Screening of consumer and industrial chemicals and pesticides as priority substances in Finnish aquatic environments

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Objectives of the screening

- Identify EU/WFD prioritized and nationally selected organic pollutants in aquatic environments near sources of discharge
- Provide information to source identification – but not single pollution sources (impact monitoring, compliance checking => enterprises)

- To develop best practices, analytical methods and cooperation between laboratories
- To identify WFD substances which should enter the national monitoring networks
31.3.2008

SUBSTANCES
• risk based selection
• EU PS + National

PROPERTIES
• water solubility
• logK_{sed-water}
• Bio Conc. Factor

PRESSURE
• municipalities
• SME industry
• large factories
• agriculture

MATRICES
• STP sludge
• STP effluent
  • surface water
  • sediment
  • fish
• stream water
• sediment

SITES
• number of samples
• pooling?
• replicates?
• number of sites?
Project: VESKA 1
Industrial & household chemicals

Map of Finland with locations marked:
- Sewage treatment plant
- Sediment & water
- Fish

VESKA 1
Lahti, Porvoonjoki

Sewage treatment plant
population > 100 000

sediment + surface water
3 km from discharge
VESKA 1
Tampere, Viinikanlahti

Sediment + surface water
Near effluent pipe <200 m

Sewage treatment plant
Treatment plant effluent indicates, what might be found in surface water

- Max observation of 12 substances not even 5 percent of the EQS\textsubscript{water} (!)
- 10 substances max 5 – 100 % of EQS\textsubscript{water}
- 6 substances max > EQS\textsubscript{water}

- MBT, DBT, DEHP, 4-tert-octylphenol, nonylphenylethoxylate, 4-n-nonylphenol
Surface water; few detected

- Very few substances even detected: chloroform, 1,2-dichlorethene < 1 µg/l -range
- HCB, lindane & α-HCH, HCBD in < 1 ng/l range

- Nonylphenyl ethoxylates (precursor to NP) found (0.4 µg/l) in the range of EQS proposal (0.3 µg/l) for NP
- NP/OP not detected

- Phthalates and PAHs found occasionally in 2006-2007 pilot monitoring
Mainly TBT exceed the estimated EQS-values in sediment

Max observed / EQS_{sediment}
SYKE TBT and TPhT in FISH 2003, 2005 (mostly pike)

BACKGROUND AREAS

LAKES, RIVERS

COASTAL

WFD calc. Quality standard (EQS) 15 µg / kg

North -> South
TBT bioaccumulates, but TPhT bioaccumulates much stronger

If sediment clearly TBT contaminated, fish *might* be contaminated

If sediment *slightly* TPhT contaminated, fish are contaminated
EQS = 0.2 ng/L corresponding to c.a. 0.1 kg/a emission

TBT Modeling at catchment/estuary scale
VESKA 2: Pesticides Regional screening 2005

- 120 water samples; over 100 pesticides analysed – 46 found

35 agricultural rivers

- Statistical sample, 2 sampling occasions
  - selection based on watershed number
  - sediment sample from most sites
  - field percentage over 25

- 5 reference areas, field percentage < 10
- 6 major rivers, monthly sampling
Many substances found, but not much

<table>
<thead>
<tr>
<th>Substances</th>
<th>Detected Amount (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCPA</td>
<td>8.8</td>
</tr>
<tr>
<td>Dichlorprop</td>
<td>4.40</td>
</tr>
<tr>
<td>Mecoprop</td>
<td>1.60</td>
</tr>
<tr>
<td>Tralkoxydim</td>
<td>0.10</td>
</tr>
<tr>
<td>Bentazone</td>
<td>0.15</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>0.14</td>
</tr>
<tr>
<td>Desaminometamitron</td>
<td>0.56</td>
</tr>
<tr>
<td>Simazine</td>
<td>0.02</td>
</tr>
<tr>
<td>Ethofumesate</td>
<td>0.31</td>
</tr>
<tr>
<td>Thifensulfuronmethyl</td>
<td>0.04</td>
</tr>
<tr>
<td>Tribenuronmethyl</td>
<td>0.08</td>
</tr>
<tr>
<td>Linuron</td>
<td>0.09</td>
</tr>
<tr>
<td>Atrazine</td>
<td>0.01</td>
</tr>
<tr>
<td>BAM</td>
<td>0.07</td>
</tr>
<tr>
<td>Metamitron</td>
<td>0.26</td>
</tr>
<tr>
<td>Azoxyostrobin</td>
<td>0.03</td>
</tr>
<tr>
<td>Dimethomorph</td>
<td>0.12</td>
</tr>
<tr>
<td>Terbutylazine</td>
<td>0.01</td>
</tr>
<tr>
<td>Fluroxypyr</td>
<td>0.35</td>
</tr>
<tr>
<td>Flutolanil</td>
<td>0.24</td>
</tr>
<tr>
<td>Pirimicarb</td>
<td>0.02</td>
</tr>
<tr>
<td>Triflusulfuron-methyl</td>
<td>0.16</td>
</tr>
<tr>
<td>Endosulfansulphate</td>
<td>0.02</td>
</tr>
</tbody>
</table>

- Low concentration (<EQS)
- Potentially harmful concentration (> EQS)
- No reference concentration to compare
## VESKA analyses and risks

<table>
<thead>
<tr>
<th>Compound Group</th>
<th>STP effluent</th>
<th>Surface water</th>
<th>Sludge</th>
<th>Sediment</th>
<th>Pike</th>
<th>PROBLEMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organotins</td>
<td>15</td>
<td></td>
<td>6</td>
<td>14</td>
<td>28</td>
<td>found constantly, observations &gt; EOS (solid)</td>
</tr>
<tr>
<td>Pesticides (mostly phenoxyherbicides)</td>
<td>160</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>detected in rivermouths, monitoring to be targeted</td>
</tr>
<tr>
<td>PBDE</td>
<td></td>
<td>10</td>
<td>5</td>
<td>30</td>
<td></td>
<td>water analysis difficult, diffuse sources</td>
</tr>
<tr>
<td>PAHs</td>
<td>40</td>
<td>20</td>
<td>14</td>
<td>10</td>
<td></td>
<td>water analysis difficult, diffuse sources</td>
</tr>
<tr>
<td>NP, NPE, OP</td>
<td>20</td>
<td>70</td>
<td>20</td>
<td></td>
<td></td>
<td>difficult to analyse, diffuse sources</td>
</tr>
<tr>
<td>Phthalates</td>
<td>10</td>
<td>40</td>
<td>6</td>
<td>14</td>
<td>10</td>
<td>easily contaminated, diffuse sources</td>
</tr>
<tr>
<td>VOC: chlor &amp; aromatic</td>
<td>40</td>
<td>70</td>
<td></td>
<td>14</td>
<td>10</td>
<td>have to be analysed rapidly</td>
</tr>
<tr>
<td>HCB, HCHt, HCBd</td>
<td>40</td>
<td>30</td>
<td>20</td>
<td>14</td>
<td>monit</td>
<td>persistent, banned, still found</td>
</tr>
<tr>
<td>SCCP</td>
<td>10</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>difficult to quantify, few analyses</td>
</tr>
<tr>
<td>Chlorophenols</td>
<td>20</td>
<td>30</td>
<td>10</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCMTB</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bronopol &amp; resorcinol</td>
<td>24</td>
<td>2</td>
<td>9</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

- **Detected, Risk**: 30 sample number
- **Unsure**: not analysed
- **Detected, no risk**: not analysed, WFD requirement, but DL > EOS
- **Not detected**:
Screening Lessons

- Organotin compounds found in all matrices => need for research, monitoring and management
- Many pesticides and few industrial chemicals (NP/NPE) are found in surface water => need for monitoring
- For some substances difficult to assess the need for monitoring: PAH, PBDE, phthalates, chlorobenzenes

- Analytical methods and equipment fairly well established – in theory, but practice lacking
- Simultaneous screening of several substance groups suitable for pesticides but not for industrial & household chemicals (several, poorly known sources)
- Natural conditions in Finland (population/water volume, lake-richness) would favour sediment and biota over water, in monitoring industrial & household chemicals
River Basin District Surveillance Monitoring for WFD reporting

Industrial & household chemicals:
- NP/NPEO, OP
- PAHs
- Phthalates (DEHP, DBP, BBP)
- Trace metals
- 10 sites
+ 6 sites only trace metals

Water phase monthly sampling
May-07 – April-08
River Basin District Surveillance Monitoring for WFD reporting

Water phase monthly sampling
May-07 – April-08

Pesticides:
>100 substances / sample
- rivers 12 samples / yr
Sites in three year rotation
+ 3 intensive rivers every year
=> max 9 rivers per year
Fish & sediment monitoring

Frequency: 2-6 yr, site specific
2006: pooled herring, vendace
2007: individual pikes (+pooled perch 2 lakes)

- Hg, Cd, Pb + other trace metals
- OCPs, PCB (12+12Copl), PCDD/F (part)
- new: PBDE, organotins

8 large lakes
2 headwater lakes
3 major rivers
7 coastal areas
2 sedimentation traps

Sediments: all sites, in 4-5/yr time
Specimen banking

Prepared, homogenized aquatic & terrestrial tissue samples stored in liquid nitrogen –196 °C

photos: Matti Verta
Prioritisation of substances and matrices

EU:
- directives
  - water, air, soil, sludge, IPPC
  - REACH
  - Env Health Strategy
  - RA & RM

International Conventions
- UNEP
- CLRTAP
- OSPAR/HELCOM
- AMAP

National Priorities
- “own substances”
- meaningful participation in EU & int. monitoring

Emission/pressure Information
- Registers/data banks

Decision on Monitoring: Screening, Threshold values (EQS), trends, RA, research, modelling
Emerging substances monitoring in future

- Better identification of sources
- Monitoring and screening activities should be internationally harmonized and optimized – cooperation!
- Importance of concentration in sediments ( & soils) and biota must be understood better
  - => realistic Environmental Quality Standards
- QA/QC in the whole information chain
  - Planning, manuals, sampling, storage, pretreatment,
  - Analyses / validation, PT schemes
  - Data storage, reporting…
- Chemical monitoring combined to biological (effects) monitoring
  - Combined effects of several compounds likely
- Link to risk management and risk research
  - no “monitoring for monitoring” => think: why, what, where, how….
Thank You!