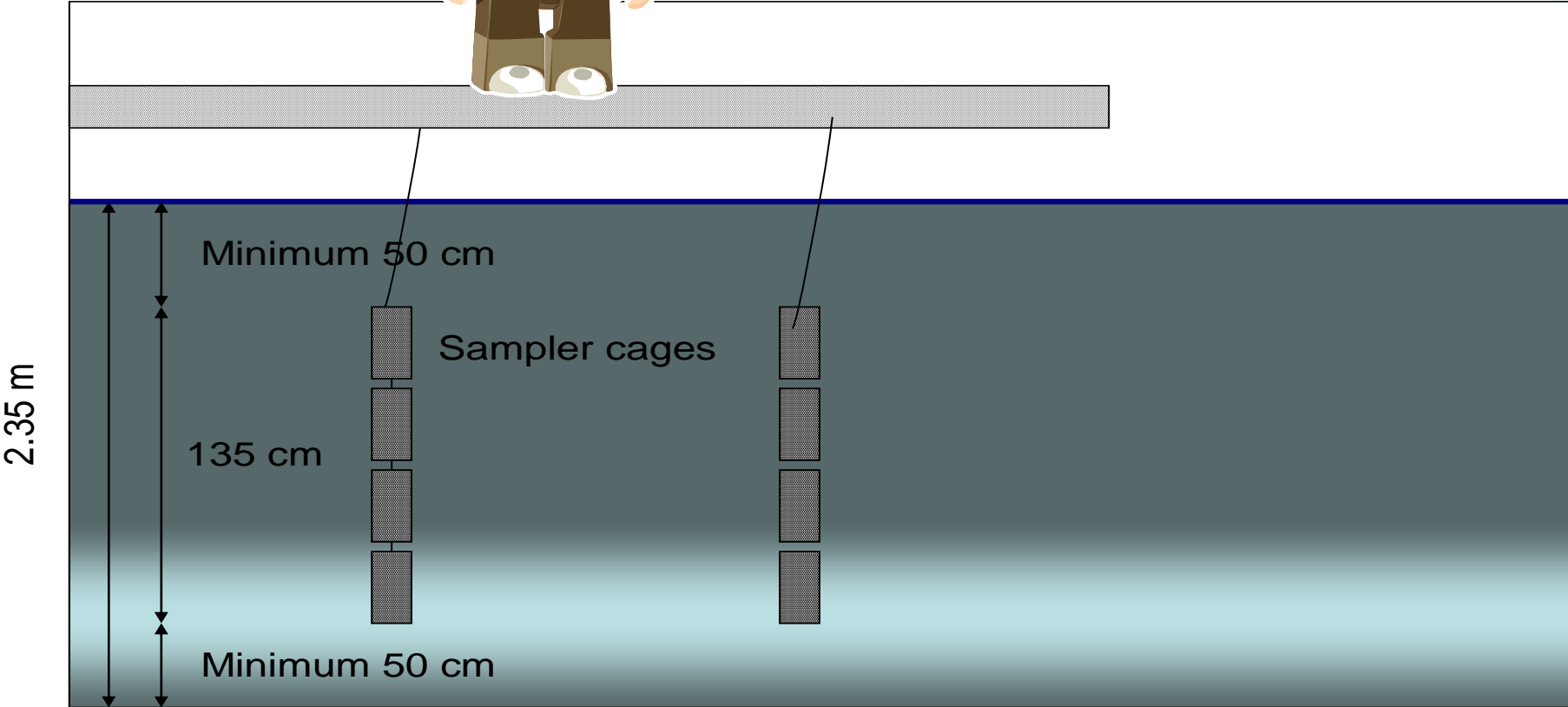
Sampler: SDB-RPS; SDB-RPS-PES
18.6.-2.7.2010; 18.6.-2.7.2010

Analysed by: Eawag



Compound name	RPS ng/disk	RPS-PES ng/disk	Irstea POCIS pharm ng/POCIS	Univ. Bordeaux POCIS pharm ng/POCIS
5-Methyl-Benzotriazole	6,092	3,720		
Atrazine	104	42		
Atrazine-Desethyl	108	54	38	
Atrazine-Desisopropyl	<LOQ	<LOQ	<LOQ	
Atrazine-Hydroxy	13	<LOQ		
Benzotriazole	1,911	2,090		
Caffeine	<LOQ	<LOQ		10
Carbamazepine	2,904	1,074		456
Carbendazim	405	144	28	
Chloridazone	<LOQ	<LOQ		
Diazinon	49	12		
Diclofenac	2,015	700		523
Diuron	511	137	137	
Irgarol	10	3		
Isoproturone	28	9		
Mecoprop	2	3		
Metolachlor	183	51	83	
Phenazone	56	30		
Sufamethoxazole	922	788		
Sulcotrion	<LOQ	<LOQ		
Terbutryn	287	77		
Terbutylazine	318	90	132	

Sampling site: discharge from WWTP Brno-Modřice



Sampler deployment



Sampler deployment



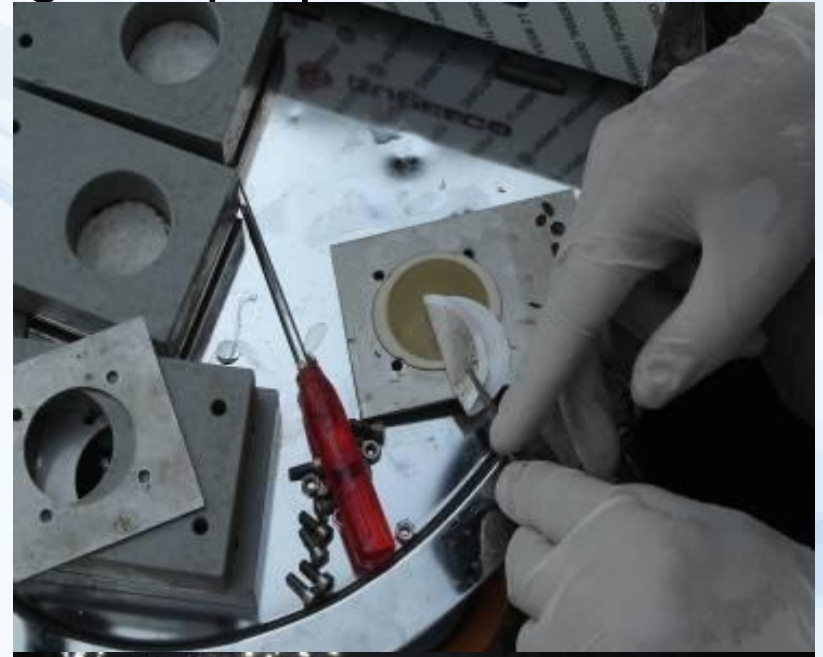
Sampler recovery



Sampler recovery



Onsite sampler cleaning and preparation



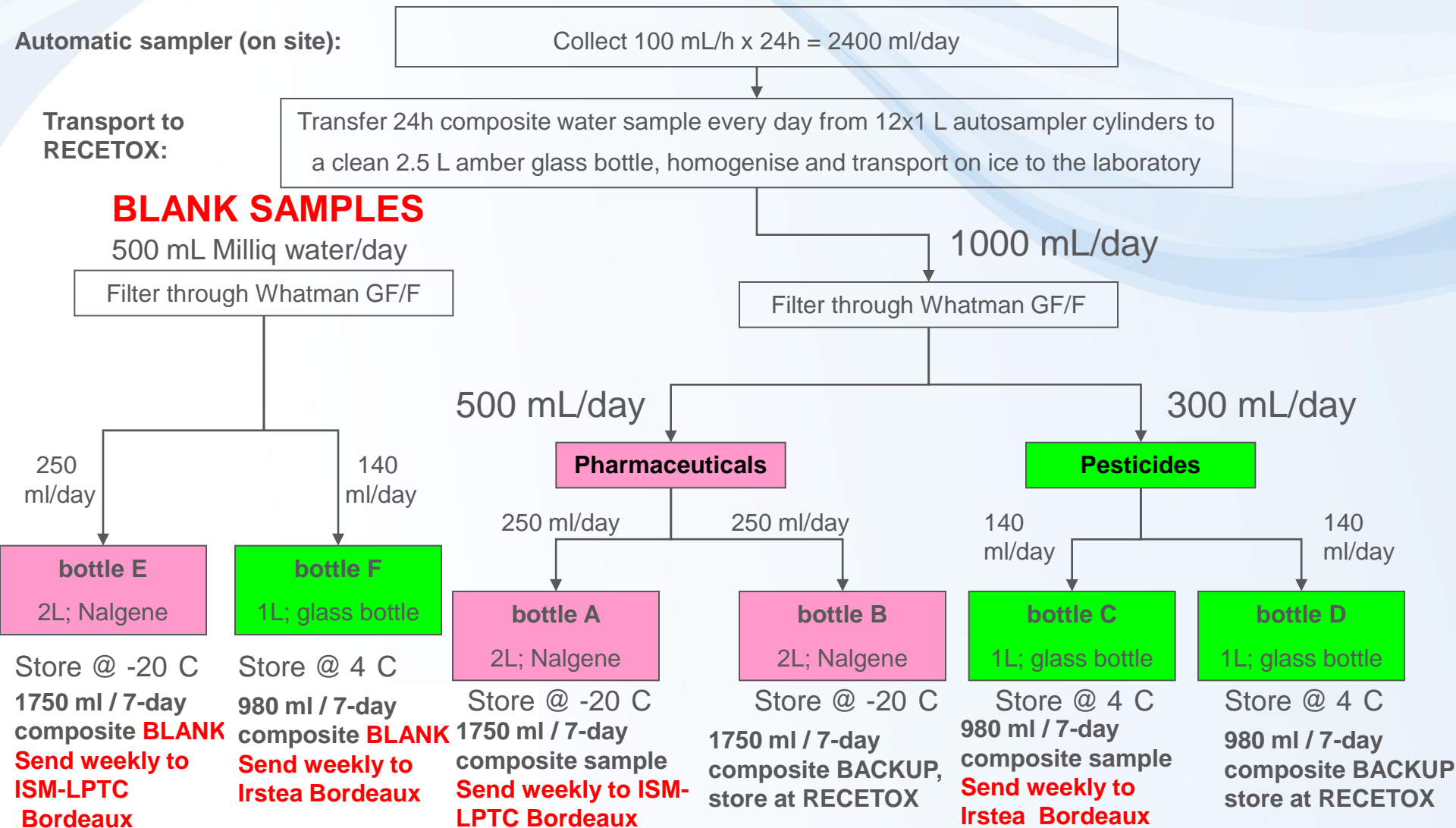
Continuous water sampling



WATER SAMPLING PROTOCOL

pesticides + pharmaceuticals

FIELD SAMPLES



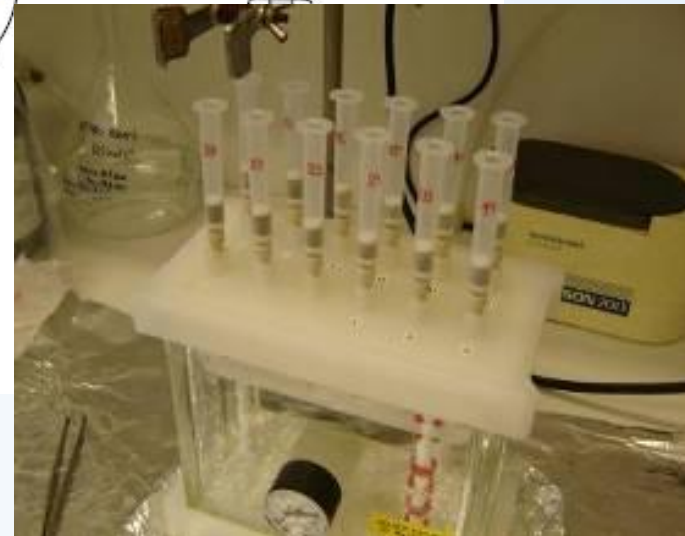
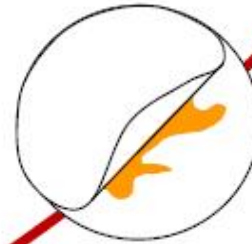
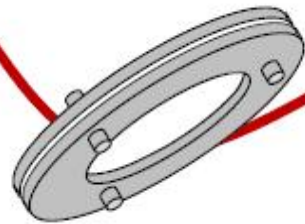
PROVIDED SAMPLER

STANDARD POCIS (pharmaceutical version)

- OASIS HLB Sorbent receiving phase
- Polyethersulphone membrane
- Standard configuration (200 mg sorbent;
45.8 cm² surface area)
- PRC test – DIA-D5 spiked (only
for polar pesticides)



Preparation of provided POCIS samplers for distribution to participants



STUDY RESULTS

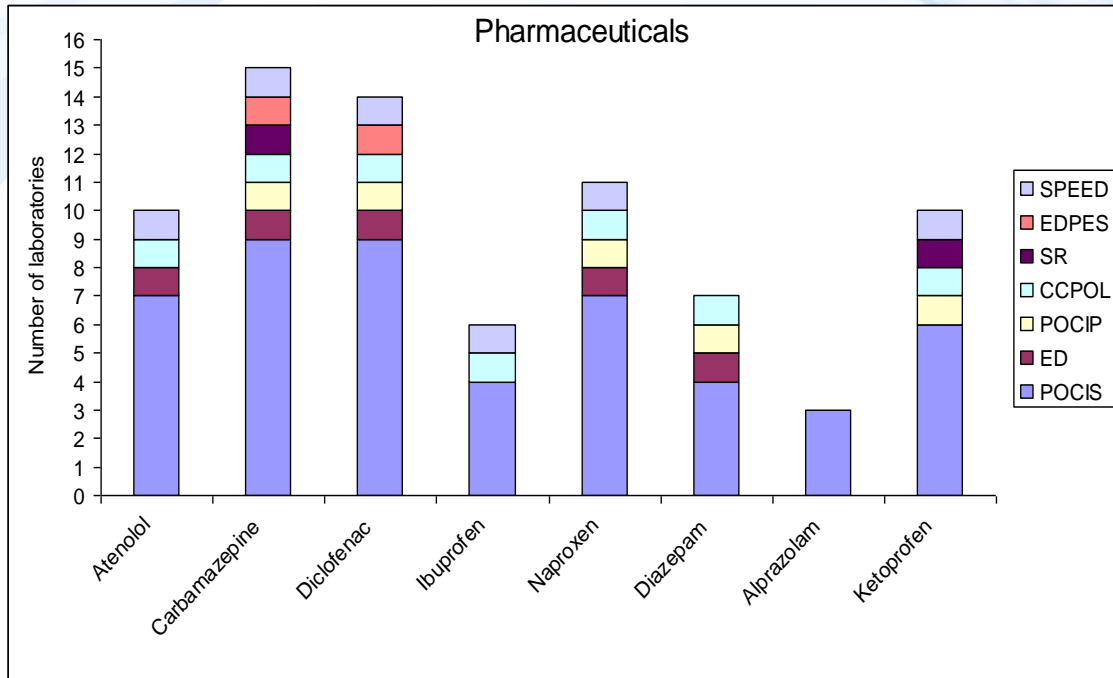
Target compounds PHARMACEUTICALS

Up to 17 participants

	Compound	CAS	Usage
1.	Alprazolam	28981-97-7	benzodiazepine drug
2.	Atenolol	29122-68-7	beta blocker drug
3.	Carbamazepine	298-46-4	anticonvulsant drug
4.	Diazepam	439-14-5	benzodiazepine drug
5.	Diclofenac	15307-86-5	non-steroidal anti-inflammatory drug
6.	Ibuprofen	15687-27-1	non-steroidal anti-inflammatory drug
7.	Naproxen	22204-53-1	non-steroidal anti-inflammatory drug

Pharmaceuticals: Categories of participant samplers

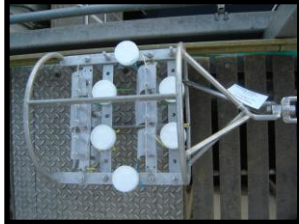
Up to 17 participants



Sampler	Abbreviation
POCIS pharmaceutical version	POCIS
Empore Disk	ED
POCIS, pesticide version	POCIP
Chemcatcher (3rd generation) polar configuration	CCPOL
silicone rubber material	SR
Empore SDB-RPS with PES-Membrane (0.1um)	EDPES
Speedisks	SPEED



POCIS



SPEED
SR



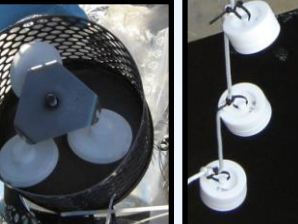
POCIP



EDPES



CCPOL

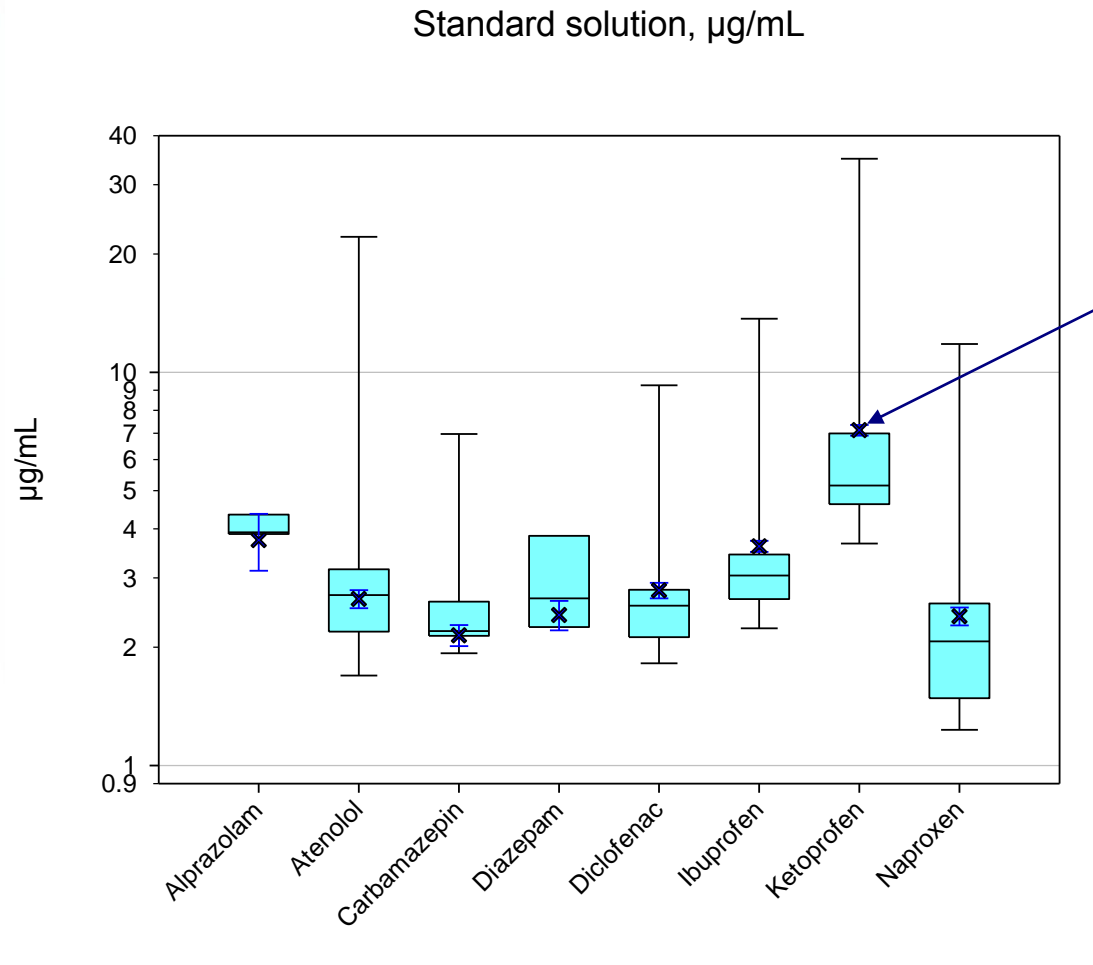


CCPOL



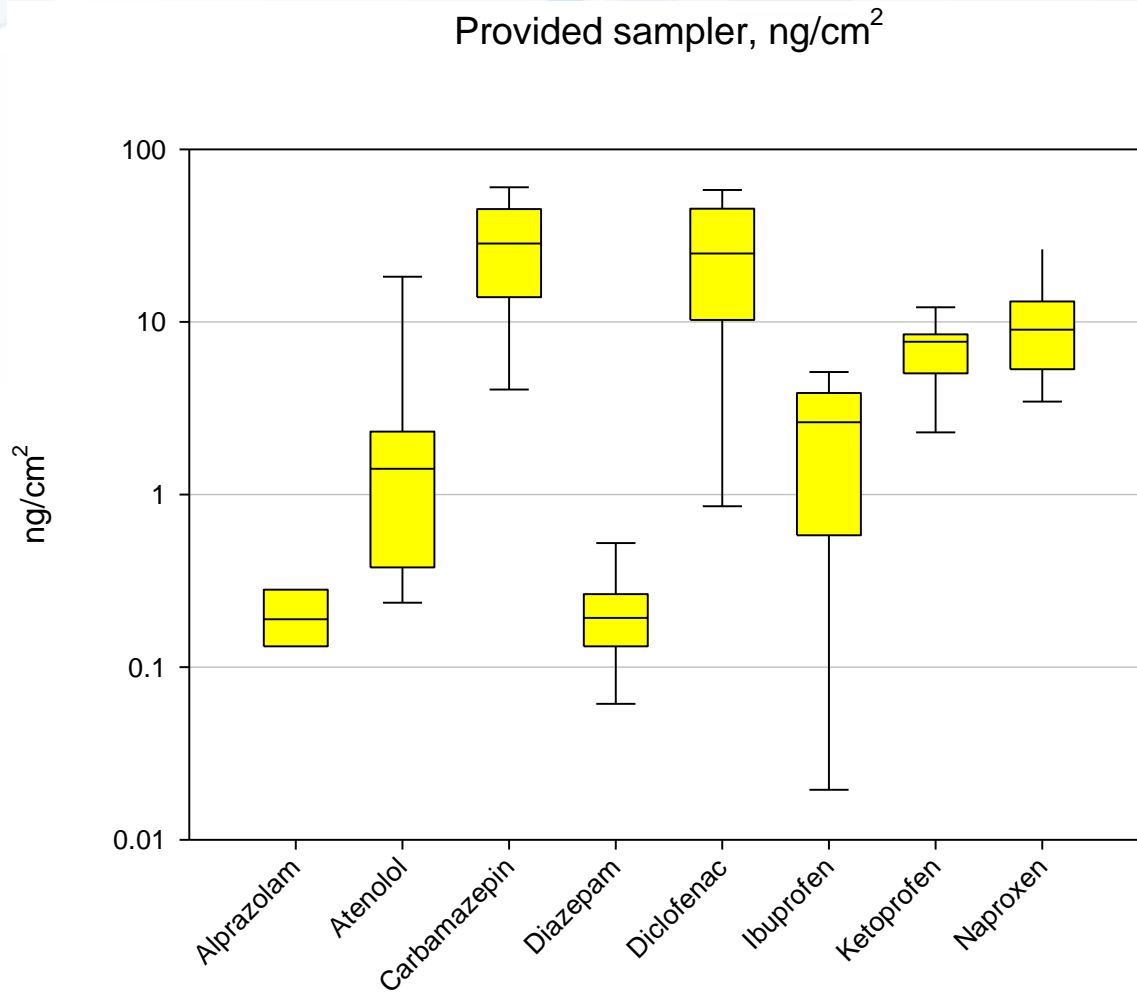
ED

Study results: pharmaceuticals

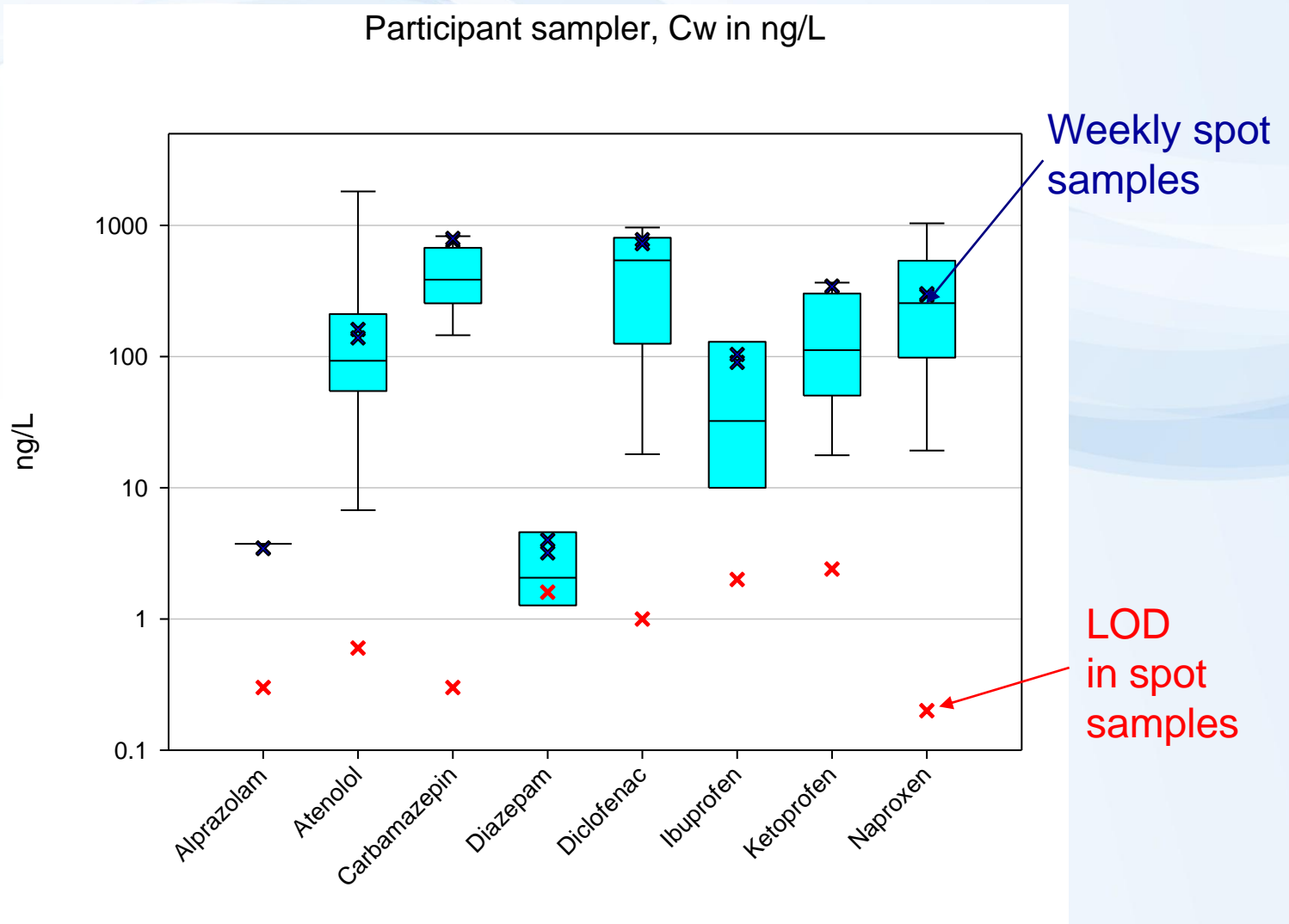


Set value
expanded
uncertainty
($k = 2$)

Study results: pharmaceuticals

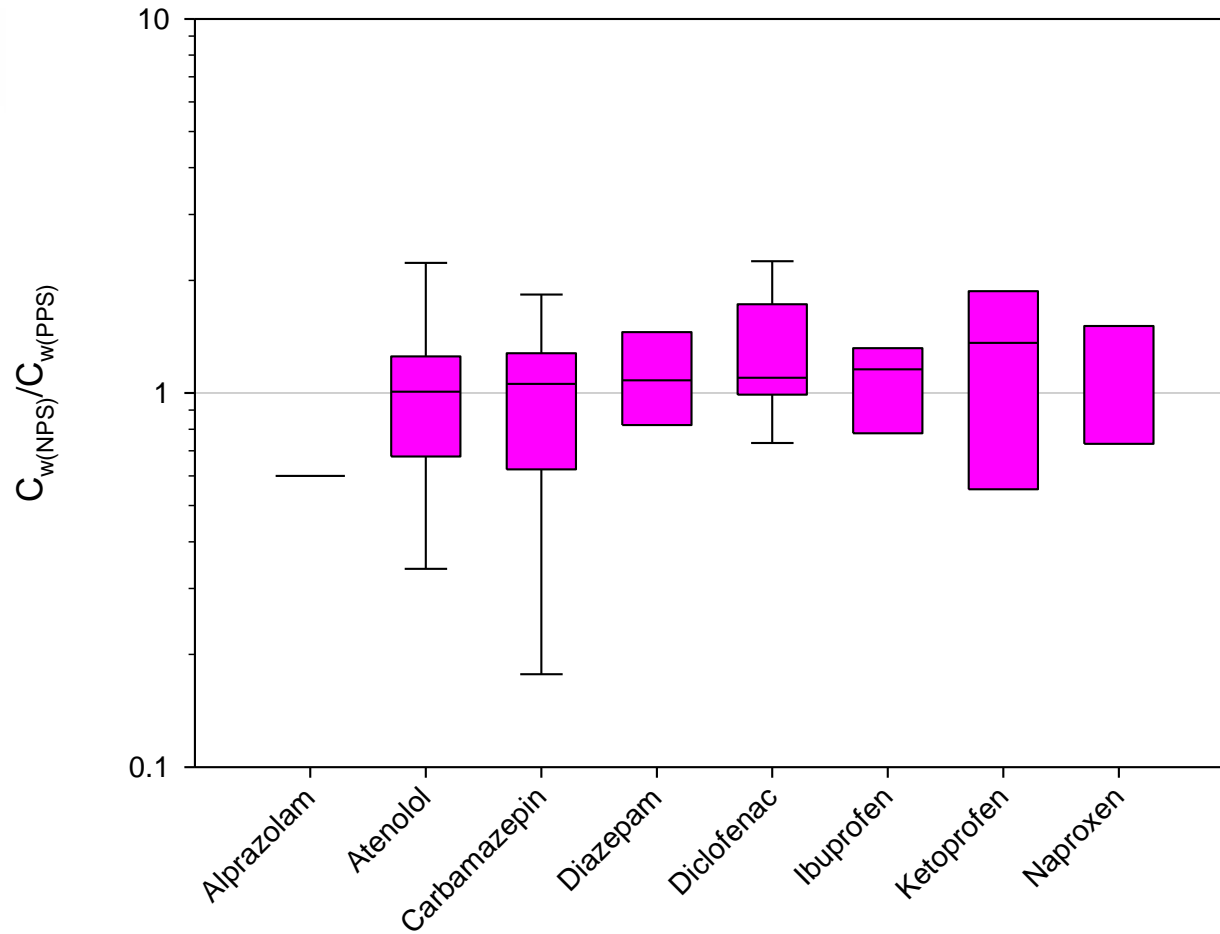


Study results: pharmaceuticals



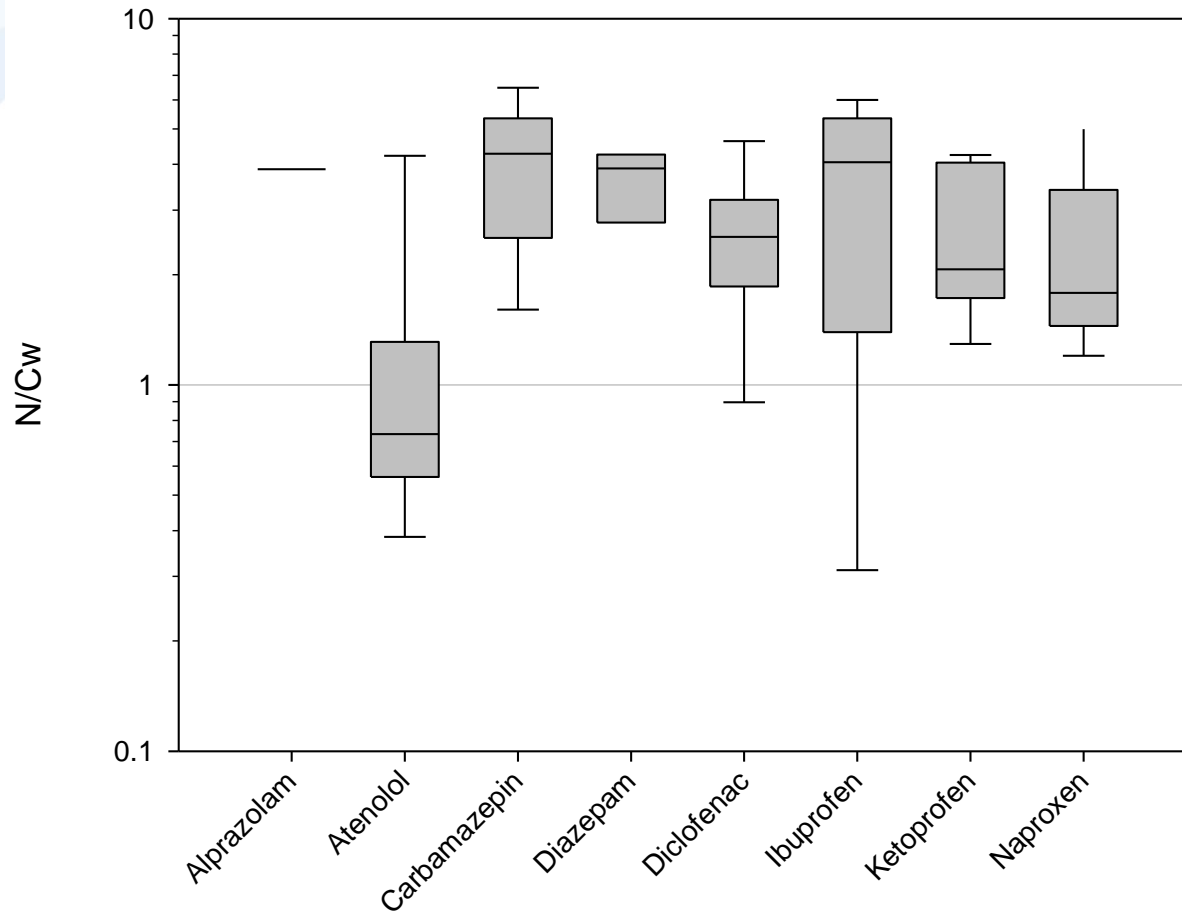
Study results: pharmaceuticals

Ratio of water concentrations provided/participant sampler



Study results: polar pesticides

Provided sampler, N/Cw ratio, L



$$N/C_w = R_s t \quad [L]$$

t = 14 days

RESULTS

Example: Carbamazepin

outliers

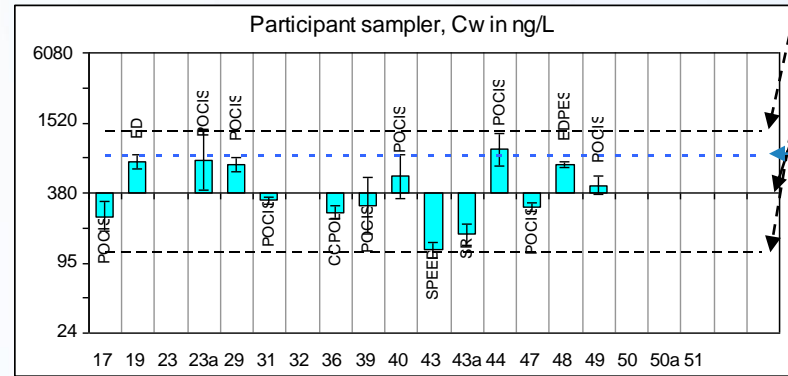
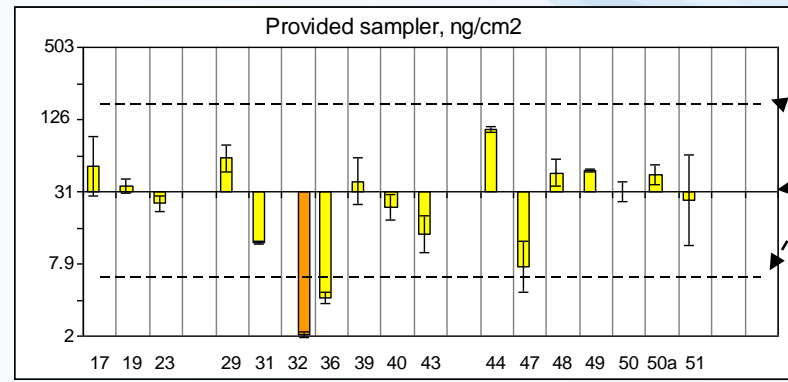
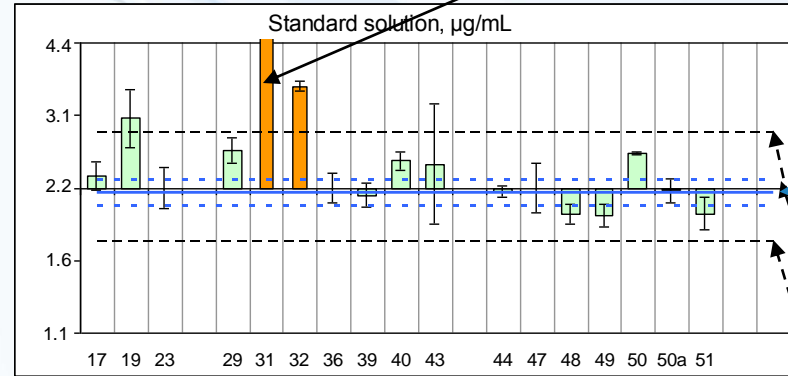
Stand. Solution	µg/mL
Medians	2.20
Standard deviations	1.2
Geomean	2.7
n	17
Outliers	2
Standard deviations excl. outliers	0.28
Refvalue	2.14
Exp. Unc	0.13

Provided Sampler uptake	ng/cm2
Medians	31.4
Standard deviations	32
Geomean	23
n	17
Outliers	1
Standard deviations excl. outliers	26

Participant Sampler	Cw
ng/L	
Medians	380
Standard deviations	230
GeomMean	386
n	14
Outliers	0

Spot samples	
Period 1	778
Period 2	794

Log₂ scale



Set value expanded Uncertainty (k = 2)

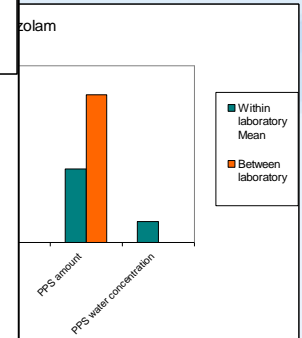
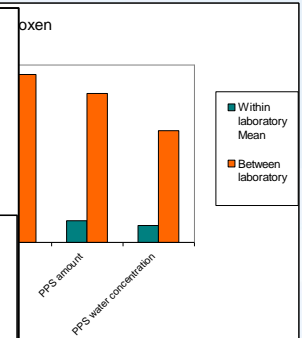
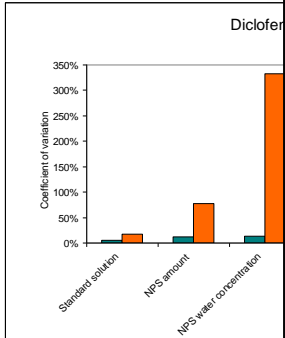
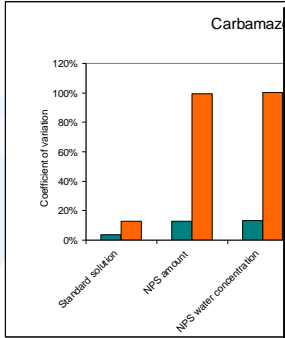
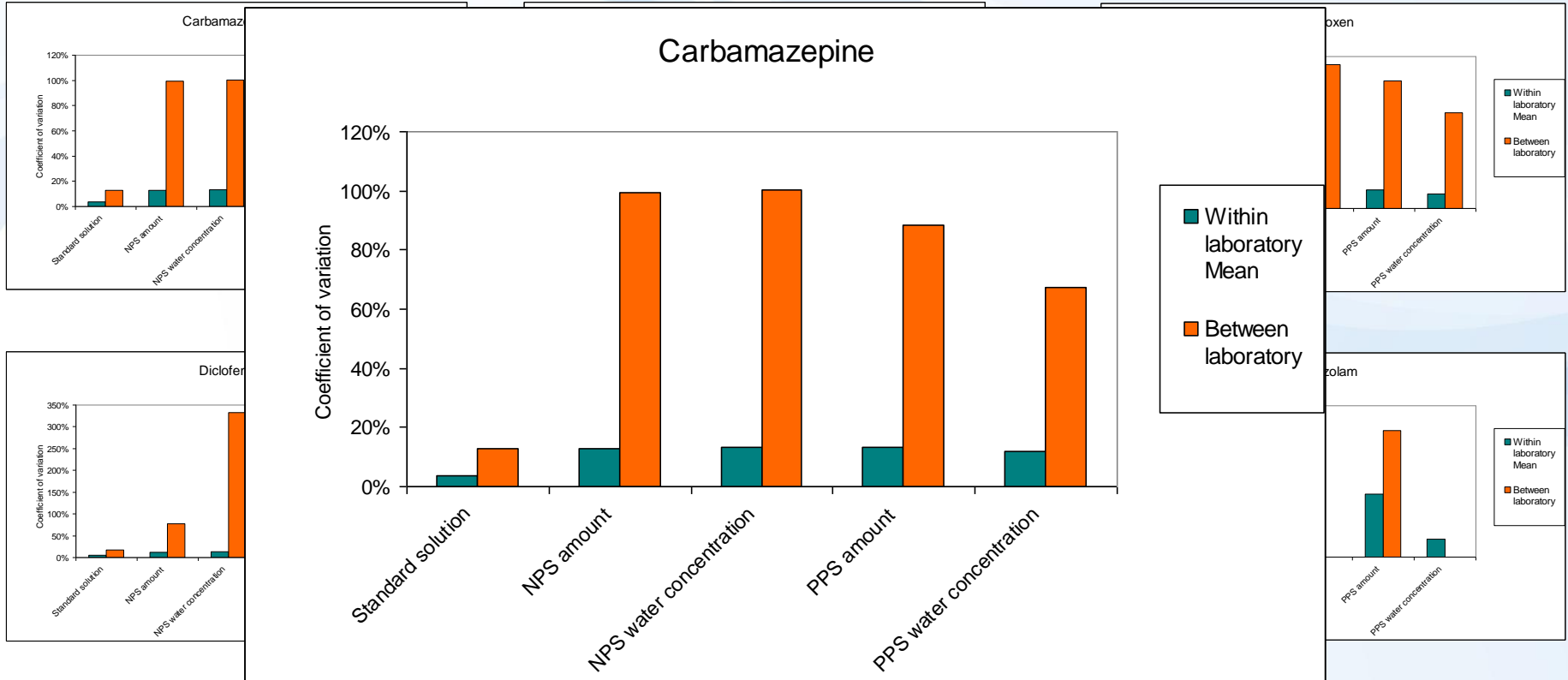
2 SD of log₂ transformed data median value

water sample mean

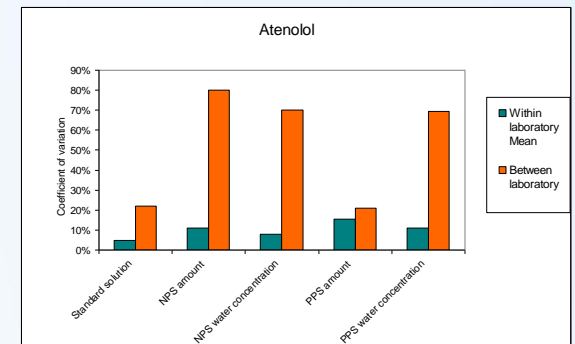
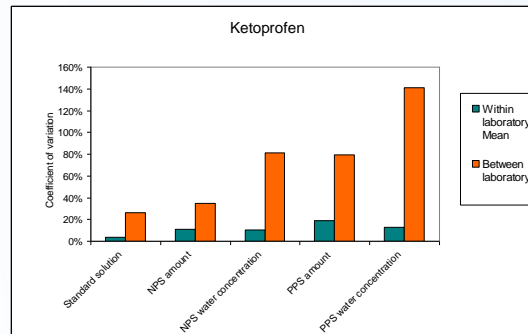
Laboratory number



Variability of results at different procedure levels



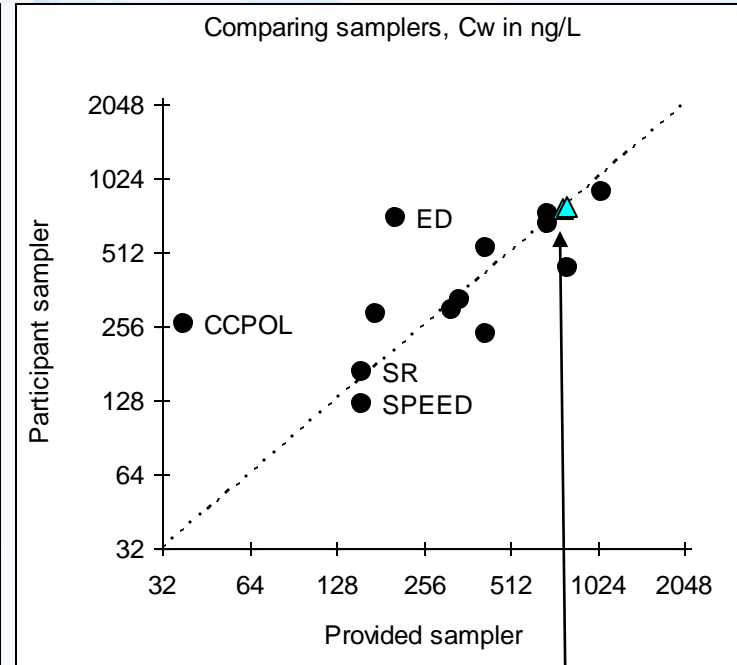
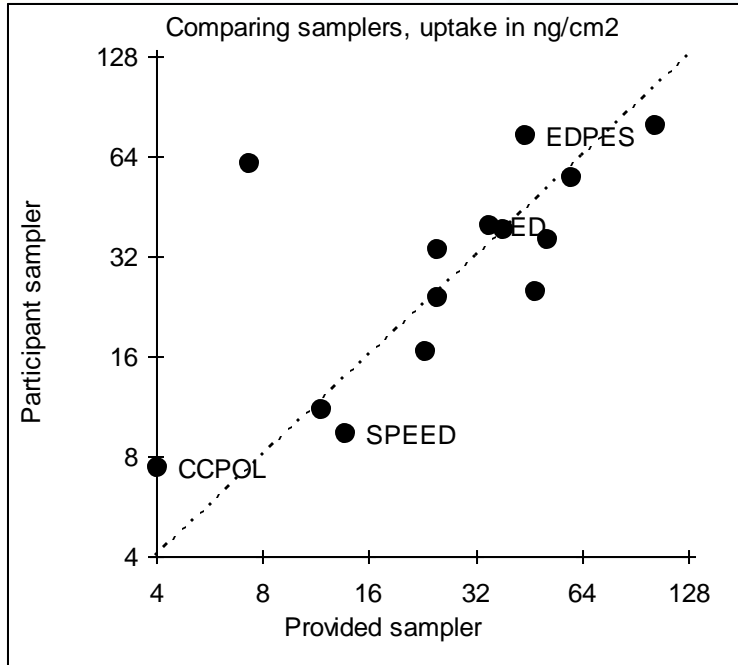
NPS – provided passive sampler
 PPS – participant passive sampler



Variability of reported results

Pharmaceuticals					
		Coefficient of variation (%)			
Variability:		Within laboratory		Between laboratory	
Matrix analysed:		Min.	Max.	Min.	Max.
	Standard solution	3%	8%	6%	35%
Provided sampler	NPS amount	11%	14%	35%	133%
	NPS water concentration	8%	13%	70%	333%
Participant sampler	PPS amount	10%	33%	13%	117%
	PPS water concentration	9%	21%	68%	205%

Comparison: participant vs. provided samplers



Composite water sample
(2 week samples per exposure)

Target compounds

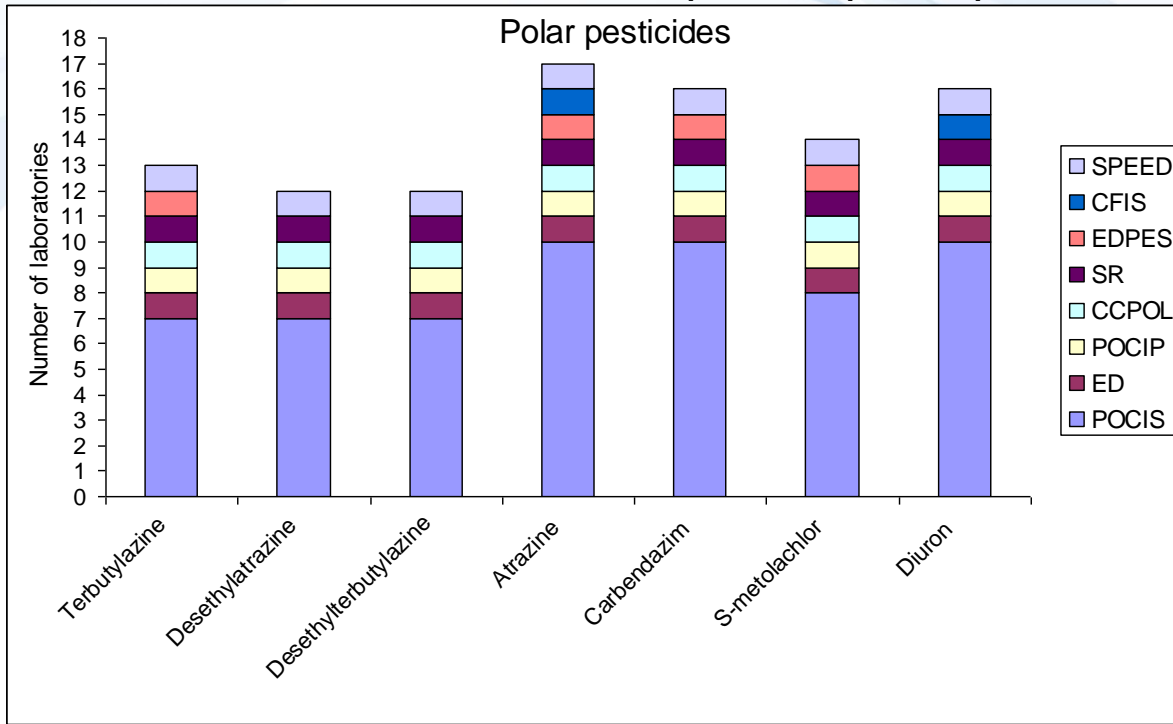
POLAR PESTICIDES

Up to 19 participants

	Compound	CAS	Usage
1.	Atrazine	1912-24-9	triazine herbicide
2.	Carbendazim	10605-21-7	benzimidazole fungicide
3.	Desethylatrazine	6190-65-4	triazine metabolite
4.	Desethylterbutylazine	30125-63-4	triazine metabolite
5.	Diuron	330-54-1	phenylurea herbicide
6.	S-metolachlor	87392-12-9	chloroacetanilide herbicides
7.	Terbutylazine	5915-41-3	triazine herbicide

Polar pesticides: Categories of participant samplers

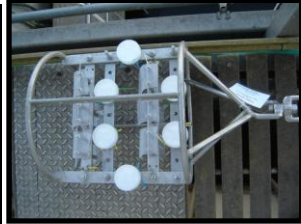
Up to 19 participants



Sampler	Abbreviation
POCIS pharmaceutical version	POCIS
Empore Disk	ED
POCIS, pesticide version	POCIP
Chemcatcher (3rd generation) polar configuration	CCPOL
silicone rubber material	SR
Empore SDB-RPS with PES-Membrane (0.1um)	EDPES
CFIS sampler	CFIS
Speedisks	SPEED



POCIS



SPEED
SR



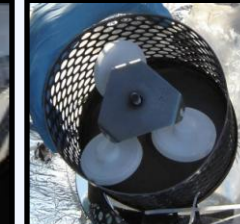
POCIP



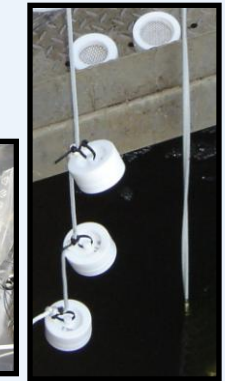
EDPES



CFIS

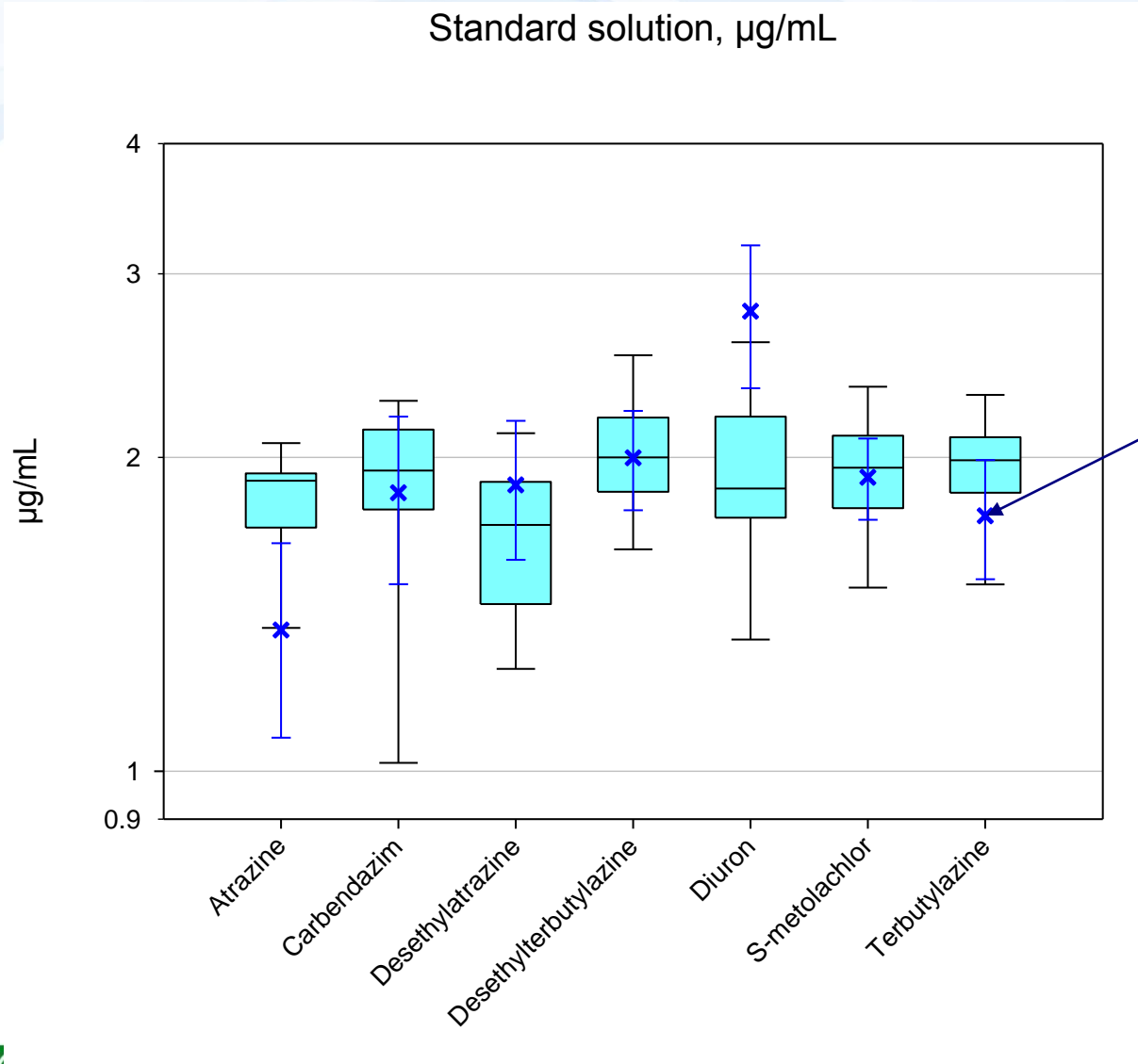


CCPOL



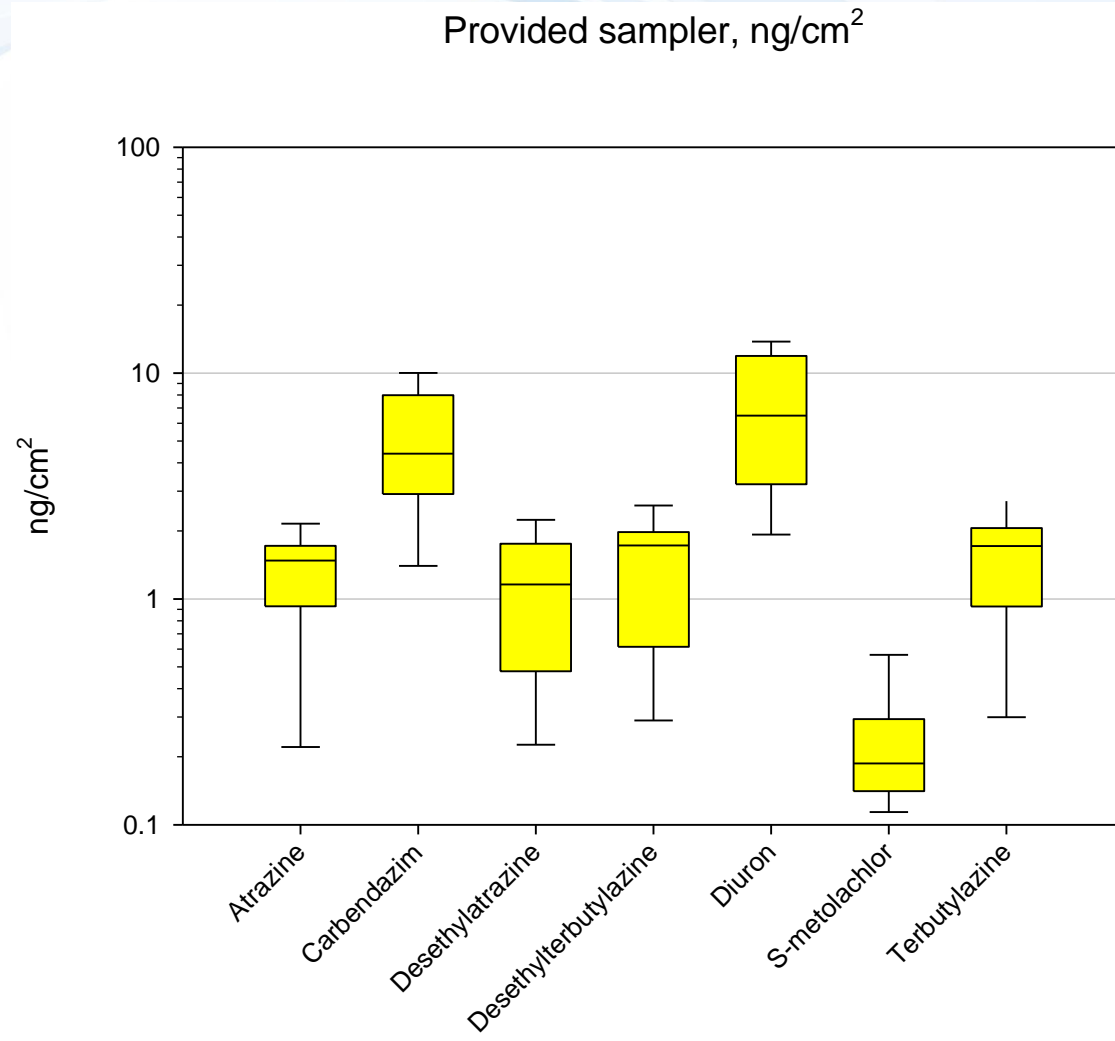
ED

Study results: polar pesticides



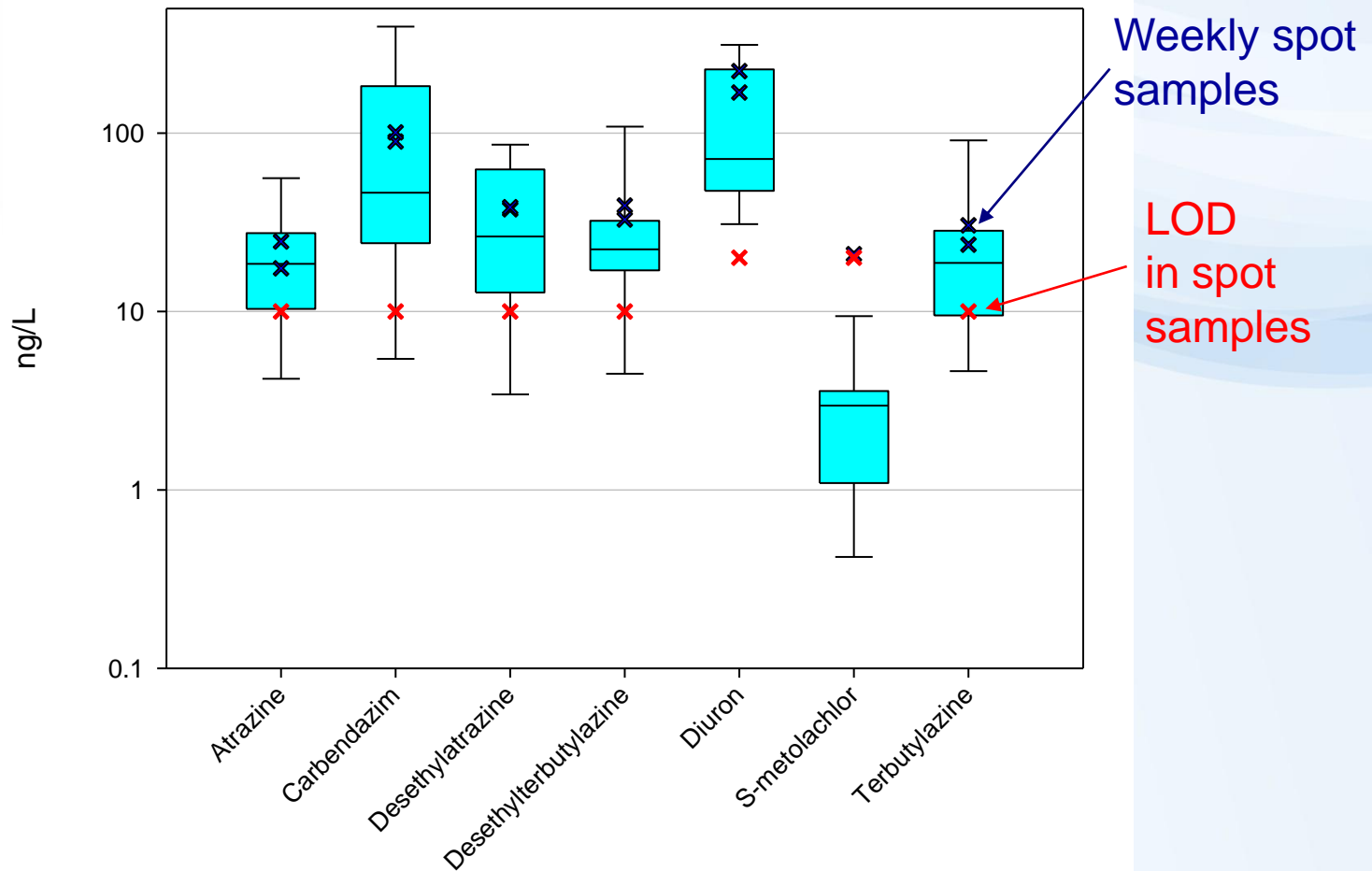
Set value
expanded
uncertainty
($k = 2$)

Study results: polar pesticides



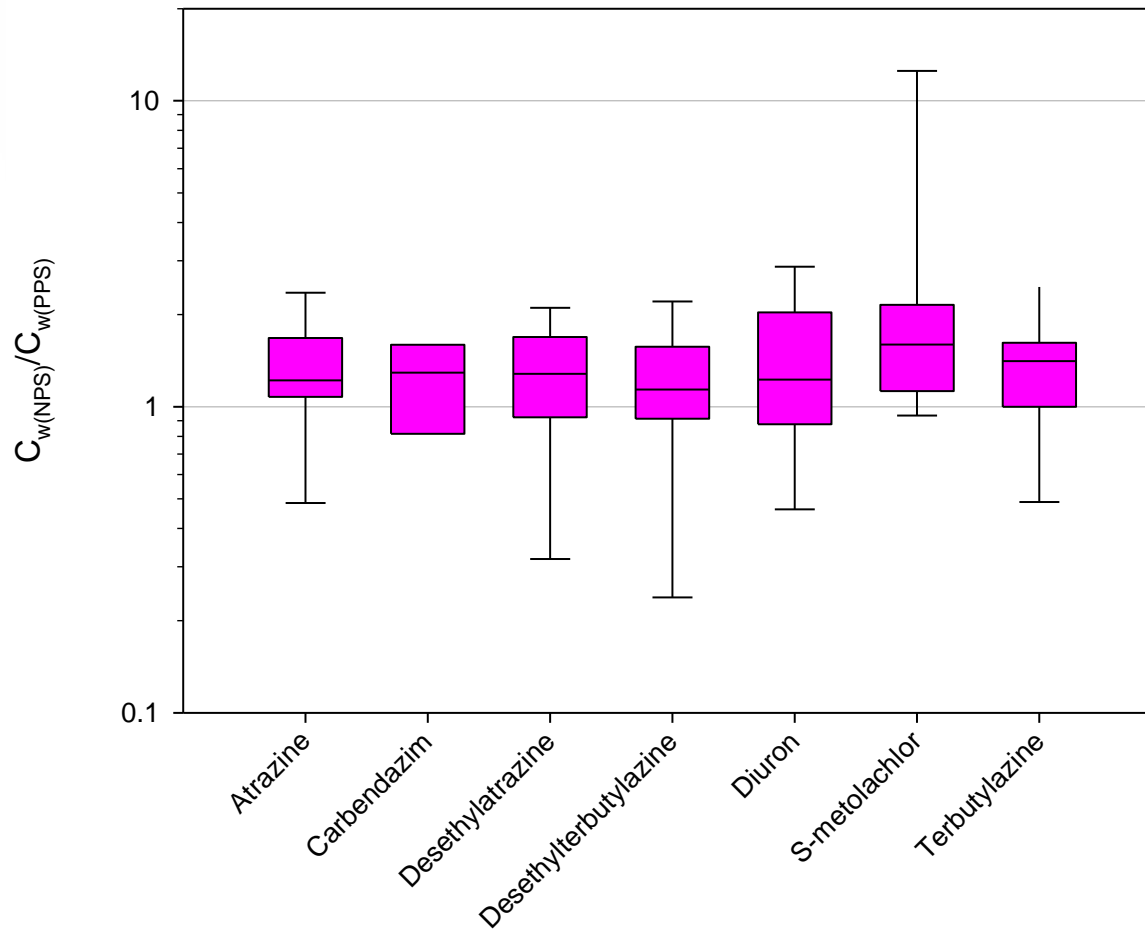
Study results: polar pesticides

Participant sampler, Cw in ng/L



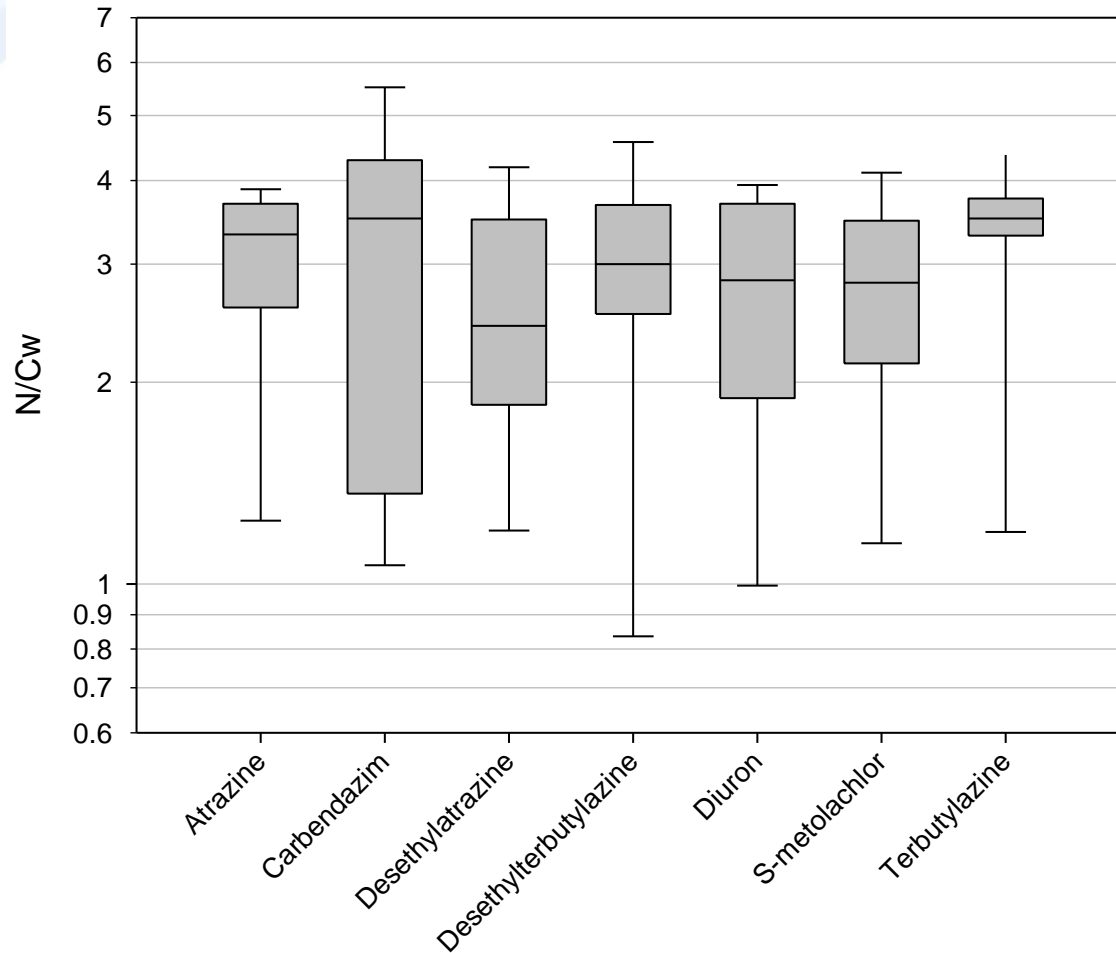
Study results: polar pesticides

Ratio of water concentrations provided/participant sampler



Study results: polar pesticides

Provided sampler, N/Cw ratio, L



$$N/C_w = R_s t \quad [L]$$

t = 14 days



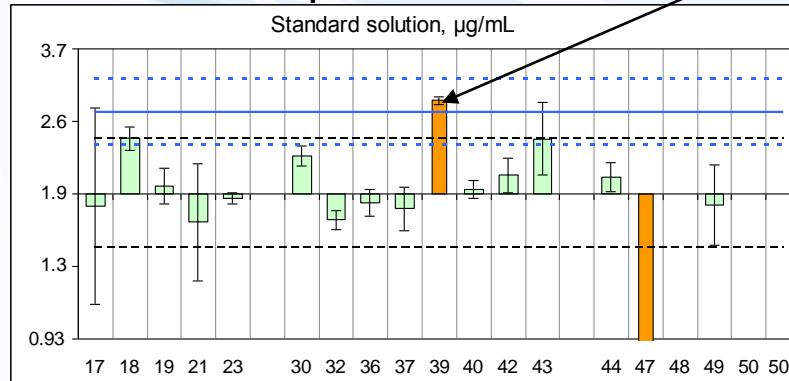
Effect of R_s applied on the C_w estimate

RESULTS

Example: Diuron

outlier

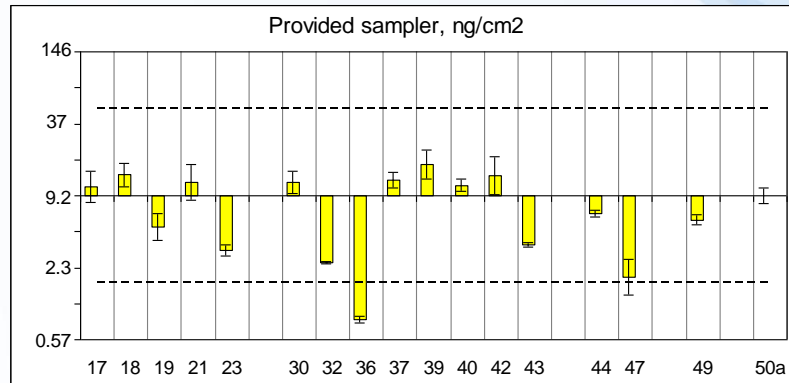
Stand. Solution	µg/mL
Median	1.87
s	0.6
Geomean	1.8
n	16
Outliers	2
s excl. outl	0.24
Refvalue	2.76
Exp. Unc	0.43



Set value expanded Uncertainty ($k = 2$)

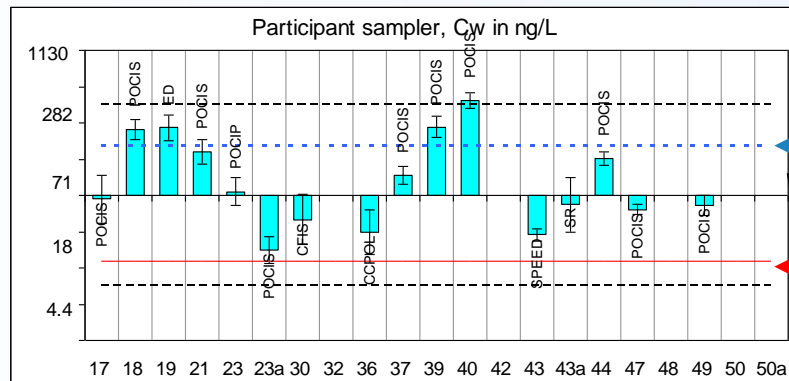
Provided Sampler uptake	ng/cm2
Median	9.2
s	7.7
Geomean	6.4
n	17
Outliers	0

Log₂ scale



2 SD of log₂ transformed data
median value

Participant Sampler	Cw
	ng/L
Median	71
s	61
GeomMean	91
n	16
Outliers	0



water sample mean

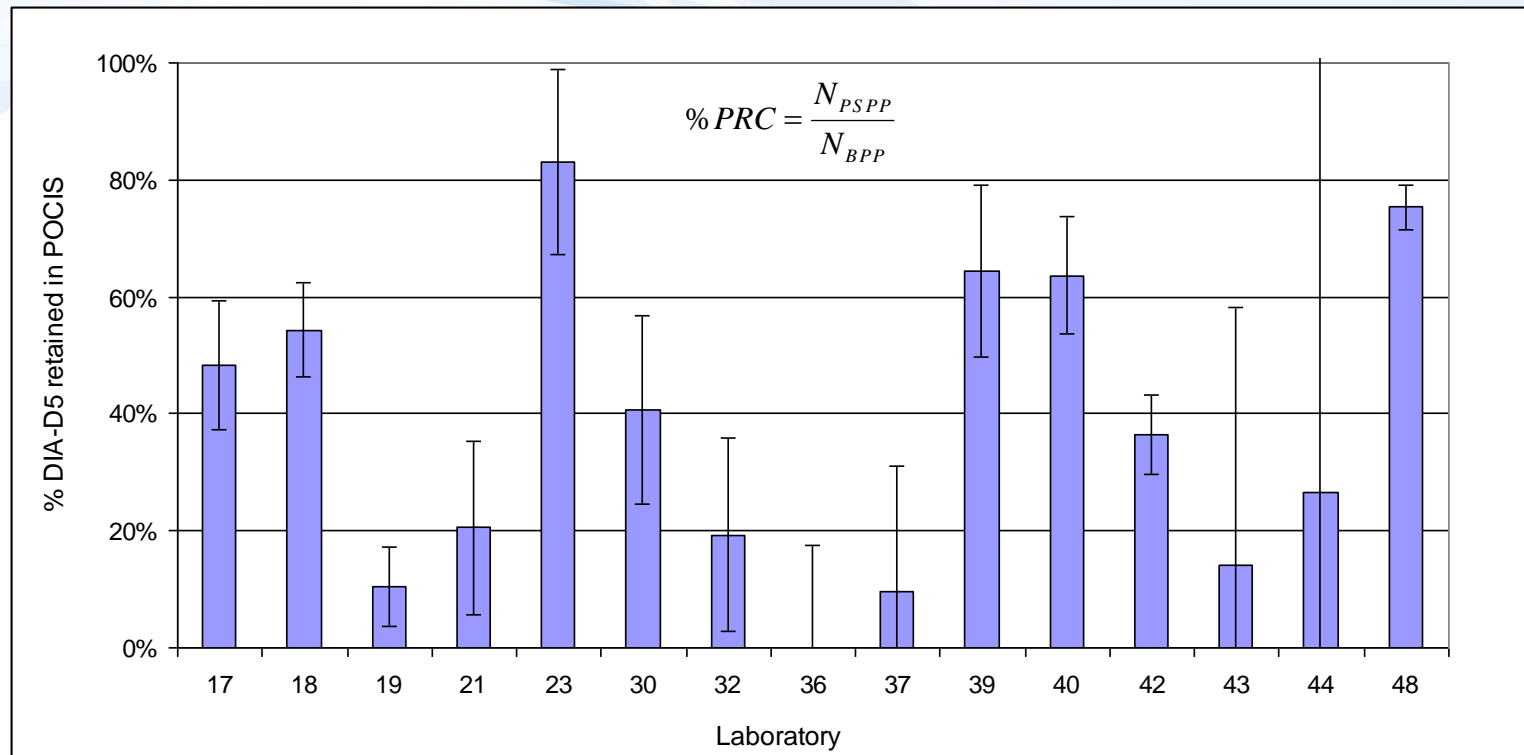
water sample LOQ

Spot samples	
Period 1	196
Period 2	169
LOQ	20

Laboratory number

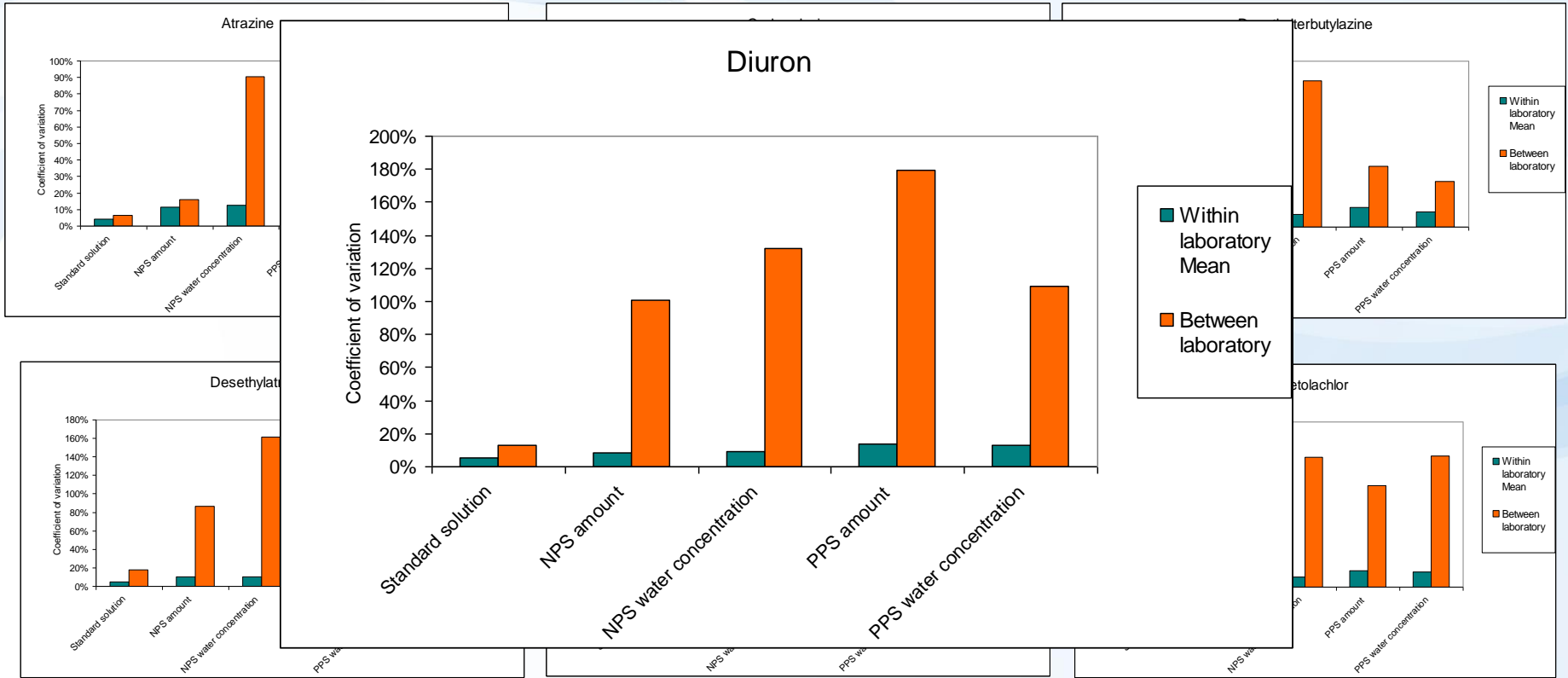


Study results: DIA-D5 = potential PRC

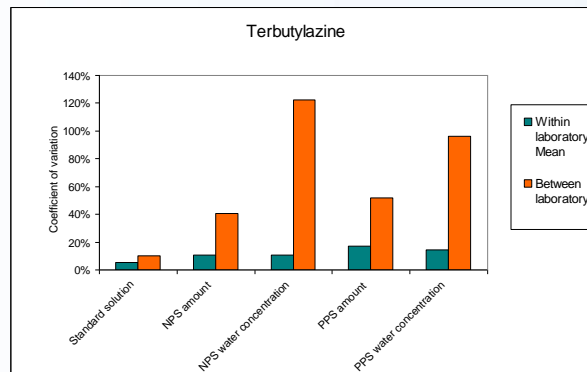


- low within laboratory and high between laboratory variability = difficulties with accuracy of DIA-D5 determination in samplers
- attention has to be paid to a reliable analysis of the compound before application as a PRC can be evaluated

Variability of results at different procedure levels



NPS – provided
passive sampler
PPS – participant
passive sampler

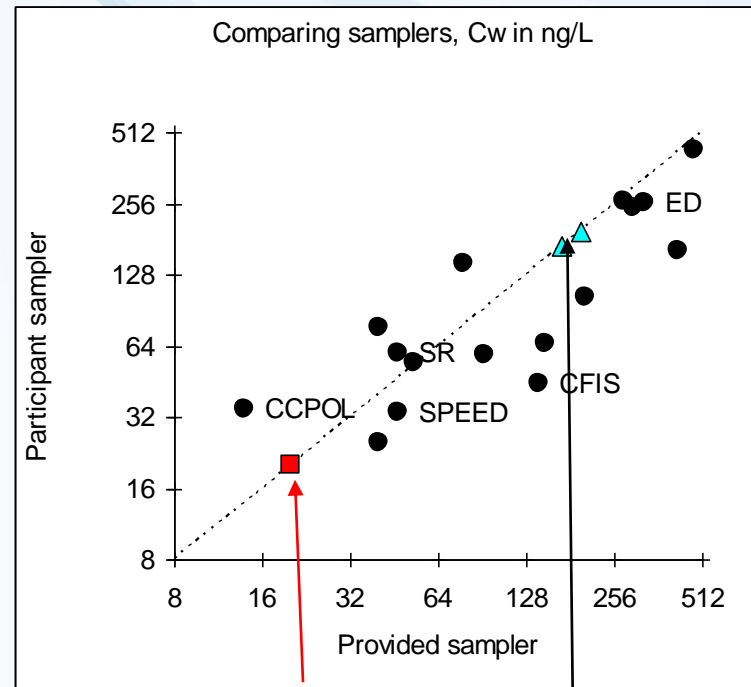
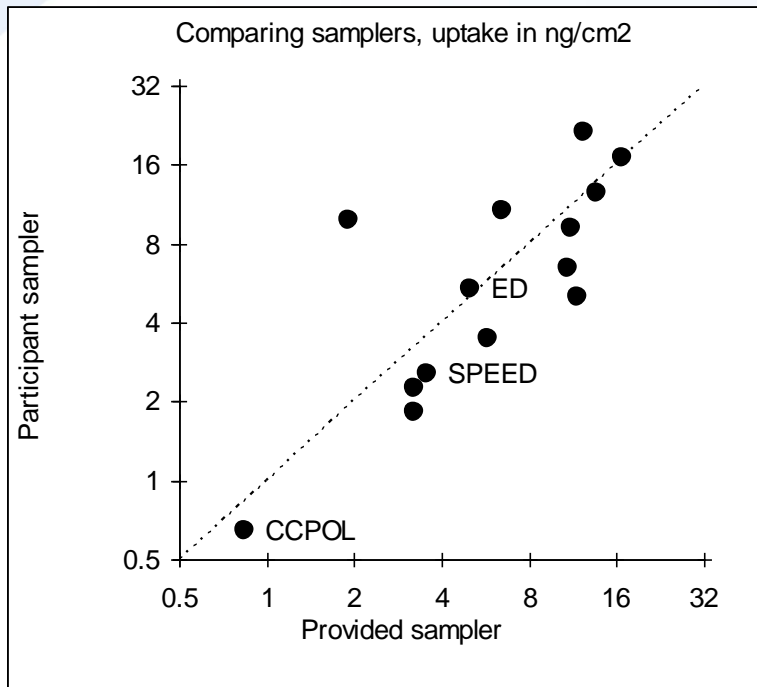


Variability of reported results

Polar pesticides					
		Coefficient of variation (%)			
Variability:		Within laboratory		Between laboratory	
Matrix analysed:		Min.	Max.	Min.	Max.
	Standard solution	4%	6%	6%	18%
Provided sampler	NPS amount	9%	12%	16%	101%
	NPS water concentration	8%	13%	89%	161%
Participant sampler	PPS amount	12%	18%	51%	179%
	PPS water concentration	11%	16%	39%	236%

Comparison: participant vs. provided samplers

Example: Diuron



LOQ of water sample

Composite water sample
(2 week samples per exposure)

STUDY RESULTS

- An acceptable within laboratory variability was observed for standard solution and samplers
- Common compounds, e.g pesticides, showed lower variability than new or rare ones
- Between laboratory variation was roughly a factor 5 larger than within laboratory variability
- However, individual laboratories found well comparable results for participant and provided sampler for uptake per surface area as well as the resulting water concentration
- Passive sampling could be evaluated versus the spot sampling method with variable differences, but mostly within the range comprised by the passive sampling results

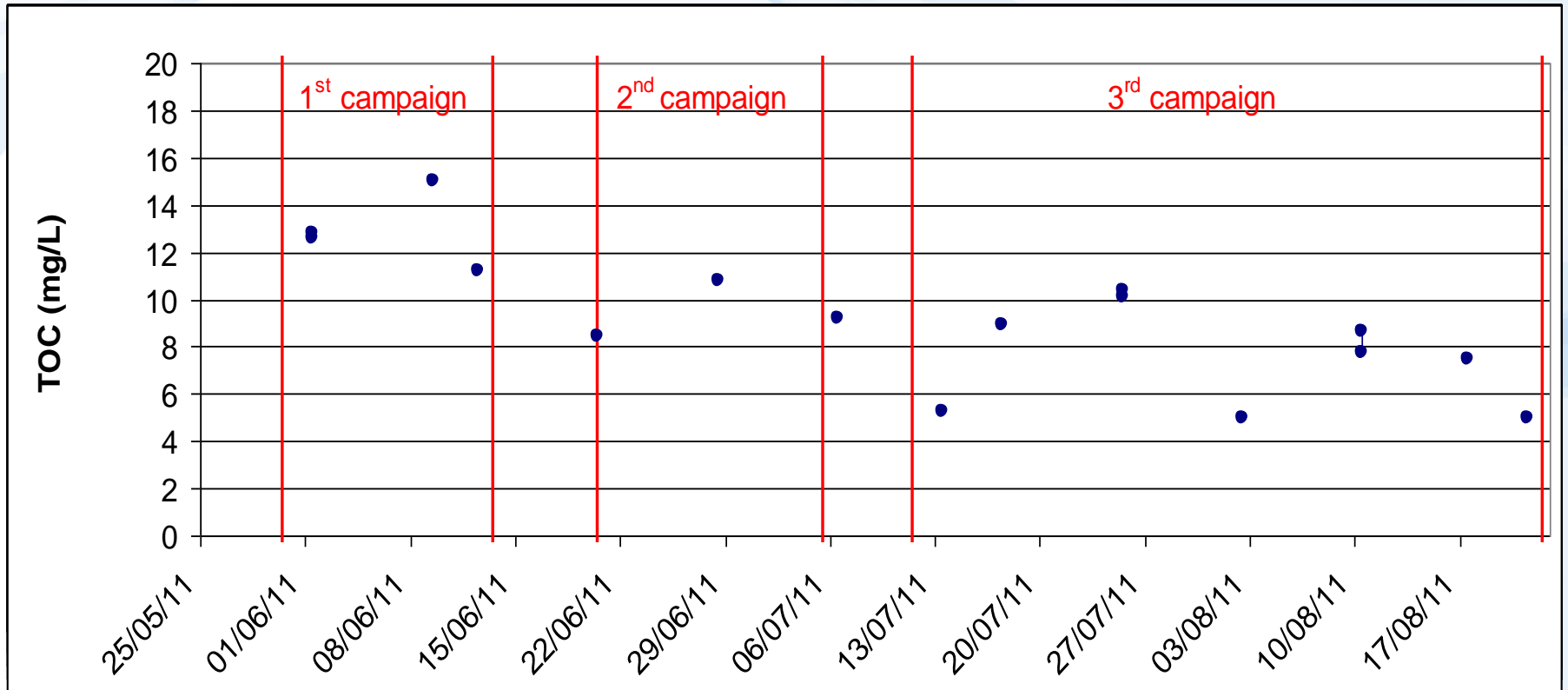
Conclusions

- **passive sampling process is not causing excessive variability** - similar results were obtained for different passive samplers
- between laboratory variability is likely related to difficulties with analysis in complex environmental matrices
- in future, effort should be made to improve accuracy of analysis of complex samples



Thank you for your attention!

Water quality parameters



Discharge

pH

Temperature

Conductivity

Suspended solids

TOC

Uncertainty of C_w estimate with passive sampling

Given the measured variables with uncertainties, $|\sigma|$, the uncertainty in the computed water concentration, σC_w is:

EQUILIBRIUM:

$$C_w = \frac{M_S}{K_{SW} V_S} \quad \sigma_{C_w} = \sqrt{\cancel{|\sigma_{M_S}|^2 \left(\frac{1}{K_{SW} V_S}\right)^2} + |\sigma_{K_{SW}}|^2 \left(\frac{M_S}{K_{SW}^2 V_S}\right)^2} \Rightarrow \frac{\sigma_{C_w}}{C_w} = \frac{\sigma_{K_{SW}}}{K_{SW}}$$

The accuracy of K_{sw} is only critical for compounds that reach sampler–water equilibrium. E.g. a bias of 0.2 log units in K_{sw} results in a bias of 0.2 log units in the C_w estimate

LINEAR UPTAKE:

$$C_w = \frac{M_S}{R_S t} \quad \sigma_{C_w} = \sqrt{\cancel{|\sigma_{M_S}|^2 \left(\frac{1}{R_S t}\right)^2} + |\sigma_{R_S}|^2 \left(\frac{M_S}{R_S^2 t}\right)^2} \Rightarrow \frac{\sigma_{C_w}}{C_w} = \frac{\sigma_{R_S}}{R_S}$$

The accuracy of C_w estimates for linear uptake strongly depends on the accuracy of R_S , which in turn largely depends on the quality of the K_{sw} values of the PRCs