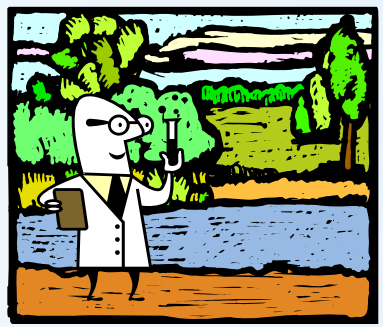
An international collaborative study on the use of passive samplers in monitoring of emerging pollutants

B. Vrana, F. Smedes, R . Prokeš, R. Loos, N. Mazzella , H. Budzinski, C. Mieg e, A. Gravell, T. Ocelka , E. Vermeirssen

Activities of NORMAN network in passive sampling 2009-2012

- An **expert group meeting** in 2009

- A **position paper** "*Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives*" in 2010



- An **interlaboratory study** in 2011-2012

Collaborative study

A sampler comparison exercise

Assessment of steps in passive sampling process

- instrumental analysis
- analysis of sampler matrix
- comparison of samplers
- comparison with spot sampling

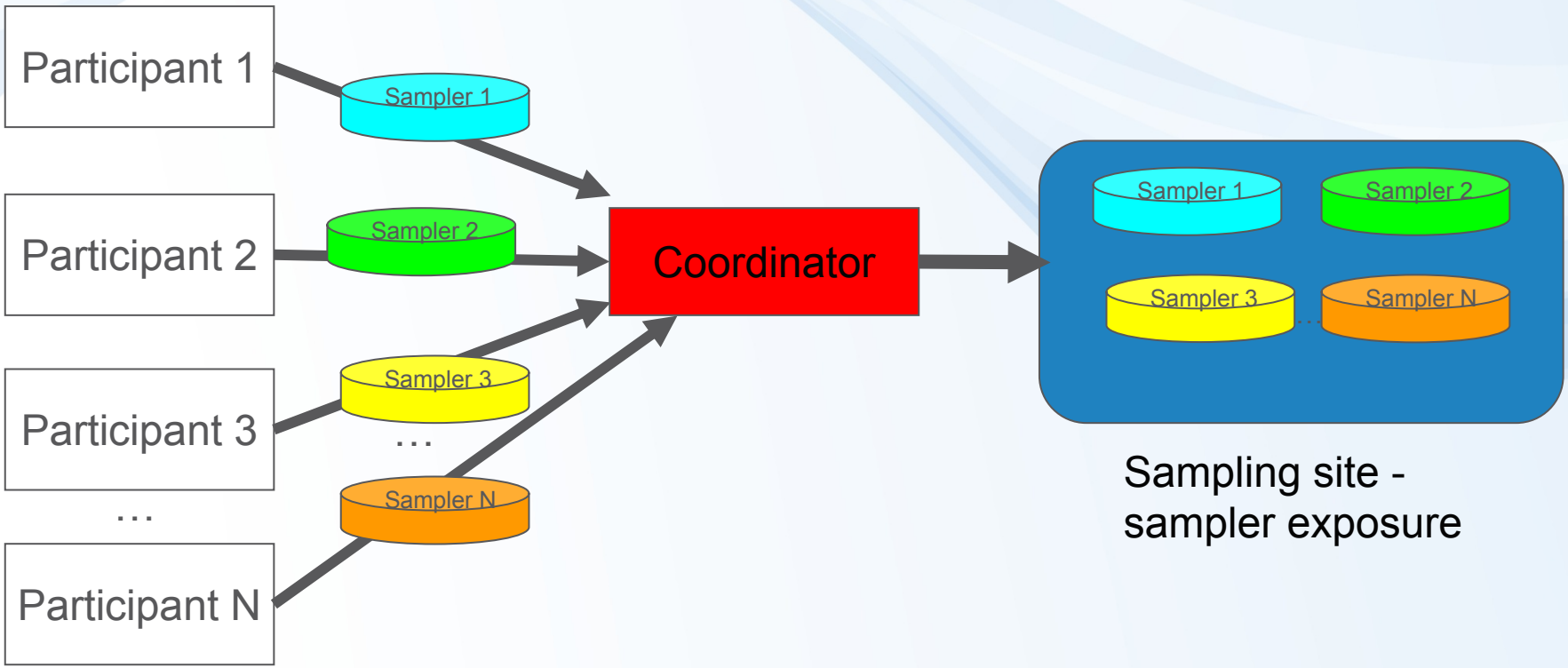
STUDY DESIGN

Target compounds

- 7 polar pesticides
- 7 pharmaceuticals
- 5 steroid hormones
- Bisfenol A
- Triclosan
- PFOA, PFOS
- 6 brominated diphenyl ethers (BDEs)

1. Exposure of passive samplers from participants

for selected analyte/analytes



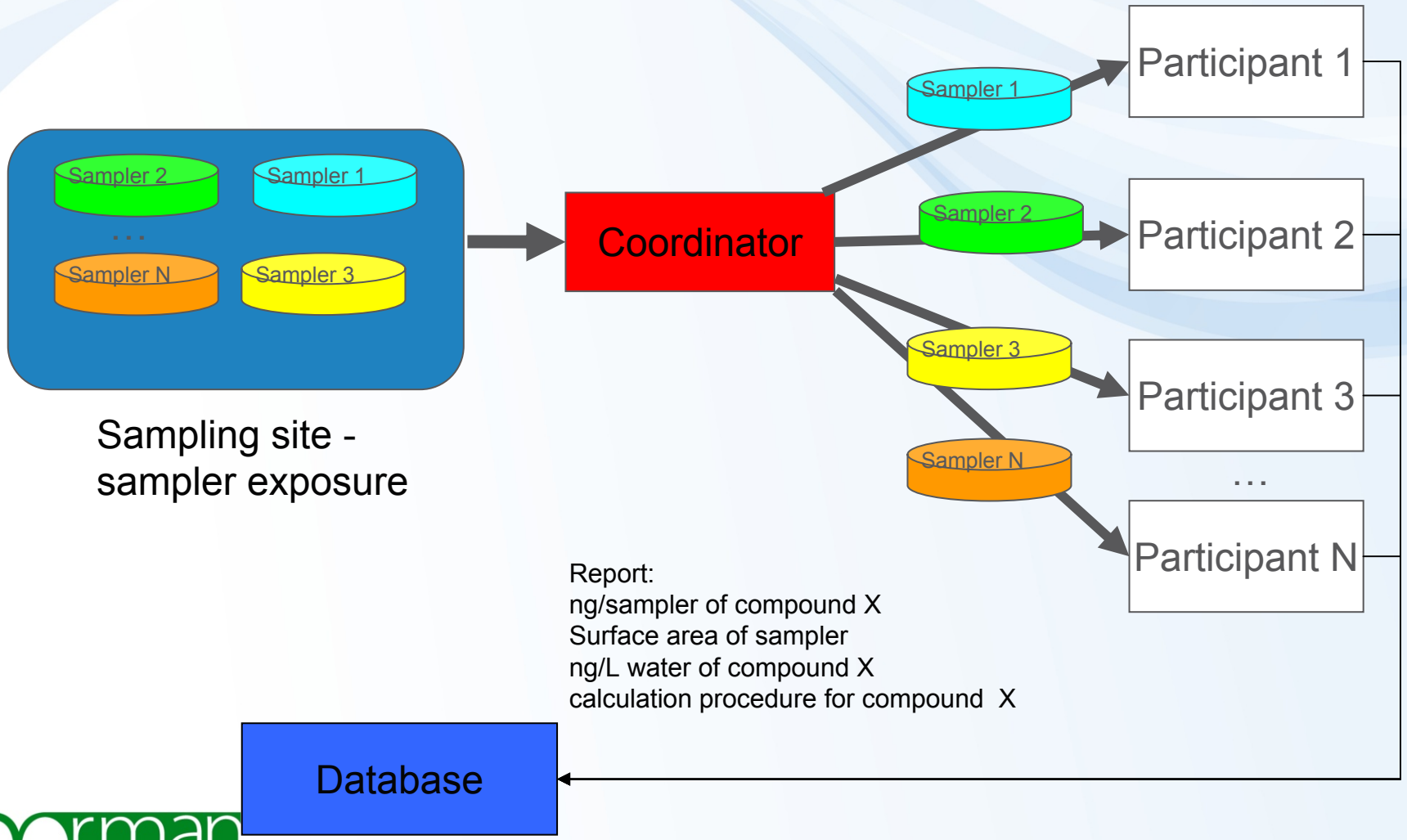
Sampling site: discharge from WWTP Brno-Modřice

Sampler deployment

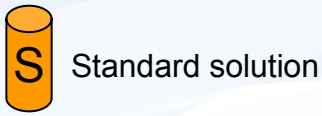
II

1. Recovery passive samplers from participants

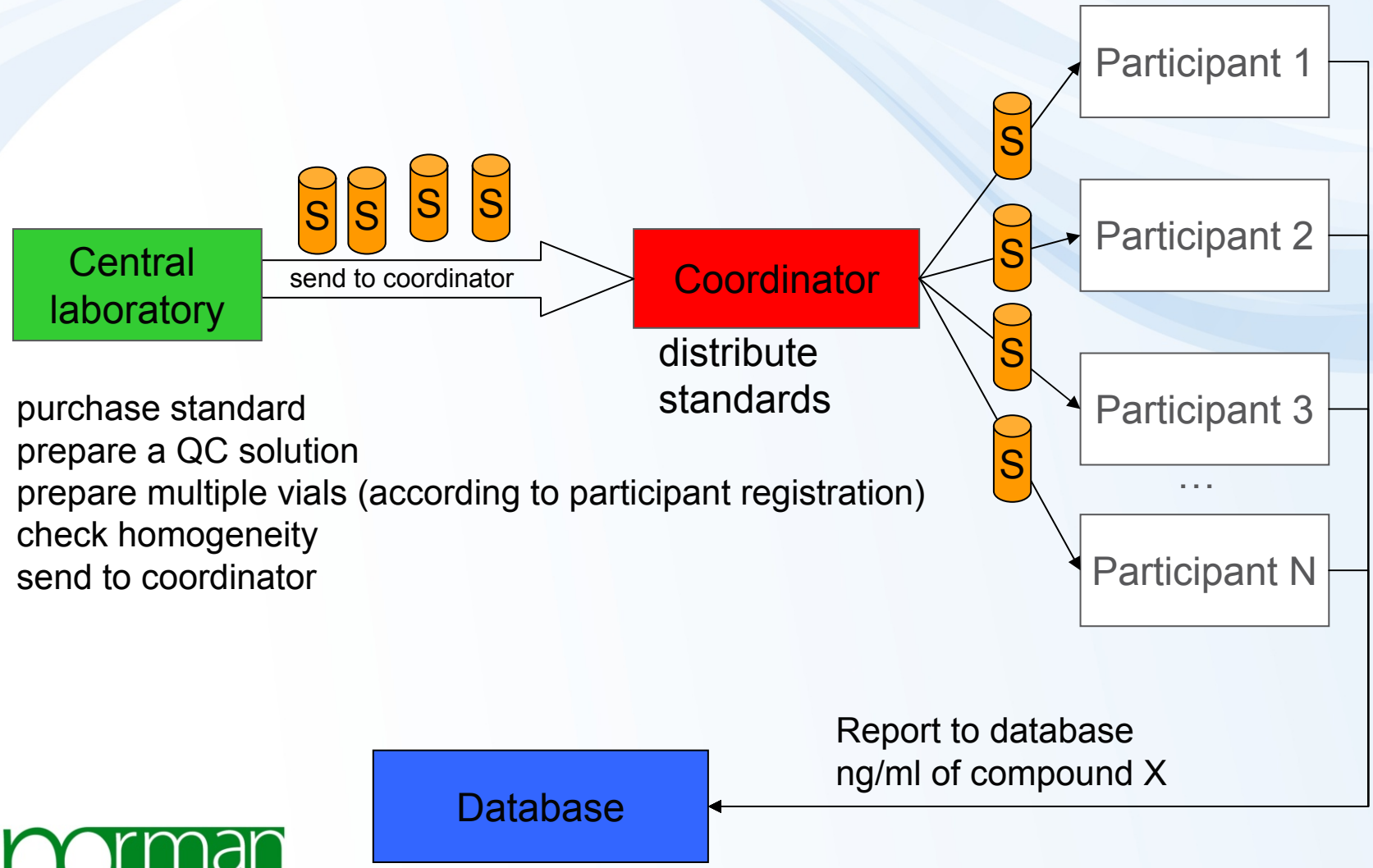
for selected analyte/analytes



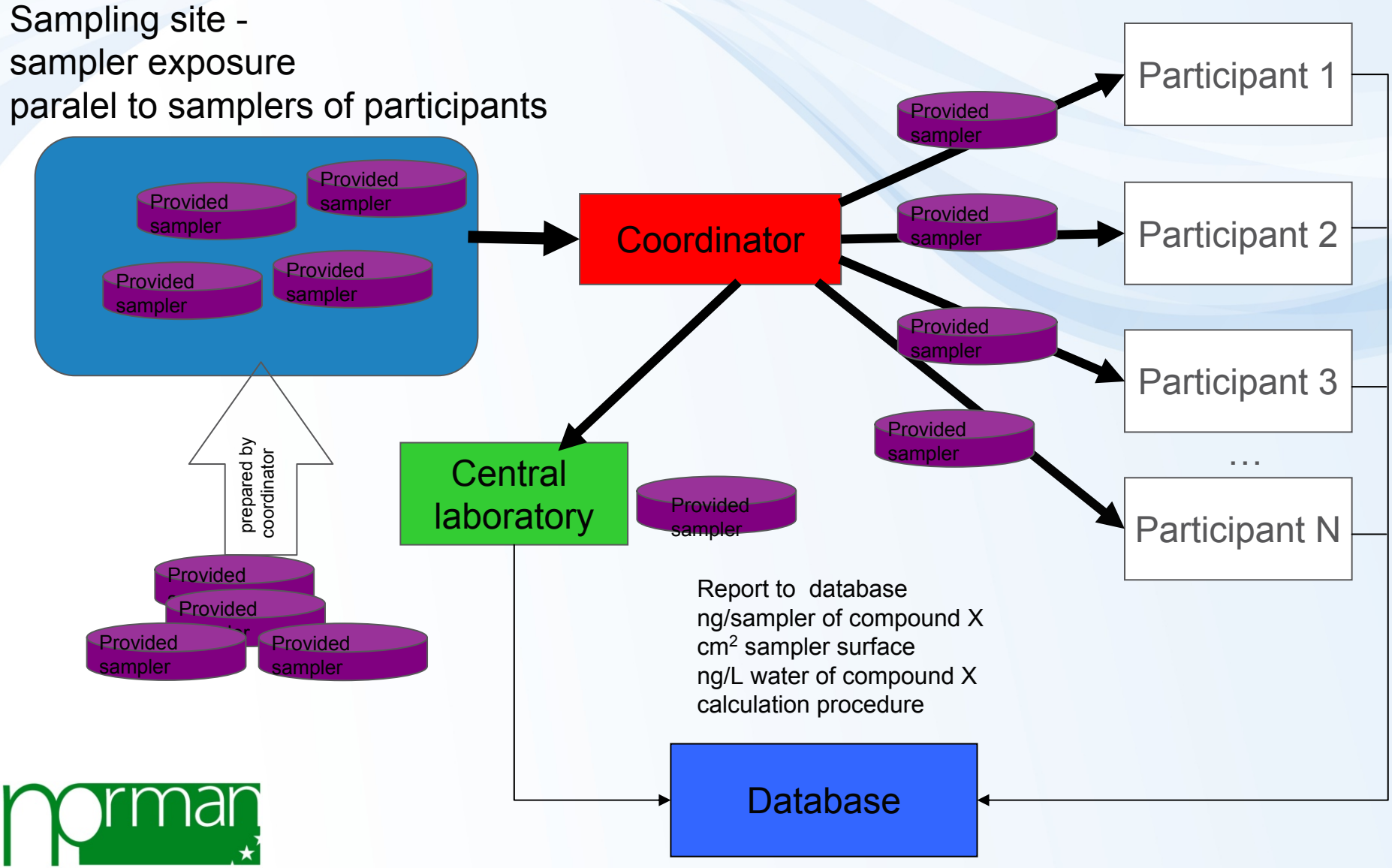
2a. Standard solution



for selected analyte/analytes



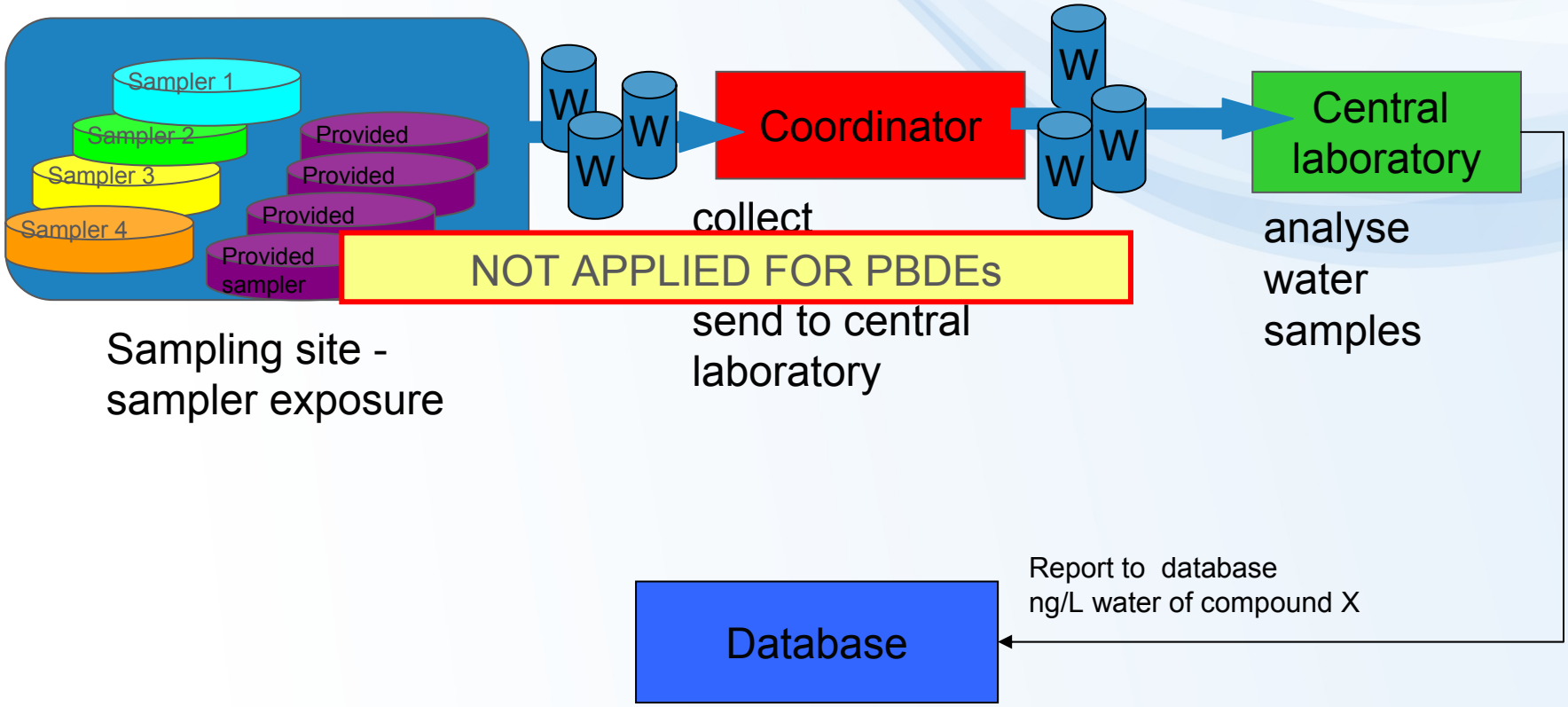
2b. Provided passive samplers



3. Water; continuous sampling

W water sample

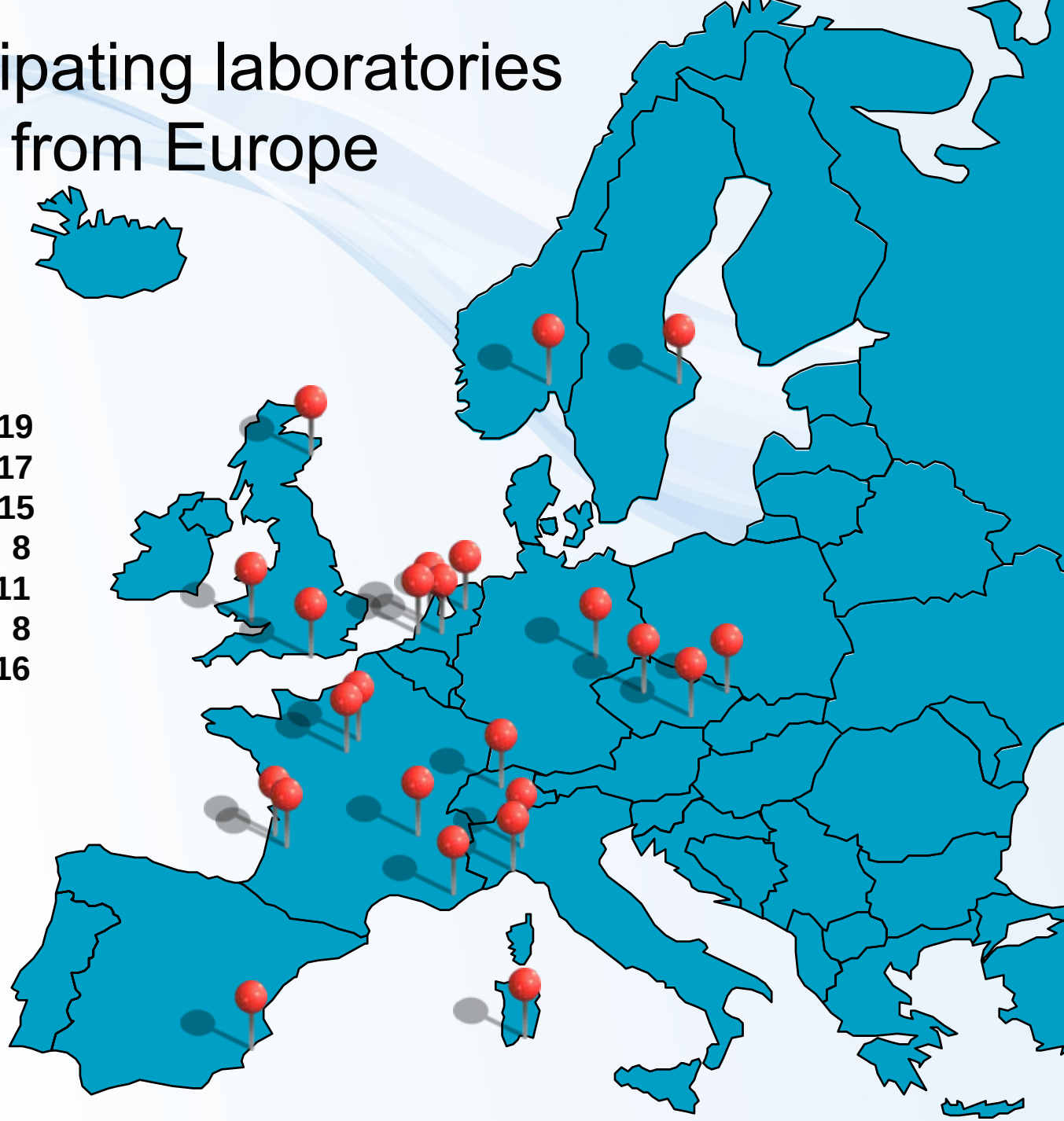
for selected analyte/analytes



STUDY REALISATION

Participating laboratories from Europe

- **Polar pesticides – 19**
- **Pharmaceuticals – 17**
- **Steroid hormones – 15**
- **Triclosan – 8**
- **Bisphenol A – 11**
- **PFOA, PFOS – 8**
- **PBDE – 16**

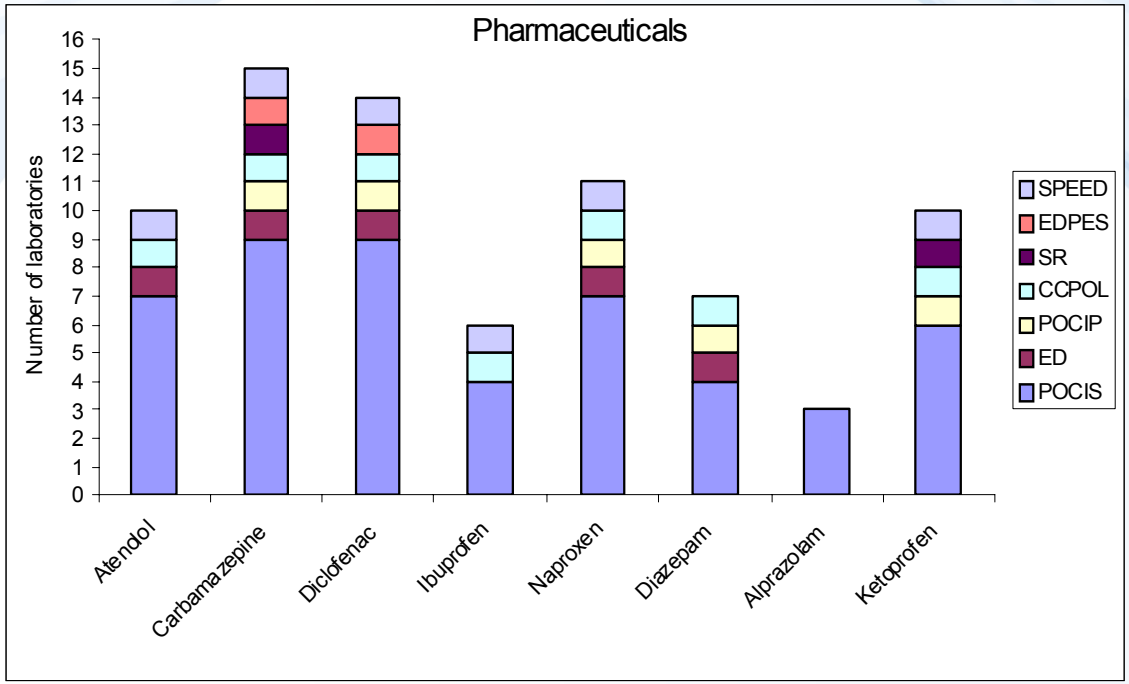


…and from the rest of the World

STUDY RESULTS

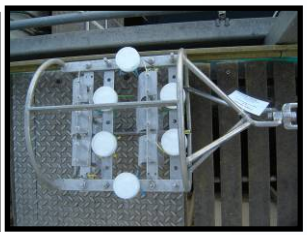
Pharmaceuticals: Categories of participant samplers

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

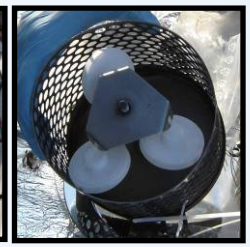


SPEED
SR

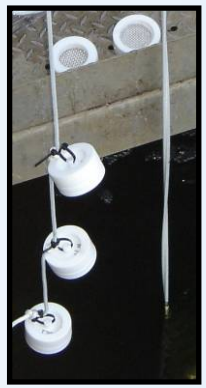
POCIP

EDPES

CCPOL

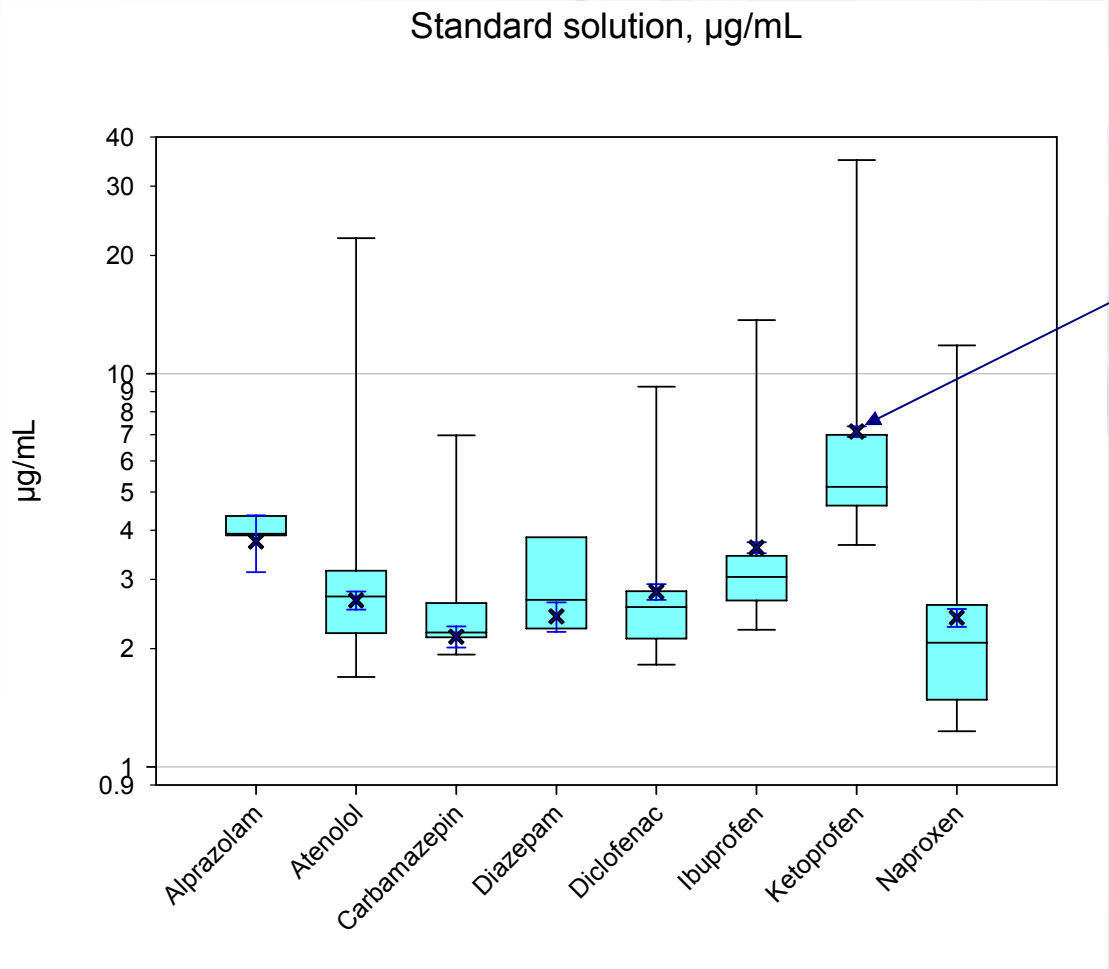


CCPOL



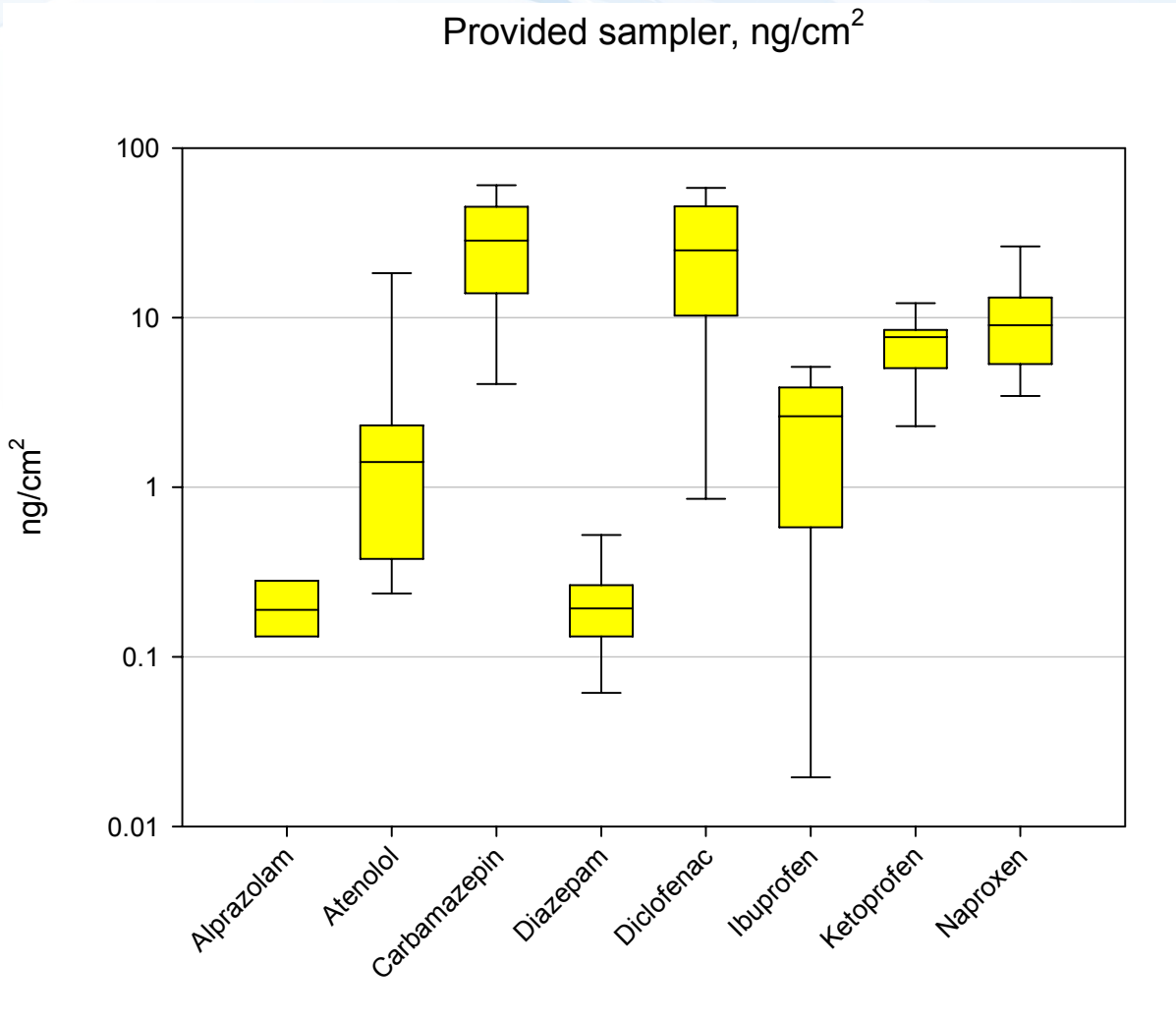
ED

Study results: pharmaceuticals

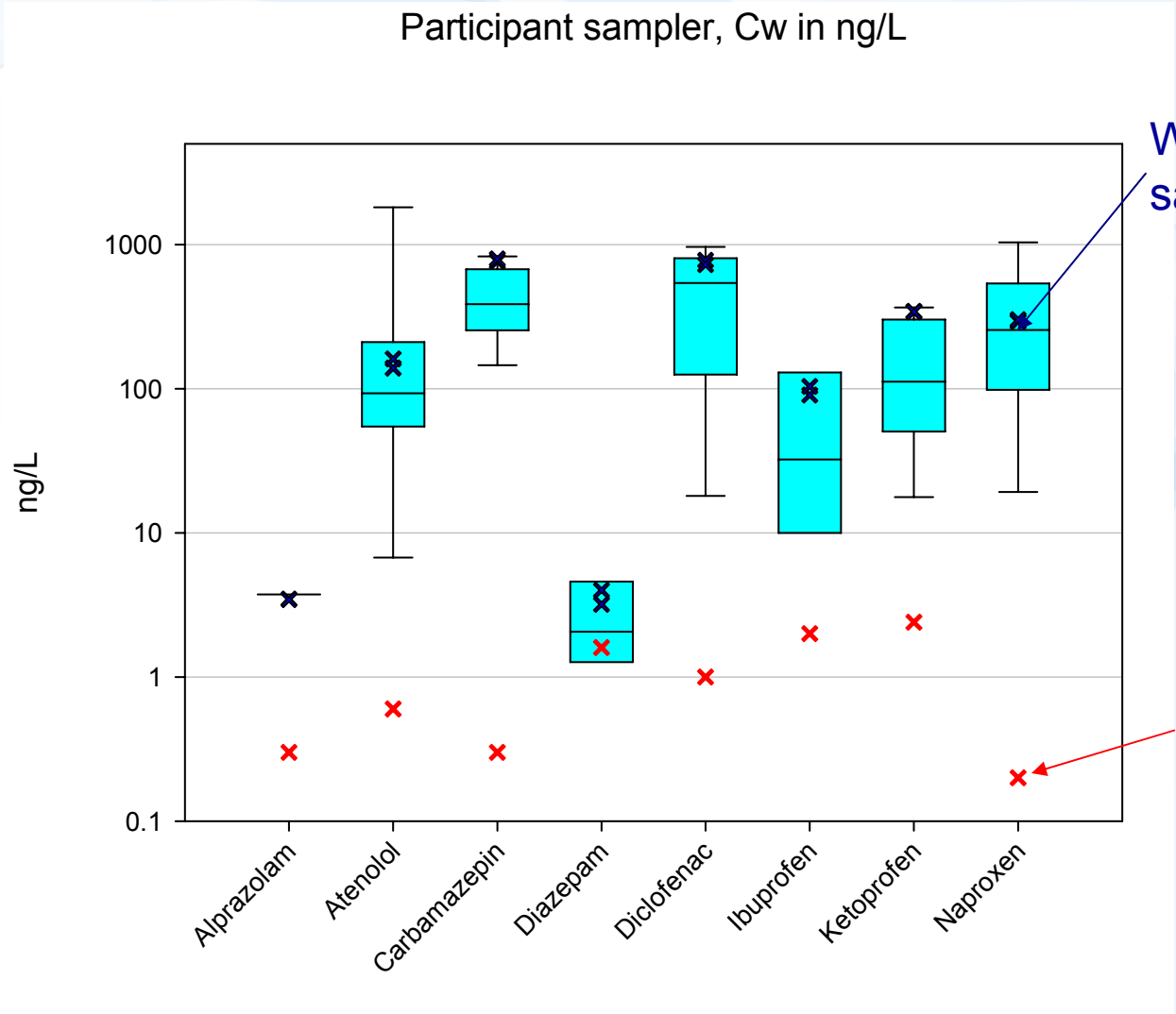


Set value ± expanded uncertainty (k = 2)

Study results: pharmaceuticals



Study results: pharmaceuticals



RESULTS

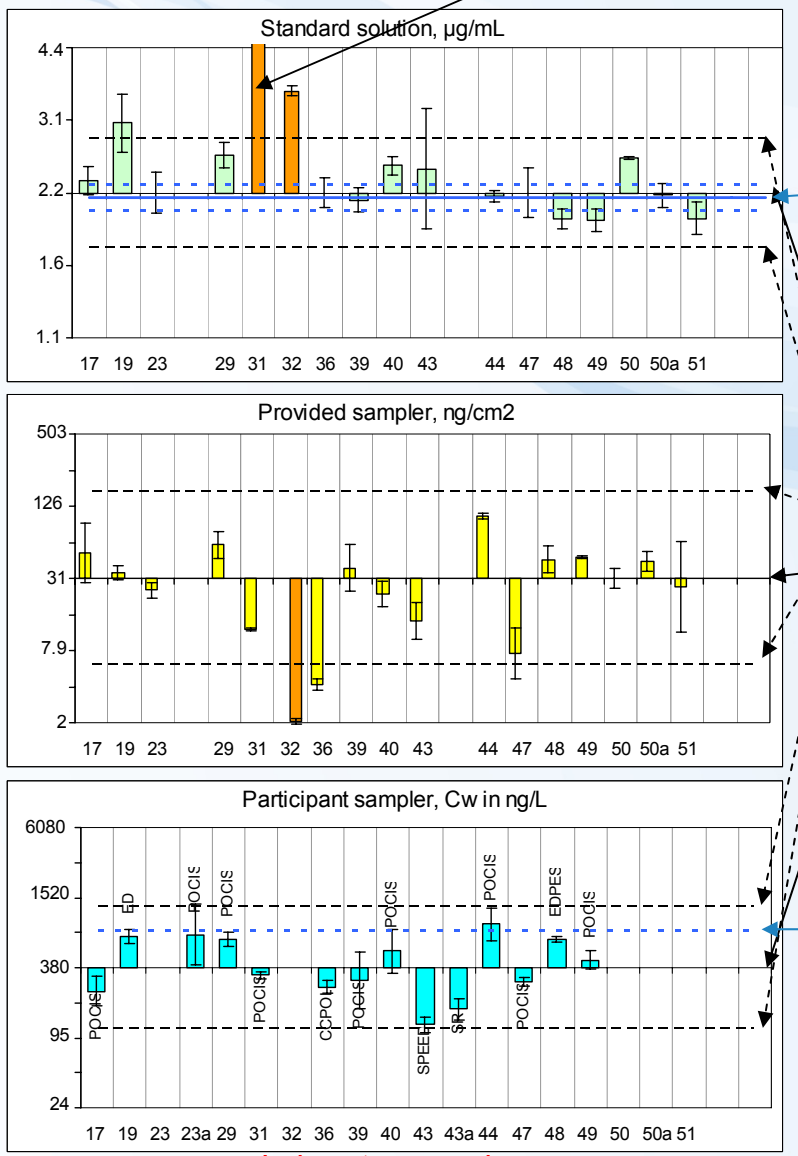
Example: Carbamazepin

	Stand. Solution µg/mL
Median	2.20
s	1.2
Geomean	2.7
n	17
Outliers	2
s excl. outl	0.28
Refvalue	2.14
Exp. Unc	0.13

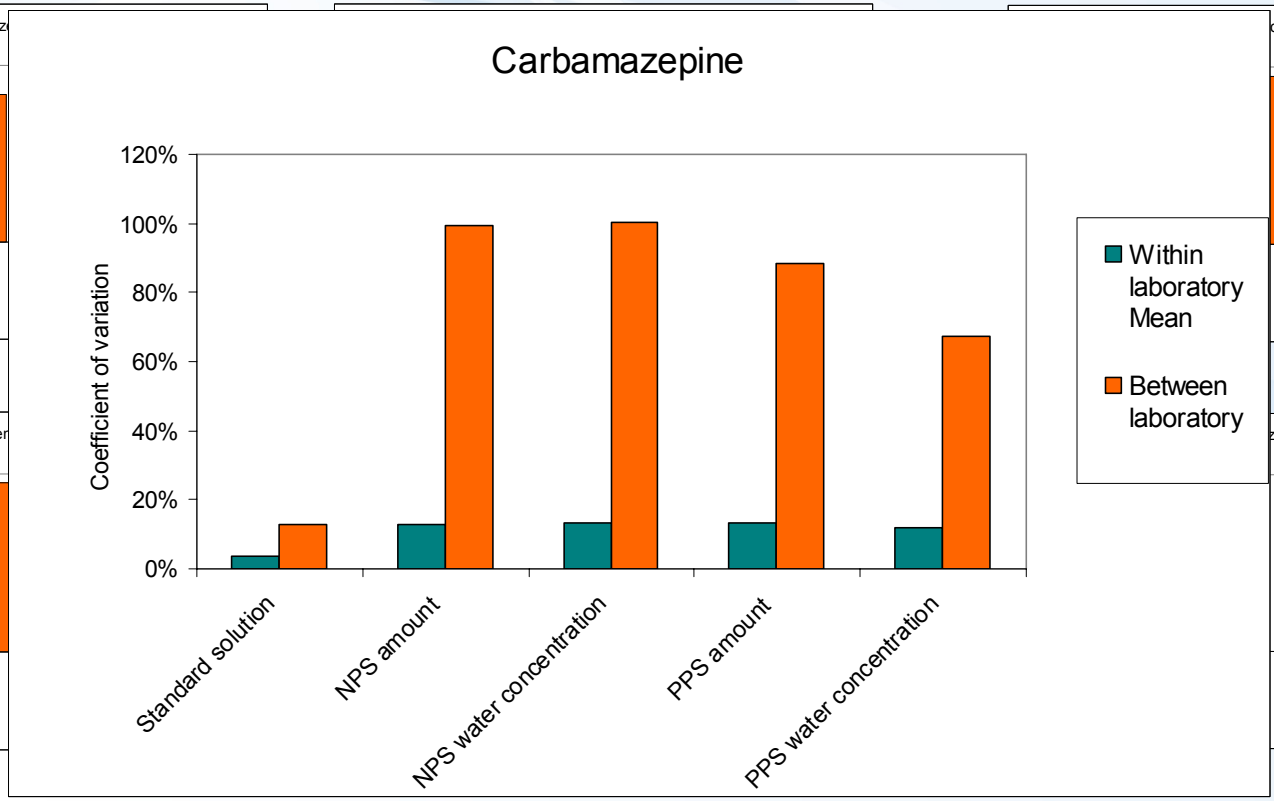
	Provided Sampler uptake ng/cm2
Median	31.4
s	32
Geomean	23
n	17
Outliers	1
s excl. outl	26

	Paricipant Sampler Cw ng/L
Median	380
s	230
GeomMean	386
n	14
Outliers	0

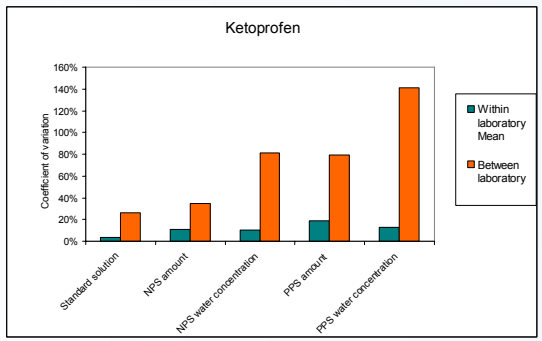
Spot samples	
Period 1	778
Period 2	794

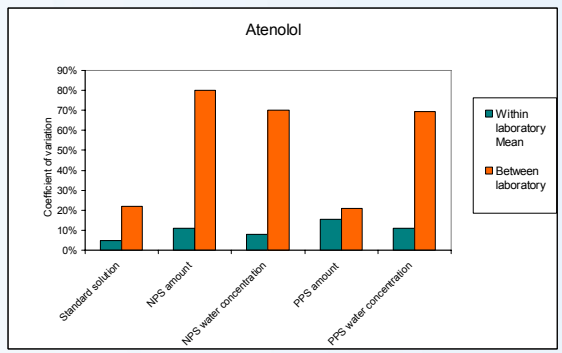


Variability of results at different procedure levels



NPS – provided passive sampler
PPS – participant passive sampler





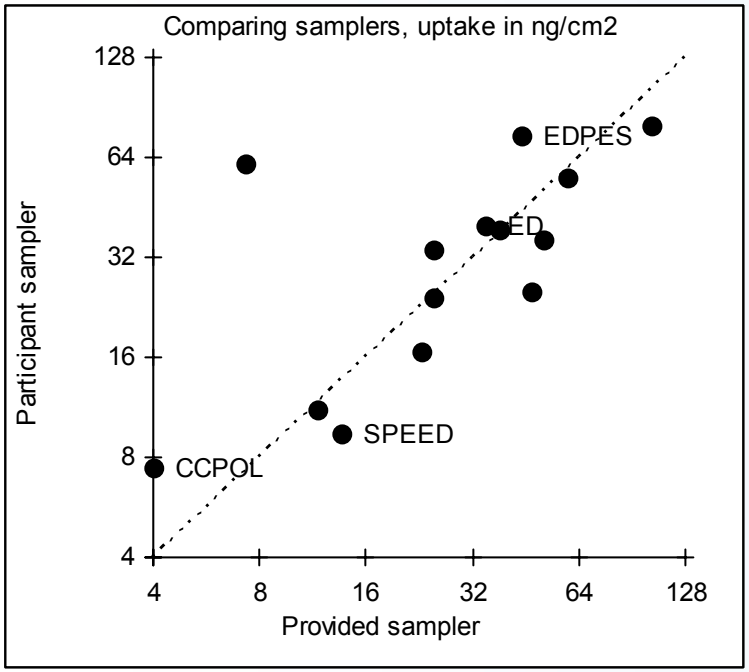
Variability of reported results

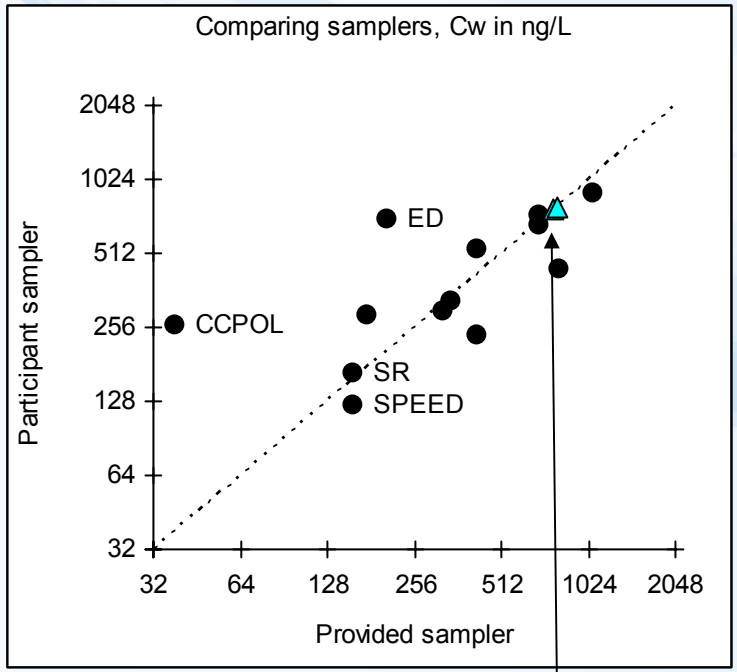
Pharmaceuticals					
		Coefficient of variation (%)			
Variability:		Within laboratory		Between laboratory	
Matrix analysed:		Min.	Max.	Min.	Max.
	Standard solution	3%	8%	6%	35%
Provided sampler	NPS amount	11%	14%	35%	133%
	NPS water concentration	8%	13%	70%	333%
Participant sampler	PPS amount	10%	33%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

NPS – provided passive sampler; PPS – participant passive sampler

Comparison: participant vs. provided samplers

CARBAMAZEPINE





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 varability 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

Acknowledgment

- NORMAN Association
- European Commission – DG JRC
- Organisers – steering committee
- Water Research Institute, Slovakia
- RECETOX, Masaryk university, Czech republic
- Deltares, The Netherlands
- Participants


Thank you for your attention!

Continuous water sampling: for polar compounds only

PHARMACEUTICALS, POLAR PESTICIDES STEROIDS, FLUORINATED SURFACTANTS, BISPHENOL A, TRICLOSAN

Provided sampler: POCIS

- OASIS HLB Sorbent receiving phase
- Polyethersulphone membrane
- Standard configuration (200 mg sorbent; 45.8 cm^2 surface area)
- For polar pesticides spiked with DIA-D5 – potential PRC

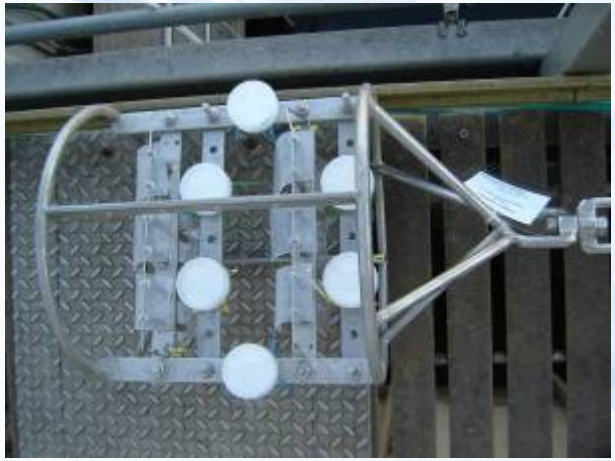
BROMINATED DIPHENYL ETHERS

Provided sampler: Altesil Silicone rubber

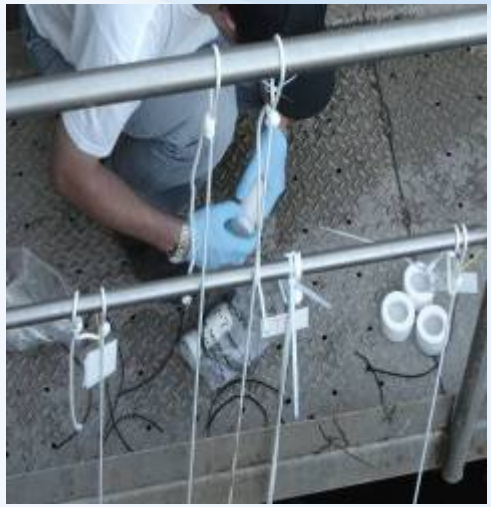
- Silicone rubber sheet consisting of 3 sheets (90x55 mm), ≈8.91 g
- Surface area: 297 cm^2
- Performance reference compounds: 7. PRCs: D10-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204

After six weeks exposure…

Sampler preparation for deployment

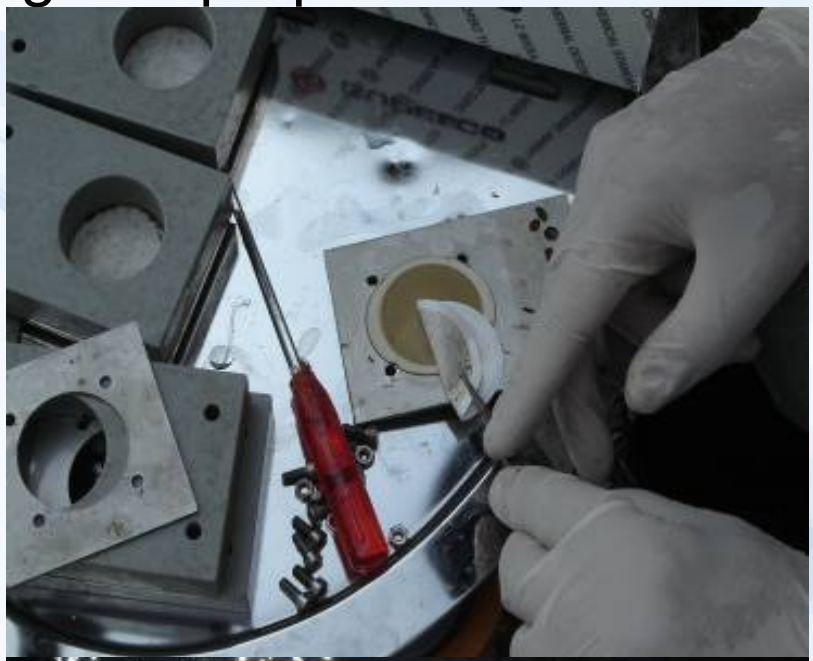







Sampler recovery

Onsite sampler cleaning and preparation



Target compounds
POLAR PESTICIDES

	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

Target compounds
PHARMACEUTICALS

	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

Target compounds
STEROID HORMONES

	Compound	CAS	Usage
1.	17-alpha-Estradiol	57-91-0	steroid hormone
2.	17-alpha-Ethinylestradiol	77538-56-8	contraceptive
3.	17-beta-Estradiol	82115-62-6	steroid hormnone
4.	Estriol	50-27-1	steroid hormnone
5.	Estrone	53-16-7	steroid hormnone

Target compounds
BISPHENOL A, TRICLOSAN, PFOA PFOS

	Compound	CAS	Usage
1.	Bisphenol A	80-05-7	monomer to make plastics
2.	Triclosan	3380-34-5	antibacterial and antifungal agent

	Compound	CAS	Usage
1.	PFOA	335-67-1	fluorosurfactant
2.	PFOS	1763-23-1	fluorosurfactant, fabric protector

Target compounds
BROMINATED DIPHENYL ETHERS

	Compound	CAS	Usage
1.	BDE 28	41318-75-6	Flame retardant
2.	BDE 47	5436-43-1	Flame retardant
3.	BDE 99	60348-60-9	Flame retardant
4.	BDE 100	189084-64-8	Flame retardant
5.	BDE 153	68631-49-2	Flame retardant
6.	BDE 154	207122-15-4	Flame retardant