NORMAN Interlaboratory study (ILS) on passive sampling of emerging pollutants **Study design and organisation**

Branislav Vrana

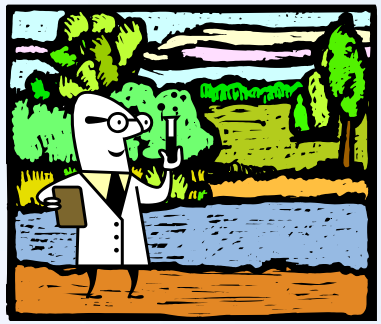
Water Research Institute, Bratislava
RECETOX, Masaryk university, Brno

Chemical Monitoring On Site (CM Onsite) organised by NORMAN Association and JRC in support of CIS WFD; 29.-30.10.2012, Ispra, Italy

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

STUDY DESIGN

Collaborative study

A sampler comparison exercise

Assessment of steps in passive sampling process

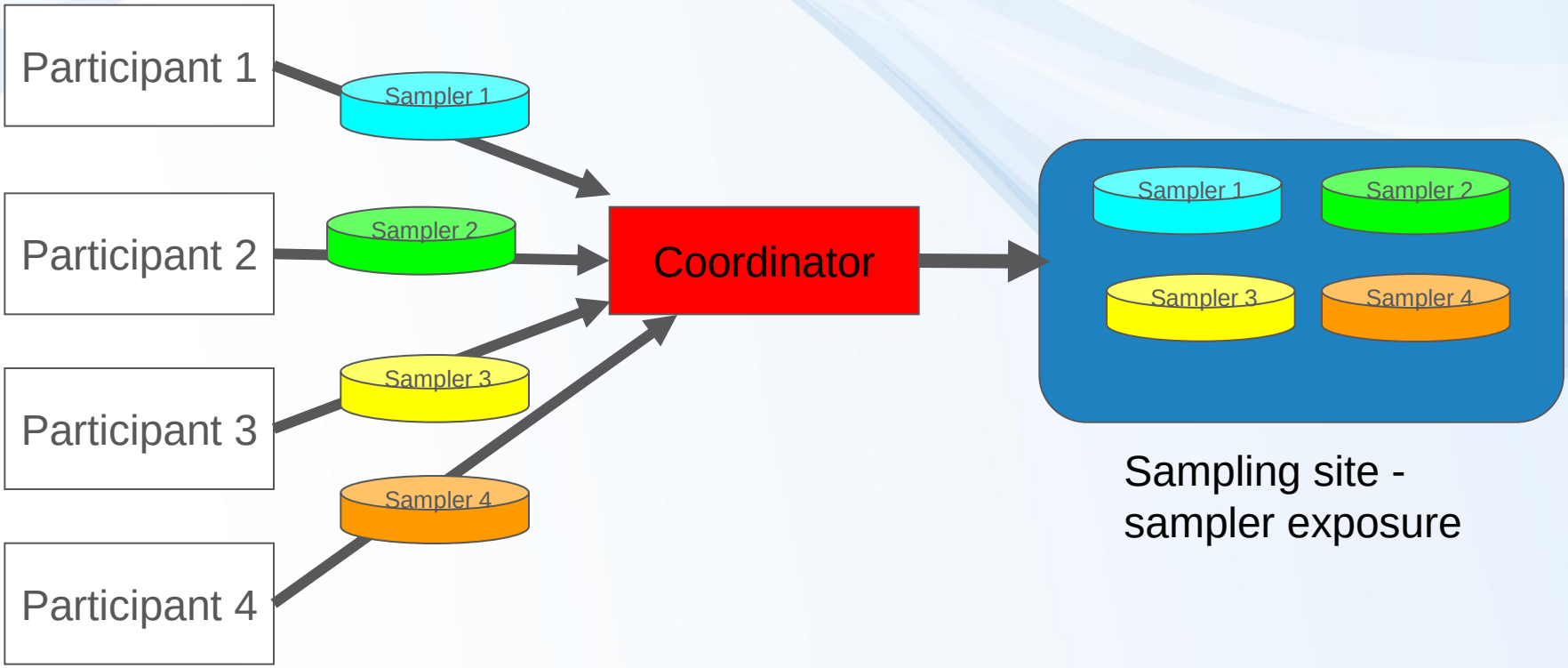
- instrumental analysis
- analysis of sampler matrix
- comparison of samplers
- comparison with spot sampling

Interlaboratory study, **Steering group**

VUVH, Slovakia (coordinator)
IRSTEA Bordeaux, France
ISM-LPTC, University of Bordeaux, France
IRSTEA Lyon, France
DG JRC IES
UK Environment Agency
DELTARES, The Netherlands
RECETOX, Masaryk University, Czech republic
Insitute of Public Health Ostrava, Czech Republic
QUASIMEME

1. Exposure of passive samplers from participants

for selected analyte/analytes

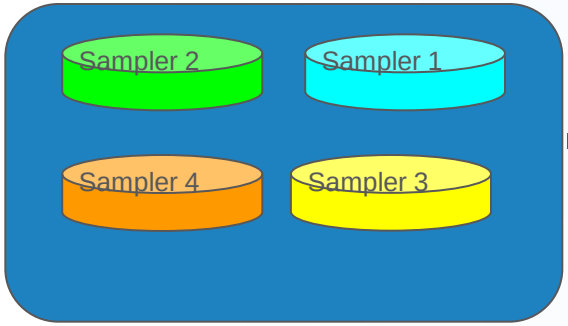


Report:
ng/sampler of compound X
Surface area of sampler
ng/L water of compound X
calculation procedure for compound X

II

1. Recovery passive samplers from participants

for selected analyte/analytes



Sampling site - sampler exposure

Coordinator

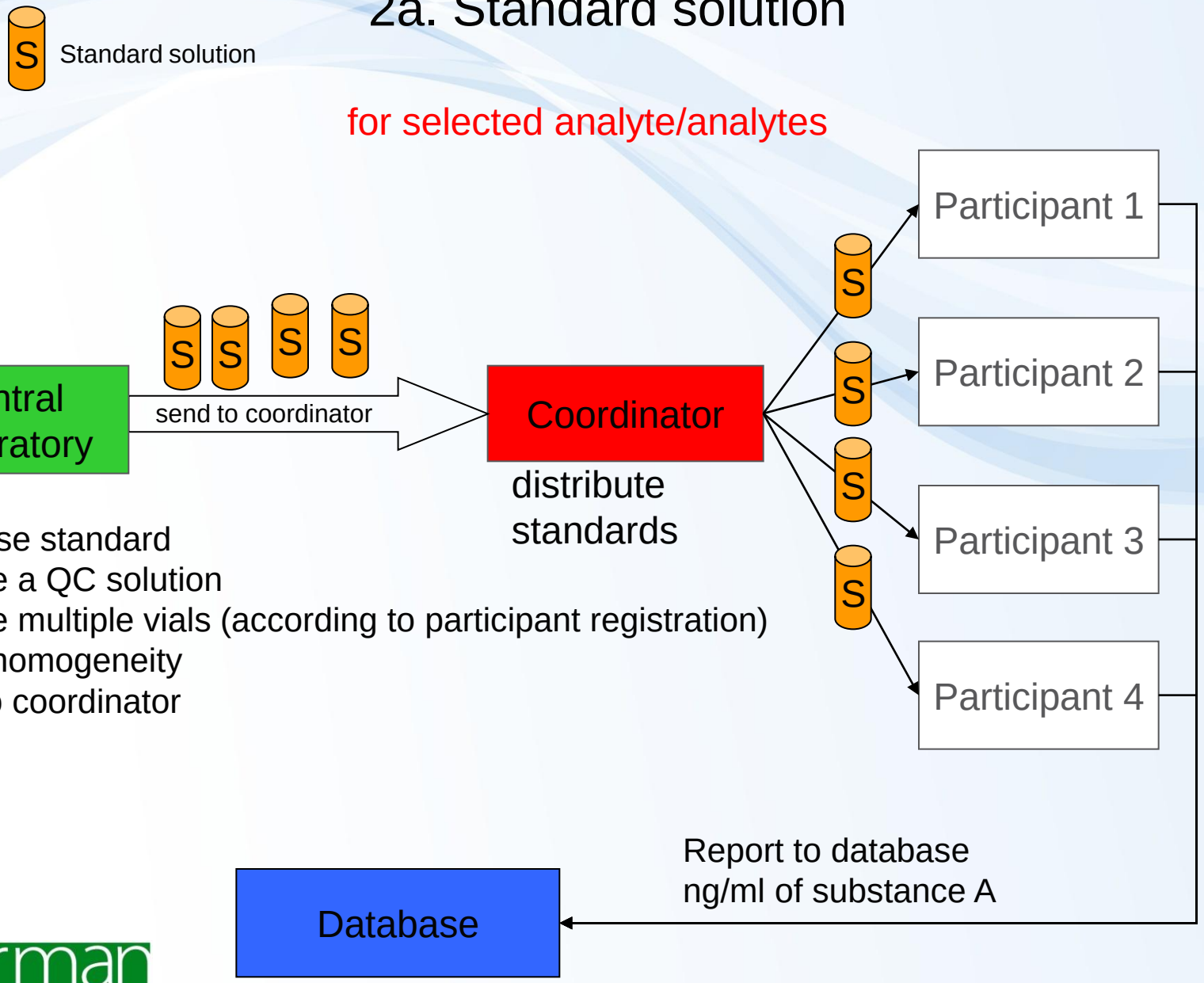
Sampler 1
Sampler 2
Sampler 3
Sampler 4

Participant 1
Participant 2
Participant 3
Participant 4

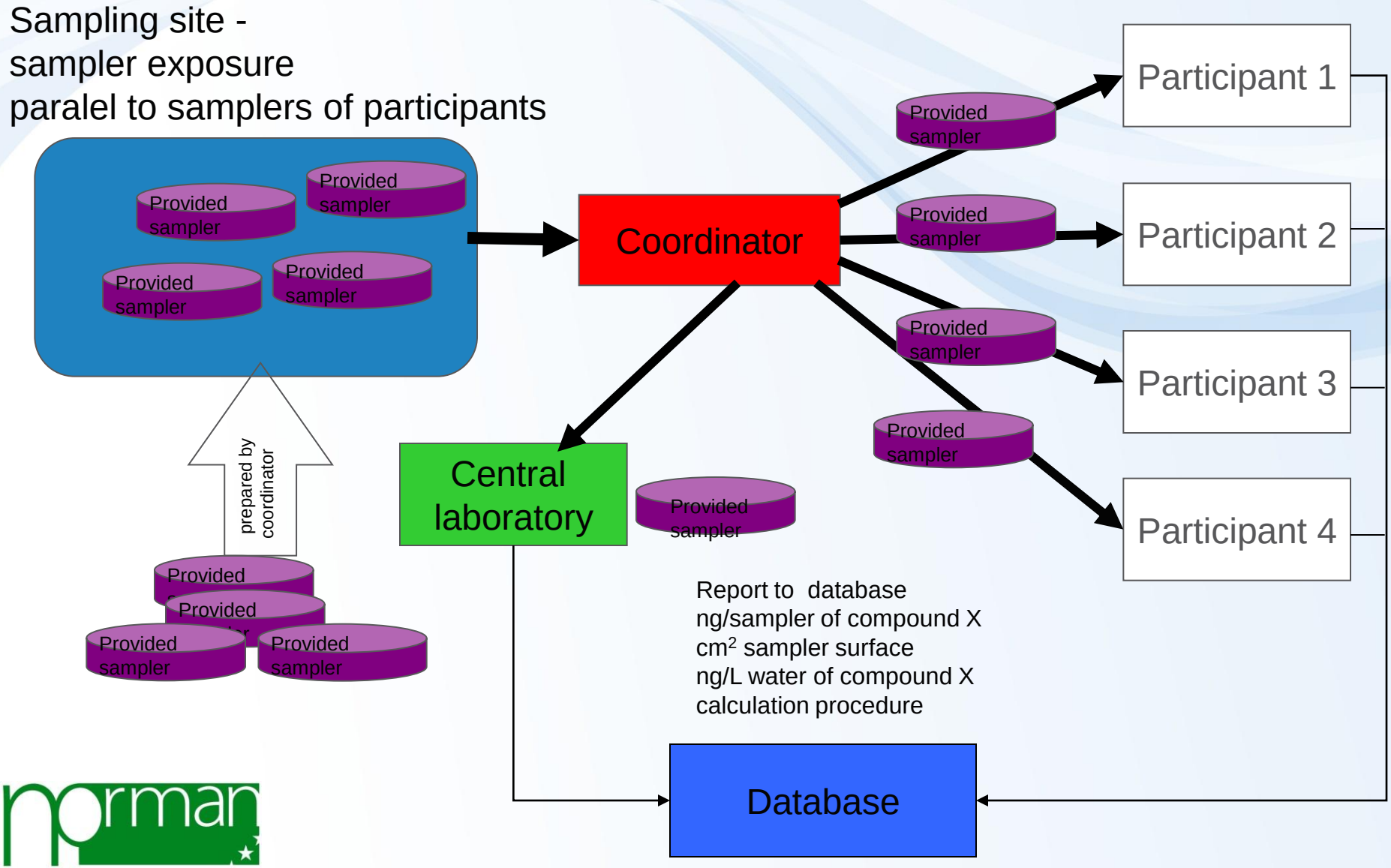
Report:
ng/sampler of compound X
Surface area of sampler
ng/L water of compound X
calculation procedure for compound X

Database

2a. Standard solution



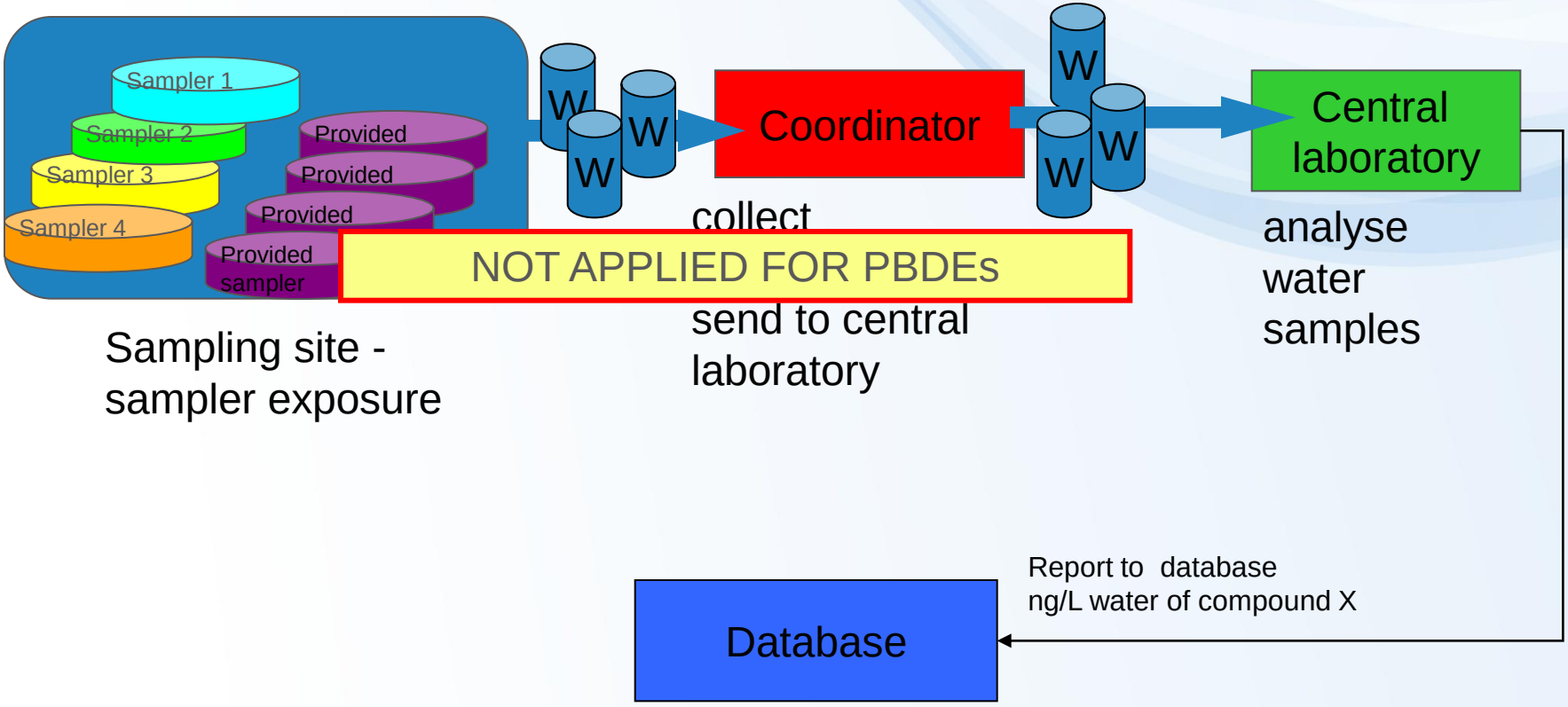
2b. Provided passive samplers



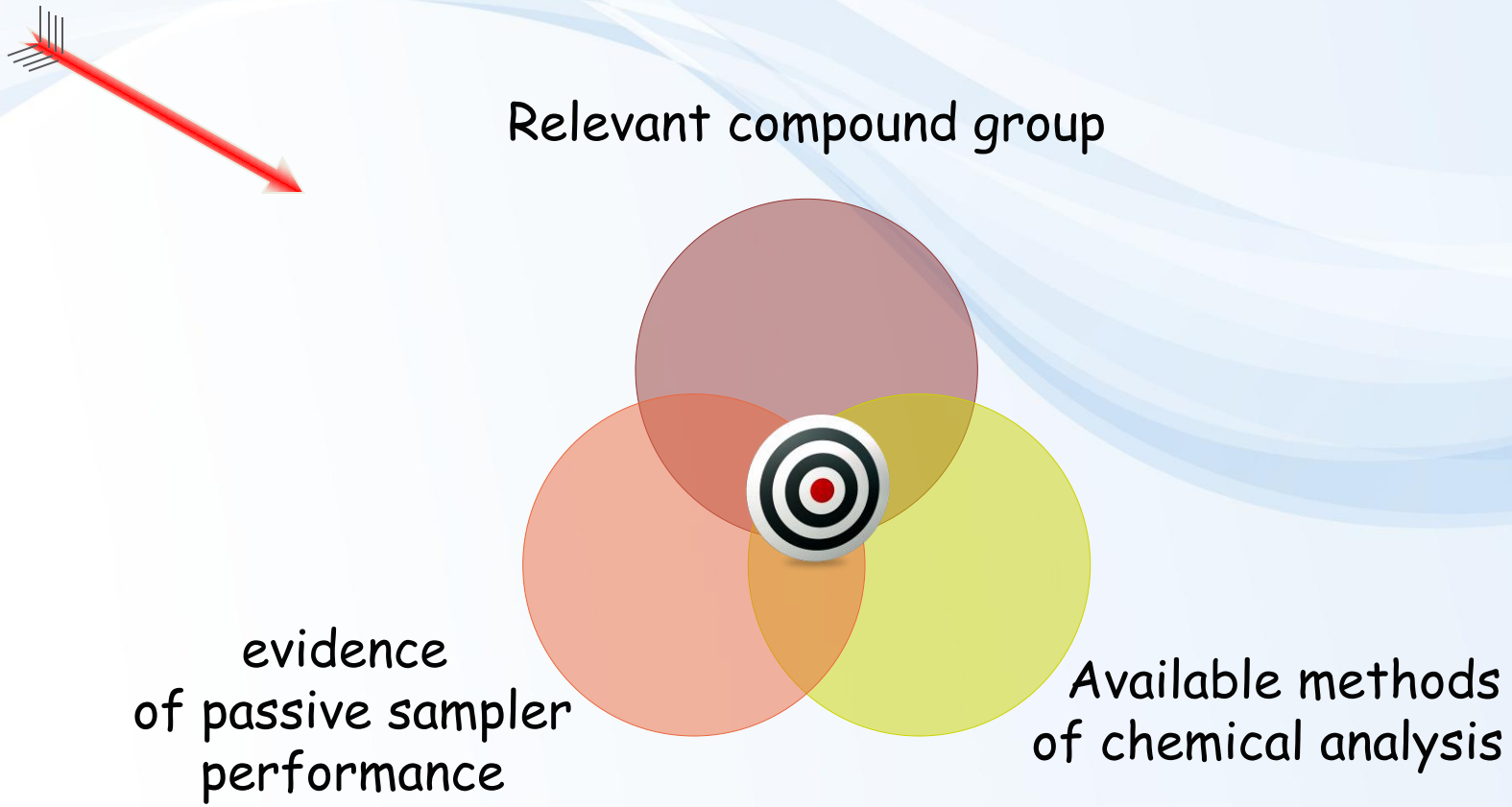
3. Water; continuous sampling

W water sample

for selected analyte/analytes



Target compounds: selection process



- NORMAN list of the most frequently discussed emerging substances
- Selection based on a questionnaire filled in by 10 expert laboratories

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

WFD priority substances; Directive 2008/105/EC

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

proposed priority substance; Directive 2008/105/EC under review

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

proposed priority substances; Directive 2008/105/EC under review

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

proposed priority substance; Directive 2008/105/EC under review

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

WFD priority substances; Directive 2008/105/EC

STUDY REALISATION

Contribution and tasks

<table>
<tr><th>Organisation</th><th>Role</th></tr>
<tr><td>WRI, Slovakia</td><td>Coordinator</td></tr>
<tr><td>Cemagref Bordeaux, France</td><td rowspan="6">Preparation of analytical QC standards,

Preparation of samplers that are provided to participants,

Analysis of parallel water samples (not BDEs)</td></tr>
<tr><td>ISM-LPTC, University of Bordeaux,</td></tr>
<tr><td>Cemagref Lyon, France</td></tr>
<tr><td>UK Environment Agency, UK</td></tr>
<tr><td>DG JRC IES</td></tr>
<tr><td>RECETOX + DELTARES</td></tr>
<tr><td>Institute of Public Health Ostrava, Czech Republic</td><td>Sampling support</td></tr>
<tr><td>RECETOX</td><td>Sampling support
Data interpretation</td></tr>
<tr><td>QUASIMEME</td><td>Data reporting</td></tr>
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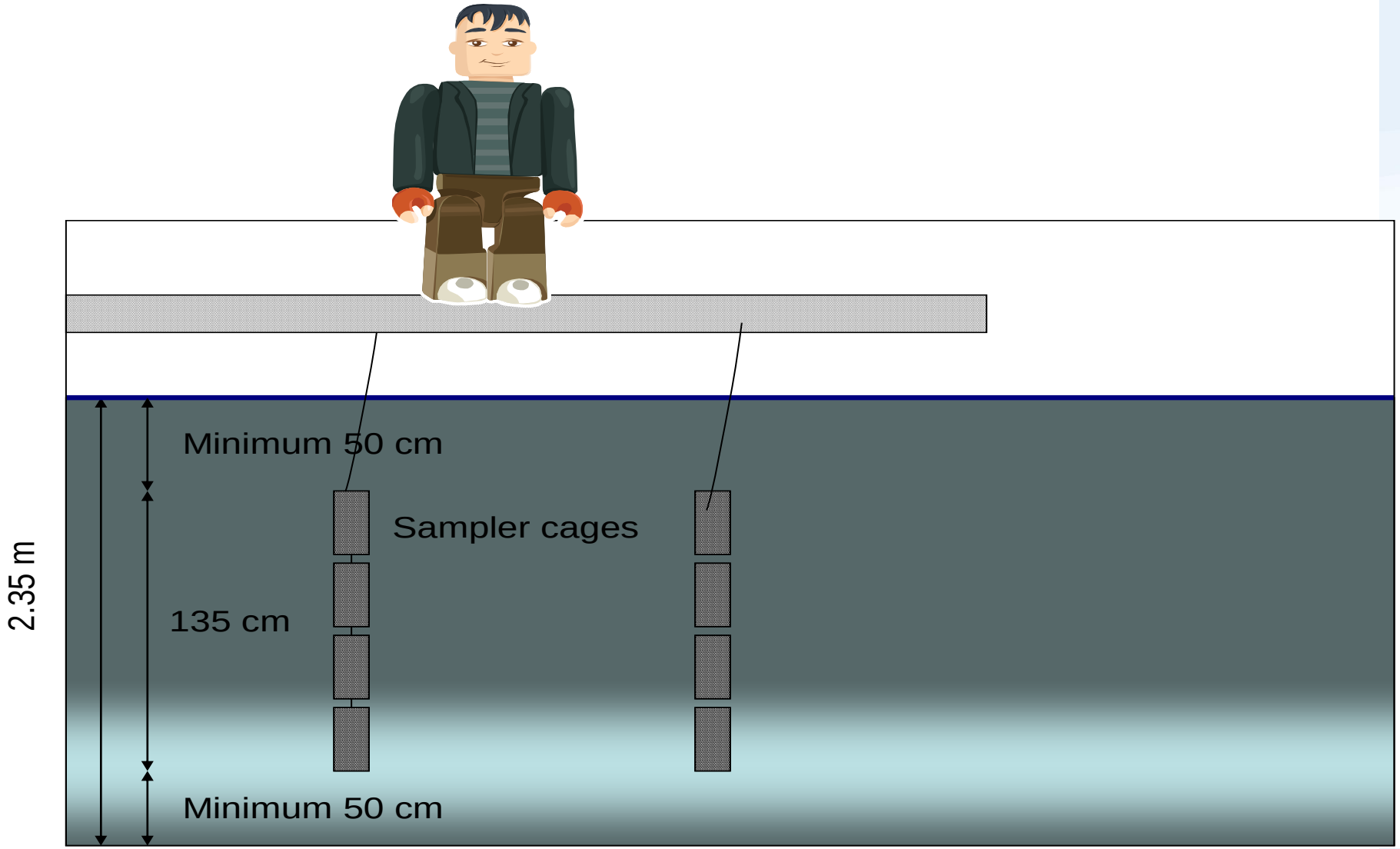
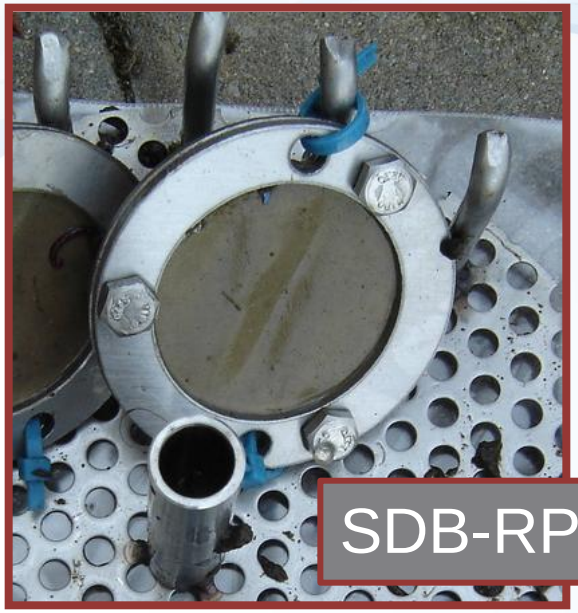
Sampling site: discharge from WWTP Brno-Modřice

Sampling site: discharge from WWTP Brno-Modřice



Study preparation: Pre-screening for presence of contaminants



SDB-RPS

SDB-RPS-PES

Silicone rubber

POCIS

Screening for presence of contaminants

Compound class	Sampler	Laboratory	Contact
Polar pesticides	POCIS	Irstea Lyon	Nicolas.Mazzella@irstea.fr
Polar pesticides, pharmaceuticals	SDB/RPS Empore disk	Eawag	Etienne.Vermeirssen@eawag.ch
Steroid hormones	POCIS, SDB-XC Empore	RECETOX	simek@recetox.muni.cz
PBDE	Silicone sheets	RECETOX	kukucka@recetox.muni.cz prokes@recetox.muni.cz
Pharmaceuticals	POCIS	University Bordeaux	h.budzinski@ism.u-bordeaux1.fr
PFOA, PFOS	POCIS	RECETOX	becanova@recetox.muni.cz
Triclosan	SPMD	IPH Ostrava	samuel.mach@zu.cz
Bisfenol A	Water sample/SBSE	VUVH	branovrana@googlemail.com

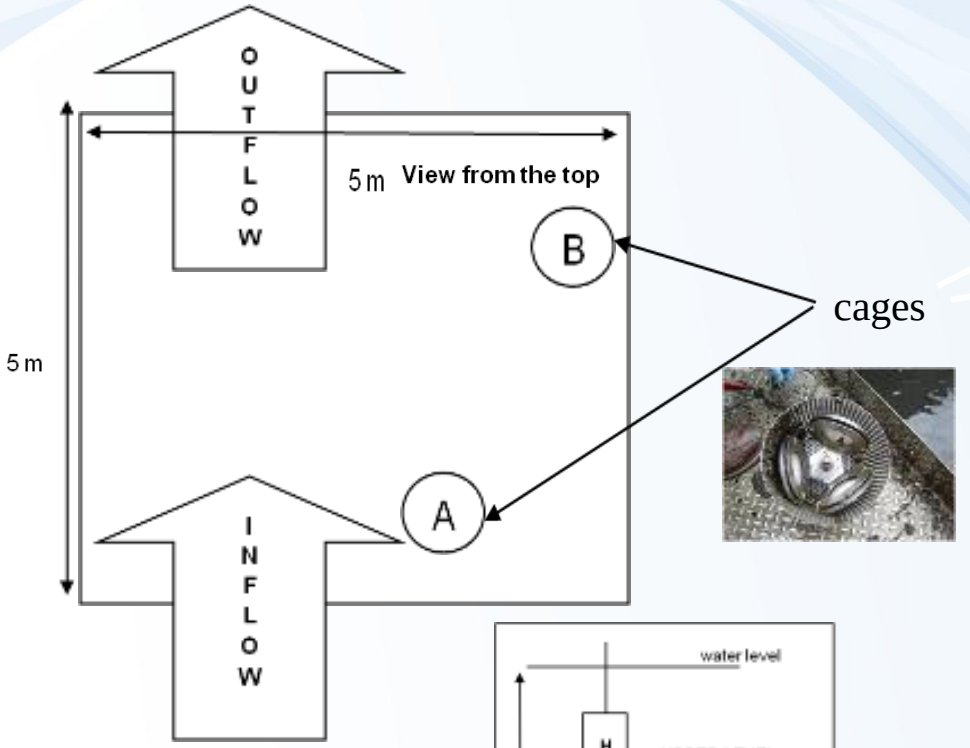
Screening for presence of contaminants: Fluorinated surfactants

Sampler: POCIS; 18.6.-2.7.2010

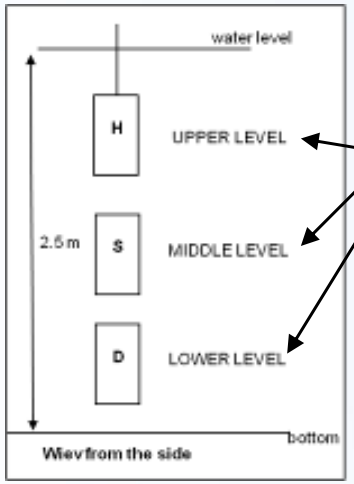
Analysed by: RECETOX

Sample Name	c (ng/sampler)					
Analytes	**Blank1**	**Blank2**	**Blank3**	**Sampler1**	**Sampler2**	**Sampler3**
PFBA	< 0,16	< 0,16	< 0,16	1.22	1.28	1.59
PFPA	0.66	0.74	0.77	1.23	1.18	1.15
PFHxA	-	-	-	0.96	1.12	1.52
PFHpA	-	-	-	1.27	1.00	1.33
PFOA	**< 0,14**	**< 0,14**	**< 0,14**	**6.28**	**7.19**	**8.08**
PFNA	< 0,25	-	< 0,25	1.56	1.31	1.54
PFDA	< 0,28	< 0,28	< 0,28	2.18	1.81	2.28
PFUnDA	< 0,37	-	-	< 0,37	< 0,37	< 0,37
PFDoDA	< 0,24	-	< 0,24	< 0,24	< 0,24	< 0,24
PFTrDA	< 0,27	-	-	< 0,27	-	-
PFTEDA	-	-	-	-	-	-
PFBS	-	-	-	0.45	0.49	0.37
PFHxS	-	-	-	0.39	0.45	0.47
PFHpS	-	-	-	< 0,07	< 0,07	< 0,07
PFOS	**-**	**-**	**-**	**2.86**	**2.67**	**3.26**
PFDS	-	-	-	< 0,08	< 0,08	< 0,08

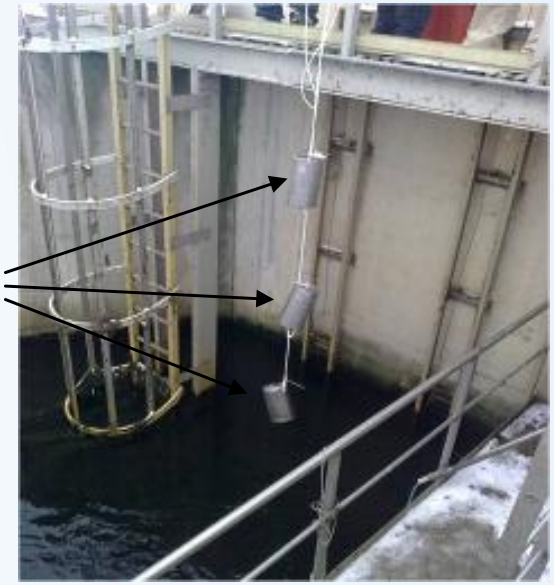
Study preparation: Passive sampling homogeneity test



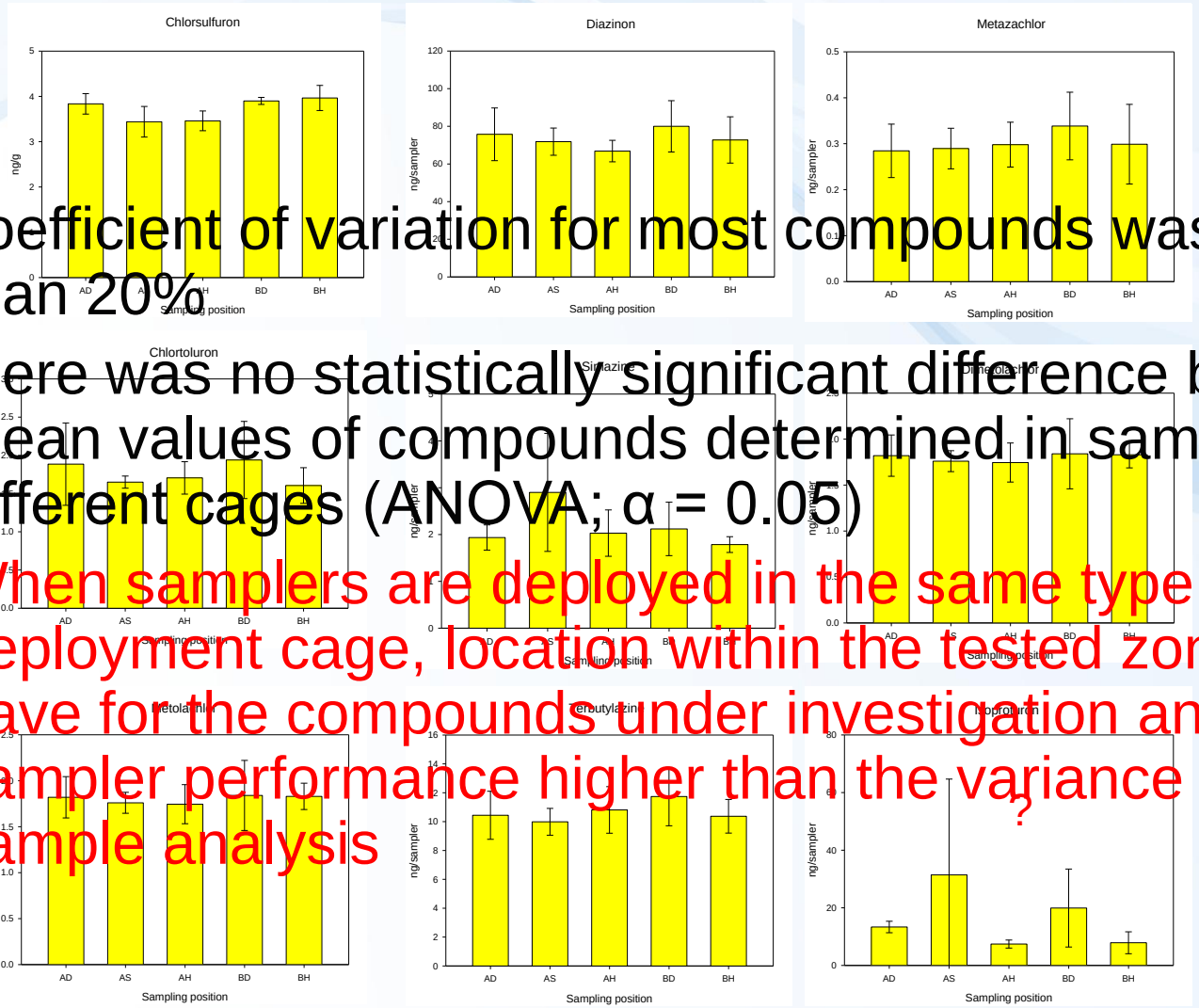
cages



cages



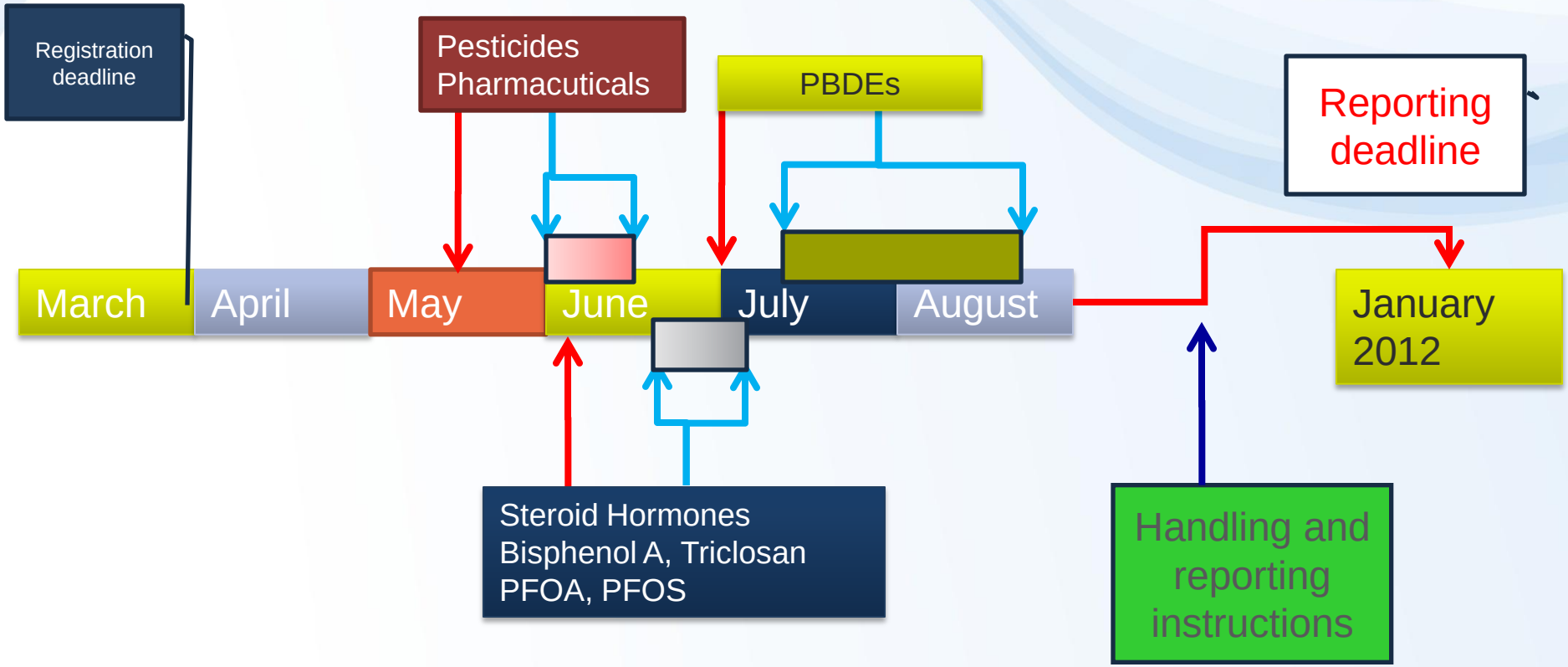
Study preparation: Passive sampling homogeneity test



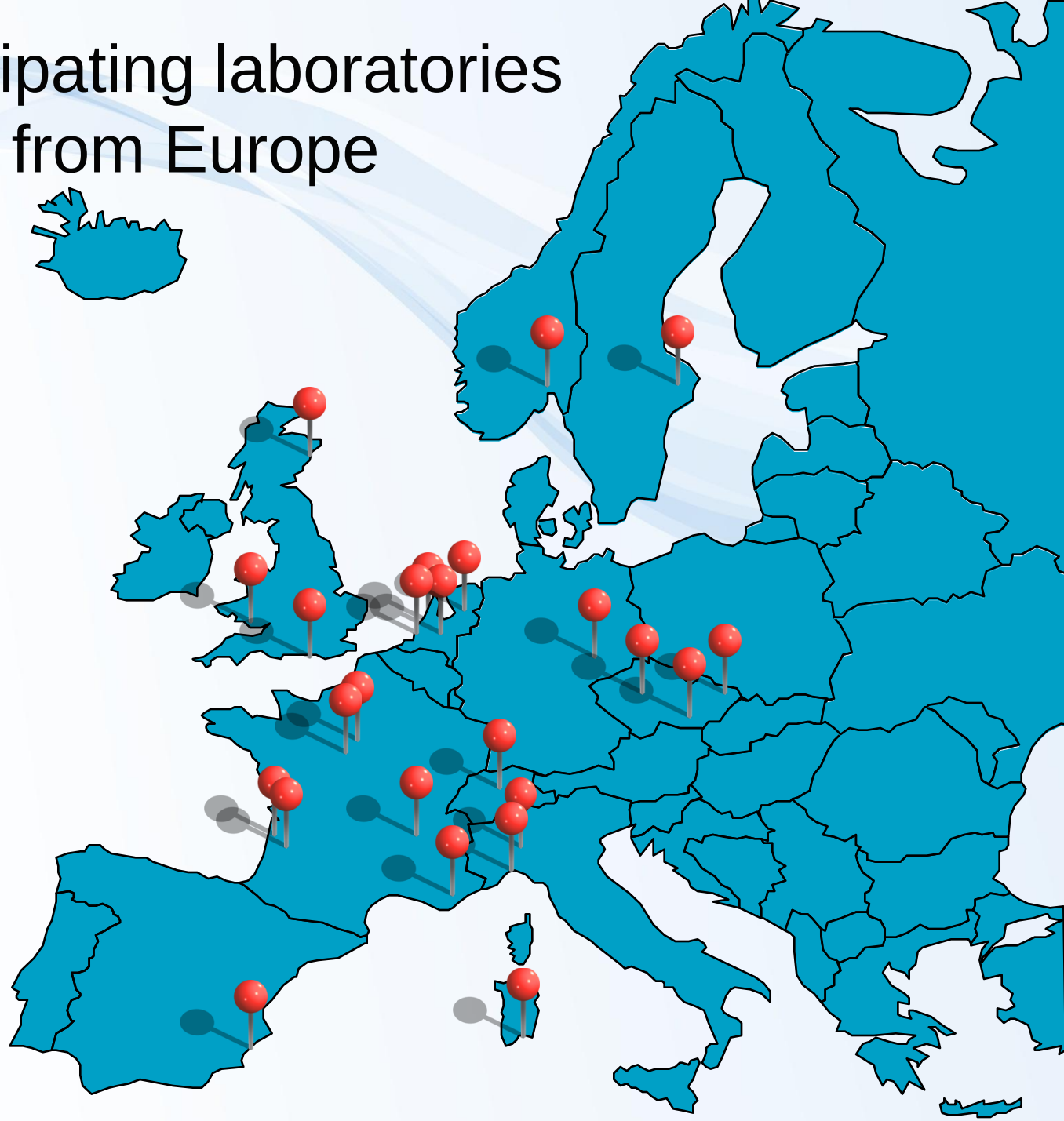
- coefficient of variation for most compounds was less than 20%
- there was no statistically significant difference between mean values of compounds determined in samplers from different cages (ANOVA; $\alpha = 0.05$)
- When samplers are deployed in the same type of deployment cage, location within the tested zone did not have for the compounds under investigation an effect on sampler performance higher than the variance of the sample analysis

?

Campaign timeline



Participating laboratories from Europe



…and from the rest of the World

Participant laboratories: self assessed expertise level

Laboratory ID	Polar pesticides	Pharmaceuticals	Steroid hormones	Fluorinated surfactants	Triclosan	Bisphenol A	Brominated flame retardants
16	A		A	A	C	A	A
17	A	A					
18	A						
19	A	B	B	B	B	B	B
20			C		B	C	B
21	C			C			C
23	A	A	B	A	A	A	A
25							B
26			C			C	C
29		A		A			A
30	A						A
31		A	A				
32	B	B					
33			A				
36	B	B	B				B
37	B		C	C			B
38							C
39	B	B	B	B		B	
40	A	A					
42	C						
43	B	B	B				A
44	C	C	C	C	C	C	C
45			B			B	
46		C					
47	B	B			B	B	
48	A	A					
49	B	B	A		A	B	
50	C	C	C		C	C	C
51							
52				A			

A-expert
B-some experience
C-limited experience

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

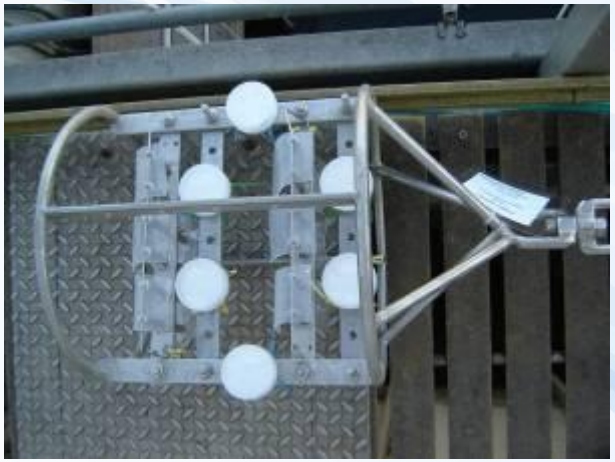
Delivery and handling of samplers prior exposure

Participants provided to the organiser for each compound class of interest at least 2 weeks before the start of sampler deployment:

4 passive samplers = 3 exposed + 1 field blank

- The system to deploy their own passive samplers (holders)
- instructions how the samplers are installed in the deployment
- system and how the sampling system should be deployed in water
- Instruction for sampler storage following exposure
- waybill for a courier service to get back their passive samplers after exposure

Sampler preparation for deployment

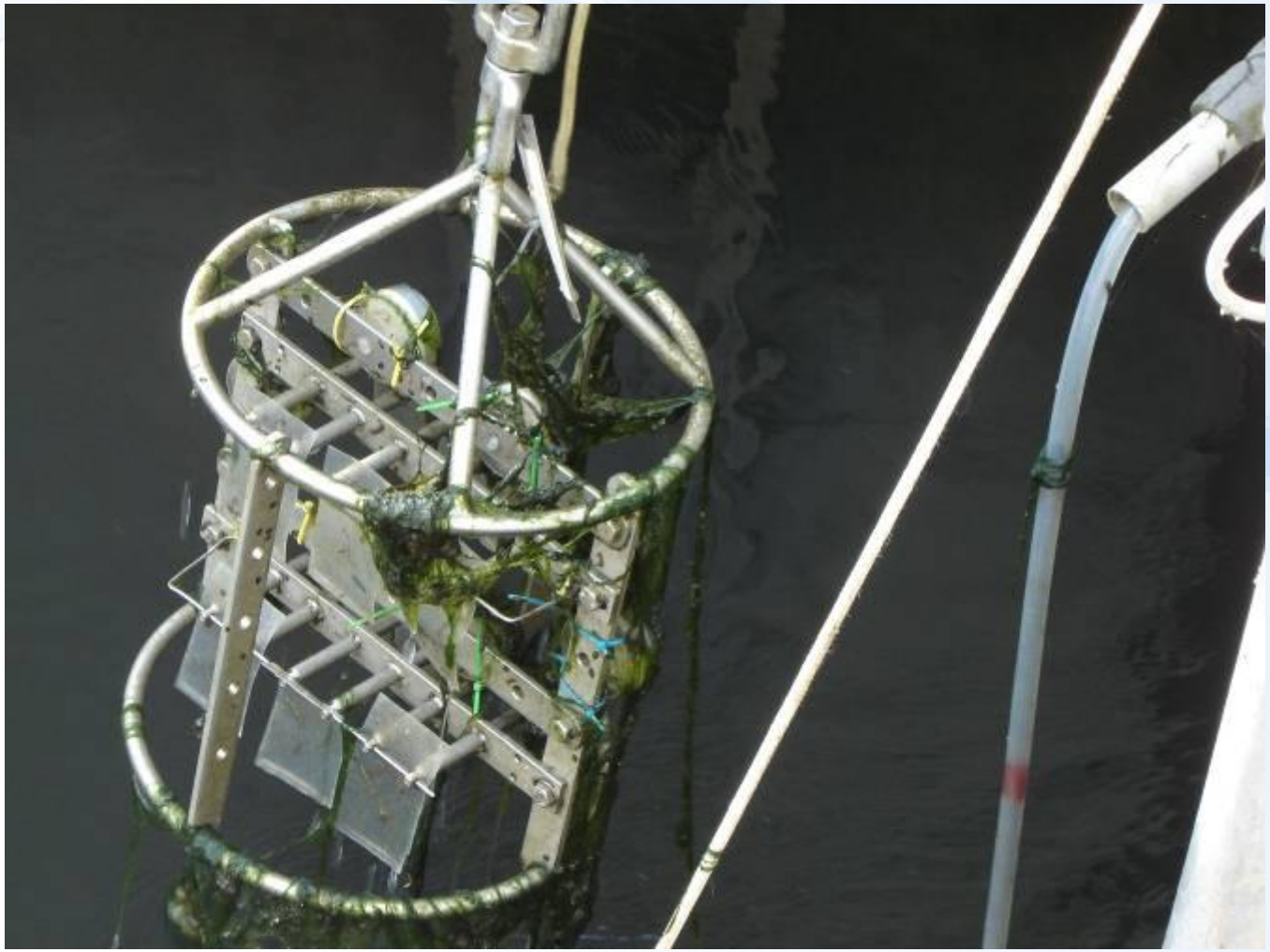


Sampler deployment

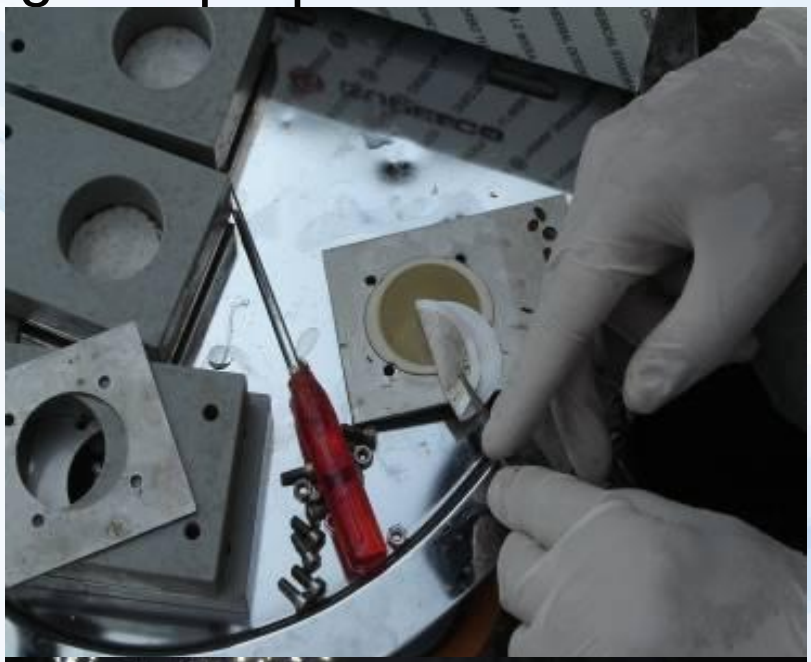
Sampler deployment

Sampler recovery

Sampler recovery



Onsite sampler cleaning and preparation



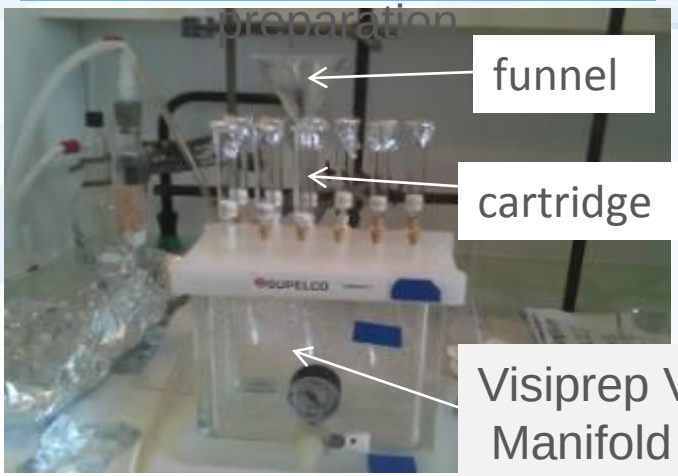
PHARMACEUTICALS, POLAR PESTICIDES STEROIDS, FLUORINATED SURFACTANTS, BISPHENOL A, TRICLOSAN

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

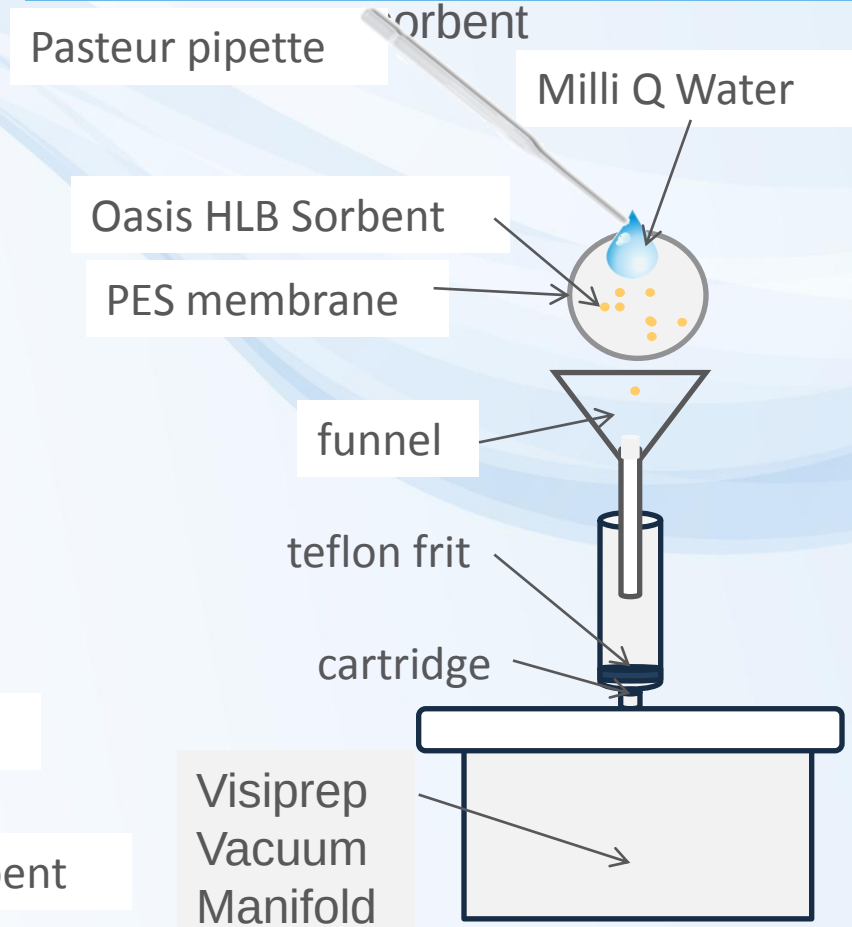
Preparation of provided POCIS samplers for distribution to participants

Step 1 : Cartridge preparation

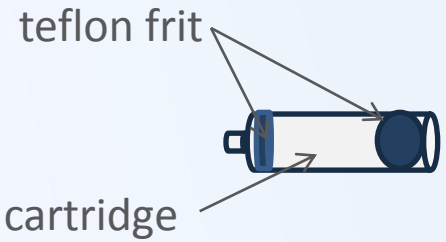


Step 2 : Pocis dismantling

Step 3 : Transfer the OASIS HLB sorbent



SAMPLERS WERE RANDOMISED !!!



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

Preparation of provided samplers

Sampler handling and delivery to participants after exposure

Following exposure the organiser arranged

- treatment and storage of samplers according participant`s instructions
- communication with participants concerning sampler delivery arrangement
- shipment of samplers to participants by a fast courier service (paid by participant)

Materials for analysis

Following the sampler exposure each participant received for each target compound class of interest (according to registration):

- standard solution of each compound class
- 3 exposed passive samplers provided by the organiser – ALWAYS RANDOMISED
- 1 field blank passive sampler provided by the organiser
- 3 exposed passive samplers provided by the participant
- 1 field blank passive sampler provided by the participant

Continuous water sampling: for polar compounds only

WATER SAMPLING PROTOCOL

STEROIDS, PFOA/PFOS, triclosan, Bishpenol A

FIELD SAMPLES

Automatic sampler (on site): Collect 100 mL/h x 24h = 2400 ml/day

Transport to RECETOX: Transfer 24h composite water sample every day from 12x1 L autosampler cylinders to a clean 2.5 L amber glass bottle, homogenise and transport on ice to the laboratory

min. 2000 mL/day

Filter through Whatman GF/F

570 mL/day | 570 mL/day | 340 mL/day | 430 mL/day

Triclosan AND Bishpenol A (570 mL/day)

285 ml/day | 285 ml/day

bottle A 2x1 L; glass bottle
Store @ 4 C
2000 ml / 7-day composite sample
Send weekly to UK EA

bottle B 2x1 L; glass bottle
Store @ 4 C
2000 ml / 7-day composite sample
Send weekly to UK EA

PFOA/PFOS (570 mL/day)

285 ml/day | 285 ml/day

bottle C 2L; Nalgene
Store @ 4 C
2000 ml / 7-day composite sample
Send weekly to DG JRC IES

bottle D 2L; Nalgene
Store @ 4 C
2000 ml / 7-day composite BACKUP, store at RECETOX

Steroid hormones (340 mL/day)

170 ml/day | 170 ml/day

bottle E 2x 1L; glass bottle
Store @ -20 C
1200 ml / 7-day composite sample
Send weekly to Cemagref Lyon

bottle F 2x 1L; glass bottle
Store @ -20 C
1200 ml / 7-day composite BACKUP store at RECETOX

bioassays (430 mL/day)

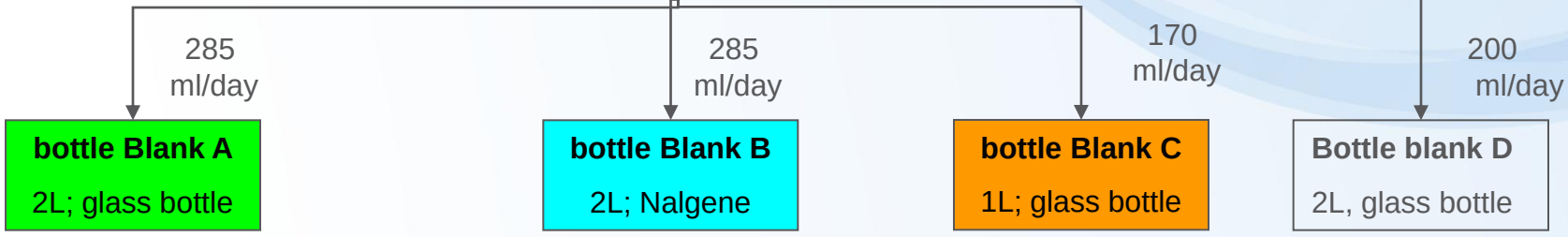
bottles G,H 2x 2L; glass bottle
Store @ -20 C
2x1500 ml / 7-day composite sample
Store at RECETOX

WATER SAMPLING PROTOCOL
STEROIDS, PFOA/PFOS, triclosan, Bishpenol A

BLANK SAMPLES

1000 mL Milliq water/day

Filter through Whatman GF/F



Store @ 4 C

2000 ml / 7-day composite BLANK triclosan and bisphenol A

Send weekly to UK EA

Store @ 4 C

2000 ml / 7-day composite BLANK PFOS/PFOA

Send weekly to DG JRC IES

Store @ -20 C

1200 ml / 7-day composite BLANK Steroids

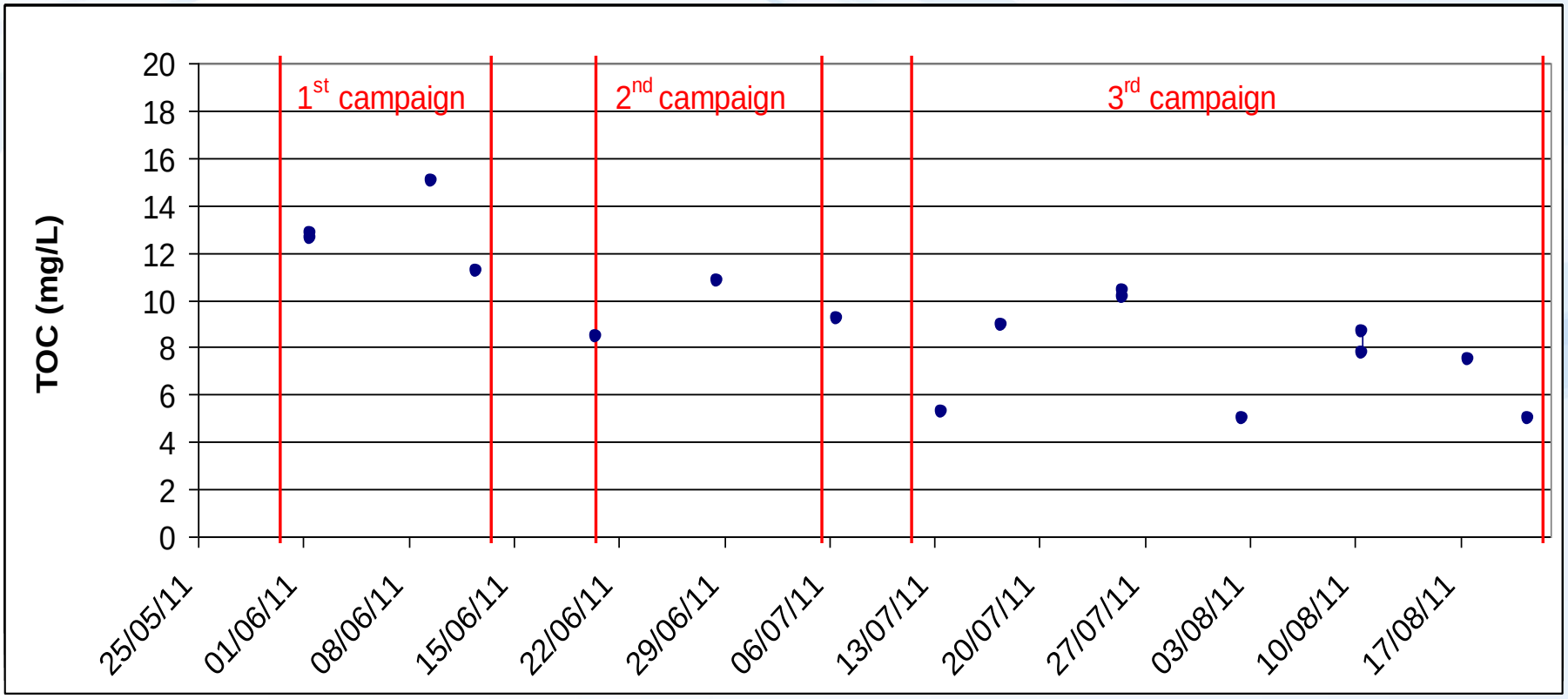
Send weekly to Irstea Lyon

Store @ -20 C

1500 ml / 7-day composite BLANK Steroids

Store at RECETOX

Water quality parameters



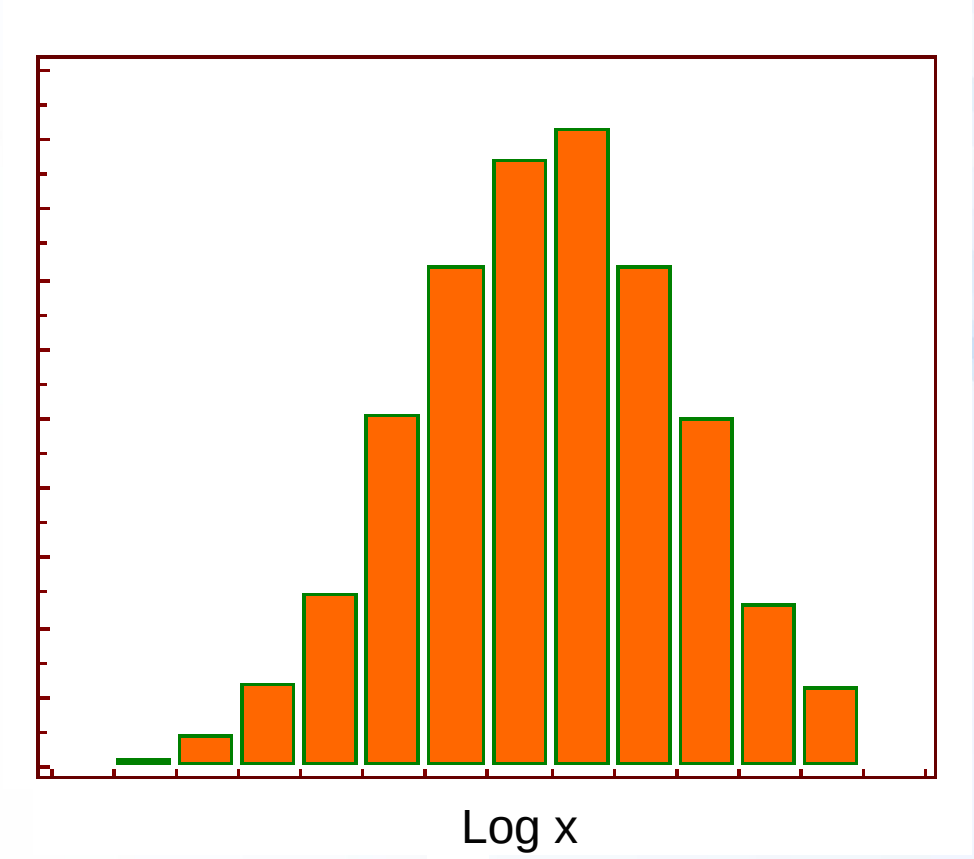
Discharge	pH
Temperature	Conductivity
Suspended solids	TOC

REPORTING

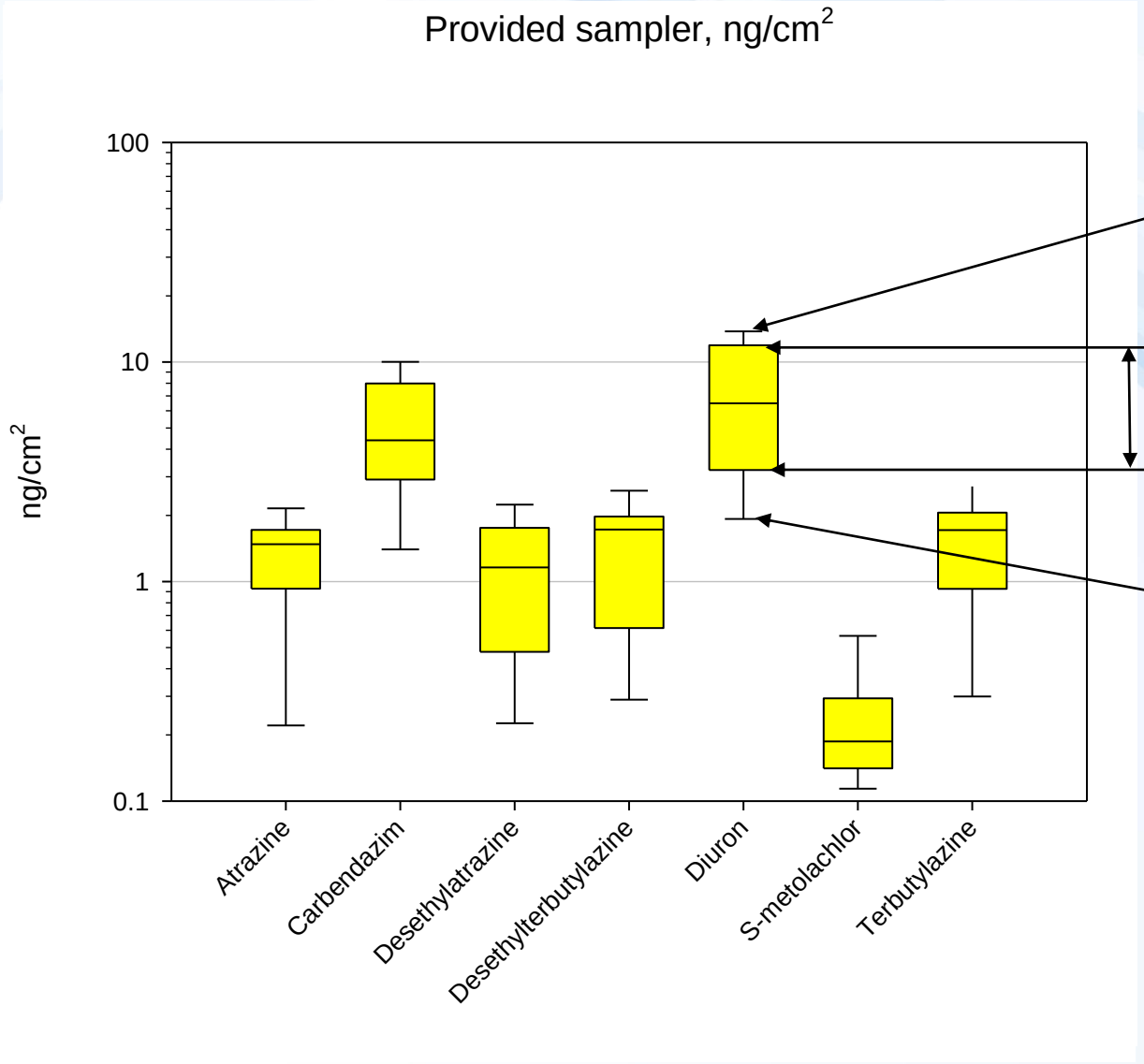
- Sharepoint sites by Quasimeme
- Reporting excel templates
- Instructions provided in October 2011
- Reporting deadline in January 2012

DATA EVALUATION

LOG TRANSFORMATION



Box-and-whisker plots



90th percentile

75th percentile = Q3

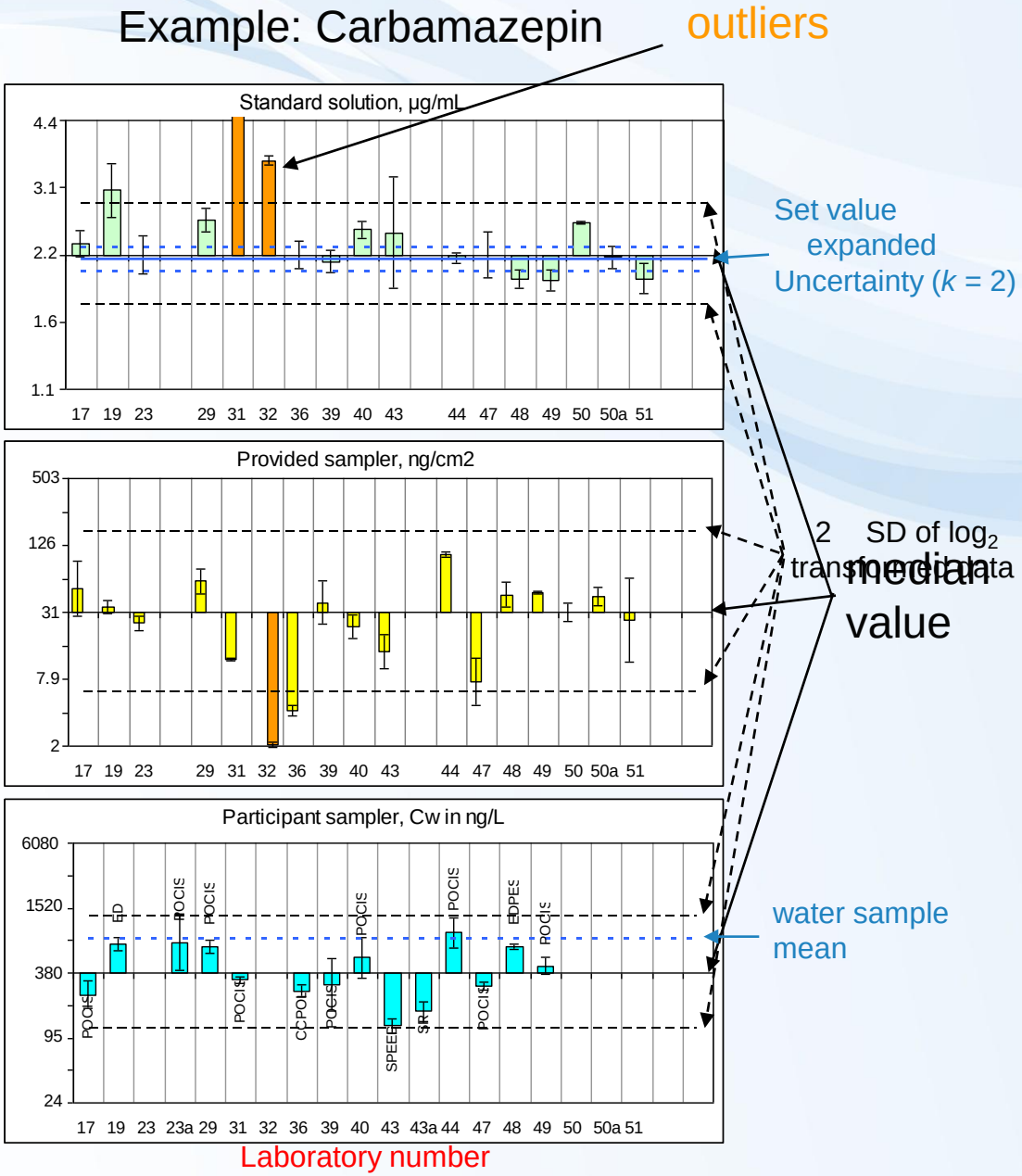
IQR

25th percentile = Q1

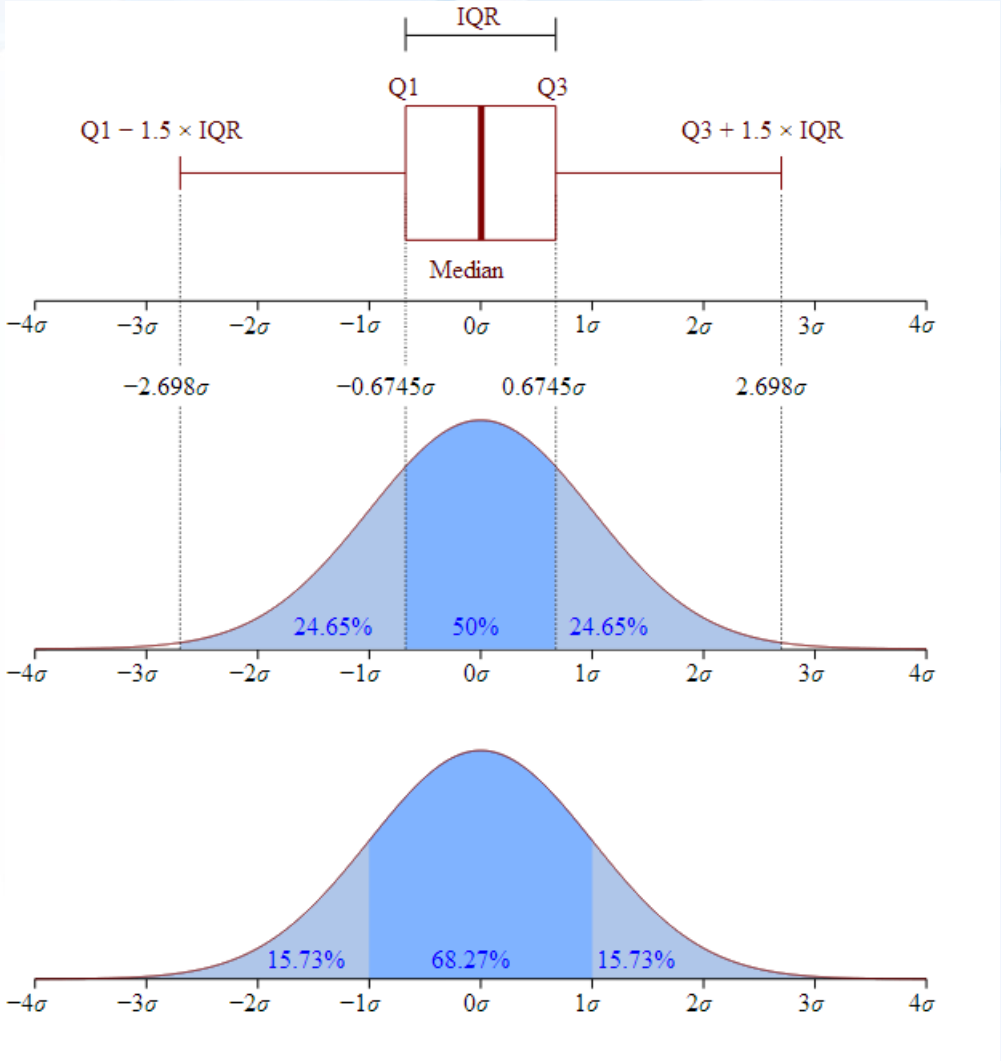
10th percentile

BAR GRAPHS

Example: Carbamazepin

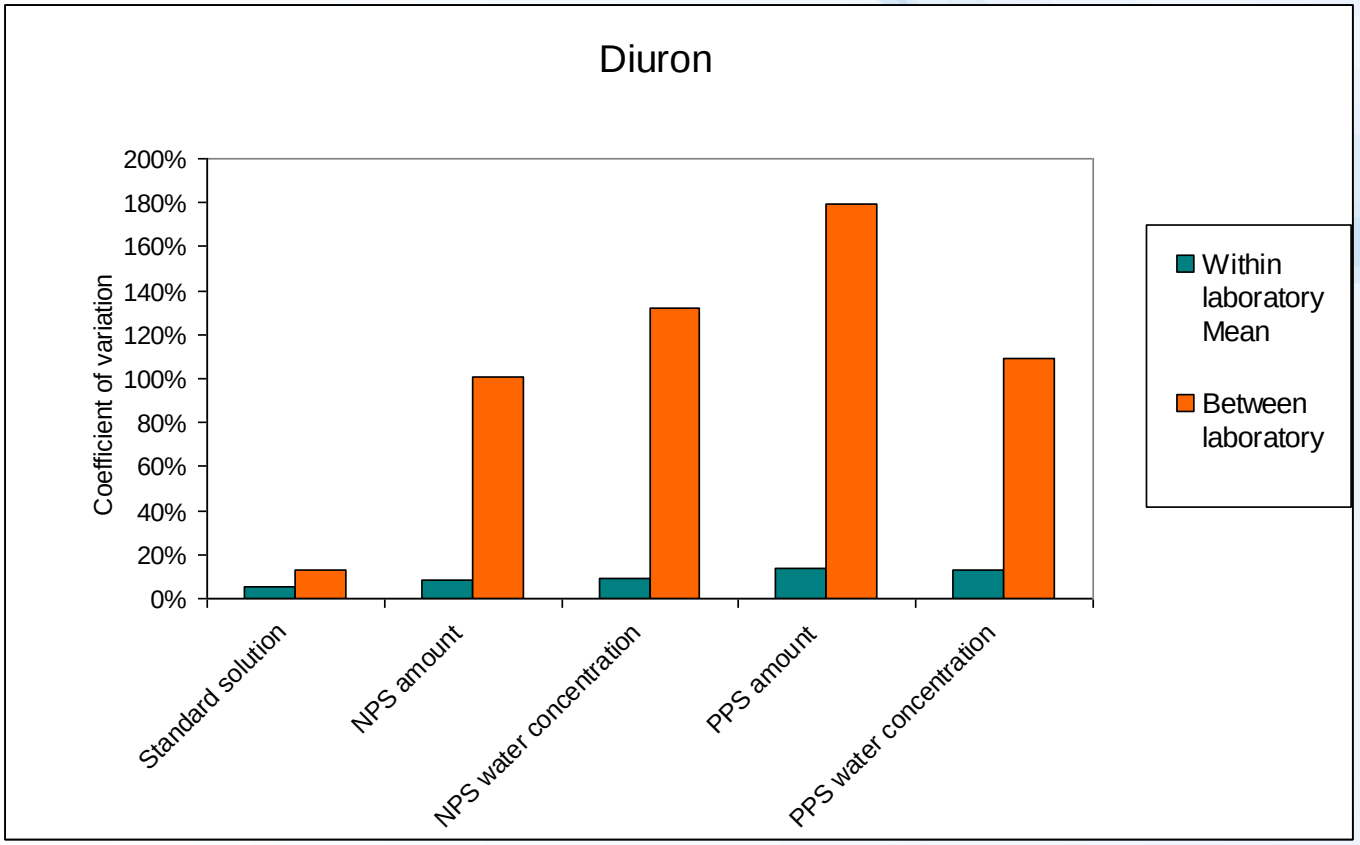


OUTLIER IDENTIFICATION



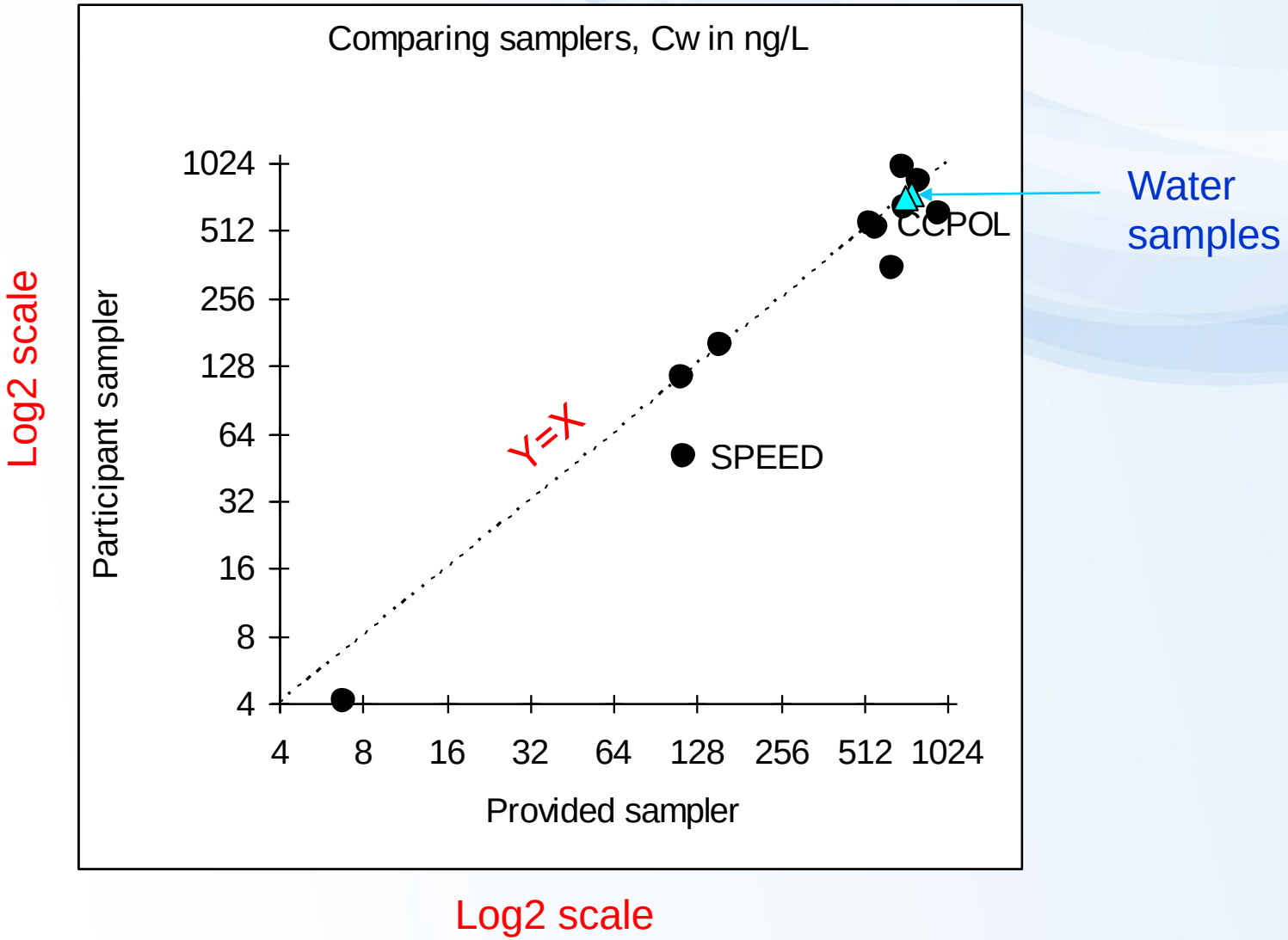
Expression of data variability

$$CV = \ln 2 \; s_{\log 2}$$



BIPLOTS: participant vs. provided samplers

Example: Diclofenac



Statistics and numbers

- 10 institutions involved in organisation
- 30 participating laboratories from 3 continents (Europe, North America and Australia)
- 29 target compounds analysed
- 6 courier service companies used for shipment
- 268 participant samplers for pesticides and pharmaceuticals
- 285 participant samplers for PFOS, steroids, bisphenol A and triclosan
- 292 provided samplers for polar compounds
- 80 provided samplers for PBDE
- 132 participant samplers for PBDE
- **Total: 1057 samplers were deployed at the reference site and distributed for analysis**

Acknowledgment

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

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Thank you for your attention!

Interlaboratory study: participant registration

- 30 participants from commercial, academic and regulatory laboratories

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

- Request to report other compounds detected