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

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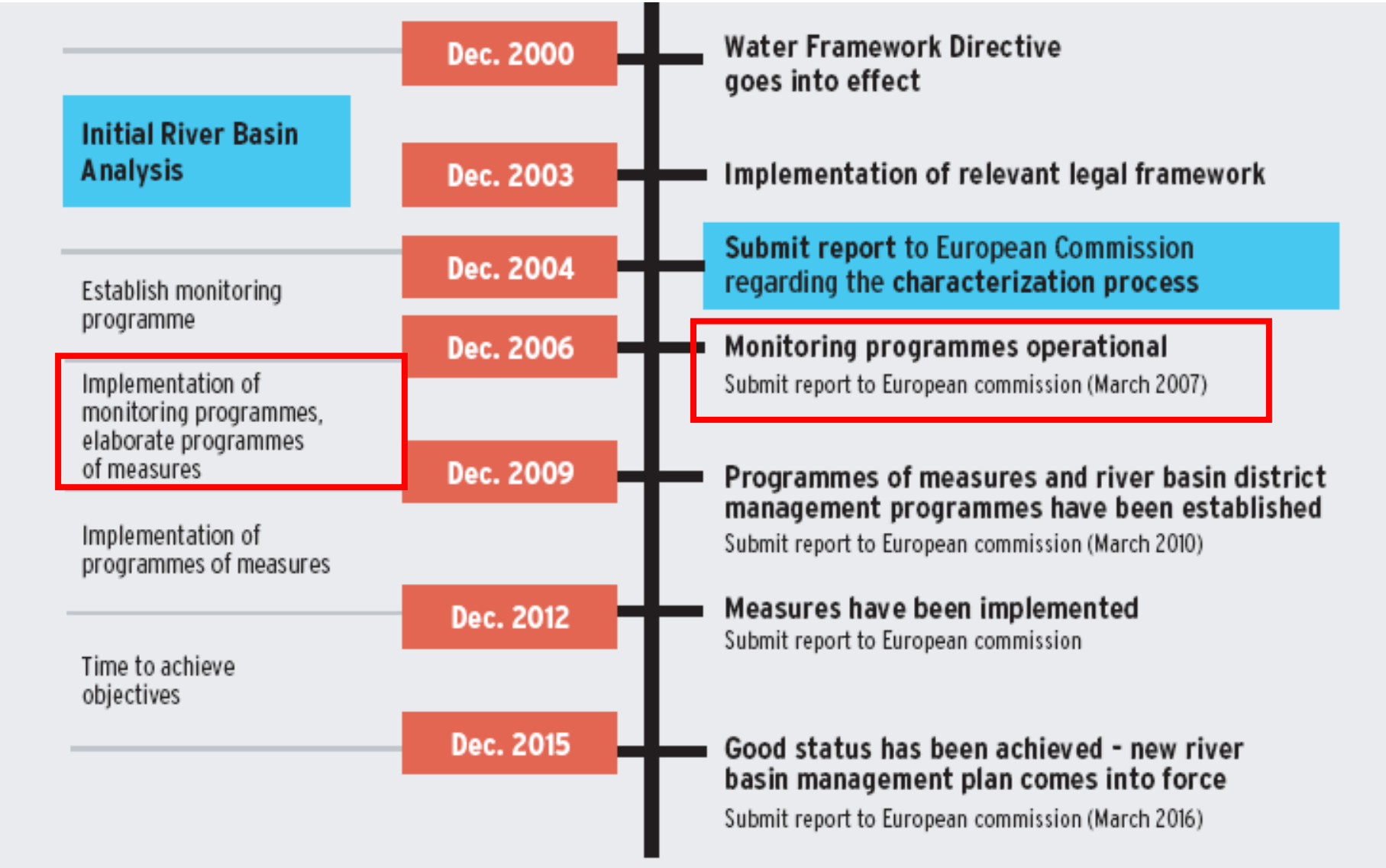
Agenda

- 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



Hundreds of River Basins in Europe

Strong needs for co-ordination and harmonisation at EU level

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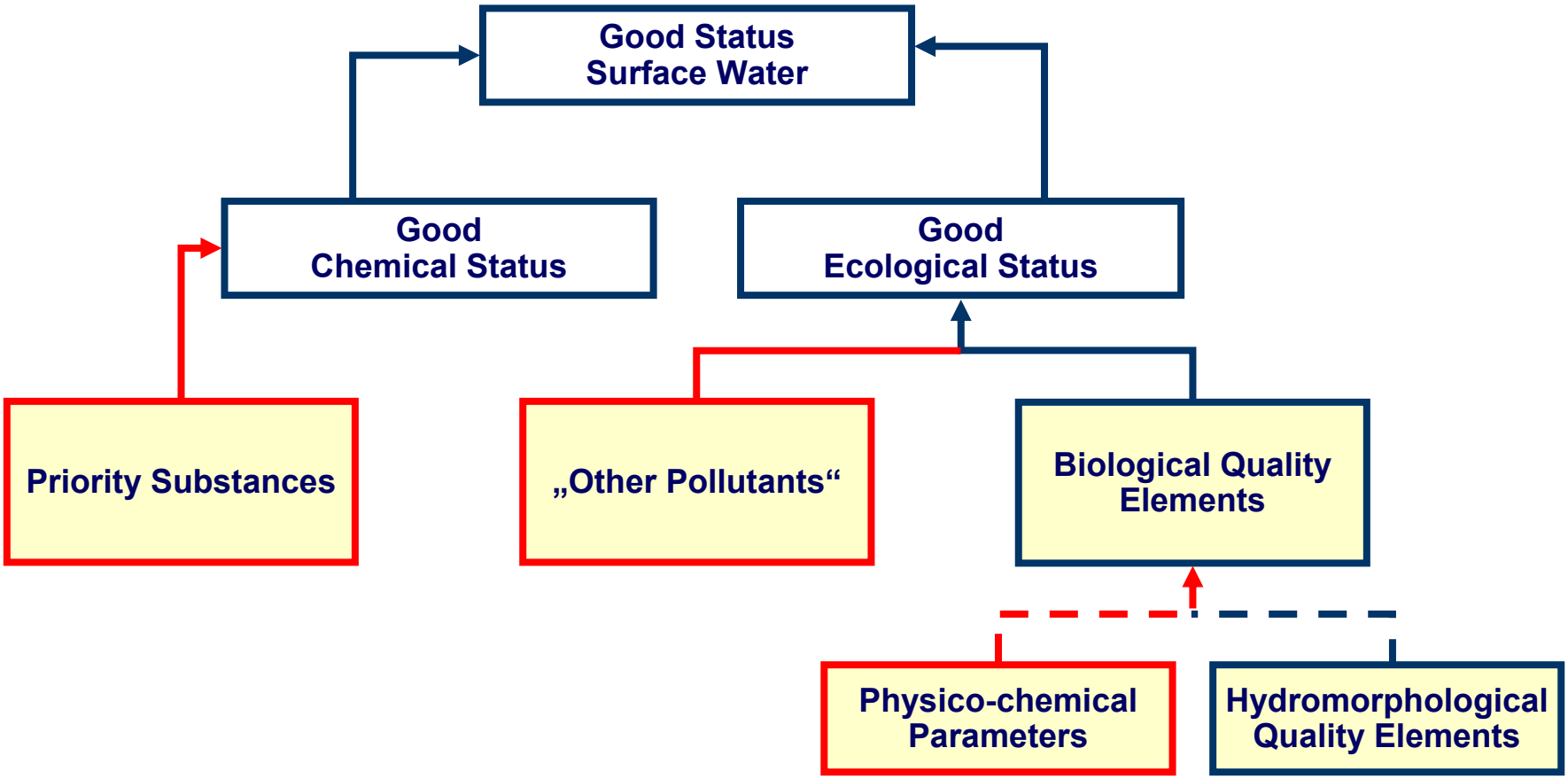
Scope of the Monitoring

- **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



Types of Monitoring

- Surveillance
- Operational
- Investigative
- Protected areas

Frequency of Monitoring

Physico-Chemical Quality Elements	Rivers	Lakes	Transitional	Coastal
Thermal Conditions	3 months	3 months	3 months	3 months
Oxygenation	3 months	3 months	3 months	3 months
Salinity	3 months	3 months	3 months	3 months
Nutrient status	3 months	3 months	3 months	3 months
Acidification status	3 months	3 months		
Other pollutants	3 months	3 months	3 months	3 months
Priority substances	**1 month**	**1 month**	**1 month**	**1 month**

- **Less frequent only if justifiable (e.g. biota, sediment)**

Frequency of Monitoring

- **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)**

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WFD Annex X – Priority Substances

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**

WFD Annex X – Priority Substances

- **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**

Priority Substances

Priority Hazardous Substances	Priority Substances under Review	Priority Substances
Pentabromodiphenylether	Anthracene	Alachlor
Cadmium and its compounds	Atrazin	Benzene
C10-C13-Chloroalkanes	Chlorpyrifos	Chlorfenvinphos
Hexachlorobenzene	Di(2-ethylhexyl)phthalate (DEHP)	1,2-Dichloroethane
Hexachlorobutadiene	Diuron	Dichloromethane
Hexachlorocyclohexane	Endosulfan	Fluoranthene
Mercury and its compounds	Isoproturon	Nickel and its compounds
Nonylphenol	Lead and its compounds	Trichloromethane
Pentachlorobenzene	Naphthalene	
Polyaromatic Hydrocarbons (PAH)	Octylphenol	
Tributyltin compounds	Pentachlorophenol	
	Simazine	
	Trichlorobenzenes	
	Trifluralin	

Derivation of Environmental Quality Standards

- **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: EQS = Lowest NOEC * 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 <u>whole</u> water samples**
- **In the case of metals the EQS refer to the <u>dissolved</u> concentration**

Environmental Quality Standards

		Inland Surface Waters		Other Surface Waters	
No	**Priority Substance**	**AA-EQS (µg/L)**	***MAQ-EQS (µg/L)***	***AA-EQS (µg/L)***	***MAQ-EQS (µg/L)***
(1)	Alachlor	0,3	0,7	0,3	0,7
(2)	Anthracene	0,1	0,4	0,1	0,4
(3)	Atrazin	0,6	2	0,6	2
(4)	Benzene	**10**	50	**8**	50
(5)	Pentabromodiphenylether	0,0005	*not applicable*	0,0002	*not applicable*
(6)	Cadmium and its compounds	**0,08 - 0,2**	**0,45 - 1,5**	0,2	0,45 - 1,5
(7)	C10-C13-Chloroalkanes	0,4	1,4	0,4	1,4
(8)	Chlorfenvinphos	0,1	0,3	0,1	0,3
(9)	Chlorpyrifos	0,03	0,1	0,03	0,1
(10)	1,2-Dichloroethane	10	*not applicable*	10	*not applicable*
(11)	Dichloromethane	20	*not applicable*	20	*not applicable*
(12)	Di(2-ethylhexyl)phthalate (DEHP)	1,3	*not applicable*	1,3	*not applicable*
(13)	Diuron	0,2	1,8	0,2	1,8
(14)	Endosulfan	0,005	0,01	0,0005	0,004
(15)	Fluoranthene	0,1	1	0,1	1
(16)	Hexachlorobenzene	0,01	0,05	0,01	0,05
(17)	Hexachlorobutadiene	0,1	0,6	0,1	0,6
(18)	Hexachlorocyclohexane	0,02	0,04	0,002	0,02
(19)	Isoproturon	0,3	1,0	0,3	1,0
(20)	Lead and its compounds	**7,2**	*not applicable*	7,2	*not applicable*

Environmental Quality Standards

		Inland Surface Waters		Other Surface Waters	
No	**Priority Substance**	**AA-EQS (µg/L)**	***MAQ-EQS (µg/L)***	***AA-EQS (µg/L)***	***MAQ-EQS (µg/L)***
(21)	Mercury and its compounds	**0,05**	**0,07**	0,05	0,07
(22)	Naphthalene	2,4	*not applicable*	1,2	*not applicable*
(23)	Nickel and its compounds	**20**	*not applicable*	20	*not applicable*
(24)	Nonylphenol	0,3	2	0,3	2
(25)	Octylphenol	0,1	*not applicable*	0,01	*not applicable*
(26)	Pentachlorobenzene	0,007	*not applicable*	0,0007	*not applicable*
(27)	Pentachlorophenol	0,4	1	0,4	1
(28)	Polyaromatic Hydrocarbons (PAH)				
	Benzo(a)pyrene	0,05	0,1	0,05	0,1
	Benzo(b)fluroanthene				
	Benzo(k)fluoranthene	**Σ=0,03**	*not applicable*	**Σ=0.03**	*not applicable*
	Benzo(g,h,i)perylene				
	Ideno(1,2,3-cd)pyrene	Σ=0,002	*not applicable*	Σ=0.002	*not applicable*
(29)	Simazine	1	4	1	4
(30)	Tributyltin compounds	0,0002	0,0015	0,0002	0,0015
(31)	Trichlorobenzenes	0,4	*not applicable*	0,4	*not applicable*
(32)	Trichloromethane	2,5	*not applicable*	2,5	*not applicable*
(33)	Trifluralin	0,03	*not applicable*	0,03	*not applicable*

Monitoring in Water

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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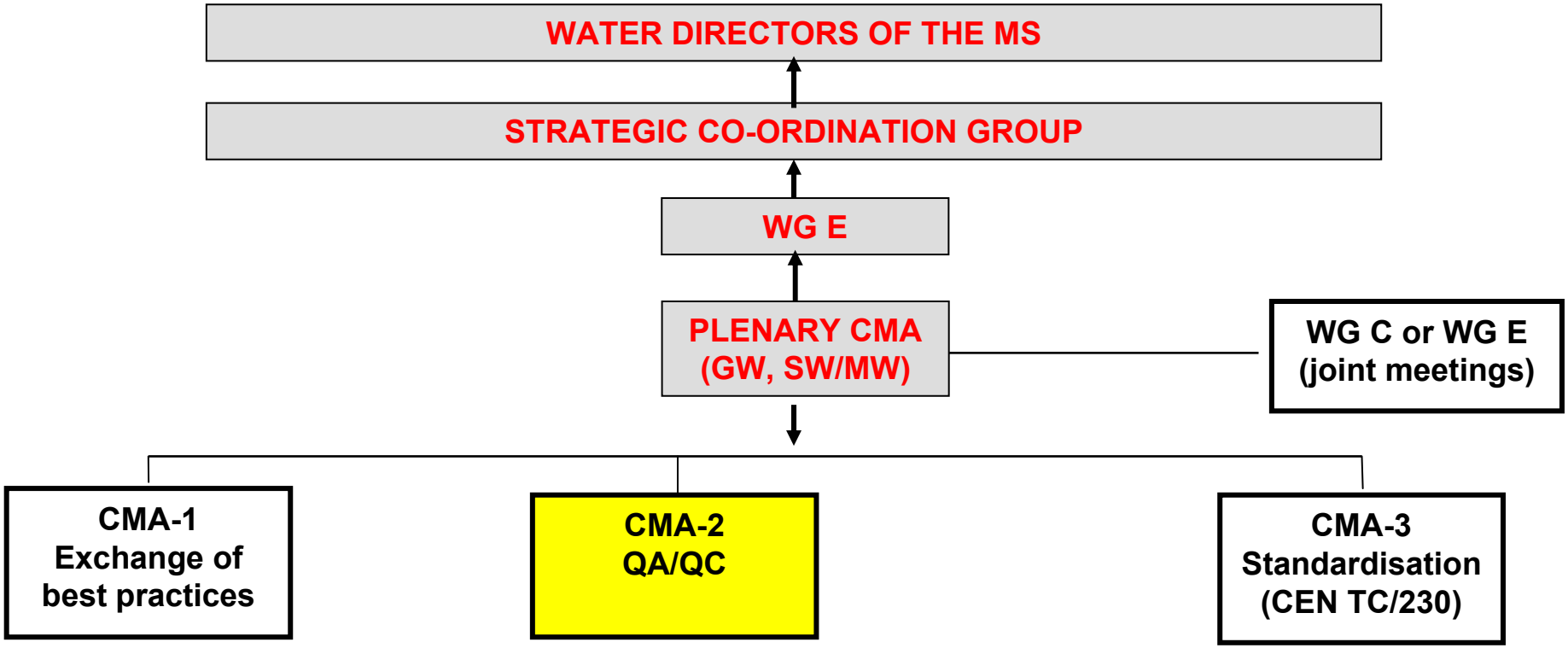
CMA 2007 – 2009 – Tasks and Deliverables



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

- Follow-up of EU Directive
- Discussion of common strategy (EAQC-WISE)

- 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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WFD Requirements for analytical methods

- **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** **key point 1**
  - **"Whole water", SPM, sediment, biota**

* Proposal for a Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC

Requirements from QA/QC Directive

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

key point 2

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

key point 3

- **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)**
  - **MAF = LOQ / 0.3 * EQS**

    - **MAF ≤ 1** fit for purpose
    - **MAF 1- 5** method needs to be improved
    - **MAF > 5** not applicable, need for method development

Evaluation of LOQ Information from European Monitoring Laboratories

	Inland	Others
No standardised method available	3	3
MAF > 5 – not applicable	1	1
MAF 1 to 5 – need for improvement	0	2
MAF ≤ 1 – applicable	42	40

Mandate to CEN TC 230

EUROPEAN COMMISSION
ENTERPRISE AND INDUSTRY DIRECTORATE-GENERAL

New Approach Industries, Tourism and CSR
Director

07 AVR. 2008

Brussels,
ENTR/I3/RG/kk D(2008)10160

Mr Gaston Michaud
Secretary General
CEN
Rue Stassart 36
B-1050 Brussels

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

EU Directive on QA/QC Issues

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

EU Directive on QA/QC Issues

- **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**

Minimum Performance Criteria for Analytical Methods / Quality of Results

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 Performance Criteria

- Minimum Limit of Quantification (LOQ)
  - LOQ ≤ 0.3 * AA-EQS
    - Cadmium 0,033 µg/l
    - Lead 2,4 µg/l
    - Mercury 0,017 µg/l
    - Nickel 7 µg/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

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
http://forum.europa.eu.int/public/irc/env/wfd/library