Use of LC-MS/MS in the Compliance Monitoring of Priority (Hazardous) Substances and Specific Pollutants under the Water Framework Directive

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Hyphenated Analytical Techniques - Fundamentals, Applications and Challenges
The State Laboratory, 19/10/2017

Presentation outline

- Introduction
- Fundamentals
  - Water Framework Directive
  - Priority (Hazardous) Substances, Specific Pollutants
  - Environmental Quality Standards
- Applications
  - Pesticides & Herbicides
- Challenges
  - Priority Substances Directive 2013
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- Conclusion

The Water Framework Directive 2000/60/EC

Water Framework Directive

Coordinated and integrated water management

Inland surface waters, transitional waters, groundwaters and coastal waters to achieve ‘‘good status’’

“Good water status” includes the requirement for “good chemical status” and “good ecological status”

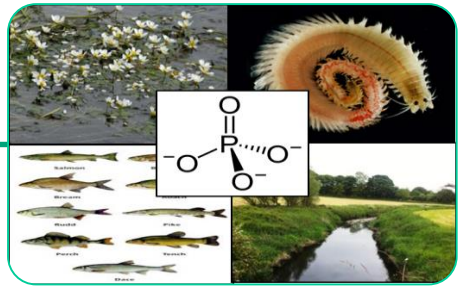
Water Framework Directive Status Objectives
Surface water status assessment

Chemical Status & **Ecological Status**

Substances selected & EQS applied at EU level

- Priority Substances (Annex X)
- Priority Hazardous Substances (Annex X)

Biological & Physico-chemical Elements



- Specific Pollutants (Annex VIII)

Substances identified & EQS derived by individual MSs

EQSs & PNECs

- Environmental Quality Standard (EQS) - Retrospective level of environmental safety
  - Concentration below which the ecological functions and the community structure of the water body are not changed (WFD 2000, Lepper 2006)
- Predicted No Effect Concentration (PNEC) - Prospective level of environmental safety
  - Concentration below which adverse effects are not expected to occur (TGD 2003)

- EQS(PNEC) = Most reliable ecotox data (µg/L) / Assessment Factor

Ecotoxicity tests

All ecotoxicity tests are based on either:

Mortality of an organism to a toxicant or an environmental sample (acute tests)

Change in some life property/sub-lethal endpoint, most commonly growth or reproduction (chronic tests)

Acute Tests (MAC-EQS)

EC_{50} for growth of an alga

LC_{50} for Daphnia

LC_{50} for fish

Chronic Tests (AA-EQS)

No Observed Effect Concentration (NOEC) values for one or more of the same species

EPA WFD micropollutant analysis; LC-MS, GC-MS, ICP-MS, IC

	Priority Hazardous Substances	Priority Substances	Specific Pollutants	Others
PAHs (GC-MS)	Ant, Fl, BbFl, BkFL, BaP, Ipyr, BghiPer			
Metals (ICP-MS)	Cd, Hg	Pb, Ni	Zn, As, Cr, Cu, F	
VOCs (GC-MS)		Benzene, DCM, 1,2-dichloroethane, Naphthalene	Toluene, xylenes (o,m,p)	
Pesticides & Herbicides (LC-MS/MS)		Simazine, atrazine, terbutryn, diuron, isoproturon	Linuron, glyphosate	Malathion, dichlobenil, 2,6-dichlorobenzamide, AMPA, 2,4-D, MCPA, mecoprop
Biota	Hg, HCB, HCBD (Marine Institute)			
Non WFD	Dioxins & BFRs (State Laboratory & Eurofins Gfa DE)			

Applications;
Old LCMS equipment - Varian 320 MS

Applications;
New LCMS equipment Agilent 6470 LC-MS

EPA LC-MS applications

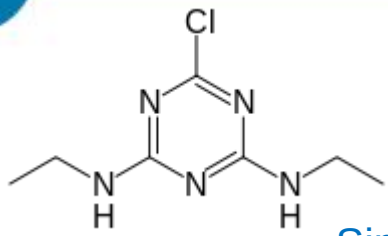
- Three groups of substances;

I. Triazine herbicides;
   - Simazine, atrazine, terbutryn.

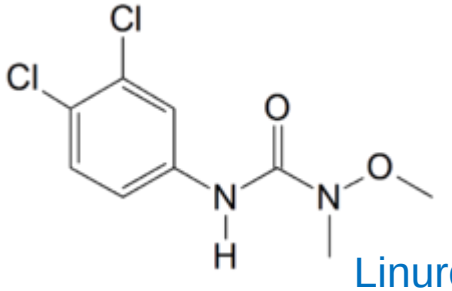
II. Uron herbicides
   - Linuron, isoproturon, diuron.

III. Phenoxyacetic acid herbicides;
   - Mecoprop, MCPA, 2,4-D

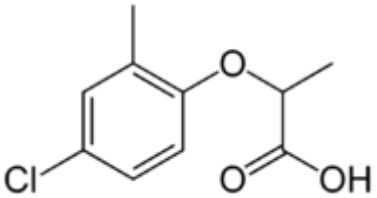
- Also glyphosate & AMPA



Simazine



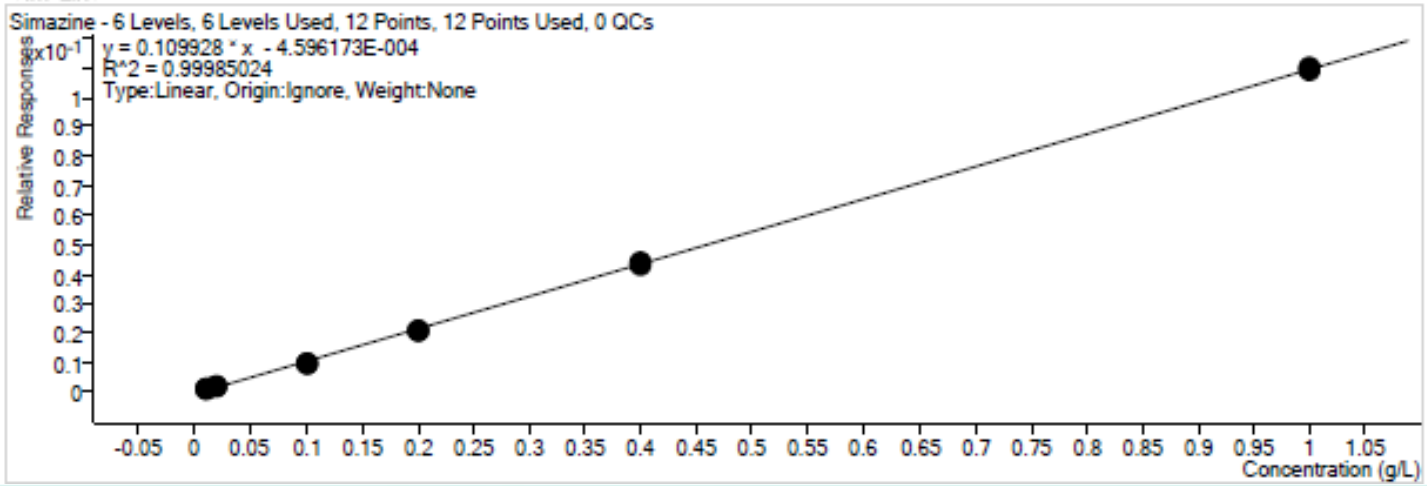
Linuron



Mecoprop

EPA LC-MS applications

- Direct injection (20µl) rather than in-line sample enrichment/SPE (5000µl)
- ESI, higher sensitivity (<10ng/L), S/N ratios, precision and scan speed
- Good working range (10-1000 ng/L), excellent linearity (r^2>0.999)
- Mobile Phases; water and acetonitrile, gradient flow
- Agilent Zorbax Eclipse Plus C18 Rapid Resolution HD 2.1 x 50mm, 1.8µm



EPA Pesticides & Herbicides Suite

Compound Name	Precursor Ion	Product Ion	Fragmentor	Collision Energy	Cell Accelerator Voltage	Polarity
Simazine	202.1	132	380	20	5	Positive
Simazine	202.1	124.1	380	20	5	Positive
Atrazine	216	174.1	380	15	3	Positive
Atrazine	216	104	380	30	3	Positive
Terbutryn	242.1	186.1	380	15	5	Positive
Terbutryn	242.1	91	380	25	5	Positive
MCPA	201	143	380	16	3	Negative
MCPA	199	141	380	8	3	Negative
Mecoprop	213	141	380	8	3	Negative
Mecoprop	213	105	380	15	3	Negative
2,4-D	221	163	380	9	7	Negative
2,4-D	219	161	380	9	7	Negative
Diuron	235	72	380	20	5	Positive
Diuron	233	72	380	20	5	Positive
Isoproturon	207.2	165.1	380	10	5	Positive
Isoproturon	207.2	72	380	20	5	Positive
Linuron	249	182	380	15	5	Positive
Linuron	249	160	380	20	5	Positive

Challenges;
12 new Priority Substances from 2018

Substance	EQS µg/l	2009/90/EC LOQ	
		µg/L	ng/L
Perfluorooctane sulfonic acid (PFOS) + derivatives	6.5×10^{-4}	0.195×10^{-3}	0.195
Dioxins and dioxin-like compounds	0.008 µg/kg	2.4×10^{-3}	2.4 ng/kg
Cypermethrin	8×10^{-5}	24×10^{-6}	0.024×10^{-3}
Heptachlor and heptachlor epoxide	2×10^{-7}	0.06×10^{-6}	0.06×10^{-3}
Aclonifen	0.12	36×10^{-3}	36
Dicofol	1.3×10^{-3}	0.39×10^{-3}	0.39
Quinoxyfen	0.15	45×10^{-3}	45
Bifenox	0.012	3.6×10^{-3}	3.6
Terbutryn	0.065	19.5×10^{-3}	19.5
Cybutryne (Irgarol)	2.5×10^{-3}	0.75×10^{-3}	0.75
Dichlorvos	6×10^{-4}	0.18×10^{-3}	0.18
Hexabromocyclododecane (HBCDD)	1.6×10^{-3}	0.48×10^{-3}	0.48

Challenges;
Watch List substances

Name of substance	LOD (ng/l)
17-Alpha-ethinylestradiol (EE2)	0.035
17-Beta-estradiol (E2)	0.4
Estrone (E1)	0.4
Diclofenac	10
2,6-Ditert-butyl-4-methylphenol	3160
2-Ethylhexyl 4-methoxycinnamate	6000
Erythromycin, clarithromycin, azithromycin	90
Methiocarb	10
Imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid	9
Oxadiazon	88
Tri-allate	670

Challenges;
Priority Substances Review Group Short list

Priority Substance Candidate	Comment
Omethoate/dimethoate	Insecticide PPP
Malathion	Insecticide PPP
Nicosulfuron	Herbicide PPP
Selenium	Metal
Silver	Metal
Uranium	Metal
Permethrin	Pyrethroid Insecticides
Deltamethrin	
Bifenthrin	
Esfenvalerate	

- EQSs currently being derived by JRC
- MSs encouraged to include these as Specific Pollutants

Conclusion - EPA current activities

- Significant investment in new laboratory equipment – LC-MS, GC-MS (X2), ICP-MS
- Involved at various levels in EU WFD Chemicals Working Groups and work with DHPLG in relation to the WFD priority substances portfolio
- Scoping study on new PSs in Irish aquatic environment
- Significant funding of the EPA Research Pillar SAFE WATER
  - Emerging pollutants, priority substances, endocrine disruptors and emerging risks such as pathogens (including antibiotic resistant bacteria and viruses), cyanotoxins and nanomaterials
- Membership of the NORMAN Network – Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances

Conclusion - Future challenges

- Challenges exist with regard to LOQs of new Priority Substances (& Watch List steroidal hormones) from 2018
- Increased workload from new Priority Substances list, Watch List, PS candidates, River Basin Specific Pollutants
- Derivation of new EQSs for Irish Specific Pollutants
- Staffing numbers to effectively fulfil new commitments?

EQSs & MCPA review

Thanks for your attention