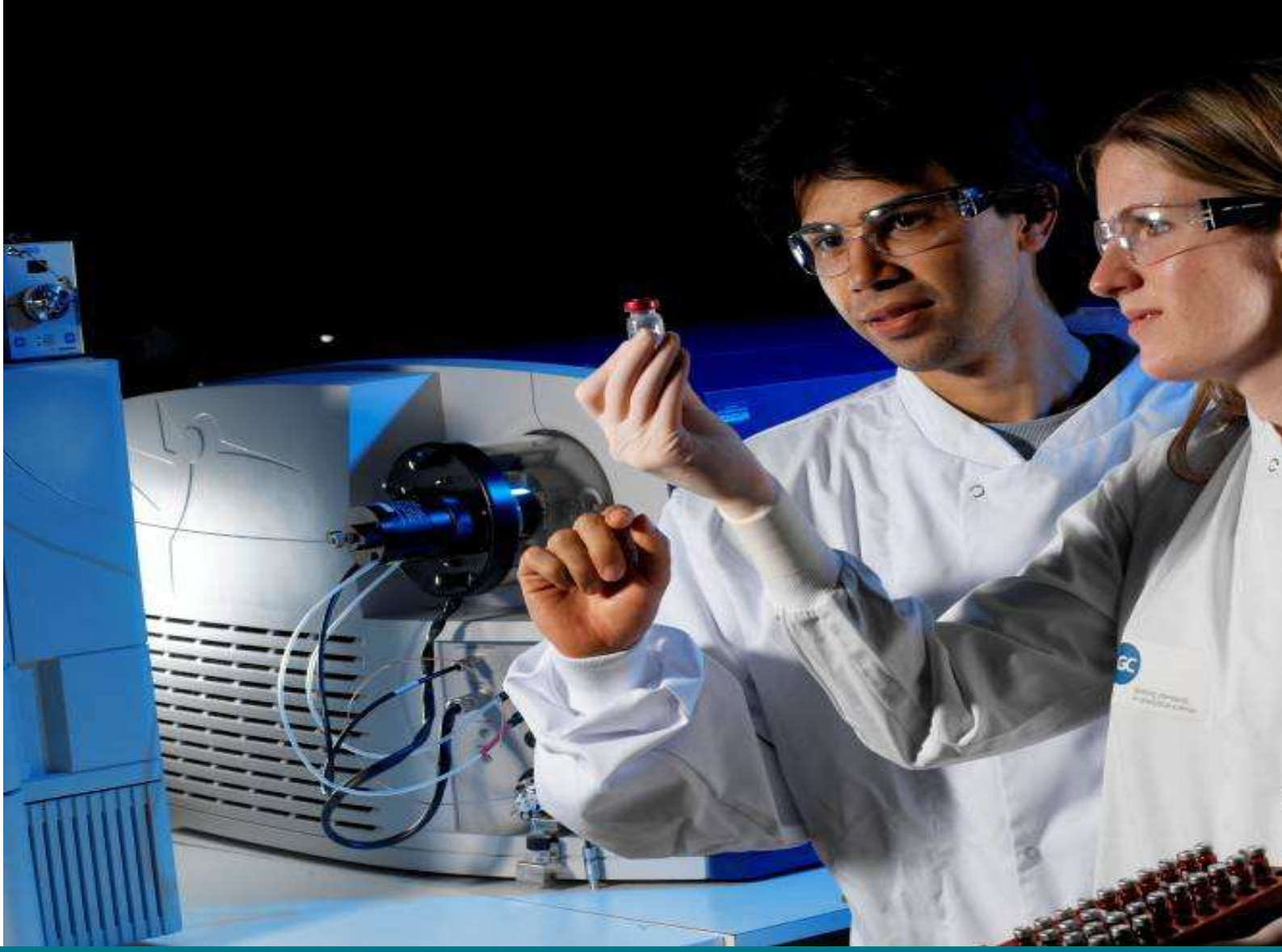

Measurement Issues relating to the EU Water Framework Directive:

Government Chemist Advisory Function Study

January 2015

LGC/R/2015/374

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1. Summary

The number of chemical pollutants which are considered to be of concern regarding European water bodies is significant and growing. It is fully expected that the number of substances which will be covered by the Water Framework Directive and its daughter directives will continue to increase over time. It is therefore of prime importance that those charged with monitoring water bodies for the presence of these substances have the analytical measurement tools at their disposal in order to carry out this task accurately and reproducibly.

The number of substances, including priority hazardous substances, where the state-of-the-art in analytical measurement methodology is inadequate, or only available in a very few laboratories and/or Member States, is worrying. The same can be said for the analytical quality assurance infrastructure, including the availability of appropriate Certified Reference Materials (CRMs) and Proficiency Testing Schemes (PTS). This report highlights where existing procedures are in place, and where the issues and problems lie. This will hopefully provide a basis for where resources and research can be prioritised in order to plug the gaps.

2. Introduction

This report aims to address the area where the regulation/legislation issues and analytical measurement issues overlap with regard to the requirements of the EU Water Framework Directive. Additionally, in order that monitoring or enforcement laboratories are able to check the efficacy of their analytical measurement procedures, the availability of certified reference materials (CRMs) and proficiency testing schemes which cover these substances in an appropriate matrix are necessary. This report will also study the availability of these and identify gaps which need to be filled.

3. The Water Framework Directive

The Water Framework Directive (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)[1] was enacted in the European Union in 2000. Its aims were to obtain 'good status' for all ground and surface waters (rivers, lakes, transitional waters, and coastal waters) in the EU. The ecological and chemical status of surface waters was assessed as follows:

- Biological quality (fish, benthic invertebrates, aquatic flora)
- Hydromorphological quality such as river bank structure, river continuity or substrate of the river bed
- Physical-chemical quality such as temperature, oxygenation and nutrient conditions
- Chemical quality that refers to environmental quality standards for river basin specific pollutants. These standards specify maximum concentrations for specific water pollutants. If even one such concentration is exceeded, the water body will not be classed as having a “good ecological status”.

The Water Framework Directive stipulated that groundwater must achieve “good quantitative status” and “good chemical status” (i.e. not polluted) by 2015. Groundwater bodies are classified as either "good" or "poor".

[1] http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32000L0060

The Directive noted that with approximately 75 % of the EU's drinking water supplies deriving from groundwater, it was of prime importance to ensure quality of groundwater. This was achieved by a series of River Basin Management Plans (RBMPs) which could focus on a particular river system which was independent of national borders. Many major rivers, such as the Danube, flow through several member states and the plan to ensure their quality could be enacted between those member states.

There are two "daughter" directives linked with the Water Framework Directive, which have been implemented in Member States.

3.1 Groundwater Daughter Directive

The Groundwater Daughter Directive (Directive 2006/118/EC)[2] mandates Member States to consider setting threshold limits for a number of pollutants which are indicative of groundwater status quality:

- Arsenic
- Cadmium
- Lead
- Mercury
- Ammonium
- Chloride
- Sulfate
- Trichloroethylene
- Tetrachloroethylene
- Conductivity

Member States set limits for the above based upon their own situations. Some pollutants are naturally-occurring, and others introduced by human activity – and some fall into each category. The natural levels of pollutants arising from the local geology have to be taken into consideration. This leads to inconsistency of limits set between Member States. The Directive states that "methods of monitoring and analysis used will conform to international quality control principles, including, if relevant, CEN or national standardized methods, to ensure equivalent scientific quality and comparability of the data provided" which should ensure that any data produced will be reliable providing that appropriate methods are available which can detect accurately these pollutants at the threshold limits set.

3.2 Directive on Environmental Quality Standards

The Directive on Environmental Quality Standards – also known as the Priority Substances Directive - (Directive 2008/105/EC)[3] establishes the concentration limits for a number of substances to be controlled under the Water Framework Directive.

The Directive has been reviewed to ensure that possible pollution threats are adequately covered, and that existing limits are appropriate to maintain the quality of water and reduce threats to the health of humans, other species and the environment. Consequently, a proposal to amend the directive by

- adding 15 additional priority substances, 6 of them designated as priority hazardous substances;
- setting stricter Environmental Quality Standards (EQS) for four existing priority substances and slightly revised EQS for three others;

[2] http://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1401349873350&uri=CELEX:32006L0118

[3] http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32008L0105

- 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.

It is important that analytical capability develops in parallel with such proposals to ensure that implementation and monitoring are fully effective. There have been signs that such an approach will be more likely in the future. However, the development of analytical measurement methods in support of new EQS levels is an activity which is devolved to EU Member States, so there is no formal parallel between the implementation of standards and the development of methodology in support of them.

4. Substances Controlled under the WFD

Many substances are controlled under the Water Framework Directive and its daughter directives. Most of these are controlled under the Priority Substances Directive.

Annex I of the Priority Substances Directive lists those substances covered, and these are reproduced in Table 1 below.

Table 1: Substances listed in Annex I of the Priority Substances Directive

Number	CAS number	EU number	Name of priority substance	Identified as priority hazardous substance	EQS[4]
1	15972-60-8	240-110-8	Alachlor	No	0.3
2	120-12-7	204-371-1	Anthracene	Yes	0.1
3	1912-24-9	217-617-8	Atrazine	No	0.6
4	71-43-2	200-753-7	Benzene	No	10
5	N/A	N/A	Brominated diphenylether	Yes	0.5 ng/L (sum of congeners
	32534-81-9	N/A	Pentabromodiphenyleth er (congener numbers 28, 47, 99, 100, 153 and 154)	No	
6	7440-43-9	231-152-8	Cadmium and its compounds	Yes	0.08 - 0.25
7	85535-84-8	287-476-5	Chloroalkanes, C10-13	No	0.4
8	470-90-6	207-432-0	Chlorfenvinphos	No	0.1
9	2921-88-2	220-864-4	Chlorpyrifos (Chlorpyrifos-ethyl)	No	0.03
10	107-06-2	203-458-1	1,2-Dichloroethane	No	10
11	75-09-2	200-838-9	Dichloromethane	No	20

[4] Environmental Quality Standard for inland surface waters in µg/L – i.e a limit value

Number	CAS number	EU number	Name of priority substance	Identified as priority hazardous substance	EQS[4]
12	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)	No	1.3
13	330-54-1	206-354-4	Diuron	No	0.2
14	115-29-7	204-079-4	Endosulfan	Yes	0.005
15	206-44-0	205-912-4	Fluoranthene	No	0.0063
16	118-74-1	204-273-9	Hexachlorobenzene	Yes	0.05
17	87-68-3	201-765-5	Hexachlorobutadiene	Yes	0.6
18	608-73-1	210-158-9	Hexachlorocyclohexane	Yes	0.03
19	34123-59-6	251-835-4	Isoproturon	No	0.2
20	7439-92-1	231-100-4	Lead and its compounds	No	1.2
21	7439-97-6	231-106-7	Mercury and its compounds	Yes	0.07
22	91-20-3	202-049-5	Naphthalene	No	2
23	7440-02-0	231-111-4	Nickel and its compounds	No	4
24	25154-52-3	246-672-0	Nonylphenols	Yes	0.3
	104-40-5	203-199-4	(4-nonylphenol)	Yes	
25	1806-26-4	217-302-5	Octylphenols	No	0.1
	140-66-9	not applicable	(4-(1,1',3,3'-tetramethylbutyl)-phenol)	No	
26	608-93-5	210-172-5	Pentachlorobenzene	Yes	0.007
27	87-86-5	201-778-6	Pentachlorophenol	No	0.04
28	N/A	N/A	Polyaromatic hydrocarbons	Yes	1.7×10^{-4} (sum)
	50-32-8	200-028-5	(Benzo(a)pyrene)	Yes	
	205-99-2	205-911-9	(Benzo(b)fluoranthene)	Yes	
	191-24-2	205-883-8	(Benzo(g,h,i)perylene)	Yes	
	207-08-9	205-916-6	(Benzo(k)fluoranthene)	Yes	
	193-39-5	205-893-2	(Indeno(1,2,3-cd)pyrene)	Yes	
29	122-34-9	204-535-2	Simazine	No	1
30	N/A	N/A	Tributyltin compounds	Yes	0.0002
	36643-28-4	N/A	(Tributyltin-cation)	Yes	
31	12002-48-1	234-413-4	Trichlorobenzenes	No	0.4
32	67-66-3	200-663-8	Trichloromethane (chloroform)	No	2.5
33	1582-09-8	216-428-8	Trifluralin	No	0.03

There are also 8 other substances not in the priority substances list, but for which environmental quality standards have not been set. These are:

- DDT
- p-p-DDT
- Cyclodiene pesticides

- Aldrin
- Dieldrin
- Endrin
- Isodrin
- Tetrachloroethylene
- Trichloroethylene

The last two of these are also listed in the Groundwater Daughter Directive (q.v.).

4.1 Proposed Changes

In 2013 The European Commission has proposed adding 15 additional priority substances to the 33 pollutants outlined above. They are listed in Table 2.

Table 2: Substances suggested for inclusion in Annex I of the Priority Substances Directive

Number	CAS number	EU number	Name of priority substance	Identified as priority hazardous substance	EQS[5]
34	115-32-2	204-082-0	Dicofol	Yes	1.3×10^{-3}
35	1763-23-1	217-179-8	Perfluorooctane sulfonic acid and its derivatives (PFOS)	Yes	6.5×10^{-4}
36	124495-18-7	N/A	Quinoxyfen	Yes	0.15
37	N/A	N/A	Dioxins and dioxin-like compounds	Yes	0.008 µg/kg total
38	74070-46-5	277-704-1	Aclonifen	No	0.12
39	42576-02-3	255-894-7	Bifenox	No	0.012
40	28159-98-0	248-872-3	Cybutryne	No	0.0025
41	52315-07-8	257-842-9	Cypermethrin	No	8×10^{-5}
42	62-73-7	200-547-7	Dichlorvos	No	6×10^{-4}
43	N/A	N/A	Hexabromocyclododecanes (HBCDD)	Yes	0.0016
44	76-44-8 / 1024-57-3	200-962-3 / 213-831-0	Heptachlor/heptachlor epoxide	Yes	2×10^{-7}
45	886-50-0	212-950-5	Terbutryn	No	0.065
46	57-63-6	200-342-2	17alpha-ethinylestradiol	No	3.5×10^{-5}
47	50-28-2	200-023-8	17beta-estradiol	No	4×10^{-4}
48	15307-79-6	239-346-4	Diclofenac	No	0.1

It was subsequently decided that only 12 of these should be added to the Priority Substances List, and that three - 17 alpha-ethinylestradiol (EE2), 17 beta-estradiol (E2) and Diclofenac – be placed on a “Watch List”, where further studies and evidence will be required before they can become priority substances.

[5] Environmental Quality Standard for inland surface waters in µg/L – i.e. a limit value

5. Analytical Measurement Issues

5.1 Introduction

It is important that priority and priority hazardous substances can be measured accurately at the levels specified in the Priority Substances Directive. Regulations which are underpinned by analytical measurements cannot be properly enforced if the available measurement methods are insufficient or inadequate for the task. Although the EQS levels in the Priority Substance Directive are set at the EU level, the responsibility for implementation – and therefore for developing and validating appropriate analytical methodology – lies with Member States. The danger inherent in this approach is that the cost of developing suitable methods where none exist can be prohibitively expensive.

Methods will generally be drawn from a narrow range of techniques:

- Inductively-coupled plasma mass spectrometry (ICP-MS) for inorganic species;
- Liquid chromatography and/or gas chromatography, linked to mass spectrometry (LC-MS and GC-MS) for organic species.

Under the WFD it is recommended any method used to determine the levels of a hazardous substance or priority hazardous should:

- Be validated according to ISO/IEC 17025;
- Have a limit of quantification (LOQ) ≤ EQS;
- Have a measurement uncertainty ≤ 50 %.

5.2 Methods available for Priority Hazardous Substances

Priority Hazardous Substances are substances with the highest potential hazard to the environment and, by extension, to human and animal health. Consequently, some of these substances have particularly low EQS values, which can be very challenging for analytical laboratories

5.2.1 Anthracene

GC-MS methods are generally employed to determine anthracene in water. A good example is that used by the US Environmental Protection Agency (USEPA)[6] which has been validated to detect down to 0.25 µg/L with a relative standard deviation (RSD) of 3.8 %.

5.2.2 Polybrominated Diphenyl Ethers (PBDEs)

This is one of the more challenging measurements needed, due to the extremely low EQS value (0.5 ng/L), which applies to the sum of all pentabromodiphenylether congeners. Therefore potentially each would need to be measured at a fraction of this concentration. GC-MS methods are usually employed, such as that by the USEPA[7], although this only goes down to the µg/L level at best, which is at least two orders of magnitude too high.

Work is currently ongoing at LGC to develop a method which can measure PBDEs at sub-pg levels as required by the Quality Standards Directive (QSD). LGC is also a partner in an EU funded project involving a number of metrology laboratories to develop methods for merging pollutants such as PBDEs at the levels specified in the QSD.

[6] http://www.epa.gov/nerlcwww/documents/method%20525_3_feb21_2012%20final.pdf

[7] http://water.epa.gov/scitech/methods/cwa/upload/M1614A_11June10.pdf

5.2.3 Cadmium and its compounds

ICP-MS is now widely used for the determination of cadmium in water, where the limit of detection can go below 0.01 µg/L, for example in a monograph from the instrument company Perkin-Elmer[8].

5.2.4 Endosulfan

Endosulfan is a widely-used pesticide which is normally determined by GC-MS. There are several published methods which claim to be able to measure endosulfan at concentrations between 0.05 and 0.1 µg/L, but the ability to measure this substance at the EQS level of 0.005 µg/L remains in question.

5.2.5 Hexachlorobenzene

Hexachlorobenzene is a widely-used organochlorine pesticide. A GC-MS method followed by the US EPA[9] is able to accurately determine this substance at concentrations below the EQS value of 0.05 µg/L.

5.2.6 Hexachlorobutadiene

Hexachlorobutadiene (HCBD) is a volatile substance which can be determined by headspace gas chromatography-mass spectrometry (HSGC-MS) at levels down to 0.003 µg/L[10], which is significantly lower than the EQS limit of 0.6 µg/L.

5.2.7 Hexachlorocyclohexane

Hexachlorocyclohexane (γ-HCH) is also known as Lindane, a pesticide with marked toxic properties. It has been measured by a method published by the US Environmental Protection Agency[11] using solid-phase extraction and GC-MS at levels down to 0.03 µg/l, the EQS limit value. Any changes to the limit value would therefore require the method to be further refined to measure accurately at lower concentrations.

5.2.8 Mercury and its compounds

For many years, the determination of mercury at low concentrations was problematical. The development of new procedures including ICP-MS has improved the situation. Cold vapour atomic absorption spectroscopy (CVAAS) methods have been used for determining total mercury for many years, but newer methods using ICP-MS are not much more sensitive. Thus mercury cannot be readily measured at the EQS limit by the majority of routine laboratories. HPLC linked with ICP-MS has been successfully used to separate mercury species[12], such as methylmercury and ethylmercury as well as mercury (II) and measure them at around 1 µg/L each.

5.2.9 Nonylphenols

Nonylphenols and their alkoxylates are considered to be endocrine disrupters, and find their way into the environment and, hence, water bodies, from their use in detergents as non-ionic surfactants. HPLC-MS methodology is usually employed in their determination and levels of 0.002 µg/L can be determined,

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[8]

[9] http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_11_06_methods_method_505.pdf

[10] http://www.gerstel.co.uk/pdf/GERSTEL_solutions_no_4_8_9.pdf

[11] http://www.epa.gov/nerlcwww/documents/method%20525_3_feb21_2012%20final.pdf

[12] http://www.cffet.net/ait/Hg_Agilent.pdf

which is well below the EQS limit. Similar methodology is available for octylphenols and their alkoxylates, which are Priority Substances under the EQS Directive.

5.2.10 Pentachlorobenzene

Like other chlorinated benzenes, pentachlorobenzene is determined by GC-MS. Work carried out on quantification of this persistent organic pollutant in South Africa[13] has shown that it can be detected down to the EQS level of 0.07 µg/L, but not accurately quantified; the LOQ is considered to be 0.7µg/L. Other workers[14] in the field claim to be able to detect pentachlorobenzene down to 0.05 ng/L, which would imply an LOQ of around 1 ng/L, or 0.001 µg/L.

5.2.11 Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons (PAHs) are a group of highly toxic organic compounds usually produced by the incomplete combustion of fossil fuels. The EQS specifically mentions five PAHs:(Benzo(a)pyrene; Benzo(b)fluoranthene; Benzo(g,h,i)perylene; Benzo(k)fluoranthene and Indeno(1,2,3-cd)pyrene.

HPLC method employing fluorescence detection, used for many years in PAH measurements, do not have the sensitivity required to check compliance with the EQS levels (0.00017 µg/L Total PAH). Detection limits for this technique are approximately two orders of magnitude higher for each PAH. Limits of detection using GC-MS are very much of the same order[15]. Current methodology therefore struggles to accurately detect and quantify PAHs in water bodies, where the worst case scenario of equal concentrations of the 5 named PAHs would require an LOQ of 0.000085 µg/L, which would appear to be well beyond current procedures.

5.2.12 Tributyltin compounds

Tributyltin has found its way into our environment following its use as an anti-fouling paint on ships and boats. Advanced GC-MS methodology, using the latest generation of triple quadrupole mass spectrometers[16], has enabled limits of quantification of 0.00005 µg/L to be achieved, below the EQS limit of 0.0002 µg/L. Although such instrumentation is not routinely available, many high-end laboratories should have access to this.

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[13] http://oatd.org/oatd/record?record=handle%5C:10321%5C%2F1118&q=id%3A%22handle%3A10321%2F1118%22

[14] http://chromsci.oxfordjournals.org/content/early/2013/05/03/chromsci.bmt043.full

[15] http://www.salltd.co.uk/about_us/method_statement?label=pahgcms

[16] http://www.thermoscientific.com/content/dam/tfs/ATG/CMD/cmd-support/trace-gc-ultra/scientific-resources/application-notes/Determination-of-Organotins-in-Water-Using-Triple-Quadrupole-GC-MS-MS.pdf

Table 3: Summary of Priority Hazardous Substances data

Substance	EQS value[1]	LOD[1]	Satisfactory?	Only measurable using high-end instruments
Anthracene	0.1	0.25	No	No
Brominated diphenylethers	0.0005	>0.001	No	Yes
Cadmium and its compounds	0.08-0.25	0.01	Yes	No
Endosulfan	0.005	0.05	No	Yes
Hexachlorobenzene	0.05	0.05	Yes	No
Hexachlorobutadiene	0.6	0.003	Yes	No
Hexachlorocyclohexane	0.03	0.03	Borderline	Yes
Mercury and its compounds	0.07	<0.001	Yes	No
Nonylphenols	0.3	0.002	Yes	No
Pentachlorobenzene	0.007	0.001-0.01	Yes	No
PAHs[2]	0.00017	ca. 0.008	No	Yes
Tributyltin	0.0002	0.00005	Yes	Yes

[1] µg/l unless otherwise stated

[2] those specified in the Directive

5.3 Methods available for proposed new priority hazardous substances

These substances are proposed to be added to the list of priority hazardous substances; the availability of suitable measurement methods is important to underpin their addition to the list.

5.3.1 Dicofol

Dicofol is an organochlorine pesticide, which is known to degrade to p,p´-dichlorobenzophenone (DCBP) during analysis unless steps are taken to prevent this (e.g. keeping the pH low)[17]. Methods used in Europe, usually employing GC-MS, for the determination of dicofol in waters have been unable to achieve a limit of quantification near the EQS level of 0.0013 µg/L[18], which makes it very difficult to monitor waters effectively for this pollutant at the necessary concentrations.

5.3.2 Perfluoroctane sulfonic acid (PFOS)

[17] http://www.eurl-pesticides.eu/library/docs/srm/EurlSrm_Observations_dicofol.pdf

[18] http://publications.jrc.ec.europa.eu/repository/bitstream/111111111/26936/1/lb-na-25532-en-n.pdf.pdf

This is another pollutant where the current state-of-the-art in measurements (LC-MS/MS) is insufficient to monitor levels at the proposed EQS level of 0.00065 µg/L[18]. Recent developments in China using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF)[19] have achieved limits of detection below 0.00065 µg/L, but this technique is not routinely available in many monitoring laboratories.

5.3.3 Quinoxyfen

Quinoxyfen is usually measured using LC-MS or LC-MS/MS, and can be determined significantly below the EQS level.

5.3.4 Dioxins and dioxin-like compounds

The EQS limit for dioxins and dioxin-lie substances in total is 0.008 µg/kg (8 ng/kg), which means that if there are several species in a sample, then the effective concentration of each may be an order of magnitude lower. This class of compound is usually determined by GC-MS, with limits of detection in the sub-ng/kg range[20] which should normally be sufficient.

5.3.5 Hexabromocyclododecanes (HBCDDs)

HBCDDs are persistent organic pollutants (POPs) which have been used as flame retardants. LC-MS methods are most commonly used, including those where other polluting flame retardants are determined simultaneously[21]. The limit of quantification for such methods is generally in the range 0.2 to 1 µg/L, which is significantly higher than the EQS value of 0.0016 µg/L.

5.3.6 Heptachlor/heptachlor epoxide

These organochlorine pesticides have one of the lowest EQS values for priority hazardous substances, 0.0000002 µg/L (0.2 pg/L). This is very challenging for analytical monitoring laboratories. State-of-the-art methods such as that developed in China[22] can only measure down to 0.2 ng/L, 2 orders of magnitude above the EQS value, using GC-MS.

Table 4: Summary of Proposed new Priority Hazardous Substances data

Substance	EQS value[1]	LOD[1]	Satisfactory?	Only measurable using high-end instruments
Dicofol	0.0013	<0.0015	No	Yes
Perfluoroctane sulfonic acid	0.00065	0.00065[2]	Borderline	Yes
Quinoxyfen	0.15	>>0.15	Yes	Yes
Dioxins and dioxin-like compounds	0.008 (total)	0.001	Yes	No
Hexabromocyclododecanes	0.0016	<0.2	No	No

[19] http://www.ncbi.nlm.nih.gov/pubmed/21645709

[20] http://www.salltd.co.uk/about_us/method_statement?label=dioxins

[21] http://link.springer.com/article/10.1007%2Fs11270-014-1866-4#page-1

[22] http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3630005/

Substance	EQS value[1]	LOD[1]	Satisfactory?	Only measurable using high-end instruments
Heptachlor/heptachlor epoxide	0.0000002	0.00002	No	Yes

[1] µg/l unless otherwise stated

[2] Not in the EU

5.4 Methods available for Priority Substances

5.4.1 Existing Priority Substances

1. Alachlor

Alachlor can be readily determined by GC-MS and many laboratories have carried this out successfully with limits of detection well below the EQS level of 0.3 µg/L.

2. Atrazine

Atrazine can also be determined by GC-MS, but the use of immunoassay techniques[23] has achieved lower detection limit values in line with those required by the EQS.

3. Benzene

This common pollutant, usually arising from fuel sources, can be successfully measured down to 0.5 µg/L using gas chromatographic-based techniques, which is well below the EQS value.

4. Chloroalkanes, C10-C13

These compounds are also known as short-chain chlorinated paraffins (SCCPs). No standard methods had been developed for this class of compounds by 2005, unlike all other priority substances. However, these compounds should be amenable to analysis using electron capture negative ionisation mass spectrometric detection techniques (GC-ECNI-MS), but incomplete resolution of the significant numbers of the compounds and poor reproducibility means that it is still not possible to determine these with any accuracy at or below the EQS value.

5. Chlorfenvinphos

Chlorfenvinphos has been measured successfully using both HPLC-UV and HPLC-MS at levels below the EQS value.[24]

6. Chlorpyrifos

This organophosphorus pesticide has been determined using GC-FPD in the past, at levels slightly above the EQS value. GC-MS methods are commonly used to measure chlorpyrifos residues in foods and agricultural products and can

[23] Evaluation of Surface Water Pollution with Atrazine, an Endocrine Disruptor Chemical, in Agricultural Areas of Turopolje (Croatia), T. Gojmerac, Z. Ostojić, D. Pauković, J. Pleadin1, M. Žurić

[24] http://www.atsdr.cdc.gov/toxprofiles/tp83-c6.pdf

be successfully adapted for water and achieve the detection limit required for the EQS level.

7. 1,2-dichlorethane

This volatile contaminant is usually determined by purge & trap GC-MS, where limits of detection can be significantly below the EQS level of 10 µg/L[25]. The same procedure can be readily followed to measure a complete suite of volatile organic compounds (VOCs) at an appropriate level in support of the Directive. These are: dichloromethane, naphthalene, trichloromethane, trichlorobenzenes,

8. Dichloromethane

See 1,2-dichlorethane above.

9. Di(2-ethylhexyl)phthalate

This commonly-found plasticiser can be readily determined in aqueous matrices using gas chromatography linked to a range of detectors (e.g. ECD, MS) where limits of detection an order of magnitude below the EQS level of 1.3 µg/L can be readily achieved.

10. Diuron

Diuron is a widely-used herbicide, and can be readily determined in water by LC-MS/MS with a limit of detection significantly below the EQS value of 0.2 µg/L.

11. Fluoranthene

Either GC-MS or LC-MS can be used to determine this polynuclear aromatic hydrocarbon. Many methods published are not capable of measuring fluoranthene at the EQS level of 0.0063 µg/L (6.3 ng/L), but a GC-MS method employing solid-phase extraction (SPE) clean-up can measure at sub-ng/L levels.[26]

12. Isoproturon

In common with other pesticides listed as priority substances, isoproturon is usually determined by LC-MS/MS following SPE clean-up, and limits of detection in the ng/L range can be achieved, which is compatible with the EQS level of 200 ng/L.

13. Lead (and its compounds)

Lead, as with many other trace metals, can be accurately determined in groundwater at sub-µg/L levels using High Resolution ICP-MS. Nickel can similarly be determined at such levels using this technique.

14. Naphthalene

See 1,2-dichlorethane above.

15. Nickel (and its compounds)

See Lead (and its compounds) above.

16. Octylphenols

[25] http://www.caslab.com/EPA-Methods/PDF/524_2.pdf

[26] http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=12520

This group of compounds can be measured in water using ultra-high-performance liquid chromatography/tandem mass spectrometry (uHPLC/MS/MS) using an isotope-labeled internal standard[27]. Limits of detection slightly below the 0.1 µg/L EQS value can be achieved suing this technique.

17. Pentachlorophenol

EPA method 515.4[28], despite being over 10 years old, can determine pentachlorophenol accurately using GC-ECD following derivatisation at levels at or below the EQS value of 0.04 µg/L.

18. Simazine

A number of procedures for determining simazine at levels significantly below the EQS value of 1 µg/L by GC-MS (some with isotope dilution) have been reported.

19. Trichlorobenzenes

See 1,2-dichlorethane above.

20. Trichloromethane

See 1,2-dichlorethane above.

21. Trifluralin

This commonly-used herbicide can be determined in waters using SPE extraction followed by GC-MS, where limits of detection just below the EQS level of 0.03 µg/L can be achieved.

Table 5: Summary of Priority Substances data

Substance	EQS value[1]	LOD[1]	Satisfactory?	Only measurable using high-end instruments
Alachlor	0.3	<0.3	Yes	No
Atrazine	0.6	<0.6	Yes	No
Benzene	10	0.5	Yes	No
Chloroalkanes, C10-13	0.4	N/A	No	Yes
Chlorfenvinphos	0.1	<0.1	Yes	No
Chlorpyriphos	0.03	<0.03	Yes	No
1,2-Dichloroethane	10	<<10	Yes	No
Dichloromethane	20	<< 20	Yes	No
Di(2-ethylhexyl)phthalate	1.3	~ 0.1	Yes	No
Diuron	0.2	<< 0.2	Yes	Yes
Fluoranthene	0.0063	< 0.001	Yes	No

[27] http://www.ncbi.nlm.nih.gov/pubmed/20740536

[28] http://www.caslab.com/EPA-Methods/PDF/EPA-Method-5154.pdf

Substance	EQS value[1]	LOD[1]	Satisfactory?	Only measurable using high-end instruments
Isoproturon	0.2	< 0.2	Yes	Yes
Lead and its compounds	1.2	< 1	Yes	No
Naphthalene	2	< 1	Yes	No
Nickel and its compounds	4	< 1	Yes	No
Octylphenols	0.1	<0.1	Yes	Yes
Pentachlorophenol	0.04	≤ 0.04	Yes	No
Simazine	1	<< 1	Yes	Yes
Trichlorobenzenes	0.4	<< 0.4	Yes	No
Trichloromethane	2.5	<< 2.5	Yes	No
Trifluralin	0.03	<0.03	Yes	No

[1] µg/l unless otherwise stated

5.4.2 Proposed New Priority Substances

1. Aclonifen

This herbicidal compound can be measured accurately by GC-MS based techniques down to levels an order of magnitude below the proposed EQS value of 0.12 µg/L.

2. Bifenox

A GC-MS method has been reported as being able to measure bifenox at 10 ng/L (proposed EQS value is 12 ng/L), but laboratories in many member states have not been able to achieve this.

3. Cybutryne

Although cybutryne can be measured relatively easily by either GC-MS or LC-MS, very few laboratories have reported being able to measure accurately at or below the proposed EQS value of 2.5 ng/L.

4. Cypermethrin

Cypermethrin has an extremely low proposed EQS value (8×10^{-5} µg/L or 0.08 ng/L), which makes accurate measurement of it in groundwater very challenging. No laboratory in the EU has reported being able to carry out measurements at this level, although it is claimed that an US EPA method[29] can achieve a limit of quantitation of 0.066 µg/L using a high resolution GC-MS procedure.

[29] http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2008_01_03_methods_method_1699.pdf

5. Dichlorvos

Dichlorvos is another chlorinated pesticide with a very low proposed EQS value (0.6 ng/L). Current analytical methodology, utilizing GC-MS or, more rarely, LC-MS, appears to be insufficient to measure dichlorvos at this level.

6. Terbutryn

Terbutryn is a triazine herbicide which can be measured by GC-MS with SPE clean-up to ng/L levels, below the proposed EQS value.

Table 6: Summary of Proposed New Priority Substances

Substance	EQS value[1]	LOD[1]	Satisfactory?	Only measurable using high-end instruments
Aclonifen	0.12	<0.1	Yes	Yes
Bifenox	0.012	0.010	Borderline	Yes
Cybutryn	0.0025	<0.0025	Yes	Yes
Cypermethrin	0.00008	0.066	No	Yes
Dichlorvos	0.0006	>0.001	No	Yes
Terbutryn	0.065	~0.001	Yes	Yes

[1] µg/l unless otherwise stated

5.5 Methods available for substances on Watch List

5.5.1 17alpha-ethinylestradiol

The proposed EQS value of 3.5 pg/L is extremely challenging for any analytical laboratory to meet accurately. GC-MS following derivatisation with BSTFA:TMCS is the most favoured method for determining this compound[30]. Many EU expert laboratories have report being able to get down to the 0.2-2 ng/L range, but the proposed limit is not currently achievable.

5.5.2 17beta-estradiol

The proposed EQS value for this steroid hormone is more than ten times greater than that for 17 alpha-ethinylestradiol, at 40 pg/L. LC-MS/MS is the preferred technique for this substance, and many laboratories have struggled to measure it at the proposed limit value.

5.5.3 Diclofenac

This common pharmaceutical compound can be readily determined in water sample matrices by both Enzyme-linked Immunosorbent Assay (ELISA) and LC-MS techniques[31] at ng/L levels, in line with the proposed EQS value of 100 ng/L.

[30] http://publications.jrc.ec.europa.eu/repository/bitstream/111111111/26936/1/lb-na-25532-en-n.pdf.pdf

[31] http://www.ncbi.nlm.nih.gov/pubmed/12966990

Table 7: Summary of Watch List Substances

Substance	EQS value[1]	LOD[1]	Satisfactory?	Only measurable using high-end instruments
17alpha-ethinylestradiol	0.000035	0.0002-0.002	No	Yes
17beta-estradiol	0.0004	>0.0004	No	Yes
Diclofenac	0.1	<0.01	Yes	No

[1] µg/l unless otherwise stated

6. Certified Reference Materials and Proficiency Testing Schemes

6.1 Certified Reference Materials (CRMs)

There still appears to be a dearth of suitable reference materials (RMs), including certified reference materials (CRMs) which contain priority substances and/or priority hazardous substances at concentrations near to the EQS level. The following, however, is available and should be considered when carrying out monitoring analytical measurement:

- ERM-CA615 is a groundwater which contains, amongst other substances, cadmium at a level of 0.106 µg/L and mercury at 0.037 µg/L.

No further reference materials which are appropriate for laboratories carrying out measurements of groundwater in support of the WFD appear to be available. This covers all the organic substances listed in the Directives. This is of serious concern and should be addressed by reference material producer, with support from national Governments and the European Commission, as soon as possible.

6.2 Proficiency Testing Schemes (PT)

It is very important for laboratories to be able to monitor their analytical performance on an ongoing basis against peer laboratories. Proficiency testing (PT) schemes allow them to achieve this, usually on a range of typical sample types with levels of important constituents or parameters across the range which may normally encountered during routine monitoring.

PT schemes which cover a number of substances listed in the Priority Substances Directive are available. In particular a network of PT providers (PT-WFD, Proficiency Testing for the Water Framework Directive[32]) was established. However, some members have left the network and the future of this group is unclear going forward. Some of the providers and their studies previously organized under this banner include:

- LGC Standards (Bury, UK[33]) has organized a number of relevant studies including organotin compounds in surface water. Some studies are still

[32] http://www.pt-wfd.eu/

[33] https://www.lgcpt.com/Default_eng.aspx

carried out and planned which support the WFD as part of the Aquacheck scheme.

- AQS Baden-Württemberg[34], part of the University of Stuttgart in Germany, has organized a number of studies which cover groups of priority substances in groundwater. Examples of this include polybrominated diphenylethers in surface water (9/14) and Priority pesticides according to the WFD in surface water (6/13). These studies are recognized by the European Co-operation for Accreditation (EA) for laboratories monitoring water in line with the WFD.

The complete range of priority substances and priority hazardous substances was not covered under the WFD-PT group, and the range of PT schemes still only covers a minority of compounds in the EQS at appropriate concentrations. There are technical issues involved in the preparation of suitable materials for these studies to be overcome. A specific barrier is the cost of providing these schemes with a limited number of laboratories in the sector in Europe and the high cost of preparing and distributing appropriate samples. This is a concern for laboratories involved in the monitoring of waters under the WFD and action is required to overcome the technical and commercial problems so that appropriate PTs can be provided in the future.

7. Conclusion

The data presented in this brief report indicates that there are currently analytical methodology problems in accurately measuring a number of existing priority hazardous substances in groundwater at the EQS values set in the EQS Directive. In addition, a similar problem exists with the majority of the proposed new priority hazardous substances, a number of the proposed new priority substances and two out of three “Watch List” substances. A number of priority hazardous substances can only be measured at or near the EQS levels using high-end analytical instrumentation, not available to most laboratories.

It is of prime importance that to monitor water bodies for good ecological quality, and to enforce appropriate European regulations regarding water quality – which are important and necessary activities – that the means of carrying these out in our monitoring laboratories are available. The development of state-of-the-art analytical measurement methods to accurately determine these substances at very low levels, with known measurement uncertainties, should take place prior to any regulation being implemented.

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[34] http://www.iswa.uni-stuttgart.de/ch/aqs/rv/