Chemical Monitoring under the Water Framework Directive (WFD)

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Surface water pollution by chemicals
Water Framework Directive

- Water Framework Directive (WFD) 2000/60/EC
- Environmental Quality Standards (EQS) Directive 2008/105/EC
- Directive 2009/90/EC on technical specifications for chemical analysis and monitoring of water status (QA/QC)
- Proposal for a new Directive on priority substances from January 2012 (COM(2011) 876 final)
WFD

- Protection of aquatic ecosystems
- No deterioration principle
- Water management based on river basin districts
- Environmental quality standards and emission controls
- „Phasing out” of priority hazardous substances
- Integration of other directives related to water issues
- **Objective: To achieve good water status (ecological and chemical) by December 2015**
Environmental Quality Standards (EQS) Directive 2008/105/EC

- sets out environmental quality standards (EQS) of certain pollutants and substances or groups of substances identified as priority on account of the substantial risk they pose to or via the aquatic environment
- **AA-EQS** - the average value or concentration of the substance concerned calculated over a one-year period. The purpose of this standard is to ensure the long-term quality of the aquatic environment;
- **MAC-EQS** the maximum allowable concentration of the substance measured specifically. The purpose of this second standard is to limit short-term pollution peaks.
- Member States must ensure **compliance with these standards**. They must also verify that the concentration of substances concerned **does not increase significantly** in sediments and/or the relevant biota.
Environmental Quality Standards (EQS)

ANNEX I

ENvironMental QUALITY STANDARDS FOR PRIoRITY SUBSTANCES AND CERTAIN OTHER POLLUTANTS

PART A: ENvironMental QUALITY STANDARDS (EQS)

AA: annual average;

MAC: maximum allowable concentration.

Unit: [μg/l]

<table>
<thead>
<tr>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
<th>(7)</th>
</tr>
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<tbody>
<tr>
<td>No</td>
<td>Name of substance</td>
<td>CAS number (°)</td>
<td>AA-EQS (°) Inland surface waters (°)</td>
<td>AA-EQS (°) Other surface waters</td>
<td>MAC-EQS (°) Inland surface waters (°)</td>
<td>MAC-EQS (°) Other surface waters</td>
</tr>
<tr>
<td>(1)</td>
<td>Alachlor</td>
<td>15972-60-8</td>
<td>0,3</td>
<td>0,3</td>
<td>0,7</td>
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<td>(2)</td>
<td>Anthracene</td>
<td>120-12-7</td>
<td>0,1</td>
<td>0,1</td>
<td>0,4</td>
<td>0,4</td>
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<tr>
<td>(3)</td>
<td>Atrazine</td>
<td>1912-24-9</td>
<td>0,6</td>
<td>0,6</td>
<td>2,0</td>
<td>2,0</td>
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<tr>
<td>(4)</td>
<td>Benzene</td>
<td>71-43-2</td>
<td>10</td>
<td>8</td>
<td>50</td>
<td>50</td>
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<tr>
<td>(5)</td>
<td>Brominated diphenylether (°)</td>
<td>32534-81-9</td>
<td>0,0005</td>
<td>0,0002</td>
<td>not applicable</td>
<td>not applicable</td>
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<tr>
<td>(6)</td>
<td>Cadmium and its compounds (depending on water hardness classes (°))</td>
<td>7440-43-9</td>
<td>≤ 0,08 (Class 1)</td>
<td>0,2</td>
<td>≤ 0,45 (Class 1)</td>
<td>≤ 0,45 (Class 1)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0,08 (Class 2)</td>
<td>0,45 (Class 2)</td>
<td>0,45 (Class 2)</td>
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</table>
## Priority Substances

### Priority Hazardous Substances
- Anthracene
- Brominated diphenylethers
- Cadmium and its compounds
- C10-C13-Chloroalkanes
- Di(2-ethylhexyl)phthalate (DEHP)
- Endosulfan
- Hexachlorobenzene (HCB)
- Hexachlorobutadiene (HCBD)
- Hexachlorocyclohexane
- Mercury and its compounds
- Nonylphenols
- Pentachlorobenzene
- Polyaromatic Hydrocarbons (PAHs)
- Tributyltin compounds
- Trifluralin

*Toxic, persistent, liable to bioaccumulate*

### Priority Substances
- Alachlor
- Atrazine
- Benzene
- Chlorfenvinphos
- Chlorpyrifos (ethyl)
- 1,2-Dichloroethane
- Dichloromethane
- Diuron
- Fluoranthene
- Isoproturon
- Lead and its compounds
- Naphthalene
- Nickel and its compounds
- Octylphenols
- Pentachlorophenol
- Simazine
- Trichlorobenzenes
- Trichloromethane

### Other specific pollutants
- DDT / p,p’-DDT
- Aldrin
- Dieldrin
- Endrin
- Isodrin
- Carbontetrachloride
- Tetrachloroethylene
- Trichloroethylene
WFD

All surface waters

- Rivers, lakes, artificial waters
- Transitional waters (partly saline)
- Coastal waters (up to one sea mile)

Types of Chemical Monitoring

- Surveillance (12 samples per year)
- Operational
- Investigative
What to Monitor?

- **Priority Substances** – Compliance with EQS
- **“Other pollutants”** relevant at river basin level – Compliance with national EQS
- **Physico-chemical parameters** supporting interpretation of biological data
- **Parameters required for interpretation of the results of chemical measurements** (e.g., DOC, Ca, SPM)
All methods should meet minimum performance criteria
Standardized or validated methods
Validation according to ISO 17025
Laboratories: Demonstrate their competence by participation in Interlaboratory Studies
Analysis of Certified Reference Materials (CRMs)
LOQ < 30% of EQS
Relative target uncertainty at EQS level: < 50%
Long term trend monitoring and analysis

- Directive 2008/105/EC: long-term trend analysis of those PS that tend to accumulate in sediment and biota
- Anthracene, PBDEs, Cd, C10-13 chloroalkanes, DEHP, Fluoranthene, HCB, Hexachlorobutadiene, HCH, Pb, Hg, Pentachlorobenzene, PAHs, TBT
- It must be ensured that concentrations do not significantly increase in S&B (no deterioration objective)
  - Mercury: EQS 20 μg/kg
  - HCB: EQS 10 μg/kg
  - Hexachlorobutadiene: EQS 55 μg/kg

- 15 additional Priority Substances (PS)
- Pesticides and biocidal products
- Industrial chemicals (POPs)
- Pharmaceuticals
- Stricter EQS for four existing PS
- Biota standards for several substances
Pesticides and Biocidal products

- **Aclonifen** (Herbicide)
- **Bifenox** (Herbicide)
- **Cybutryne = Irgarol** (Triazine herbicide = algicide)
- **Cypermethrin** (Pyrethroide Insecticide)
- **Dichlorvos** (Phospho-ester Insecticide)
- **Dicofol** (Miticide)
- **Heptachlor (epoxide)** (Insecticide)
- **Quinoxyfen** (Fungicide)
- **Terbutryyn** (Triazine herbicide = algicide)
Hexabromocyclododecane (HBCDD)
(Brominated flame retardant)

2,3,7,8-Tetrachlorodibenzodioxin

PCBs

PFOS
(Fluorosurfactant)
Pharmaceutical compounds

**Diclofenac**
(Non-Steroidal Anti-Inflammatory Drug)

**17α-ethyl-estradiol**
(Contraceptive pill)

**17β-estradiol**
(Estradiol is the predominant sex hormone present in females)
Brominated Diphenylethers (BDEs)

\[ \sum \text{BDE28, BDE47, BDE99, BDE100, BDE153 and BDE154} \]

Commercial “pentaBDE” is a technical mixture of different PBDE congeners, with **BDE-47** (2,2',4,4'-tetrabromodiphenyl ether) and **BDE-99** (2,2',4,4',5-pentabromodiphenyl ether) as the most abundant.

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**EQS (2008)**

**AA-EQS:**
- Fresh water: 0.5 ng/l
- Salt water: 0.2 ng/l

**Proposal 2012**

**AA-EQS:**
- 49 fg/l
- 2.4 fg/l

**MAC-EQS:**
- Fresh: 0.14 \( \mu g/l \)
- Salt: 0.014 \( \mu g/l \)

**Biota:** \( 0.0085 \ \mu g/kg \)

\[ = 8.5 \text{ ng/kg} \]
Polyaromatic Hydrocarbons (PAHs)

EQS (2008)
AA-EQS
0.05 µg/l

Proposal 2012
AA-EQS
Σ 0.03 µg/l

Σ 0.002 µg/l

Σ 0.17 ng/l

Σ Biota EQS
2 µg/kg for fish
5 µg/kg for crustaceans
10 µg/kg for molluscs
Tributyltin compounds

ISO/DIS 17353 (year 2002)

Organotin compounds in water are ethylated with sodium tetraethyl-borate (NaBEt₄) and extracted with hexane. The extract can be cleaned with silica. After concentration, the tetra-substituted OTC are separated by capillary gas chromatography and detected with a suitable system (MS, FPD, AED). The concentration is determined by calibration over the total procedure using an internal standard mixture. The working range is 10 – 1000 ng/l.


AA-EQS
0.2 ng/l

Proposal 2012
No change; no biota EQS
SCCPs: C10-C13 Chloroalkanes

- Complex mixture of branched and straight-chained alkanes ranging from C10–C13 with varying degrees of chlorination
- Priority Hazardous Substances (carcinogenic)
- Analysis of SCCPs is extremely difficult owing to their complex composition containing thousands of homologues and isomers
- ISO 12010:2012; Water quality - Determination of short-chain polychlorinated alkanes (SCCPs) in water - Method using gas chromatography-mass spectrometry (GC-MS) and negative-ion chemical ionization (NCI)

Sverko et al.: Improving the quality of environmental measurements on short chain chlorinated paraffins to support global regulatory efforts
Endosulfan

Technical endosulfan is a 7:3 mixture of $\alpha$- and $\beta$-endosulfan stereoisomers

**EQS Directive (2008)**

**AA-EQS**

- 5 ng/l
- 0.5 ng/l (for other surface waters)

**Proposal 2012**

- No change; no biota EQS
Hexachlorocyclohexane

Different Isomers

Gamma-HCH = Lindane

AA-EQS
0.02 µg/l
0.002 µg/l (for other surface waters)

Proposal 2012
No change; no biota EQS
Cyclodiene pesticides

Aldrin, Dieldrin, Endrin, Isodrin


AA-EQS

Sum: 0.01 µg/l

Sum 0.005 µg/l (for other surface waters)

Proposal 2012

No change; no biota EQS
Commercial DDT is a mixture of several closely-related compounds. The major component (77%) is the $p,p'$-isomer. The $o,p'$ isomer is also present in significant amounts (15%).

**Chemical Structures:**
- **p-p’-DDT**
- **o-p’-DDT**
- **DDE**
- **DDD**

**EQS Directive (2008)**

**AA-EQS**

- **DDT total** 0.025 µg/l
- **p-p’-DDT** 0.010 µg/l

**Proposal 2012**

- No change; no biota EQS
Pentachlorobenzene

AA-EQS
7 ng/l
0.7 ng/l (for other surface waters)

Proposal 2012
No change; no biota EQS
Problematic Chemicals of new Proposal (EQS in pg/l range)

- **Cypermethrin**: 80 pg/l (8 pg/l for coastal salt waters)
- **Dichlorvos**: 0.6 ng/l (60 pg/l in coastal waters)
- **Dicofol**: 1.3 ng/l (32 pg/l in coastal waters)
- **17-alpha-ethinylestradiol**: 35 pg/l (7 pg/l in coastal waters)
- **17-beta-estradiol**: 0.4 ng/l (80 pg/l in coastal waters)
- **Heptachlor/Heptachlorepoxide**: 0.2 pg/l (10 fg/l)
- **PFOS**: 0.65 ng/l (0.13 ng/l in coastal waters)
- **Dicofol, Heptachlor/Heptachlorepoxide, PFOS**: biota EQS
Conclusions

• Some PS are very difficult to analyse
  (Tributyltin, Chloroalkanes)
• Very low EQS values
• New PS proposal: BDEs, PAHs, Cypermethrin, Dichlorvos,
  Dicofol, Estradiols, Heptachlor/ Heptachlorepoxide, PFOS
• Biota analysis
• River basin specific pollutants
• Compliance with the QA/QC Directive
• Analysis of whole water samples
Need for research and development

- methods of analysis of organic compounds in non-filtered water samples – whole water analysis
- distribution of chemicals between suspended particulate matter and the dissolved phase
- methods for analysis in sediment and biota

- For quality assurance it is necessary to:
  - Organise interlaboratory studies designed according to WFD requirements (concentrations close to EQS, representative water samples)
  - Field studies that focus comparison of sampling methods
Thank you for your attention!