Emerging and Priority Pollutants: the need for ultra-low level monitoring

Emerging contaminants in waters and soils, practical considerations: - Sampling, analysis and consequences

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Summary

- **Introduction**
  - Emerging Substances, Priority Substances and Priority Hazardous Substances
  - Environmental Quality Standards
- **The Water Framework Directive**
  - The Water Framework Directive
  - Environmental Quality Standards Directive
  - Priority Substances Directive
- **Chemical and Biological monitoring**
  - Analytical methods for Priority substances and emerging pollutants
  - Biota monitoring
  - Bioassays, Passive sampling and other approaches
- **Next Steps**

Emerging Substances and Priority Substances

➢ Emerging Pollutants

Pollutants that are currently not included in routine monitoring programmes at the European level and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments

➢ Priority Pollutants

Substances that require progressive reduction or phasing out and those which are thought to pose the greatest threat are further identified as 'priority hazardous substances'.

- Resistant to chemical transformation – Persistent, bioaccumulative, toxic to aquatic life or adversely impact human health
- Continual release of a substance to a media (such as a waterbody) having an adverse effect

The Water Framework Directive

- Expand the scope of water protection to all waters, surface waters and groundwater
- To establish a framework for the management, protection and improvement of water resources across the EU
- To achieve ‘‘good status’’ by 2015 (extended to 2021 or by 2027 at the latest)
- Good status includes both “good chemical status” and “good ecological status”
- Undertaking integrated water management based on river basins across Europe – working across member states and internationally
- Having a "combined approach" of emission limit values and quality standards
- Involving citizens and streamlining legislation

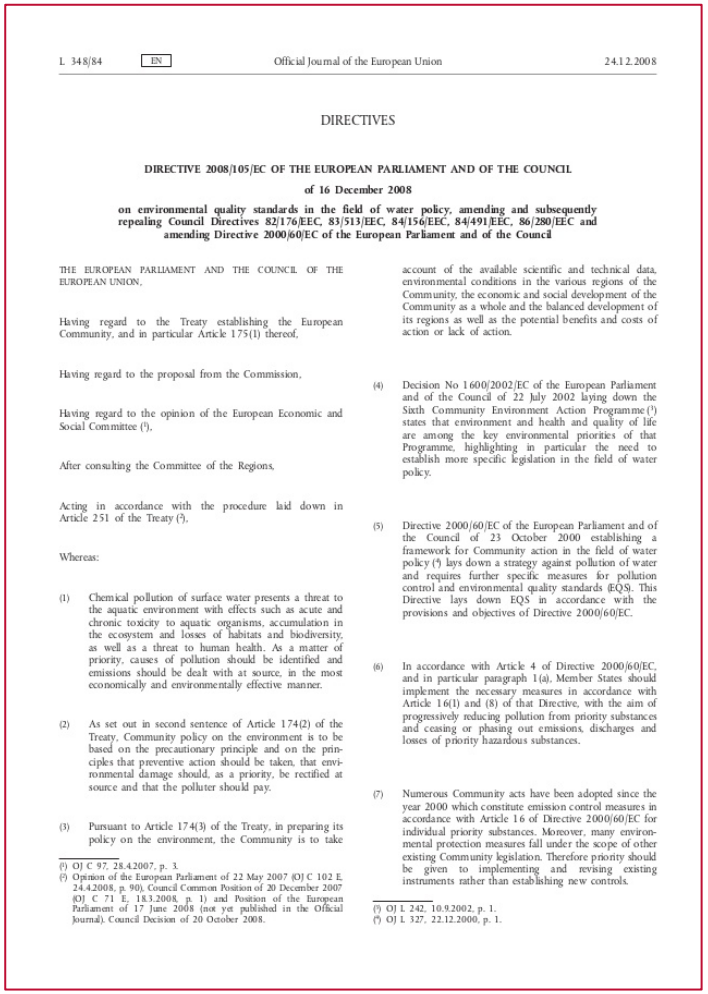
WFD & Priority Substances

- Article 16 of the Water Framework Directive (2000/60/EC) (WFD) sets out **"Strategies against pollution of water"**
- Decision 2455/2001/EC a first list of priority substances to become **Annex X** of the WFD. These substances were selected from amongst those presenting a significant risk to or via the aquatic environment
- This first list was replaced by Annex II of the Directive on Environmental Quality Standards (Directive 2008/105/EC) (EQSD), also known as the **Priority Substances Directive**
- The Environmental Quality Standard Directive (2008/105/EC) established EQSs for **33 priority substances and 8 priority hazardous substances** in surface waters (plus EQS for some substances in sediment and biota).

The Environmental Quality Standard Directive (2008/105/EC)

In order to cover both long- and short-term effects resulting from exposure to substances, two water column EQSs will be required to meet compliance:

- a long-term standard, expressed as an **annual average concentration (AA-EQS)** and normally based on chronic toxicity data
- a short-term standard, referred to as a **maximum acceptable concentration EQS (MAC-EQS)** which is based on acute toxicity data.



L 348/84 EN Official Journal of the European Union 24.12.2008

DIRECTIVES

DIRECTIVE 2008/105/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 16 December 2008

on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 175(1) thereof,

Having regard to the proposal from the Commission,

Having regard to the opinion of the European Economic and Social Committee [1],

After consulting the Committee of the Regions,

Acting in accordance with the procedure laid down in Article 251 of the Treaty [2],

Whereas:

(1) Chemical pollution of surface water presents a threat to the aquatic environment with effects such as acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem and losses of habitats and biodiversity, as well as a threat to human health. As a matter of priority, causes of pollution should be identified and emissions should be dealt with at source, in the most economically and environmentally effective manner.

(2) As set out in second sentence of Article 174(2) of the Treaty, Community policy on the environment is to be based on the precautionary principle and on the principles that preventive action should be taken, that environmental damage should, as a priority, be rectified at source and that the polluter should pay.

(3) Pursuant to Article 174(3) of the Treaty, in preparing its policy on the environment, the Community is to take account of the available scientific and technical data, environmental conditions in the various regions of the Community, the economic and social development of the Community as a whole and the balanced development of its regions as well as the potential benefits and costs of action or lack of action.

(4) Decision No 1600/2002/EC of the European Parliament and of the Council of 22 July 2002 laying down the Sixth Community Environment Action Programme [3] states that environment and health and quality of life are among the key environmental priorities of that Programme, highlighting in particular the need to establish more specific legislation in the field of water policy.

(5) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy [4] lays down a strategy against pollution of water and requires further specific measures for pollution control and environmental quality standards (EQS). This Directive lays down EQS in accordance with the provisions and objectives of Directive 2000/60/EC.

(6) In accordance with Article 4 of Directive 2000/60/EC, and in particular paragraph 1(a), Member States should implement the necessary measures in accordance with Article 16(1) and (8) of that Directive, with the aim of progressively reducing pollution from priority substances and ceasing or phasing out emissions, discharges and losses of priority hazardous substances.

(7) Numerous Community acts have been adopted since the year 2000 which constitute emission control measures in accordance with Article 16 of Directive 2000/60/EC for individual priority substances. Moreover, many environmental protection measures fall under the scope of other existing Community legislation. Therefore priority should be given to implementing and revising existing instruments rather than establishing new controls.

[1] OJ C 97, 28.4.2007, p. 3.
[2] Opinion of the European Parliament of 22 May 2007 (OJ C 102 E, 24.4.2008, p. 90), Council Common Position of 20 December 2007 (OJ C 71 E, 18.3.2008, p. 1) and Position of the European Parliament of 17 June 2008 (not yet published in the Official Journal). Council Decision of 20 October 2008.
[3] OJ L 242, 10.9.2002, p. 1.
[4] OJ L 327, 22.12.2000, p. 1.

Biota EQS

The WFD requires biota EQSs to protect:

- **humans from adverse effects** resulting from consumption of chemical-contaminated food (fish, molluscs, crustaceans, etc.)
- top predators such as birds and mammals from **risks of secondary poisoning** by consuming toxic chemicals in their prey
- benthic and pelagic predators (e.g. predatory fish) that may also be at risk from **secondary poisoning**.
- The choice of species to be monitored should depends upon the **identified protection goal** (e.g. humans, top predators); where there are a variety of protection objectives, it is preferable to choose a species that can satisfy all of the aims

EQS WFD Annex X

Name of substance		AA-EQS	MAC-EQS
	CAS number	Inland surface waters	Inland surface waters
Alachlor	15972-60-8	0,3	0,7
Anthracene	120-12-7	0,1	0,4
Atrazine	1912-24-9	0,6	2,0
Benzene	71-43-2	10	50
Brominated diphenylether (5)	32534-81-9	0,0005	not applicable
Cadmium and its compounds	7440-43-9	≤ 0,08 (Class 1)	≤ 0,45 (Class 1)
(depending on water hardness classes) (6)		0,08 (Class 2)	0,45 (Class 2)
		0,09 (Class 3)	0,6 (Class 3)
		0,15 (Class 4)	0,9 (Class 4)
		0,25 (Class 5)	1,5 (Class 5)
Carbon-tetrachloride (7)	56-23-5	12	not applicable
C10-13 Chloroalkanes	85535-84-8	0,4	1,4
Chlorfenvinphos	470-90-6	0,1	0,3
Chlorpyrifos (Chlorpyrifos-ethyl)	2921-88-2	0,03	0,1

EQS WFD Annex X

Name of substance		AA-EQS (2)	MAC-EQS (4)
	CAS number (1)	Inland surface waters (3)	Inland surface waters (3)
Cyclodiene pesticides:		Σ = 0,01	not applicable
Aldrin (7)	309-00-2		
Dieldrin (7)	60-57-1		
Endrin (7)	72-20-8		
Isodrin (7)	465-73-6		
DDT total (7) (8)	not applicable	0,025	not applicable
para-para-DDT (7)	50-29-3	0,01	not applicable
1,2-Dichloroethane	107-06-2	10	not applicable
Dichloromethane	75-09-2	20	not applicable
Di(2-ethylhexyl)-phthalate (DEHP)	117-81-7	1,3	not applicable
Diuron	330-54-1	0,2	1,8
Endosulfan	115-29-7	0,005	0,01
Fluoranthene	206-44-0	0,1	1
Hexachloro-benzene	118-74-1	0,01 (9)	0,05
Hexachloro-butadiene	87-68-3	0,1 (9)	0,6
Hexachloro-cyclohexane	608-73-1	0,02	0,04

EQS WFD Annex X

Name of substance		AA-EQS (2)	MAC-EQS (4)
	CAS number (1)	Inland surface waters (3)	Inland surface waters (3)
Isoproturon	34123-59-6	0,3	1,0
Lead and its compounds	7439-92-1	7,2	not applicable
Mercury and its compounds	7439-97-6	0,05 (9)	0,07
Naphthalene	91-20-3	2,4	not applicable
Nickel and its compounds	7440-02-0	20	not applicable
Nonylphenol (4-Nonylphenol)	104-40-5	0,3	2,0
Octylphenol ((4-(1,1′,3,3′-tetramethylbutyl)- phenol))	140-66-9	0,1	not applicable
Pentachloro-benzene	608-93-5	0,007	not applicable
Pentachloro-phenol	87-86-5	0,4	1
Polyaromatic hydrocarbons (PAH) (10)	not applicable	not applicable	not applicable
Benzo(a)pyrene	50-32-8	0,05	0,1
Benzo(b)fluor-anthene	205-99-2	Σ = 0,03	not applicable
Benzo(k)fluor-anthene	207-08-9		
Benzo(g,h,i)-perylene	191-24-2	Σ = 0,002	not applicable
Indeno(1,2,3-cd)-pyrene	193-39-5		
Simazine	122-34-9	1	4
Tetrachloro-ethylene (7)	127-18-4	10	not applicable
Trichloro-ethylene (7)	79-01-6	10	not applicable
Tributyltin compounds (Tributhyltin-cation)	36643-28-4	0,0002	0,0015
Trichloro-benzenes	12002-48-1	0,4	not applicable
Trichloro-methane	67-66-3	2,5	not applicable
Trifluralin	1582-09-8	0,03	not applicable

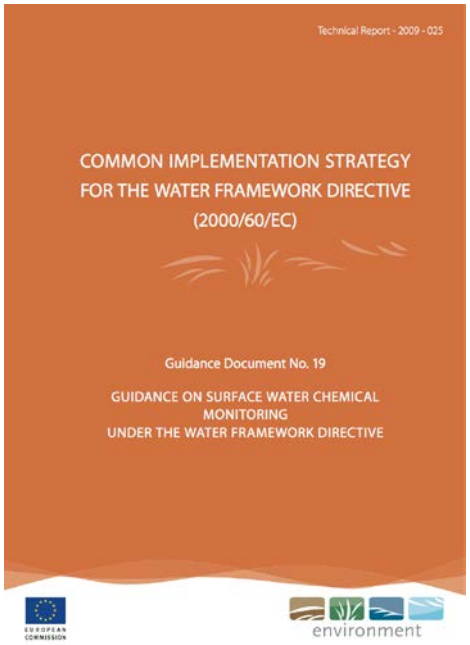
Proposal for a Directive amending the WFD and EQSD (COM(2011)876)

This proposal (COM(2011)876) includes a revised (second) list of priority substances, and provisions to improve the functioning of the legislation. The main features of the proposal are:

- 15 additional priority substances, 6 of them designated as priority hazardous substances;
- stricter EQS for four existing priority substances and slightly revised EQS for three others;
- the designation of two existing priority substances as priority hazardous substances;
- the introduction of biota standards for several substances;
- provisions to improve the efficiency of monitoring and the clarity of reporting with regard to certain substances behaving as ubiquitous persistent, bioaccumulative and toxic (PBT) substances;
- a provision for a watch-list mechanism designed to allow targeted EU-wide monitoring of substances of possible concern to support the prioritisation process in future reviews of the priority substances list.

Analytical Laboratories: meeting EQS Directive

- Commission Directive 2009/90/EC (QA/QC Directive):
  - Limit of Quantitation (LOQ) < 30% EQS
  - Expanded uncertainty <50% at EQS level.

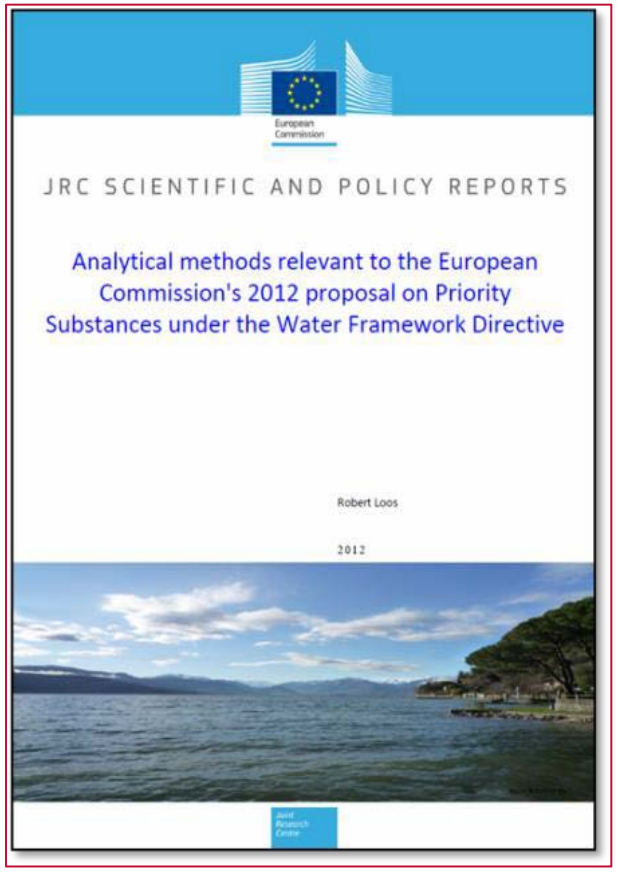


Minimum performance criteria for methods of analysis

- the minimum performance criteria for all methods of analysis applied are based on **uncertainty of measurement of 50% or below** (k = 2) estimated at the level of relevant environmental quality standards and a limit of quantification equal or below a value of 30% of the relevant environmental quality standards; and
- in the absence of relevant environmental quality standard for a given parameter, or in the absence of a method of analysis meeting the minimum performance criteria set out in paragraph, that monitoring is carried out using best available techniques **not entailing excessive costs.**

Analytical methods relevant to the EC 2012 proposal on priority substances under the WFD

- Analytical methods for the new proposed priority substances of the Europen Water Framework Directive (WFD) relevant to the EC's 2012 proposal on
  Priority Substances under the WFD
- Reviewed chemical analysis methods for new proposed Priority Substances (PS) and for some existing PS for which the EQS have been changed
- Analytical 'standard methods' (ISO, CEN, US EPA) were searched.
- Member states reported national reference standards and detection limits

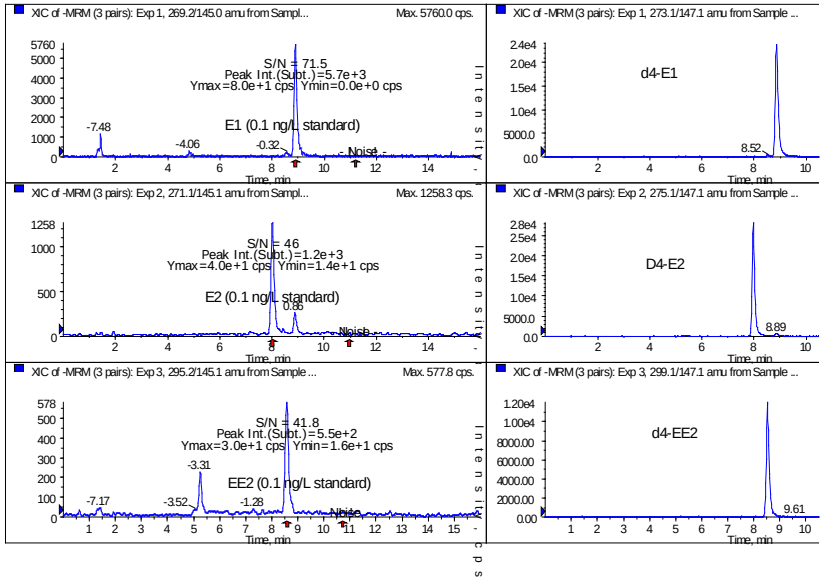


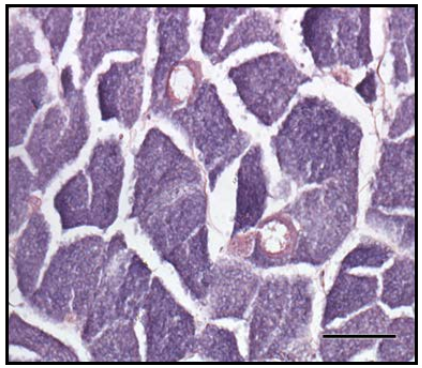
Available at; http://publications.jrc.ec.europa.eu/repository/bitstream/111111111/26936/1/lb-na-25532-en-n.pdf

α-Ethynylestradiol

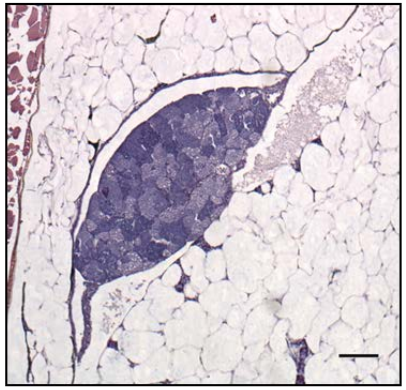
Feminisation due to estrogenic exposure via wastewaters

AA-EQS
Fresh = 35 pg/L
Salt= 7 pg/L
UK Bluebook = 30-50 pg/L

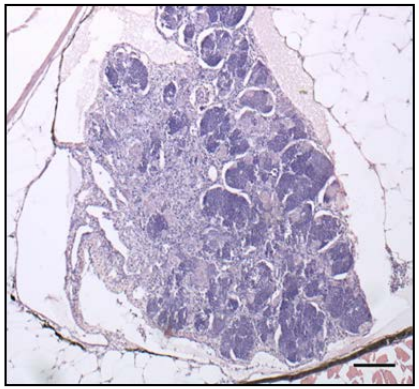




Oocytes in testis



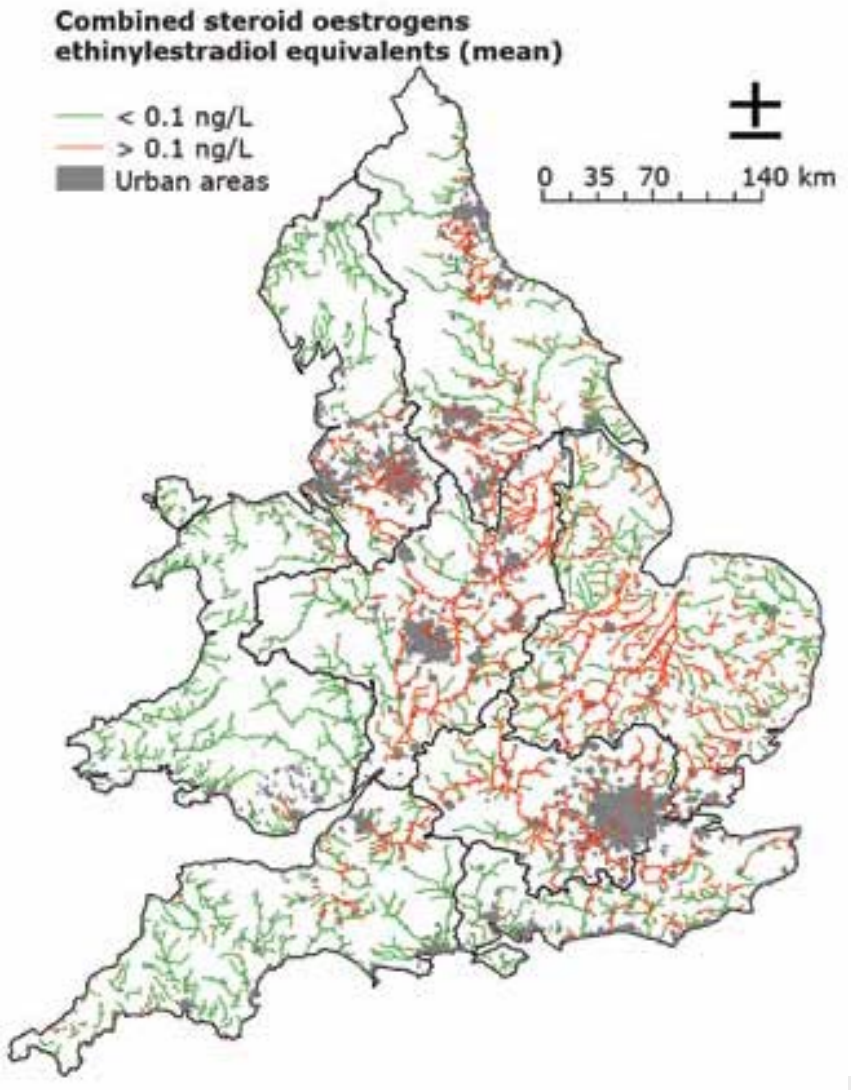
Feminised sperm duct



Disruption to Spermatogenesis/ testicular organisation

Baynes et al. 2012

UK rivers and streams exceeding the PNEC for EE2



Jobling & Owen 2012

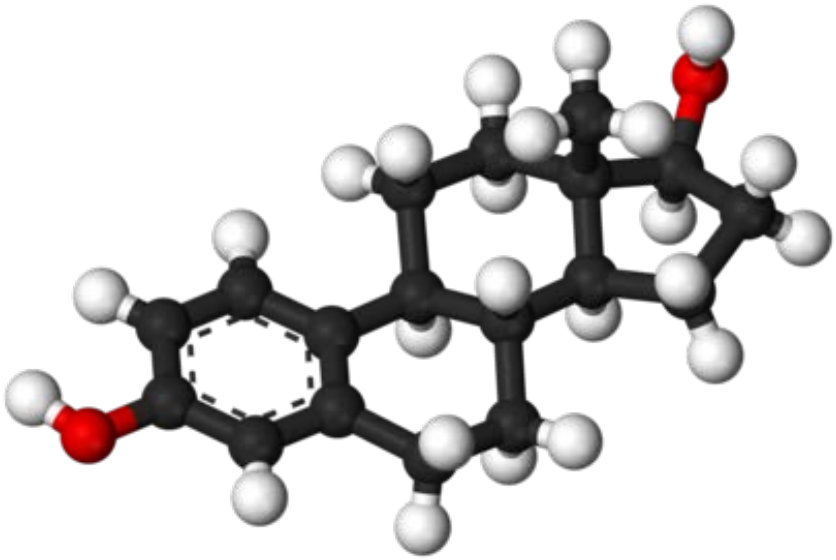
β-Estradiol

AA-EQS

Fresh =0.4 ng/L
Sea = 80 pg/L

Analysis is complex and costly requires extraction, cleanup and high sensitivity MS

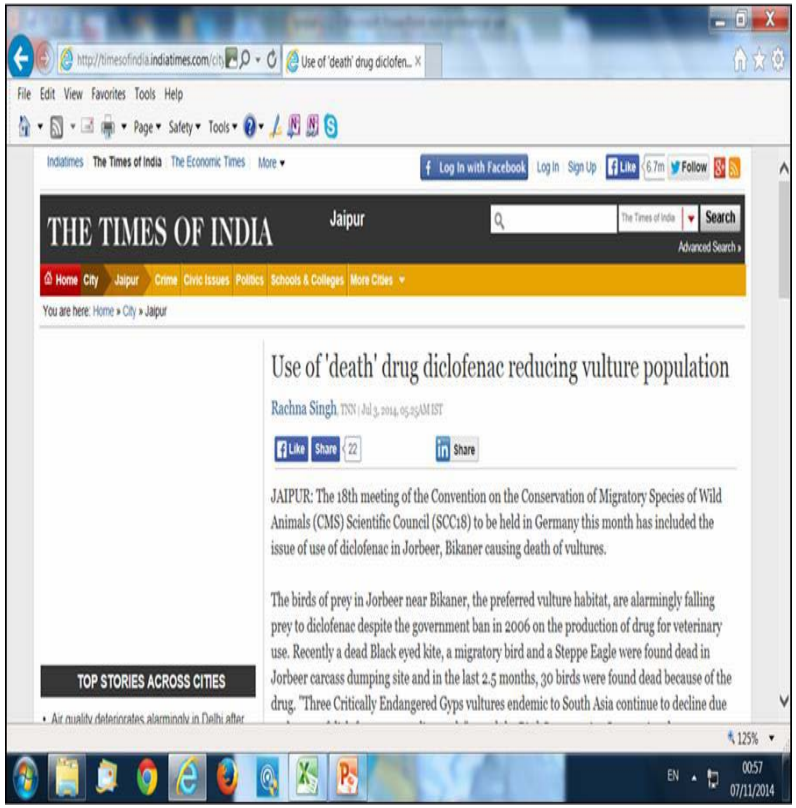
LC-QQQ
LC-TOF
LC-Orbitrap



Altenatively bioassays such as YES and ER-CALUX can be used to report estradiol equivalents. Provides "total" estrogenicity of sample.

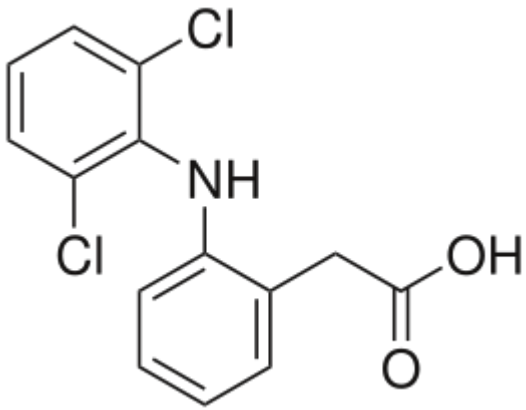
Diclofenac

- In the 80's there were 80 million white-rumped vultures (*Gyps bengalensis*) in India
- The 90s saw a rapid decline in vulture population in India - a 95% decline by 2003 and a 99.9% decline by 2008.
- In 2004 Oaks et al reported the cause to be vultures eating the carcasses of livestock which were administered veterinary diclofenac, which resulted in renal failure
- Drug banned in India, Pakistan and Napel and replaced with Meloxicam which is safe for vultures



Oaks, J. Lindsay; Gilbert, Martin; Virani, Munir Z.; Watson, Richard T.; Meteyer, Carol U.; Rideout, Bruce A.; Shivaprasad, H. L.; Shakeel Ahmed; Muhammad Jamshed Iqbal Chaudhry; Muhammad Arshad; Shahid Mahmood; Ahmad Ali and Aleem Ahmed Khan; 'Diclofenac residues as the cause of vulture population decline in Pakistan'; *Nature, 427 (12 February 2004), p. 630*

Diclofenac



- AA-EQS

- Fresh 0.1 ug/L
- Salt 0.01 ug/L = 10 ng/L

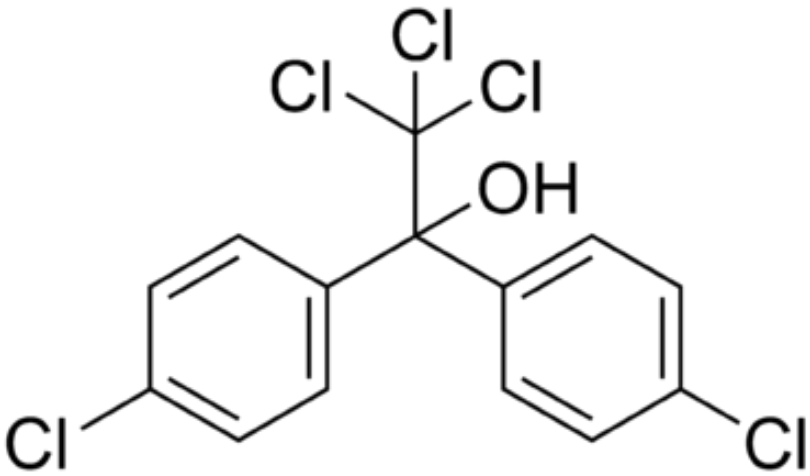
- GCMSMS following derivatisation
- Or LC-QQQ or LC-ion trap MSMS

- Grujic et al 2009 reports LOD 0.15 ng/L; LOQ 0.49 ng/L
- Martinez Bueno et al 2007 LOD 0.4 ng/L; LOQ 1 ng/L

- **Inland surface water compliance (0.3 x EQS = 30 ng/L) is sufficient and literature values show costal surface water LOQ of 3 ng/L is also achievable**

Dicofol

Dicofol is highly toxic to fish, aquatic invertebrates, and algae. The LC50 is 0.12 mg/L in rainbow trout, 0.37 mg/L in sheepshead minnow, 0.06 mg/L in mysid shrimp, 0.015 mg/L in shell oysters, and 0.075 mg/L in algae.



The EQS requires pg/L sensitive methods.

No standard methods available.

Reported method: Liq-Liq extraction GCMS methods LODs in the range 5-10 ng/L

LOD not sufficient for compliance monitoring

AA-EQS	**MAC-EQS**	**EQS biota**
Fresh 1.3 10^{-3} = 0.0013 = **1.3 ng/l**	not applicable	33 µg/kg
Salt 3.2 10^{-5} = 0.000032 = **32 pg/l**		

PFOS

According to a study by the Environmental Directorate of the OECD *"PFOS is persistent, bioaccumulative and toxic to mammalian species."*

AA EQS

Freshwater 0.65 ng/L
Salt 0.13 ng/L

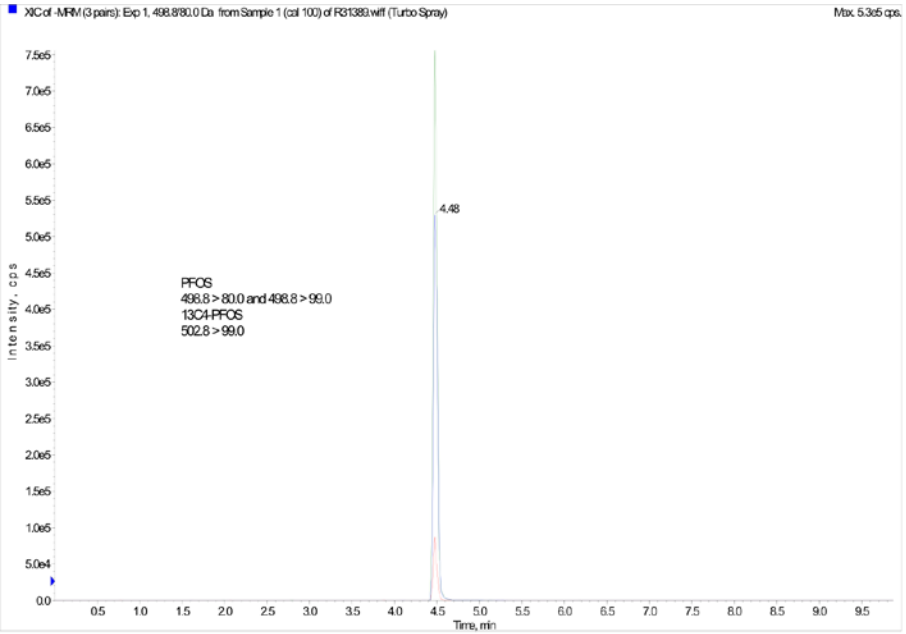
MAC EQS

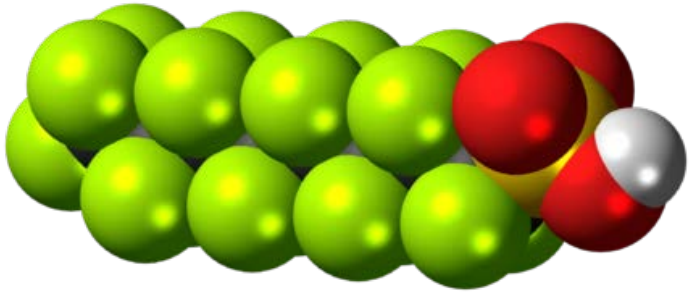
Freshwater 36 ug/L
Salt 7.2 ug/L

Standard method ISO 25101 has a LOD of 2ng/L

LCMSMS : reported LOQs in pg/L range using SPE and LCMSMS (Yamashita et al 2004)

Biota compliance (9.1 ug/Kg)
Needs LOD of 2.73 ng/g
Methods reported at 0.2 ng/g

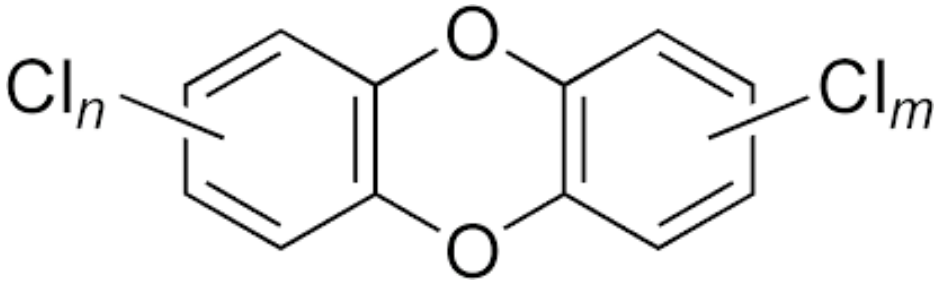




Dioxins and dioxin like compounds

- 75 PCDD (7 are specifically toxic)
- 135 PCDF (10 have dioxin like properties)
- There are 209 congeners of organochlorides with 1 to 10 chlorine atoms (12 have dioxin like properties)
- Biota EQS = 8 ng/Kg TEQ (LOD required =

0.3 x 8 = 2.4 ng/Kg). Methods are available across Europe for compliance.



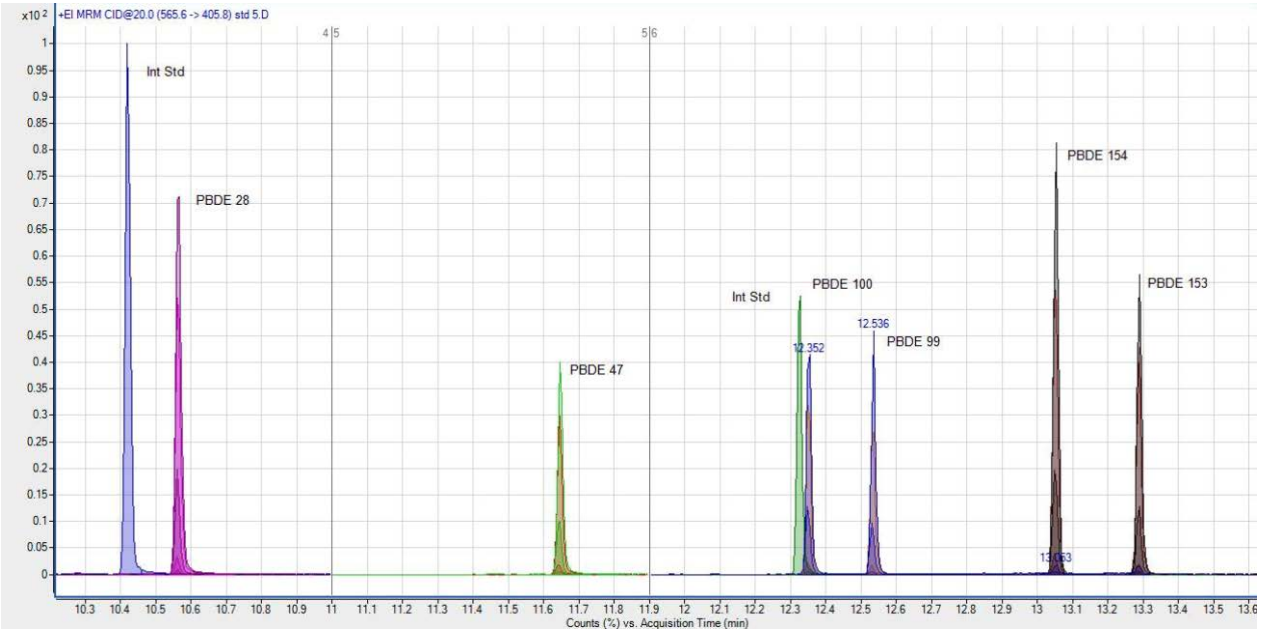
AutoSpec Premier Dioxin magnetic sector Mass Spectrometer

Polybrominated diphenyl ethers

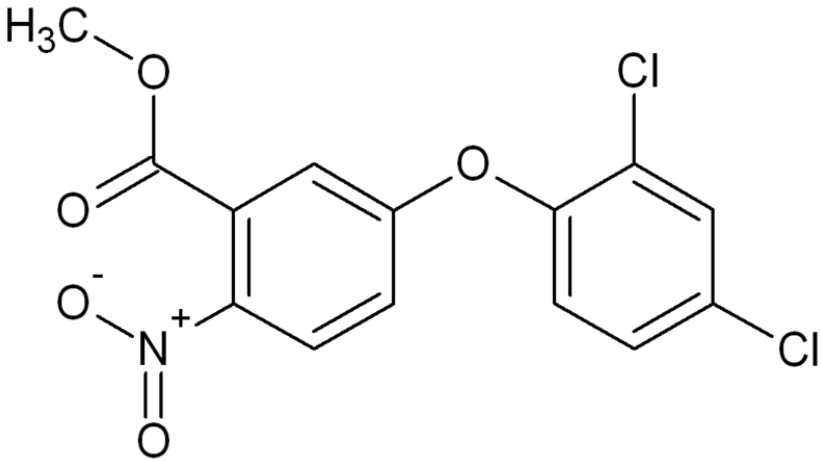
There is also growing concern that PBDEs share the environmental long life and bioaccumulation properties of polychlorinated dibenzodioxins.

AA-EQS 49 fg/L (Fresh) and 2.4 fg/L salt or 8.5 ng/Kg in biota

Low pg/L detection limits have been reported using un-managable sample volumes (upto 100 litres) . Biota LODs are achievable.



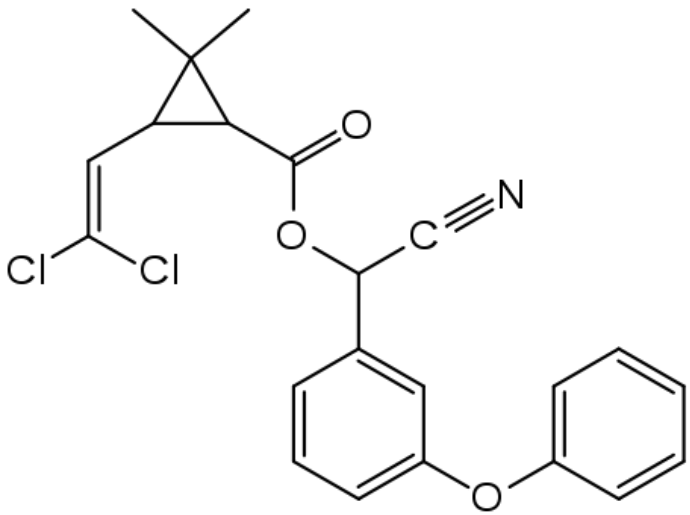
Bifenox

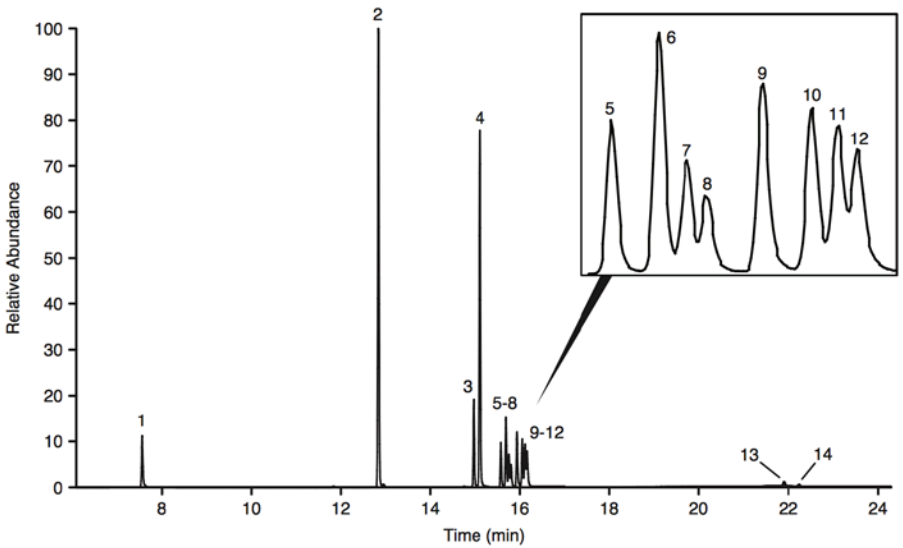


- Bifenox AA-EQS: fresh 12ng/L, MAC-EQS: 40ng/L; and in salt = 1.2 ng/L, : 4ng/L
- Standard methods are not yet available for Bifenox.
- Germany: Lowest reported LOQ: 0.01 µg/l = 10 ng/l (according to ISO 6468; GC-MS).
- Sweden: LOQ: 0.050 µg/l = 50 ng/l using LCMS

Cypermethrin

GCMS Analysis of cypermethrin isomers (peak 9-11) from ThermoFischer Scientific

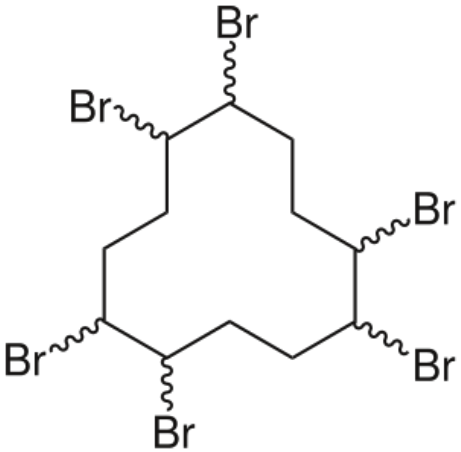




- Cypermethrin AA-EQS: 80pg/L MAC-EQS: 0.6ng/L in fresh water
- LOQ: 0.5-15 ng/l (Xue et al, 2005) and 66 pg/L using EPA 1699
- Current methods not sensitive enough to meet EQS -LOD

The Effect of the Autosampler Vial's Glass Surface on GC-MS Analysis of Pyrethroid Pesticides at ppb Levels. Brian W King and Anila I Khan, Thermo Fisher Scientific, Runcorn, UK. Poster Reference number PSCCS 0512 588.

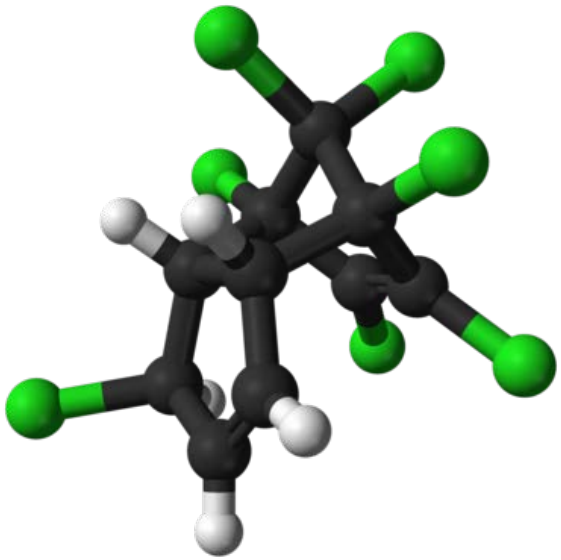
Hexabromocyclododecane (HBCDD)

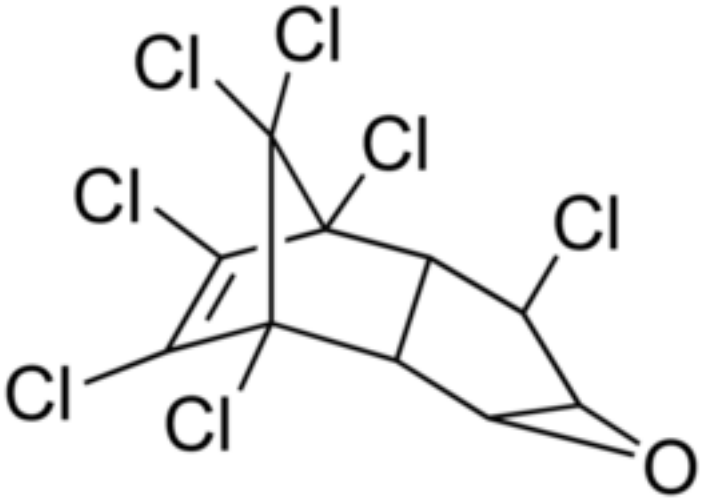


Due to its persistence, toxicity, and ecotoxicity, the **Stockholm Convention on Persistent Organic Pollutants** decided in May 2013 to list hexabromocyclododecane in Annex A to the Convention with specific exemptions for production and use

- HBCDD AA-EQS: 1.6ng/L MAC-EQS: 0.5µg/L in fresh water and 167 ug/Kg in biota
- No standard method available for HBCDD LCMS or GCMS (total HBCDD)).
- Biota analysis at 30% of the EQS (0.3 × EQS = 50.1 µg/kg) is possible – Morris et al 2006; Hajslova et al 2009

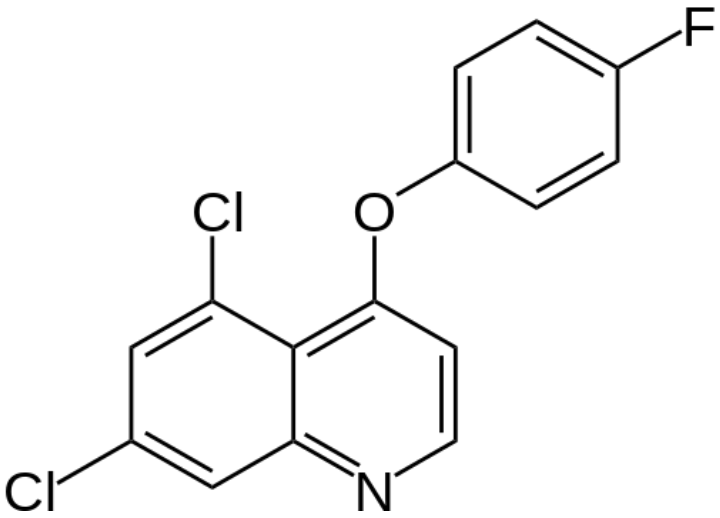
Heptachlor and Heptachlor epoxide





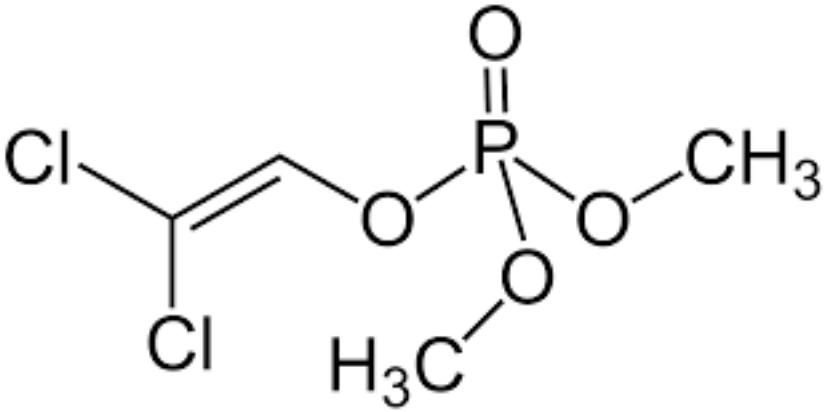
- Heptachlor AA-EQS: 0.2pg/L MAC-EQS: 0.3ng/L in fresh water and 6.7 ng/Kg in biota
- USEPA 1699 Heptachlor = 7pg/L and heptachlorepoxide 12 pg/L 0.3 ng/Kg in biota
- Biota analysis at 30% of the EQS (0.3 × EQS = 2.25 ng/kg) is possible

Quinoxyfen



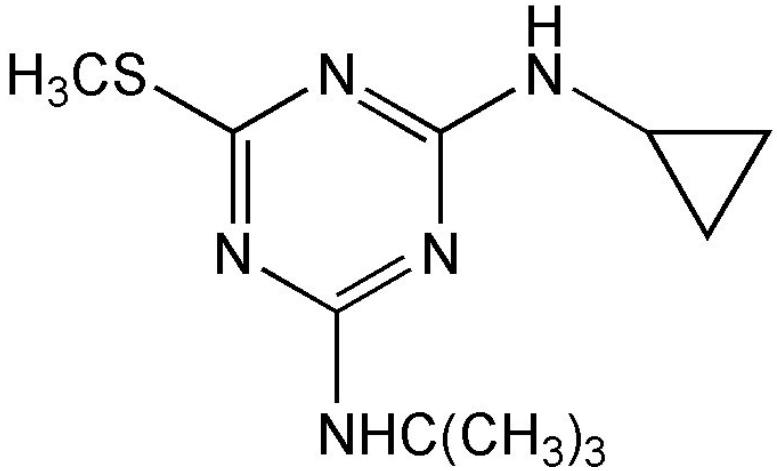
- Quinoxyfen AA-EQS: 0.15 ug/L (15 ng/L salt) MAC-EQS: 2.7 µg/L in fresh water (0.54 ug/L salt)
- No standard method available
- Sweden method OMK 51 has a LOQ 2ng/L

Dichlorvos



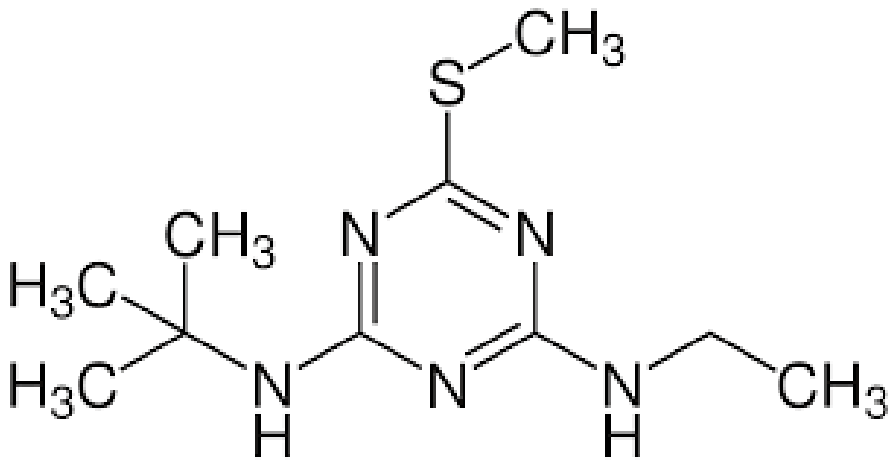
- Dichlovos AA-EQS: 0.6 ng/L (60 pg/L salt) MAC-EQS: 0.7 ng/L in fresh water (70 pg/L salt)
- EN 12918 LOQ 10 ng/L

Cybutryne - Irgarol



- Cybutryne AA-EQS: 2.5 ng/L (fresh & salt) MAC-EQS: 16 ng/L in fresh and salt water
- No standard method is available
- SwedenOMK 57 On line SPE LCMS LOQ 0.002 ug/L = 2 ng/L

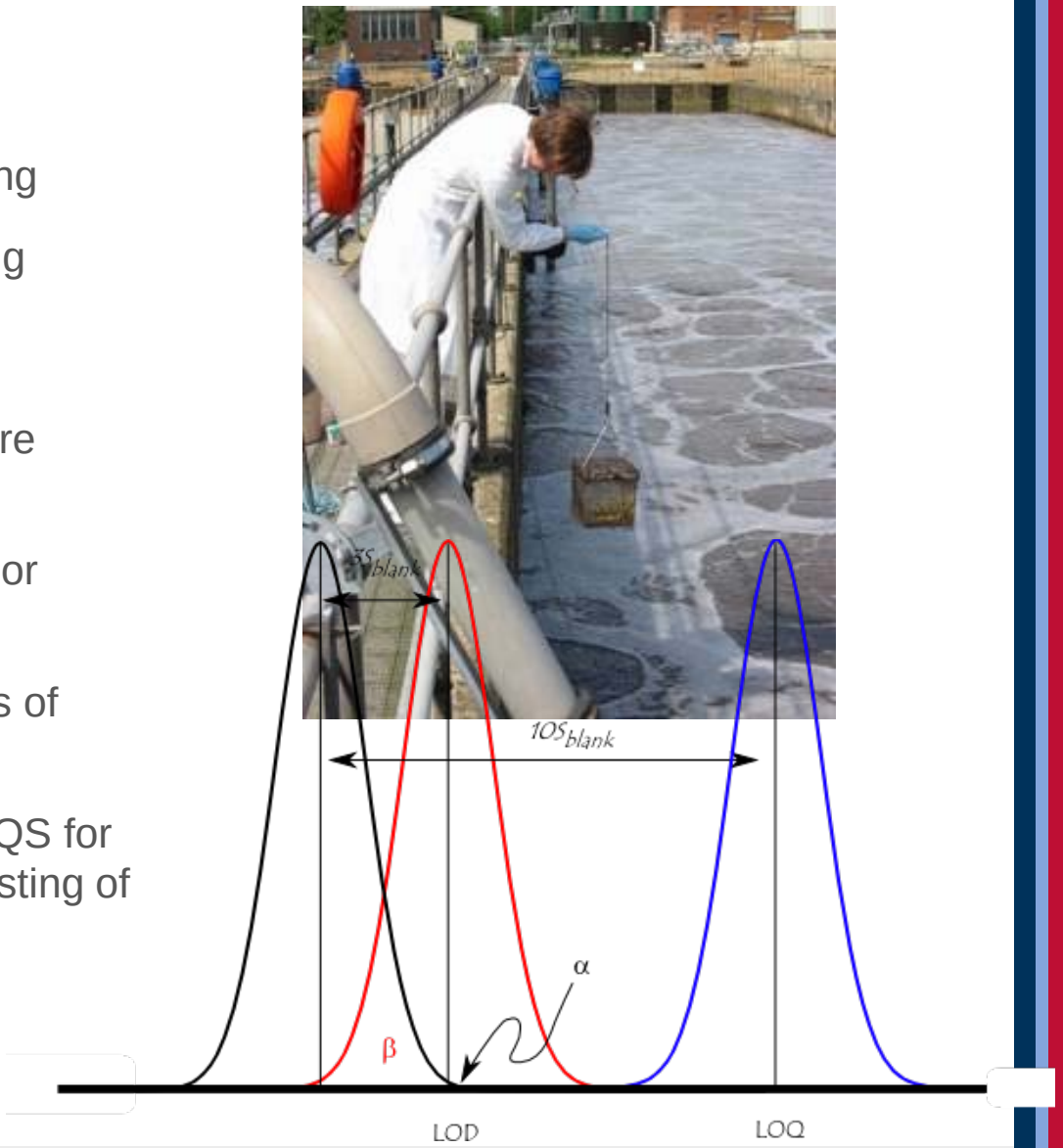
Terbutryn



- Terbutryn AA-EQS: 65 ng/L (6.5 ng/L salt) MAC-EQS: 0.34 ug/L in fresh water (0.034 ug/L salt)
- EPA 619 LOQ = 50 ng/L; SPE LCMS EL Mrabet et al 2006 = 80 pg/L

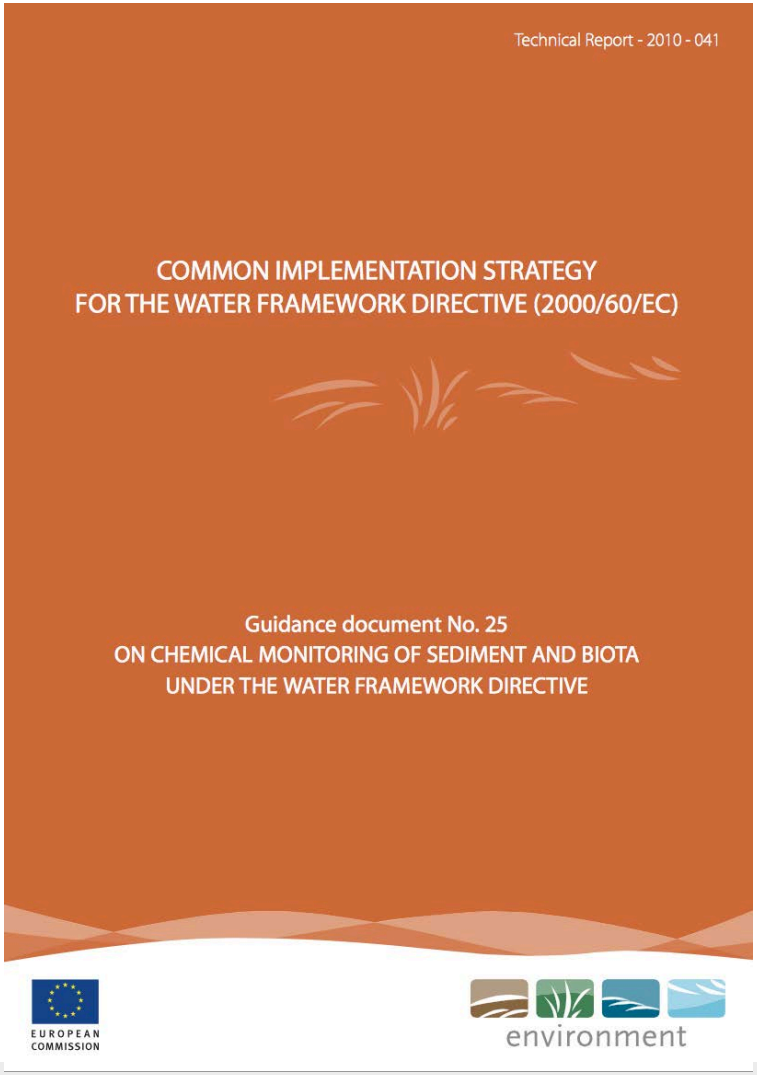
Issues - Water Samples

- EQS in water samples are challenging
- Standard methods (validated and ring tested) are not available for many determinands
- Literature values of LOD and LOQ are derived differently
- uncertainty of measurement of 50% or below at EQS
- ISO/TS 13530 (ISO, 2009) LOD = 3s of blank samples and LOQ = 3 X LOD
- Limits of detection based on 0.3 x EQS for water samples for compounds consisting of isomers is not achievable



Issues with biota monitoring

- Guidance Document No. 25 addresses EQS biota
- If different biota are used how will the data be standardised and compared
- Normalise to lipid content, dry weight, gender, age?



Summary

- EC predicts that only half of European waters will meet the water quality objectives of WFD at present.
- There are significant data gaps concerning ES & PS in the environment
- Robust environmental monitoring is essential for the assessment of the chemical status of water bodies.
- Data reported to the EC shows that 40% of surface water bodies in the EU have unknown chemical status and many member states are not monitoring priority substances.
- Some of the reasons for a lack of monitoring are associated with analytical difficulties, such as meeting limits of detection or other performance targets.
- Other barriers include the high costs of meeting analytical requirements of ultra-low measurements.

Summary

- For many chemicals more environmental data is needed (chemical and ecotoxicological) to improve and harmonise monitoring strategies.
- Restrictions on the use of certain substances
- For many substances there is a lack of ecotoxicological data.
- Knowledge gaps include the assessment of risks to human health associated with long-term exposure to low concentrations of ES
- Combined effects of mixtures of ES and PS needs to be addressed

QUESTIONS?

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