THE CHEMICAL MONITORING ACTIVITY (CMA) UNDER THE WATER FRAMEWORK DIRECTIVE (WFD)

- STATE OF THE ART AND ANALYTICAL CHALLENGES -

EURAMET 924 – Project Meeting
09 – 10 April 2008, Braunschweig

Ulrich Borchers, IWW Water Centre (D)
Peter Lepom and Anja Duffek, UBA (D)
Agenda

- Introduction to the Water Framework Directive
- The Chemical Monitoring under the WFD
- Priority Substances
- The Chemical Monitoring Activity (CMA)
- Analytical Aspects and Challenges
  - Requirements to the methods
  - Existing methods / Standards
  - Problems and new approaches
  - QA/QC requirements (new EU directive)
What are the main objectives of the WFD?

- Protection of aquatic ecosystems
- Objective by 2015:
  - Good status (ecological and chemical)
  - No deterioration principle
- Water management based on river basin districts
- Environmental quality standards and emission control
- „Phasing out“ of priority hazardous substances
- Use of economic instruments
- Public participation
- Integration of other directives related to water
## Implementation Schedule for the WFD

<table>
<thead>
<tr>
<th>Date</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dec. 2003</td>
<td>Implementation of relevant legal framework</td>
</tr>
<tr>
<td>Dec. 2004</td>
<td>Submit report to European Commission regarding the characterization process</td>
</tr>
<tr>
<td>Dec. 2006</td>
<td>Monitoring programmes operational</td>
</tr>
<tr>
<td></td>
<td>Submit report to European commission (March 2007)</td>
</tr>
<tr>
<td>Dec. 2009</td>
<td>Programmes of measures and river basin district management programmes have been established</td>
</tr>
<tr>
<td></td>
<td>Submit report to European commission (March 2010)</td>
</tr>
<tr>
<td>Dec. 2012</td>
<td>Measures have been implemented</td>
</tr>
<tr>
<td></td>
<td>Submit report to European commission</td>
</tr>
<tr>
<td>Dec. 2015</td>
<td>Good status has been achieved - new river basin management plan comes into force</td>
</tr>
<tr>
<td></td>
<td>Submit report to European commission (March 2016)</td>
</tr>
</tbody>
</table>
Hundreds of River Basins in Europe

Strong needs for co-ordination and harmonisation at EU level
Agenda

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  - Requirements to the methods
  - Existing methods / Standards
  - Problems and new approaches
  - QA/QC requirements (COM Decision)
Scope of the Monitoring

- Covers all types of waters
  - Rivers, lakes and groundwater
  - Transitional waters
  - Coastal waters up to one sea mile
  - For the chemical status also territorial waters, which may extend to 12 sea miles from the territorial baseline of a Member State
What is to be monitored?

- **Priority Substances**
  - Compliance with **European Environmental Quality Standards (EQS)**

- **River-basin-specific substances**
  - Compliance with **National EQS (Other pollutants)**

- **Physico-chemical parameters**
  - To support the interpretation of biological data
  - Parameters (e.g. DOC, Hardness, SPM)
  - Required for interpretation of the results of chemical measurements
Chemical Monitoring – Status Assessment

Good Status Surface Water

Good Chemical Status

Priority Substances

„Other Pollutants“

Good Ecological Status

Biological Quality Elements

Physico-chemical Parameters

Hydromorphological Quality Elements
Types of Monitoring

- Surveillance
- Operational
- Investigative
- Protected areas
### Frequency of Monitoring

<table>
<thead>
<tr>
<th>Physico-Chemical Quality Elements</th>
<th>Rivers</th>
<th>Lakes</th>
<th>Transitional</th>
<th>Coastal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conditions</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
</tr>
<tr>
<td>Oxygenation</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
</tr>
<tr>
<td>Salinity</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
</tr>
<tr>
<td>Nutrient status</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
</tr>
<tr>
<td>Acidification status</td>
<td>3 months</td>
<td>3 months</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other pollutants</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
<td>3 months</td>
</tr>
<tr>
<td>Priority substances</td>
<td>1 month</td>
<td>1 month</td>
<td>1 month</td>
<td>1 month</td>
</tr>
</tbody>
</table>

Less frequent only if justifiable (e.g. biota, sediment)
More frequent samplings may be necessary
- to detect short term changes and pollution loads
- to take account of variability resulting from natural and anthropogenic conditions
- to achieve acceptable levels of confidence in assessing the status of water bodies

In general, it is advisable to take samples in equidistant time intervals over a year (monthly, quarterly)
Introduction to the Water Framework Directive

The Chemical Monitoring under the WFD

Priority Substances

The Chemical Monitoring Activity (CMA)

Analytical Aspects and Challenges

- Requirements to the methods
- Existing methods / Standards
- Problems and new approaches
- QA/QC requirements (new EU directive)
Decision 2455/2001/EG

List of Priority Substances (33)

- Priority Substances
  - present a significant general risk to or via the aquatic environment

- Priority Hazardous Substances
  - Subset of priority substances, which are
    - toxic,
    - persistent,
    - liable to bio-accumulate or
    - give rise to equivalent level of concern
The goals in the light of the WFD:

- Priority substances
  - Progressive reduction of discharges, emissions and losses

- Priority hazardous substances (PHS)
  - Cessation of discharges, emissions and losses or phasing-out by 2020
<table>
<thead>
<tr>
<th>Priority Hazardous Substances</th>
<th>Priority Substances under Review</th>
<th>Priority Substances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentabromodiphenylether</td>
<td>Anthracene</td>
<td>Alachlor</td>
</tr>
<tr>
<td>Cadmium and its compounds</td>
<td>Atrazin</td>
<td>Benzene</td>
</tr>
<tr>
<td>C10-C13-Chloroalkanes</td>
<td>Chlorpyrifos</td>
<td>Chlorfenvinphos</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>Di(2-ethylhexyl)phthalate (DEHP)</td>
<td>1,2-Dichloroethane</td>
</tr>
<tr>
<td>Hexachlorobutadiene</td>
<td>Diuron</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>Hexachlorocyclohexane</td>
<td>Endosulfan</td>
<td>Fluoranthene</td>
</tr>
<tr>
<td>Mercury and its compounds</td>
<td>Isoproturon</td>
<td>Nickel and its compounds</td>
</tr>
<tr>
<td>Nonylphenol</td>
<td>Lead and its compounds</td>
<td>Trichloromethane</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>Naphthalene</td>
<td></td>
</tr>
<tr>
<td>Polyaromatic Hydrocarbons (PAH)</td>
<td>Octylphenol</td>
<td></td>
</tr>
<tr>
<td>Tributyltin compounds</td>
<td>Pentachlorophenol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Simazine</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trichlorobenzenes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Trifluralin</td>
<td></td>
</tr>
</tbody>
</table>
Environmental Quality Standards (EQS)
- At this stage, set up only for surface water
- Ecotoxicological assessment according to the Technical Guidance Document on Risk Assessment of Chemicals
- Rule of thumb: $\text{EQS} = \text{Lowest NOEC} \times 0.1$

**AA-EQS:**
- Environmental quality standard expressed as *annual average* concentration

**MAC-EQS:**
- Environmental quality standard expressed as *maximum allowable* concentrations
Compliance with EQS

- **AA-EQS**
  - For each representative point within the water body, the arithmetic mean of the concentrations measured at different times during the year is below the EQS

- **MAC-EQS**
  - The measured concentration at any representative monitoring point within the whole water body must not exceed the EQS

- With the exception of metals, EQS refer to total concentration in the whole water samples

- In the case of metals the EQS refer to the dissolved concentration
<table>
<thead>
<tr>
<th>No</th>
<th>Priority Substance</th>
<th>Inland Surface Waters</th>
<th>Other Surface Waters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AA-EQS (µg/L)</td>
<td>MAQ-EQS (µg/L)</td>
</tr>
<tr>
<td>(1)</td>
<td>Alachlor</td>
<td>0,3</td>
<td>0,7</td>
</tr>
<tr>
<td>(2)</td>
<td>Anthracene</td>
<td>0,1</td>
<td>0,4</td>
</tr>
<tr>
<td>(3)</td>
<td>Atrazin</td>
<td>0,6</td>
<td>2</td>
</tr>
<tr>
<td>(4)</td>
<td>Benzene</td>
<td>10</td>
<td>50</td>
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<tr>
<td>(5)</td>
<td>Pentabromodiphenylether</td>
<td>0,0005</td>
<td>not applicable</td>
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<tr>
<td>(6)</td>
<td>Cadmium and its compounds</td>
<td>0,08 - 0,2</td>
<td>0,45 - 1,5</td>
</tr>
<tr>
<td>(7)</td>
<td>C10-C13-Chloroalkanes</td>
<td>0,4</td>
<td>1,4</td>
</tr>
<tr>
<td>(8)</td>
<td>Chlorfenvinphos</td>
<td>0,1</td>
<td>0,3</td>
</tr>
<tr>
<td>(9)</td>
<td>Chlorpyrifos</td>
<td>0,03</td>
<td>0,1</td>
</tr>
<tr>
<td>(10)</td>
<td>1,2-Dichloroethane</td>
<td>10</td>
<td>not applicable</td>
</tr>
<tr>
<td>(11)</td>
<td>Dichloromethane</td>
<td>20</td>
<td>not applicable</td>
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<td>(12)</td>
<td>Di(2-ethylhexyl)phthalate (DEHP)</td>
<td>1,3</td>
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<td>(13)</td>
<td>Diuron</td>
<td>0,2</td>
<td>1,8</td>
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<tr>
<td>(14)</td>
<td>Endosulfan</td>
<td>0,005</td>
<td>0,01</td>
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<tr>
<td>(15)</td>
<td>Fluoranthene</td>
<td>0,1</td>
<td>1</td>
</tr>
<tr>
<td>(16)</td>
<td>Hexachlorobenzene</td>
<td>0,01</td>
<td>0,05</td>
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<tr>
<td>(17)</td>
<td>Hexachlorobutadiene</td>
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<td>0,6</td>
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<td>(18)</td>
<td>Hexachlorocyclohexane</td>
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<td>0,04</td>
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<td>(19)</td>
<td>Isoproturon</td>
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<td>1</td>
</tr>
<tr>
<td>(20)</td>
<td>Lead and its compounds</td>
<td>7,2</td>
<td>not applicable</td>
</tr>
</tbody>
</table>
Environmental Quality Standards

<table>
<thead>
<tr>
<th>No</th>
<th>Priority Substance</th>
<th>Inland Surface Waters</th>
<th>Other Surface Waters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AA-EQS (µg/L)</td>
<td>MAQ-EQS (µg/L)</td>
</tr>
<tr>
<td>(21)</td>
<td>Mercury and its compounds</td>
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<td>0,07</td>
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<tr>
<td>(22)</td>
<td>Naphthalene</td>
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<tr>
<td>(23)</td>
<td>Nickel and its compounds</td>
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<td>not applicable</td>
</tr>
<tr>
<td>(24)</td>
<td>Nonylphenol</td>
<td>0,3</td>
<td>2</td>
</tr>
<tr>
<td>(25)</td>
<td>Octylphenol</td>
<td>0,1</td>
<td>not applicable</td>
</tr>
<tr>
<td>(26)</td>
<td>Pentachlorobenzene</td>
<td>0,007</td>
<td>not applicable</td>
</tr>
<tr>
<td>(27)</td>
<td>Pentachlorophenol</td>
<td>0,4</td>
<td>1</td>
</tr>
<tr>
<td>(28)</td>
<td>Polyaromatic Hydrocarbons (PAH)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Benzo(a)pyrene</td>
<td>0,05</td>
<td>0,1</td>
</tr>
<tr>
<td></td>
<td>Benzo(b)fluoranthene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Benzo(k)fluoranthene</td>
<td>Σ=0,03</td>
<td>not applicable</td>
</tr>
<tr>
<td></td>
<td>Benzo(g,h,i)perylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ideno(1,2,3-cd)pyrene</td>
<td>Σ=0,002</td>
<td>not applicable</td>
</tr>
<tr>
<td>(29)</td>
<td>Simazine</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>(30)</td>
<td>Tributyltin compounds</td>
<td>0,0002</td>
<td>0,0015</td>
</tr>
<tr>
<td>(31)</td>
<td>Trichlorobenzenes</td>
<td>0,4</td>
<td>not applicable</td>
</tr>
<tr>
<td>(32)</td>
<td>Trichloromethane</td>
<td>2,5</td>
<td>not applicable</td>
</tr>
<tr>
<td>(33)</td>
<td>Trifluralin</td>
<td>0,03</td>
<td>not applicable</td>
</tr>
</tbody>
</table>
For the time being, there are only EQS for water

Metals
  - Filtered water sample (dissolved)
    ▪ Natural background has to be considered
    ▪ DOC, pH, hardness ➔ Bioavailability

Organic compounds
  - Results have to be referred to whole water
    ▪ Analysis of whole water samples
    ▪ Separate analysis of solid particulate matter (SPM) and the liquid phase and calculation of the content
  - SPM or the filtered water samples may be used as substitute for the whole water sample if justified
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CMA 2007 – 2009 – Tasks and Deliverables

WATER DIRECTORS OF THE MS

STRATEGIC CO-ORDINATION GROUP

PLENARY CMA (GW, SW/MW)

WG E

WG C or WG E (joint meetings)

CMA-1
Exchange of best practices
- Sharing best practices
- Identification of gaps and needs
- Analytical methods, sampling
- Practical exercises
- Sediment and biota

CMA-2
QA/QC
- Follow-up of EU Directive
- Discussion of common strategy (EAQC-WISE)

CMA-3
Standardisation (CEN TC/230)
- Identification of standards
- Follow-up of CEN work
- Links with RTD
CMA-2 Core Activities

- To develop a common strategy
  - at European,
  - national and
  - river basin level

for quality assurance and control

- The finalisation of the "QA/QC Directive"

- Development of a common and integrated strategy for quality assurance and control
  - based on recommendations arising from the EAQC-WISE project
  - aiming to an efficient and sustainable pan-EU QA/QC system in support of the WFD implementation
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Article 8.3
- Technical specifications and standardised methods for analysis and monitoring of water status shall be laid down in accordance with the procedure laid down in Article 21

Annex V, paragraph 1.3.6
- the provision of chemical data by MS shall be ensured by analytical methods
  - that conform to relevant international or national standards
  - or alternatively by analytical methods that are not standardised but provide data of equivalent or better scientific quality and comparability
Requirements from the EQS Daughter Directive*

- **EQS values (Article 2)**
  - In conjunction with Limit of Quantification (LOQ) requirements in the QA/QC Directive

- **Matrix**
  - "Whole water", SPM, sediment, biota

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Sampling and sample treatment
- ... shall follow recommendations of relevant international guidelines and standards, including relevant parts of ISO 5667

Limit of quantification (LOQ)
- ... equal or below a value of 0.3 of the relevant quality standards (EQS)

Uncertainty, relative
- ... uncertainty of measurement of 50% or below \((k = 2)\) estimated at the level of relevant EQS
Are the Existing Standard Methods Fit for the Purpose of WFD Monitoring?

- Survey under European labs whether they are able to meet the most important requirements

- Method Applicability Factor (MAF)
  - $\text{MAF} = \frac{\text{LOQ}}{0.3 \times \text{EQS}}$
  - $\text{MAF} \leq 1$ fit for purpose
  - $\text{MAF} 1-5$ method needs to be improved
  - $\text{MAF} > 5$ not applicable, need for method development
Evaluation of LOQ Information from European Monitoring Laboratories

- No standardised method available: 3
- MAF > 5 – not applicable: 1
- MAF 1 to 5 – need for improvement: 0
- MAF ≤ 1 – applicable: 42

Inland / Others:
- 3
- 1
- 2
- 40
Subject: M/424 Mandate addressed to CEN for the development or improvement of standards in support of the Water Framework Directive
List of 5 mandated chemical methods

- **Cyclodiene pesticides**
  - (e.g. Aldrin, Dieldrin, Endrin and Isodrin)

- **Pentabromodiphenylether**
  - Problems with the sensitivity of the method(s) (LOQ)

- **Tributyl tin compounds**
  - Extreme requirements on LOQ: proposed EQS is 0.2 ng/L

- **Short-chain chlorinated paraffins (SCCP)**

- **PAH (5- and 6-ring PAH)**
  - Sensitivity for some parameters (in particular for the 6-ring Isomers) not sufficient with respect to the low EQS
  - Method is not suitable to cope with samples with SPM content (whole water samples)!
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- Guidance Document on Chemical Monitoring
COMMISSION OF THE EUROPEAN COMMUNITIES

Brussels, [Day Month] 2007
C 2007 XYZ [CHECK]

Draft by Commission
[Version of 7th March 2008]

COMMISSION DIRECTIVE

of [Day Month 2008]

laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status
Important QA/QC issues in the field of chemical monitoring under the WFD

- should be prescribed in addition to accreditation rules (ISO/IEC 17025)
- should be harmonised on the European scale
- should be clarified in the case of lacks in existing documents
Analytical Methods

- Member States shall ensure that all methods of analysis used for the purposes of chemical monitoring programmes carried out under Directive 2000/60/EC are validated and documented in accordance with EN ISO/IEC-17025

- For operationally defined parameters (e.g. TOC) use of standard analytical methods adopted by ISO or CEN is recommended
Minimum Performance Criteria

- Minimum Limit of Quantification (LOQ)
  - $\text{LOQ} \leq 0.3 \times \text{AA-EQS}$
    - Cadmium $0.033 \ \mu g/l$
    - Lead $2.4 \ \mu g/l$
    - Mercury $0.017 \ \mu g/l$
    - Nickel $7 \ \mu g/l$

- The minimum performance criteria for all methods of analysis applied are based on an uncertainty of measurement of 50% or below ($k = 2$) estimated at the level of relevant EQS.
Minimum Performance Criteria

- In the absence of relevant EQS values for a given parameter, or
- In the absence of method of analysis meeting the minimum performance criteria
  - Member States shall ensure that monitoring is carried out using best available techniques not entailing excessive costs.
Quality of Results (QA/QC)

- MS shall ensure that labs or parties contracted by laboratories apply quality management system practices in accordance with EN ISO/IEC-17025

- MS shall ensure that laboratories or parties contracted by laboratories demonstrate their competences by:
  - (a) participation in proficiency testing programmes
  - (b) analysis of available reference materials that are representative of collected samples which contain appropriate levels of concentrations in relation to relevant EQS
PT schemes

- PT programmes shall be organised by accredited organisations or internationally or nationally recognised organisations which meet the requirements of ISO/IEC guide 43-1 (ISO 17043)

- The results of participation in those programmes shall be evaluated on the basis of the scoring systems set out in ISO/IEC guide 43-1 (ISO 17043) or in ISO-13528
Information on the European Water Framework Directive