

The Water Framework Directive and some of the impacts this has had on UK laboratories

- with particular reference to Priority Substances and the Chemical Investigation Programme



Environmental Science



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- **Water Framework Directive (WFD)**
 - Priority Substances
 - Watch List
- **UK Water Industry Research (UKWIR)**
 - Chemical Investigation Programme 1 (CIP1)
 - Chemical Investigation Programme 2 (CIP2)

The 33 Priority Substances

Alachlor	Anthracene
Atrazine	Benzene
BDEs	Cadmium
Chloroalkanes	Chlorfenvinphos
Chlorpyrifos	1,2-Dichloroethane
Dichloromethane	DEHP
Diuron	Endosulfan
Fluoranthene	Hexachlorobenzene
Hexachlorobutadiene	Hexachlorocyclohexane
Isoproturon	Lead
Mercury	Naphthalene
Nickel	Nonylphenols
Octylphenols	Pentachlorobenzene
PCP	Benzo(a)pyrene
Simazine	Tributyltin
Trichlorobenzenes	Trichloromethane
Trifluralin	

The 33 + 15 Priority Substances

Alachlor	Anthracene	17a ethinylestradiol
Atrazine	Benzene	17b oestradiol
BDEs	Cadmium	Aclonifen
Chloroalkanes	Chlorfenvinphos	Bifenox
Chlorpyrifos	1,2-Dichloroethane	Cybutryne
Dichloromethane	DEHP	Cypermethrin
Diuron	Endosulfan	Dichlorvos
Fluoranthene	Hexachlorobenzene	Diclofenac
Hexachlorobutadiene	Hexachlorocyclohexane	Dicofol
Isoproturon	Lead	Dioxins
Mercury	Naphthalene	HCBDD
Nickel	Nonylphenols	Heptachlor + epoxide
Octylphenols	Pentachlorobenzene	PFOS
PCP	Benzo(a)pyrene	Quinoxifen
Simazine	Tributyltin	Terbutryn
Trichlorobenzenes	Trichloromethane	
Trifluralin		

The 33 + 15 Priority Substances with EQSs (ng/l)

Aalachlor	300	Anthracene	100	17a ethinylestradiol	1.3
Atrazine	600	Benzene	10000	17b oestradiol	150
BDEs	0.000049	Cadmium	80	Aclonifen	120
Chloroalkanes	400	Chlorfenvinphos	100	Bifenox	2.5
Chlorpyriphos	30	1,2-Dichoroethane	10000	Cybutryne	0.6
Dichloromethane	20000	DEHP	1300	Cypermethrin	0.0002
Diuron	200	Endosulfan	5	Dichlorvos	0.035
Fluoranthene	6.3	Hexachlorobenzene	50	Diclofenac	100
Hexachlorobutadiene	600	Hexachlorocyclohexane	20	Dicofol	0.65
Isoproturon	300	Lead	1200	Dioxins	8ng/kg
Mercury	70	Naphthalene	2000	HCBDD	12
Nickel	4000	Nonylphenols	300	Heptachlor + epoxide	0.08
Octylphenols	100	Pentachlorobenzene	7	PFOS	1.6
PCP	400	Benzo(a)pyrene	0.17	Quinoxifen	65
Simazine	1000	Tributyltin	0.2	Terbutryn	0.04
Trichlorobenzenes	400	Trichloromethane	2500		
Trifluralin	30				

1st Watch List

- 17-alpha-Ethinylestradiol (EE2)
- 17-beta-Estradiol (E2)
- Estrone (E1)
- Diclofenac
- 2,6-ditertbutyl-4-methylphenol
- 2-ethylhexyl
- Erythromycin
- Clarithromycin
- Azithromycin
- Methiocarb
- Oxadiazon
- Triallate
- Imidacloprid
- Thiacloprid
- Thiamethoxam
- Clothianidin
- Acetamiprid

2nd & 3rd Watch List (proposals)

- Amoxicillin
- Ciprofloxacin
- Permethrin
- Esfenvalerate
- Deltamethrin
- 4-methoxycinnamate
- Diflubenzuron
- Pyridaben
- Dimoxystrobin
- Etofenprox
- Fenpyroximate
- Metaflumazone
- Proquinazide
- Venlafaxine
- Free Cyanide

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CIP 1 Parameters and Quality Criterion (ng/l)

diethylhexylphthalate	260	triclosan	100
BDEs	0.5	bentazone	430000
nonylphenol 4-	300	bisphenol-A	100
nonylphenol	300	mecoprop	6000
tributyltin	0.2	EDTA	50000
anthracene	100	ibuprofen	10
fluoranthene	6.3	propranolol	10
naphthalene	2000	erythromycin	10
benzo(a)pyrene	0.17	ofloxacin	10
benzo(b)fluoranthene	17	oxytetracycline	10
benzo(k)fluoranthene	17	fluoxetine	10
benzo(g,h,i)perylene	2	oestrone (E1)	3
indeno(1,2,3-cd)pyrene	2	17 β oestradiol (E2)	0.4
glyphosate	100000	17 α ethinyloestradiol (E3)	0.035
Aminomethyl phosphonic acid	80000	diclofenac	10

CIP 2 Parameters and Quality Criterion (ng/l)

	Required LOD	Required LOD for rivers	Determinand	Required LOD	Required LOD for rivers
Diethylhexyl-phthalate	300	200	para-hydroxy-atorvastatin	10	-
BDEs	0.5	0	propranolol	10	-
perfluorooctane sulfonic acid	0.65	0.09	atenolol	10	-
perfluorooctanoic acid	0.65	0.09	erythromycin	100	-
hexabromocyclododecane	1.6	0.23	norerythromycin	100	-
nonylphenol, 4-nonylphenol and ethoxylates	100	40	azithromycin	5	-
octylphenols	100	14	clarithromycin	10	-
tributyltin compounds	0.2	0.03	ciprofloxacin	10	-
fluoranthene	6.3	0.9	metformin	100	-
benzo(a)pyrene	0.17	0.02	ranitidine	100	-
triclosan	100	14	carbamazepine	100	-
cypermethrin	0.08	0.01	10,11- epoxy-carbamazepine	100	-
oestrone	1	-	sertraline	10	-
17 β oestradiol	0.3	-	norsertaline	10	-
17 α ethinyloestradiol	0.03	-	fluoxetine	10	-
diclofenac	10	-	tamoxifen	5	-
ibuprofen	10	-	Trixylenyl phosphate	10	-
atorvastatin	10	-	1,2,3 Benzotriazole	2	-
ortho-hydroxy-atorvastatin	10	-	Tolyltriazole (4,5 methyl BZT)	2	-

Some of the challenges facing laboratories

- **Market constraints**

- Insufficient market capacity & capability
- Collaboration between laboratories

- **Supplier**

- Instrumentation
- Standards

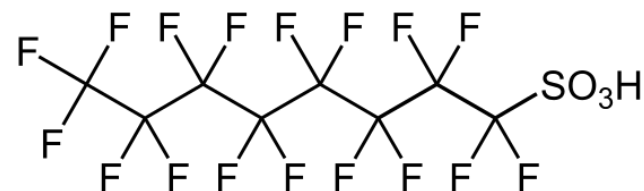
- **Contamination**

- Sampling/field Laboratory contamination

- **Technical**

- Matrix issues
- Background interference
- Limits of detection
- Method development & validation

Perfluorooctane sulphonate (PFOS)



- Former uses:
 - in cleaning products, firefighting foams, and as an impregnating agents in carpets, furniture, paper, textiles and leather

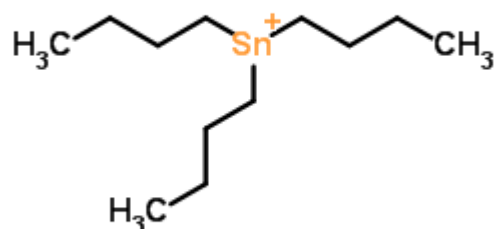
- Current uses:
 - in metal plating and semi-conductor industries and in aviation hydraulic fluids

- Analysis:
 - almost exclusively by liquid chromatography coupled to either tandem mass spectrometry (LC-MS/MS) or time of flight (ToF)

- LODs:

CIP EQS	0.60ng/l	WFD EQS	1.6ng/l
CIP LOQ	0.18ng/l	WFD LOQ	0.50ng/l
CIP LOD	0.09ng/l	WFD LOD	0.20ng/l

Tributyltin (TBT)



- Uses:

- as a biocide in anti-fouling paints, as a disinfectant, fungicidal wood preservative and a stabilizer in PVC resins and variously in the paper/pulp, textile and leather industries

- Analysis:

- various, but those using gas chromatography require derivatisation of the extracted compound to make it amenable to GC. We use GC-MS/MS

- LODs:

CIP & WFD EQS 0.20ng/l

CIP & WFD LOQ 0.06ng/l

CIP & WFD LOD 0.03ng/l



Pharmaceuticals

- Analysis:
 - Direct injection LC-MS/MS in three different modes

- LODs (ng/l)

diclofenac	10	clarithromycin	10
ibuprofen	10	ciprofloxacin	10
atorvastatin	10	metformin	100
ortho-hydroxy-atorvastatin	10	ranitidine	100
para-hydroxy-atorvastatin	10	carbamazepine	100
propranolol	10	epoxy-carbamazepine	100
atenolol	10	sertraline	10
erythromycin	100	norsertaline	10
norerythromycin	100	fluoxetine	10
azithromycin	5	tamoxifen	5



- The future...



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