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

www.norman-network.net
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

<table>
<thead>
<tr>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>VUVH, Slovakia (coordinator)</td>
</tr>
<tr>
<td>IRSTEA Bordeaux, France</td>
</tr>
<tr>
<td>ISM-LPTC, University of Bordeaux, France</td>
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<td>IRSTEA Lyon, France</td>
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<tr>
<td>DG JRC IES</td>
</tr>
<tr>
<td>UK Environment Agency</td>
</tr>
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<td>DELTARES, The Netherlands</td>
</tr>
<tr>
<td>RECETOX, Masaryk University, Czech republic</td>
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<tr>
<td>Insitute of Public Health Ostrava, Czech Republic</td>
</tr>
<tr>
<td>QUASIMEME</td>
</tr>
</tbody>
</table>
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
Participant 1

Sampler 2
Participant 2

Sampler 3
Participant 3

Sampler 4
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

for selected analyte/analytes

Central laboratory

send to coordinator

purchase standard
prepare a QC solution
prepare multiple vials (according to participant registration)
check homogeneity
send to coordinator

Coordinator

distribute standards

Participant 1

Participant 2

Participant 3

Participant 4

Report to database
ng/ml of substance A

Database
 Provided passive samplers

Sampling site - sampler exposure parallel to samplers of participants

Coordinator

Participant 1

Participant 2

Participant 3

Participant 4

Central laboratory

Provided sampler

Provided sampler

Provided sampler

Provided sampler

Prepared by coordinator

Database

Report to database ng/sampler of compound X cm² sampler surface ng/L water of compound X calculation procedure
3. Water; continuous sampling

For selected analyte/analytes

Sampling site - sampler exposure

Water sample

Coordinator

Central laboratory

Sampler 1
Sampler 2
Sampler 3
Sampler 4

Provided sampler

Collect water samples

Send to central laboratory

Not applied for PBDEs

Report to database ng/L water of compound X

Database
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

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.</strong> Atrazine</td>
<td>1912-24-9</td>
<td>triazine herbicide</td>
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<tr>
<td><strong>2.</strong> Carbendazim</td>
<td>10605-21-7</td>
<td>benzimidazole fungicide</td>
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<td><strong>3.</strong> Desethylatrazine</td>
<td>6190-65-4</td>
<td>triazine metabolite</td>
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<tr>
<td><strong>4.</strong> Desethylterbutylazine</td>
<td>30125-63-4</td>
<td>triazine metabolite</td>
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<td><strong>5.</strong> Diuron</td>
<td>330-54-1</td>
<td>phenylurea herbicide</td>
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<td><strong>6.</strong> S-metolachlor</td>
<td>87392-12-9</td>
<td>chloroacetanilide herbicides</td>
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<td><strong>7.</strong> Terbutylazine</td>
<td>5915-41-3</td>
<td>triazine herbicide</td>
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WFD priority substances; Directive 2008/105/EC
### Target compounds

**PHARMACEUTICALS**

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<tr>
<th>Compound</th>
<th>CAS</th>
<th>Usage</th>
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</thead>
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<tr>
<td>1. Alprazolam</td>
<td>28981-97-7</td>
<td>benzodiazepine drug</td>
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<td>2. Atenolol</td>
<td>29122-68-7</td>
<td>beta blocker drug</td>
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<td>3. Carbamazepine</td>
<td>298-46-4</td>
<td>anticonvulsant drug</td>
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<td>4. Diazepam</td>
<td>439-14-5</td>
<td>benzodiazepine drug</td>
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<td>5. Diclofenac</td>
<td>15307-86-5</td>
<td>non-steroidal anti-inflammatory drug</td>
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</table>

proposed priority substance; Directive 2008/105/EC under review
**Target compounds**

**STEROID HORMONES**

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<td>1. 17-alpha-Estradiol</td>
<td>57-91-0</td>
<td>steroid hormone</td>
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<td>2. 17-alpha-Ethinylestradiol</td>
<td>77538-56-8</td>
<td>contraceptive</td>
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<td>3. 17-beta-Estradiol</td>
<td>82115-62-6</td>
<td>steroid hormone</td>
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<td>4. Estriol</td>
<td>50-27-1</td>
<td>steroid hormone</td>
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<tr>
<td>5. Estrone</td>
<td>53-16-7</td>
<td>steroid hormone</td>
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*proposed priority substances; Directive 2008/105/EC under review*
## Target compounds

**BISPHENOL A, TRICLOSAN, PFOA PFOS**

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<tr>
<td>1. Bisphenol A</td>
<td>80-05-7</td>
<td>monomer to make plastics</td>
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<tr>
<td>2. Triclosan</td>
<td>3380-34-5</td>
<td>antibacterial and antifungal agent</td>
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</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS</th>
<th>Usage</th>
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<tr>
<td>1. PFOA</td>
<td>335-67-1</td>
<td>fluorosurfactant</td>
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<tr>
<td>2. PFOS</td>
<td>1763-23-1</td>
<td>fluorosurfactant, fabric protector</td>
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</table>

*proposed priority substance; Directive 2008/105/EC under review*
Target compounds
BROMINATED DIPHENYL ETHERS

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<td>1. BDE 28</td>
<td>41318-75-6</td>
<td>Flame retardant</td>
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<td>2. BDE 47</td>
<td>5436-43-1</td>
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<td>3. BDE 99</td>
<td>60348-60-9</td>
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<td>4. BDE 100</td>
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<td>5. BDE 153</td>
<td>68631-49-2</td>
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<td>6. BDE 154</td>
<td>207122-15-4</td>
<td>Flame retardant</td>
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WFD priority substances; Directive 2008/105/EC
STUDY REALISATION
# Contribution and tasks

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<th>Organisation</th>
<th>Role</th>
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<tbody>
<tr>
<td>WRI, Slovakia</td>
<td>Coordinator</td>
</tr>
<tr>
<td>Cemagref Bordeaux, France</td>
<td>Preparation of analytical QC standards,</td>
</tr>
<tr>
<td>ISM-LPTC, University of Bordeaux,</td>
<td>Preparation of samplers that are provided to participants,</td>
</tr>
<tr>
<td>Cemagref Lyon, France</td>
<td></td>
</tr>
<tr>
<td>UK Environment Agency, UK</td>
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<tr>
<td>DG JRC IES</td>
<td></td>
</tr>
<tr>
<td>RECETOX + DELTARES</td>
<td>Analysis of parallel water samples (not BDEs)</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>
</tbody>
</table>
Sampling site: discharge from WWTP Brno-Modřice
Sampling site: discharge from WWTP Brno-Modřice

Water depth: 2.35 m

Minimum 50 cm

135 cm

Sampler cages

Water flow in at depth 1 - 2 m

cca 2 m

cca 3 m
Study preparation: Pre-screening for presence of contaminants

- Silicone rubber

- SDB-RPS

- SDB-RPS-PES

- POCIS
## Screening for presence of contaminants

<table>
<thead>
<tr>
<th>Compound class</th>
<th>Sampler</th>
<th>Laboratory</th>
<th>Contact</th>
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</thead>
<tbody>
<tr>
<td>Polar pesticides</td>
<td>POCIS</td>
<td>Irstea Lyon</td>
<td><a href="mailto:Nicolas.Mazzella@irstea.fr">Nicolas.Mazzella@irstea.fr</a></td>
</tr>
<tr>
<td>Polar pesticides, pharmaceuticals</td>
<td>SDB/RPS Empore disk</td>
<td>Eawag</td>
<td><a href="mailto:Etienne.Vermeirssen@eawag.ch">Etienne.Vermeirssen@eawag.ch</a></td>
</tr>
<tr>
<td>Steroid hormones</td>
<td>POCIS, SDB-XC Empore</td>
<td>RECETOX</td>
<td><a href="mailto:simek@recetox.muni.cz">simek@recetox.muni.cz</a></td>
</tr>
<tr>
<td>PBDE</td>
<td>Silicone sheets</td>
<td>RECETOX</td>
<td><a href="mailto:kukucka@recetox.muni.cz">kukucka@recetox.muni.cz</a> <a href="mailto:prokes@recetox.muni.cz">prokes@recetox.muni.cz</a></td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>POCIS</td>
<td>University Bordeaux</td>
<td><a href="mailto:h.budzinski@ism.u-bordeaux1.fr">h.budzinski@ism.u-bordeaux1.fr</a></td>
</tr>
<tr>
<td>PFOA, PFOS</td>
<td>POCIS</td>
<td>RECETOX</td>
<td><a href="mailto:becanova@recetox.muni.cz">becanova@recetox.muni.cz</a></td>
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<tr>
<td>Triclosan</td>
<td>SPMD</td>
<td>IPH Ostrava</td>
<td><a href="mailto:samuel.mach@zu.cz">samuel.mach@zu.cz</a></td>
</tr>
<tr>
<td>Bisfenol A</td>
<td>Water sample/SBSE</td>
<td>VUVH</td>
<td><a href="mailto:branovrana@googlemail.com">branovrana@googlemail.com</a></td>
</tr>
</tbody>
</table>
Screening for presence of contaminants: Fluorinated surfactants

Sampler: POCIS; 18.6.-2.7.2010
Analysed by: RECETOX

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>c (ng/sampler)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Blank1</td>
</tr>
<tr>
<td>PFBA</td>
<td>&lt;0,16</td>
</tr>
<tr>
<td>PFPA</td>
<td>0.66</td>
</tr>
<tr>
<td>PFHxA</td>
<td>-</td>
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<tr>
<td>PFHpA</td>
<td>-</td>
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<tr>
<td>PFOA</td>
<td>&lt;0,14</td>
</tr>
<tr>
<td>PFNA</td>
<td>&lt;0,25</td>
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<tr>
<td>PFDA</td>
<td>&lt;0,28</td>
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<tr>
<td>PFUnDA</td>
<td>&lt;0,37</td>
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<tr>
<td>PFDaDA</td>
<td>&lt;0,24</td>
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<tr>
<td>PFTDA</td>
<td>&lt;0,27</td>
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<td>PFTEDA</td>
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<td>PFBS</td>
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<td>PFHpS</td>
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<tr>
<td>PFOS</td>
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<tr>
<td>PFDS</td>
<td>-</td>
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</tbody>
</table>
Study preparation: Passive sampling homogeneity test
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; α = 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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sampling position</th>
<th>ng/sampler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>AD, AS, AH, BD, BH</td>
<td>0, 10, 20, 30, 40, 50, 60, 70</td>
</tr>
<tr>
<td>Chlortoluron</td>
<td>AD, AS, AH, BD, BH</td>
<td>0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0</td>
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<tr>
<td>Chlorpyrifos</td>
<td>AD, AS, AH, BD, BH</td>
<td>0.0, 0.1, 0.2, 0.3, 0.4, 0.5</td>
</tr>
<tr>
<td>Chlorsulfuron</td>
<td>AD, AS, AH, BD, BH</td>
<td>0, 1, 2, 3, 4, 5</td>
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<td>Diazinon</td>
<td>AD, AS, AH, BD, BH</td>
<td>0, 20, 40, 60, 80, 100, 120</td>
</tr>
<tr>
<td>Dimetolachlor</td>
<td>AD, AS, AH, BD, BH</td>
<td>0.0, 0.5, 1.0, 1.5, 2.0, 2.5</td>
</tr>
<tr>
<td>Metazachlor</td>
<td>AD, AS, AH, BD, BH</td>
<td>0, 0.1, 0.2, 0.3, 0.4, 0.5</td>
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<tr>
<td>Metolachlor</td>
<td>AD, AS, AH, BD, BH</td>
<td>0.0, 0.5, 1.0, 1.5, 2.0, 2.5</td>
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<tr>
<td>Terbutylazine</td>
<td>AD, AS, AH, BD, BH</td>
<td>0, 2, 4, 6, 8, 10, 12, 14, 16</td>
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<tr>
<td>Isoproturon</td>
<td>AD, AS, AH, BD, BH</td>
<td>0, 20, 40, 60, 80</td>
</tr>
</tbody>
</table>

*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; α = 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

- Registration deadline: March
- Pesticides, Pharmaceuticals: April
- PBDEs: May
- Steroid Hormones, Bisphenol A, Triclosan, PFOA, PFOS: June
- Reporting deadline: July
- Handling and reporting instructions: August
Participating laboratories from Europe
...and from the rest of the World
## Participant laboratories: self assessed expertise level

<table>
<thead>
<tr>
<th>Laboratory ID</th>
<th>Polar pesticides</th>
<th>Pharmaceuticals</th>
<th>Steroid hormones</th>
<th>Fluorinated surfactants</th>
<th>Triclosan</th>
<th>Bisphenol A</th>
<th>Brominated flame retardants</th>
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- **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
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
- Cartridge
- Funnel
- Teflon frit
- Visiprep Vacuum Manifold

Step 2: Pocis dismantling
- PES membrane
- Oasis HLB Sorbent

Step 3: Transfer the OASIS HLB sorbent
- Pasteur pipette
- Milli Q Water
- Oasis HLB Sorbent
- PES membrane
- Funnel
- Teflon frit
- Cartridge

Visiprep Vacuum Manifold

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 cm²
- 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

Bühler 1029
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

Filter through Whatman GF/F

min. 2000 mL/day

570 mL/day

PFOA/PFOS

Steroid hormones

Triclosan AND Bishpenol A

2x1 L; glass bottle

bottle A

285 ml/day

2x1 L; glass bottle

bottle B

285 ml/day

2L; Nalgene

bottle C

285 ml/day

2L; Nalgene

bottle D

285 ml/day

2x 1L; glass bottle

bottle E

170 ml/day

2x 1L; glass bottle

bottle F

170 ml/day

bottles G,H

430 mL/day

bioassays

2x 2L; glass bottle

2x1500 ml / 7-day composite sample

Store at RECETOX

2000 ml / 7-day composite sample

Send weekly to UK EA

Store @ 4 C

2000 ml / 7-day composite sample

Send weekly to UK EA

Store @ 4 C

2000 ml / 7-day composite sample

Send weekly to DG JRC IES

Store @ 4 C

2000 ml / 7-day composite sample

Send weekly to Cemagref Lyon

Store @ -20 C

2000 ml / 7-day composite sample BACKUP, store at RECETOX

Store @ -20 C

1200 ml / 7-day composite sample BACKUP store at RECETOX

2000 ml / 7-day composite sample

Send weekly to UK EA

Store @ 4 C

2000 ml / 7-day composite sample

Send weekly to DG JRC IES

Store @ 4 C

2000 ml / 7-day composite sample

Send weekly to Cemagref Lyon

Store @ -20 C

2000 ml / 7-day composite sample BACKUP, store at RECETOX

Store @ -20 C

1200 ml / 7-day composite sample BACKUP store at RECETOX

2x1500 ml / 7-day composite sample

Store at RECETOX
WATER SAMPLING PROTOCOL
STEROIDS, PFOA/PFOS, triclosan, Bisphenol A

BLANK SAMPLES
1000 mL Milliq water/day
Filter through Whatman GF/F

- **Bottle Blank A**
  - 2L; glass bottle
  - 285 ml/day
  - Store @ 4°C
  - 2000 ml / 7-day composite BLANK triclosan and bisphenol A
  - Send weekly to UK EA

- **Bottle Blank B**
  - 2L; Nalgene
  - 285 ml/day
  - Store @ 4°C
  - 2000 ml / 7-day composite BLANK triclosan and bisphenol A
  - Send weekly to DG JRC IES

- **Bottle Blank C**
  - 1L; glass bottle
  - 170 ml/day
  - Store @ -20°C
  - 1200 ml / 7-day composite BLANK Steroids
  - Send weekly to Irstea Lyon

- **Bottle Blank D**
  - 2L, glass bottle
  - 200 ml/day
  - Store @ -20°C
  - 1500 ml / 7-day composite BLANK Steroids
  - Store at RECETOX
Water quality parameters

Discharge
Temperature
Suspended solids

pH
Conductivity
TOC
REPORTING

• Sharepoint sites by Quasimeme
• Reporting excel templates
• Instructions provided in October 2011
• Reporting deadline in January 2012
DATA EVALUATION
LOG TRANSFORMATION

Log x
Box-and-whisker plots

Provided sampler, ng/cm\(^2\)

90\(^{th}\) percentile
75\(^{th}\) percentile = Q3
25\(^{th}\) percentile = Q1
10\(^{th}\) percentile

IQR
BAR GRAPHS

Example: Carbamazepin

1. Provided sampler, ng/cm²
2. Standard solution, µg/mL
3. Participant sampler, Cw in ng/L

- Log₂ scale
- Set value expanded
- Uncertainty (k = 2)
- SD of log₂ transformed data
- Median value
- Water sample mean
- Laboratory number

Outliers
OUTLIER IDENTIFICATION

- IQR
- Q1 - 1.5 × IQR
- Q1
- Q3
- Q3 + 1.5 × IQR
- Median

- -2.698σ
- -0.6745σ
- 0.6745σ
- 2.698σ

- 24.65%
- 50%
- 24.65%

- 15.73%
- 68.27%
- 15.73%
Expression of data variability

\[ CV = \ln 2 \ s_{\log 2} \]

Diuron

- Standard solution
- NPS amount
- NPS water concentration
- PPS amount
- PPS water concentration

Within laboratory Mean
- Between laboratory
BIPLOTS: participant vs. provided samplers

Example: Diclofenac

Comparing samplers, Cw in ng/L

Log2 scale

Provided sampler

Participant sampler

Water samples
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
Acknowledgment

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• Karel Brabec from RECETOX, Masaryk University, for on-site measurement of local flow velocity profiles.
• Tomáš Ocelka from IPH Ostrava for providing equipment necessary for deployment of provided passive samplers.
• Pavla Kosková and Anna Kutláková for processing composite water samplers during experiments.
• Eva Figuliová, Veronika Grigerová and Patrik Kiss for their assistance in preparation of provided passive samplers.
• Martin Bene, Jarmila Makovinská, Richard Matula, Katarína Šilhárová and Peter Tölgyessy for their help with installation and retrieval of passive samplers.
• Wanda Kutášová, Eva Podrazilová and Pavel Hucko for assistance with administrative issues.
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