An interlaboratory calibration study

NORMAN expert group meeting
Prague, 27th May 2009
An interlaboratory calibration study

- It is important to demonstrate the reliability of the technology to the scientific community, environment and health agencies and public authorities managing chemical contaminants.
- Prior to implementation in international monitoring programmes technical guidelines for monitoring should be available and analytical methods should have been tested in different laboratories.
- Intercomparison schemes should be in place.
- Interlaboratory proficiency tests are required for a full method validation.
- Participation to proficiency tests (laboratory evaluating interlaboratory tests) is considered mandatory for laboratories accredited according to ISO 17025 and EN 45003.
Decisions and agreement needed

DEFINE OBJECTIVES

- Compounds
- Sampled medium
- Sampling techniques
- Central expert laboratory
- Study setup
- Interested participants
A key to a successful intercalibration

Relevant compound group

Mature passive sampling technology

Available methods of chemical analysis or bioassays
Objectives of intercalibration

- extend the validation of the use of passive samplers for monitoring emerging substances in water
- transfer knowledge of the methods more widely within the NORMAN community and beyond
- to gain experience in the use of passive samplers
- estimate the contribution of the analytical component to total variability
- to contribute to mapping of the occurrence of emerging substances in Europe
- to compare the results of the spot sampling of water with the results obtained by passive sampling – may be difficult in some cases
- to assess the possibility of using this tool for compliance checking with the WFD
Selection of a compound group

- The most important decision
  - must be an emerging pollutant group
    (no priority compounds but can be candidates)
  - sufficient evidence of environmental hazard
  - occurrence in freshwater environment
  - presence identified/expected Europe-wide
    (or global)
  - might be troublesome substances for monitoring
    using conventional “bottle” sampling – a challenge
Selection of compounds – overlap with available analytical methods

- Validated methods for instrumental analysis should be available – „mature emerging pollutants“
- Methods for instrumental analysis should be either:
  - available in the participating laboratories
  - not too challenging to setup in terms of infrastructure, instrumentation, method demands
  - passive sampler calibration data available
# Candidate compounds

ANNEX III of the DIRECTIVE 2008/105/EC on EQS in the field of water policy

SUBSTANCES SUBJECT TO REVIEW FOR POSSIBLE IDENTIFICATION AS PRIORITY SUBSTANCES OR PRIORITY HAZARDOUS SUBSTANCES

<table>
<thead>
<tr>
<th>CAS number</th>
<th>EU number</th>
<th>Name of substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1066-51-9</td>
<td>--</td>
<td>AMPA</td>
</tr>
<tr>
<td>25057-89-0</td>
<td>246-585-8</td>
<td>Bentazon</td>
</tr>
<tr>
<td>80-05-7</td>
<td></td>
<td>Bisphenol-A</td>
</tr>
<tr>
<td>115-32-2</td>
<td>204-082-0</td>
<td>Dicofol</td>
</tr>
<tr>
<td>60-00-4</td>
<td>200-449-4</td>
<td>EDTA</td>
</tr>
<tr>
<td>57-12-5</td>
<td></td>
<td>Free cyanide</td>
</tr>
<tr>
<td>1071-83-6</td>
<td>213-997-4</td>
<td>Glyphosate</td>
</tr>
<tr>
<td>7085-19-0</td>
<td>230-386-8</td>
<td>Mecoprop (MCPP)</td>
</tr>
<tr>
<td>81-15-2</td>
<td>201-329-4</td>
<td>Musk xylene</td>
</tr>
<tr>
<td>1763-23-1</td>
<td></td>
<td>Perfluorooctane sulphonic acid (PFOS)</td>
</tr>
<tr>
<td>124495-18-7</td>
<td>--</td>
<td>Quinoxyfen (5,7-dichloro-4-(p-fluorophenoxy)quinoline)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PCB</td>
</tr>
</tbody>
</table>
Candidate compounds under WFD

- EU Member States are currently in the process of identifying the substances that are relevant at river basin level (i.e. pollutants which are likely to cause a large number of water bodies within the river basin district to fail the objective of „good ecological status“).

- Possible approach: Compare lists of river basin specific compounds in countries of participating laboratories and find overlaps.
EU Wide Monitoring Survey of Polar Persistent Pollutants (PPP)

- Organised by Joint Research Centre, Institute for Environment and Sustainability
  - European river waters (FATE - EUMORE)
  - groundwater (FATE - GROWS)
  - sewage sludges and effluents (FATE - SEES) in preparation
  - compost (FATE – COMES) in preparation

- FATE – EUMORE
  - 122 individual water samples
  - 100 European rivers, streams or similar water bodies from
  - 27 European Countries
  - 35 selected compounds
FATE – EUMORE compounds

- Perfluorinated compounds
- Pharmaceuticals
- Pesticides
- Industrial chemicals (nitrophenols, benzotriazoles)
- Endocrine disrupting compounds (EDC)
## FATE – EUMORE compounds

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CAS No.</th>
<th>Structure</th>
<th>Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Nitrophenol</td>
<td>100-02-7</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>Nitrophenols are refractory organic compounds which are mainly used in the production of pesticides, explosives, dyes and plasticizers. They enter the environment via wastewater discharges from industry, motor vehicle emissions and contaminant degradations or atmospheric inputs, and thus they are ubiquitous environmental contaminants.</td>
<td>Zhou and Lei, 2006 Sabio et al., 2006</td>
</tr>
<tr>
<td>2,4-Dinitrophenol</td>
<td>51-28-5</td>
<td><img src="image2.png" alt="Structure" /></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bentazon</td>
<td>25057-89-0</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>Diazan: contact herbicide; low affinity for particulate or organic carbon; log $K_{ow}$ 0.35</td>
<td>URL2</td>
</tr>
<tr>
<td>2,4-D (Dichlorophenoxyacetic acid)</td>
<td>94-75-7</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>One of the most widely used herbicides in the world; aqueous aerobic half-life of ~15 days</td>
<td>URL2</td>
</tr>
<tr>
<td>Ketoprofen</td>
<td>22071-13-4</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>NSAID with analgesic and antipyretic effects</td>
<td>Gros et al., 2006 Tixier et al., 2003</td>
</tr>
<tr>
<td>Naproxen</td>
<td>22204-53-1</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>NSAID commonly used for the reduction of moderate to severe pain, fever, and inflammation caused by conditions such as osteoarthritis, rheumatoid arthritis, injury (like fractures), and menstrual cramps.</td>
<td>Gros et al., 2006 Joss et al., 2005 Tixier et al., 2003</td>
</tr>
</tbody>
</table>
### FATE – EUMORE compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Further Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bezafibrate</td>
<td>Fibrate drug used for the treatment of hyperlipidemia; it helps to lower LDL cholesterol and triglyceride in the blood, and increase HDL.</td>
</tr>
<tr>
<td>Mecroprop</td>
<td>Hormone-type phenoxy herbicide affecting enzyme activity and plant growth; used on sports turf, for forest site preparation, wheat, barley, and oats, etc.</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>NSAID (analgesic, antipyretic); it is an important non-prescription drug used widely; slowly degraded in aqueous media to hydroxy- and carboxy-ibuprofen</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>NSAID used in human medical care as an analgesic, antirheumatic, antiphlogistic compound for reducing pain in conditions such as in arthritis or acute injury</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>Fibrate drug used to lower lipid levels</td>
</tr>
<tr>
<td><strong>Perfluorinated compounds</strong></td>
<td></td>
</tr>
<tr>
<td>PFHpA, perfluorohexanoate</td>
<td>6839-11-0</td>
</tr>
<tr>
<td>PFOA, perfluorooctanoate</td>
<td>335-87-1</td>
</tr>
<tr>
<td>PFOA, perfluorooctanoate</td>
<td>The most common use of PFOA is as polymerization aid and in the production of fluoropolymers such as polytetrafluoroethylene (PTFE), Teflon®, Gore-Tex®. APFO is the ammonium salt of PFOA and the chemical form used in fluoropolymer manufacturing</td>
</tr>
<tr>
<td>PFNA, perfluorononanoate</td>
<td>375-95-3</td>
</tr>
<tr>
<td>PFOS, perfluorooctanesulfonate</td>
<td>EDF-508, Acid: 1763-23-1, NH₄⁺</td>
</tr>
</tbody>
</table>

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<tbody>
<tr>
<td>29081-56-9</td>
<td></td>
<td>costing additives, or in fire-fighting foams</td>
<td></td>
</tr>
<tr>
<td>PFDA, perfluorodecanoate</td>
<td>325-78-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFUnA, perfluoroundecanoate</td>
<td>20378-94-8</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Positive mode (method 2)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caffeine</td>
<td>58-08-2</td>
<td>Xanthine alkaloid compound that acts as a psychoactive stimulant drug</td>
<td>Moldavan, 2006 URL2</td>
</tr>
<tr>
<td>1H-Benzotriazole</td>
<td>95-14-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Methyl-1H-benzotriazole (Tolytriazole)</td>
<td>13351-73-0</td>
<td>Anticorrosives used e.g. in dish washers</td>
<td>Weiss and Reents, 2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Weiss et al., 2006</td>
</tr>
<tr>
<td>Atrazine-desethyl</td>
<td>6190-65-4</td>
<td>Persistent metabolite of atrazine</td>
<td>Claver et al., 2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Planas et al., 2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rodriguez-Mozaz et al., 2006b</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>723-46-6</td>
<td>Sulfonamide bacteriostatic antibiotic; relatively persistent in water</td>
<td>Gros et al., 2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hu et al., 2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Josi et al., 2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tamam et al., 2008</td>
</tr>
<tr>
<td>Terbutylazine-desethyl</td>
<td>30125-63-4</td>
<td>Persistent metabolite of terbutylazine</td>
<td>Claver et al., 2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Noppe et al., 2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rodriguez-Mozaz et al., 2004b</td>
</tr>
<tr>
<td>Simazine</td>
<td>122-34-9</td>
<td>Triazine herbicide similar to atrazine</td>
<td>Claver et al., 2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Noppe et al., 2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rodriguez-Mozaz et al., 2004b</td>
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<th>Compound</th>
<th>CAS</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>1912-24-9</td>
<td>Triazine herbicide used globally to stop pre- and post-emergence broadleaf and grassy weeds in major crops; it is one of the most widely used herbicides in the USA, but it has been banned in the EU; quite persistent in water and soil; degradation to desethylatex and hydroxyl metabolites.</td>
<td>Blanchaud et al., 2007. Claver et al., 2006. Neppe et al., 2007. Rodriguez-Mozaz et al., 2004b.</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>34123-39-6</td>
<td>Phenylurea herbicide; mobile in soil; in water, it is quite persistent with a half-life of about 30 days.</td>
<td>Claver et al., 2006. Blanchaud et al., 2007. Rodriguez-Mozaz et al., 2004b.</td>
</tr>
<tr>
<td>Diazon</td>
<td>330-54-1</td>
<td>Phenylurea herbicide; its main use is as an anti-feeding agent in food products; relatively persistent in natural waters.</td>
<td>Claver et al., 2006. Rodriguez-Mozaz et al., 2004b.</td>
</tr>
<tr>
<td>Terbutylazine</td>
<td>5915-41-3</td>
<td>Triazine herbicide which replaces atrazine in the EU; less mobile than atrazine.</td>
<td>Claver et al., 2006. Neppe et al., 2007.</td>
</tr>
<tr>
<td>Phenolic compounds</td>
<td></td>
<td>Endocrine disrupting compound (EDC) used in plastic materials (see section 3.5).</td>
<td>Fromme et al., 2002. Céspedes et al., 2006. Loo et al., 2007b. Rodriguez-Mozaz et al., 2004b.</td>
</tr>
<tr>
<td>Bisphenol A (BPA)</td>
<td>80-05-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nonylphenoxycarboxylic acid NPE4C</td>
<td>3115-49-9</td>
<td>Alkylyphenol ethoxycarboxylates (APEXs) are recalcitrant metabolites of theAPECO surfactants; the most prominent species is nonylphenoxycarboxylic acid (NPE, C).</td>
<td>Jonkers et al., 2001.</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonylphenol (NP)</td>
<td>84832-13-3</td>
<td>Alkylphenols are important degradation products of alkylphenol ethoxylates (APEOs) which are nonionic surfactants widely used in agricultural, industrial, and domestic applications; 80% of the APEO surfactants used are NPEOs, while the remaining 20% are almost entirely octylphenol isomers (OPEOs).</td>
</tr>
<tr>
<td>tert-Octylphenol (OP)</td>
<td>140-66-9</td>
<td>Octylphenol has a higher endocrine disrupting potential than NP because it is a single branched isomer.</td>
</tr>
<tr>
<td>Steroid estrogens</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Estrone</td>
<td>53-16-7</td>
<td></td>
</tr>
<tr>
<td>17β-Estradiol</td>
<td>50-28-2</td>
<td>Metabolite of estradiol</td>
</tr>
<tr>
<td>17α-Ethinylestradiol</td>
<td>57-63-6</td>
<td>Natural hormone</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Synthetic hormone used in anti-baby pills</td>
</tr>
</tbody>
</table>

Gabet et al., 2007
Rodriguez-Mozaz et al., 2004
Céspedes et al., 2006
Loos et al., 2007

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Candidate compounds

- Besides the WFD, other programmes are identifying new candidate emerging substances and regularly reviewing their priority lists as scientific knowledge advances:
  - OSPAR
  - HELCOM
  - AMAP
  - BSC
  - UNEP POP

- Kees Booij prepared an overview (for ICES WGMS) of the established and expected performance of PS’s in monitoring priority pollutants
Candidate compounds:
Calibration data availability

Sampling rates (RS) of pharmaceuticals by polar organic chemical integrative sampler (POCIS) and test parameters used during the experiments


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Sampled medium

- Drinking water
- Surface water
- Wastewater
- Sediment?
Selection of passive sampling techniques

- Availability of a suitable „mature“ technique in terms of performance criteria
- Agreement needed between research groups using different samplers
- Comparison of a few different samplers for one group of compounds possible in one study, but the number should not be too large – otherwise the number of samples to be processed too high
Selection of passive sampling techniques

- Sub areas of passive sampling of aquatic pollutants:
  - hydrophobic organic compounds, e.g. POPs
  - polar (hydrophilic) organic compounds such as pharmaceuticals, polar pesticides and illicit drugs
  - trace metals and organometallic compounds
Selection of passive sampling techniques

- Techniques for sampling hydrophobic organic compounds are most advanced
- Samplers for polar (hydrophilic) organic compounds – under development, sometimes difficulties in data interpretation
- Trace metals – well advanced technology
- Organometallic compounds – depends on the compound
Problems with PT setup

- Laboratory–based proficiency schemes using certified reference materials are not straightforward - large volumes of standard solutions required for calibration procedures
  - use of stable pelletised formulations that can be dispersed under standard conditions to produce large volumes of calibration solutions
  - the use of reference field sites, as have been used for studies of sediments
Previous intercalibration studies

- STAMPS intercalibration of Chemcatcher
- ICES passive sampling trial survey
- IPSIC analytical PT for field exposed SPMD, DGT – recent initiative
Intercalibration setup

Use the approach from the pioneer work of ICES PSTS

- CENTRAL EXPERT LABORATORY
  - Preparation of samplers
  - Distribution of samplers

- LAB 1
  - Sampler exposure
  - Analysis of ½ samplers

- LAB 2
  - Sampler exposure
  - Analysis of ½ samplers

- LAB 3
  - Sampler exposure
  - Analysis of ½ samplers

- LAB 4
  - Sampler exposure
  - Analysis of ½ samplers

- CENTRAL EXPERT LABORATORY
  - Analysis of replicate samples returned from participating laboratories
Intercalibration setup

Central expert laboratory

Send a portion of samplers for analysis

LAB 1
Sampler exposure and analysis

Report results

PASSIVE SAMPLING

Comparison

WATER SAMPLING

Adsorption of polar compounds to particles is generally low, which in principle enables comparison

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QA/QC

Preparation
↓
Storage
↓
Transport
↓
Deployment
↓
Exposure
↓
Retrieval
↓
Storage
→
Transport
↓
Processing
↓
Analysis

Fabrication controls

Field controls

Performance reference compounds

Field controls

Fabrication controls
Reagent controls
Recovery spikes
Decisions and agreement needed

DEFINE OBJECTIVES

- Compounds
- Sampled medium
- Sampling techniques
- Central expert laboratory
- Study setup
- Interested participants

BUDGET

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