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).
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.
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 depend 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

<table>
<thead>
<tr>
<th>Name of substance</th>
<th>CAS number</th>
<th>AA-EQS Inland surface waters</th>
<th>MAC-EQS Inland surface waters</th>
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<td>Alachlor</td>
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<td>Inland surface waters (3)</td>
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<td>Name of substance</td>
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<td>Benzo(k)fluor-anthene</td>
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<td>Trichloro-methane</td>
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<td>Trifluralin</td>
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<td>0,03</td>
<td>not applicable</td>
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</tbody>
</table>
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

  - 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 European 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

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

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

Alternatively 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**

<table>
<thead>
<tr>
<th></th>
<th>AA-EQS</th>
<th>MAC-EQS</th>
<th>EQS biota</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>1.3 $10^{-3}$</td>
<td>0.0013 = 1.3 ng/l</td>
<td>33 µg/kg</td>
</tr>
<tr>
<td>Salt</td>
<td>3.2 $10^{-5}$</td>
<td>not applicable</td>
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</tbody>
</table>
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-manageable sample volumes (upto 100 litres) . Biota LODs are achievable.

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![Graph showing detection of PBDEs](image-url)
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

- 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

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: 0.2 pg/L MAC-EQS: 0.3 ng/L in fresh water and 6.7 ng/Kg in biota
- USEPA 1699 Heptachlor = 7 pg/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 µg/L (15 ng/L salt) MAC-EQS: 2.7 µg/L in fresh water (0.54 µg/L salt)
- No standard method available
- Sweden method OMK 51 has a LOQ 2ng/L
Dichlorvos

- Dichlorvos 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
- Sweden OMK 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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