

Chemical Monitoring under the Water Framework Directive (WFD) - Current Challenges

NORMAN Inter-Laboratory Study (ILS) on *Passive Sampling of Emerging Pollutants*
Chemical Monitoring on site in support of WFD implementation
Dissemination Workshop / JRC Innovation Transfer Event
Ispra, 29-30 October 2012

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- **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)**

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]

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

- **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**



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

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

All surface waters

- **Rivers, lakes, artificial waters**
- **Transitional waters** (partly saline)
- **Coastal waters** (up to one sea mile)
- **Groundwaters (no upward trends)**

Types of Chemical Monitoring

- **Surveillance (12 samples per year)**
- **Operational**
- **Investigative**

- **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 %**

Sediment & Biota Monitoring (S&B)



- **Directive 2008/105/EC: long-term trend analysis** of those PS that tend to accumulate in S&B
- **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**
- **Mercury: EQS 20 µg/kg**
- **HCB: EQS 10 µg/kg**
- **Hexachlorobutadiene: EQS 55 µg/kg**

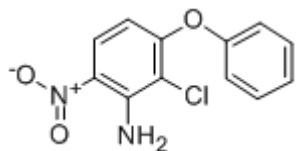


- **15 additional Priority Substances (PS)**
- **Pesticides and biocidal products**
- **Industrial chemicals (POPs)**
- **Pharmaceuticals**
- **Stricter EQS for four existing PS**
- **Biota standards for several substances**

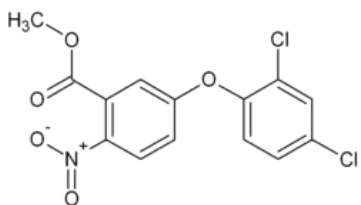
Pesticides and Biocidal products

European
Commission

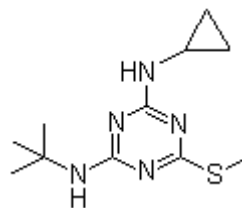
Aclonifen
(Herbicide)



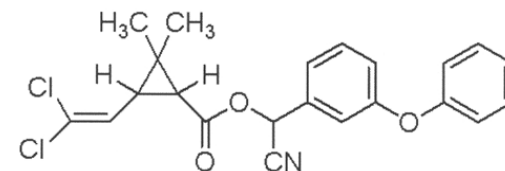
Bifenox (Herbicide)



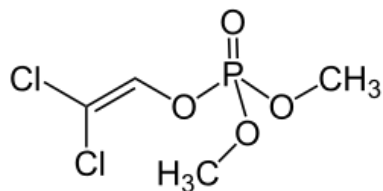
Cybutryne = Irgarol
(Triazine herbicide = algicide)



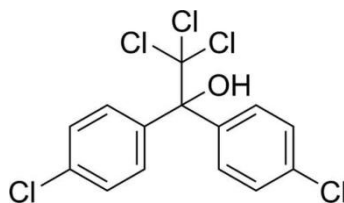
Cypermethrin
(Pyrethroide Insecticide)



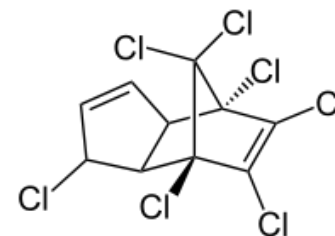
Dichlorvos
(Phospho-ester Insecticide)



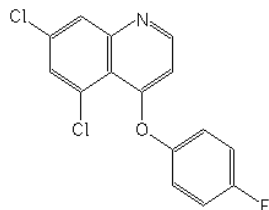
Dicofol
(Miticide)



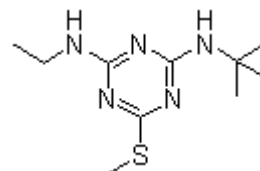
Heptachlor (epoxide)
(Insecticide)



Quinoxifen
(Fungicide)



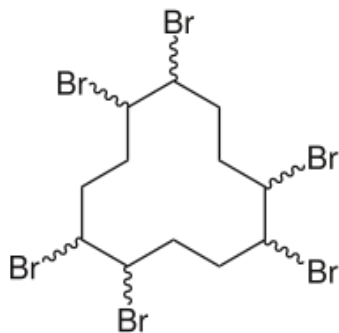
Terbutryn
(Triazine herbicide = algicide)



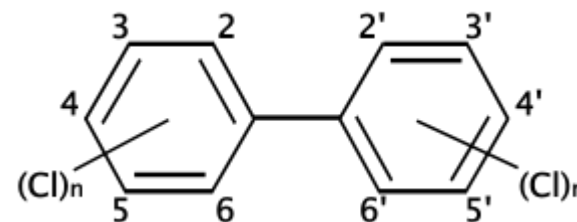
POPs - Industrial chemicals

European
Commission

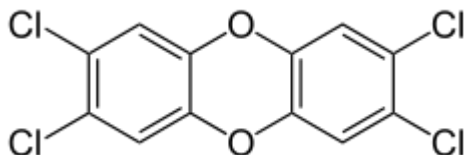
Hexabromocyclododecane (HBCDD) (Brominated flame retardant)



PCBs



2,3,7,8-Tetrachlorodibenzodioxin



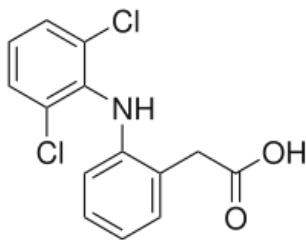
PFOS

(Fluorosurfactant)



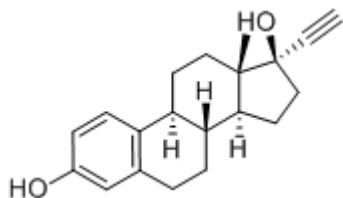
Diclofenac

(Non-Steroidal Anti-Inflammatory Drug)



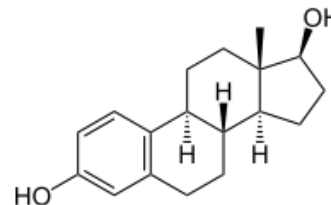
17 α -ethinyl-estradiol

(Contraceptive baby pill)



17 β -estradiol

(Estradiol is the predominant sex hormone present in females)



ANNEX III

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

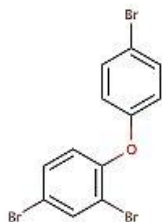
CAS number	EU number	Name of substance
1066-51-9	—	AMPA
25057-89-0	246-585-8	Bentazon
80-05-7		Bisphenol-A
115-32-2	204-082-0	Dicofol
60-00-4	200-449-4	EDTA
57-12-5		Free cyanide
1071-83-6	213-997-4	Glyphosate
7085-19-0	230-386-8	Mecoprop (MCP)
81-15-2	201-329-4	Musk xylene
1763-23-1		Perfluorooctane sulphonic acid (PFOS)
124495-18-7	—	Quinoxifen (5,7-dichloro-4-(p-fluorophenoxy)quinoline) Dioxins PCB

Brominated Diphenylethers (BDEs)

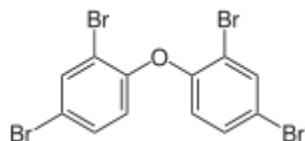
Σ BDE28, BDE47, BDE99, BDE100, BDE153 and BDE154

European
Commission

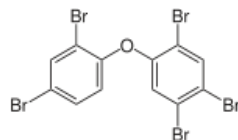
Commercial "pentaBDE" is a technical mixture of different PBDE congeners, with **BDE-47** (2,2',4,4'-tetrabromodiphenyl ether) and **BDE-99** (2,2',4,4',5-pentabromodiphenyl ether) as the most abundant.



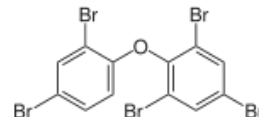
BDE28



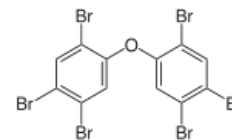
BDE47



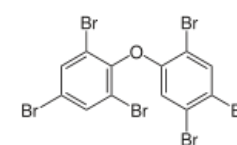
BDE99



BDE100



BDE153



BDE154

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 µg/l

Salt: 0.014 µg/l

Biota: 0.0085 µg/kg

= 8.5 ng/kg

Brominated Diphenylethers (BDEs)



- **BDEs have been extensively monitored during the last years in biota, sediment, humans, milk, food, dust, etc.**
- **Little information on **water analysis** available**
- **Concentrations in the pg/l**
- **Large volume extraction – GC-NCI-MS**
- **Biota analysis (fish)**
- **Biota levels are higher than 8.5 ng/kg (EQS)**

Guan et al., *Environ. Sci. Technol.* 2007, 41, 6007-6013

Oros et al., *Environ. Sci. Technol.* 2005, 39, 33-41

Streets et al., *Environ. Sci. Technol.* 2006, 40, 7263-7269

Wurl et al., *Chemosphere* 2006, 65, 1660-1666



EQS 8.5 ng/kg

Elbe and Vltava rivers (CZ)

	Bream	Chub	Perch
Σ BDEs	9.5 µg/kg	5 µg/kg	4 µg/kg

Hajslova et al., Chemosphere 69 (2007) 1195–1203.

Eels in Mediterranean coastal lagoons (Fr)

Σ BDEs **0.15-0.66 µg/kg**

Labadie et al., Anal. Chim. Acta 675 (2010) 97–105.

French Coast

Benthic or bottom feeder fish from estuarine or coastal areas

BDE-47 **0.002-0.05 µg/kg**

Munsch et al., Sci. Tot. Environ. 409 (2011) 4618–4627.

Polyaromatic Hydrocarbons (PAHs)



Benzo(a)pyrene

Benzo(b)fluoranthene

Benzo(k)fluoranthene

Benzo(g,h,i)perylene

Indeno(1,2,3-cd)pyrene

EQS (2008)

AA-EQS

0.05 µg/l

Σ 0.03 µg/l

Σ 0.002 µg/l

Proposal 2012

AA-EQS

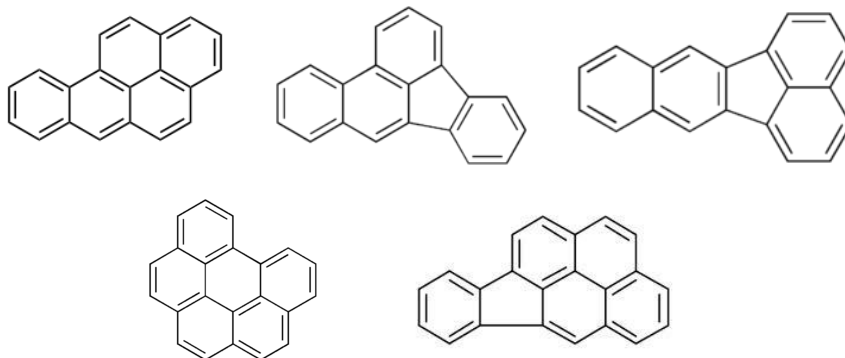
Σ 0.17 ng/l

Σ Biota EQS

2 µg/kg for fish

5 µg/kg for crustaceans

10 µg/kg for molluscs



Chemical Monitoring Exercises

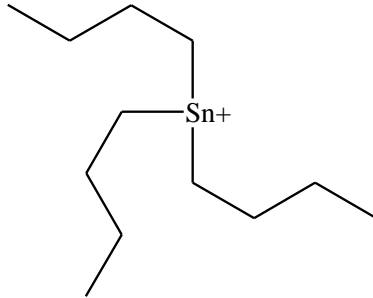


- **JRC and IRSA-CNR organized three intercomparison exercises on the Rivers Po (2006), Danube (2008) and Meuse (2010)**
- **Member State laboratories sampled simultaneously**
- **Target compounds: PBDEs, PAHs, Nonyl- and Octylphenols**

	AA-EQS	AA-EQS
Directive 2008	0.5 ng/l	
Proposal 2012	49 fg/l	0.17 ng/l
	Σ BDEs	Σ PAHs
Po River	0.37 ng/l	10 ng/l
Danube	0.30 ng/l	7.6 ng/l
Meuse	0.23 ng/l	34 ng/l

Σ of Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene in all cases > 2 ng/l

G. Hanke, S. Polesello, et al., *Trends Anal. Chem.* 36 (2012) 25-35.



ISO/DIS 17353 (year 2002)

Organotin compounds in water are ethylated with sodium tetraethyl-borate (NaBEt_4) 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.**

EQS Directive (2008)

AA-EQS

0.2 ng/l

Proposal 2012

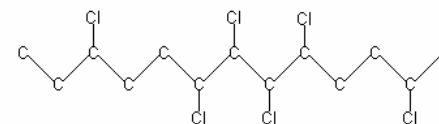
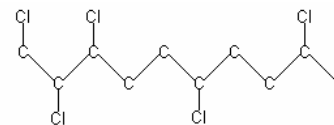
No change; no biota EQS

SCCPs: C10-C13 Chloroalkanes

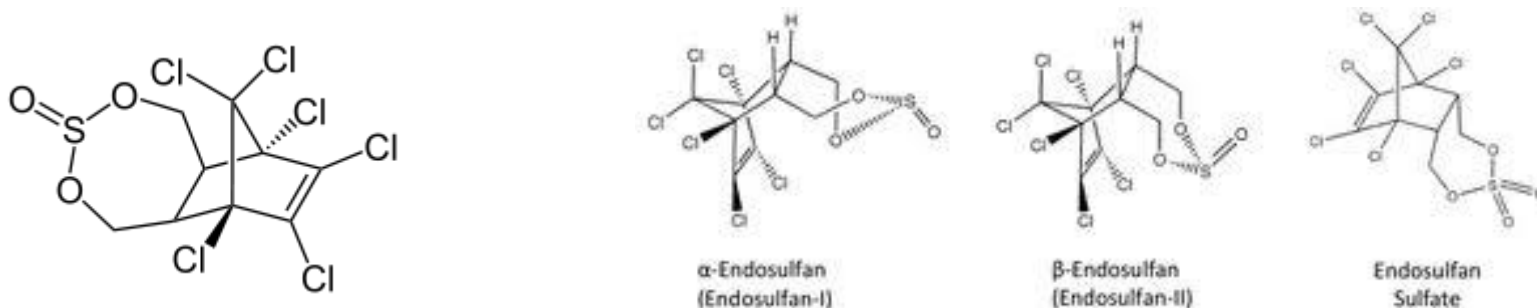


- **Complex mixture of branched and straight-chained alkanes ranging from C10–C13 with varying degrees of chlorination**
- **Priority Hazardous Substances (carcinogenic)**
- **Analysis of SCCPs is extremely difficult** owing to their complex composition containing thousands of homologues and isomers
- **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
Environ. Sci. Technol. 46 (2012) 4697–4698.



Technical endosulfan is a 7:3 mixture of α - and β -endosulfan stereoisomers



EQS Directive (2008)

AA-EQS

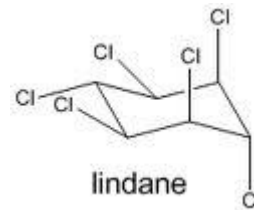
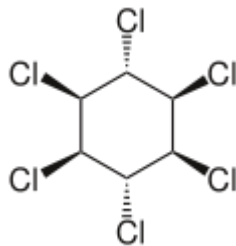
5 ng/l

0.5 ng/l (for other surface waters)

Proposal 2012

No change; no biota EQS

Different Isomers



**Gamma-HCH
= Lindane**

EQS Directive (2008)

AA-EQS

0.02 µg/l

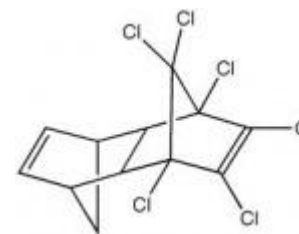
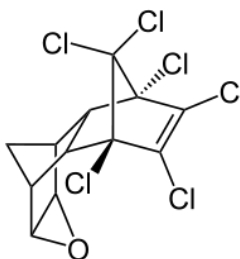
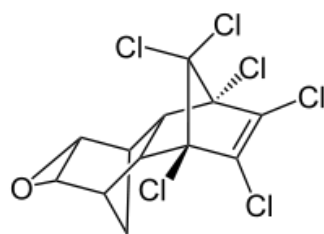
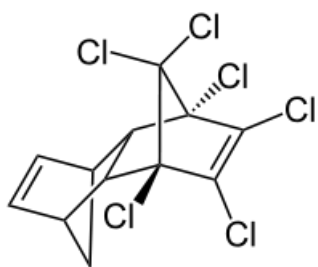
0.002 µg/l (for other surface waters)

Proposal 2012

No change; no biota EQS



Aldrin, Dieldrin, Endrin, Isodrin



EQS Directive (2008)

AA-EQS

Sum: 0.01 µg/l

Sum 0.005 µg/l (for other surface waters)

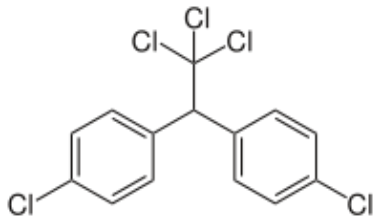
Proposal 2012

No change; no biota EQS

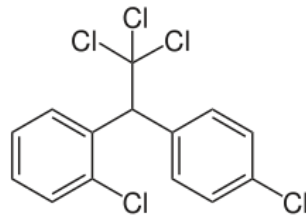
DDTs (total)



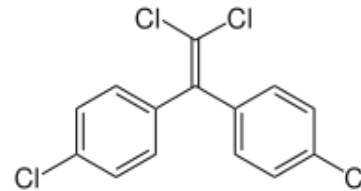
Commercial DDT is a mixture of several closely-related compounds. The major component (77%) is the *p,p'*-isomer. The *o,p'* isomer is also present in significant amounts (15%).



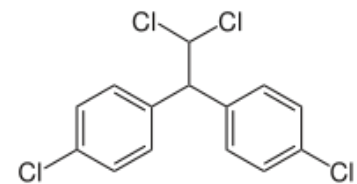
***p-p'*-DDT**



***o-p'*-DDT**



DDE



DDD

EQS Directive (2008)

AA-EQS

DDT total

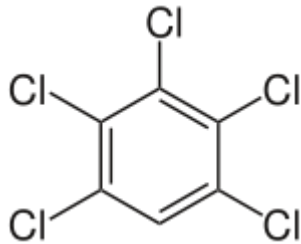
0.025 µg/l

***p-p'*-DDT**

0.010 µg/l

Proposal 2012

No change; no biota EQS



EQS Directive (2008)

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/Heptachlorepoide:** 0.2 pg/l (10 fg/l)
- **PFOS:** 0.65 ng/l (0.13 ng/l in coastal waters)
- **Dicofol, Heptachlor/Heptachlorepoide, PFOS:** biota EQS

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



- **Coquery et al.:**
Priority substances of the European Water Framework Directive: analytical challenges in monitoring of water quality
Trends Anal. Chem. 24 (2005) 117-125.
- **R. Loos, et al.:**
Laboratory intercomparison study for the analysis of nonylphenol and octylphenol in river water
Trends Anal. Chem. 27 (2008) 89-95.
- **P. Lepom, B. Brown, G. Hanke, R. Loos, P. Quevauviller, J. Wollgast:**
Needs for reliable analytical methods for monitoring chemical pollutants in surface water under the European Water Framework Directive
Journal of Chromatography A, 1216 (2009) 302-315.
- **G. Hanke, S. Polesello, et al.:**
Chemical-monitoring on-site exercises to harmonize analytical methods for priority substances in the European Union
Trends Anal. Chem. 36 (2012) 25-35.
- **R. Loos:**
Analytical Methods for the new proposed Priority Substances of the European Water Framework Directive (WFD) - Revision of the Priority Substance List (2012)
JRC Technical Report, 2012