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programmes

Guidelines for Monitoring the Chemical
Status of Surface Water Bodies



Draft

Environmental Protection of International River Basins

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Guidelines for Monitoring the Chemical Status of Surface Water Bodies

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Author: Paul Buijs

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Abbreviations and Acronyms

AA-EQS	annual average - environmental quality standard
AAS	atomic absorption spectrophotometry/ spectrophotometer
AFS	atomic fluorescence spectrometer
CEN	Comité Européen de Normalisation (European Committee for Standardization)
CIS	Common Implementation Strategy for the Water Framework Directive
COD	chemical oxygen demand
EECCA	Eastern Europe, Caucasus and Central Asia
EN	European Standard
EPIRB	International Protection of International River Basins
EQS	environmental quality standard
EU	European Union
GC-MS	gas chromatograph/chromatography with mass spectrometer/spectrometry
GD	Guidance Document
HPLC	high performance liquid chromatograph
ICP-MS	inductively coupled plasma mass spectrometer/ spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometer/spectrometry
ISO	International Standards Organization
MAC-EQS	maximum allowable concentration - environmental quality standard
PAH	polyaromatic hydrocarbon
PS	Priority substance / Priority substances and certain other pollutants
SPM	suspended particulate matter
WFD	Water Framework Directive

1 INTRODUCTION

The project Environmental Protection of International River Basins (EPIRB), funded by the European Union (EU), encompasses a range of tasks and activities that aim at enhancing capacities of the project's beneficiary countries¹ in applying principles following the EU Water Framework Directive (WFD)². Key areas addressed by the EPIRB project include:

- 1) Monitoring and assessment of the status of water bodies.
- 2) Preparation of pilot river basin management plans.

The Guidelines for Monitoring the Chemical Status of Surface Water Bodies were prepared to support the beneficiary countries in further development of their monitoring programmes in compliance with WFD requirements. This document does not intend to repeat all information that is provided under the Common Implementation Strategy (CIS), notably in the Guidance Documents such as:

- №7: Monitoring under the Water Framework Directive.
- № 19: Guidance on Surface Water Chemical Monitoring under the Water Framework Directive.
- № 25: On Chemical Monitoring of Sediment and Biota under the Water Framework Directive.³

While summarizing the quintessence of these and other guidance documents, the present guidelines focus on some key elements, deemed relevant on the basis of practical experiences in introducing the WFD-monitoring requirements in Western EECCA (Eastern Europe, Caucasus and Central Asia) countries. This includes experiences the Joint Field Surveys that have been organised under the EPIRB project.

The EPIRB issued furthermore a 'Guidance Document addressing Chemical Status of Surface Water Bodies for a Pressure-Impact Analysis/Risk Assessment according to the EU WFD' [Buijs, 2014]. This document would be a decent starting point for – preparation of – desk-based studies on the potential presence/absence of priority substances (refer to the sections 2.3 and 8.4 for further details).

¹ Armenia (AM), Azerbaijan (AZ), Belarus (BY), Georgia (GE), Moldova (MD) and Ukraine (UA).

² 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*.

³ The CIS Guidance Documents, as well as other useful information about the WFD, can be retrieved from the EU CIRCABC (Communication and Information Resource Centre for Administrations, Businesses and Citizens) site at <https://circabc.europa.eu> One can find the areas of interest via Main Menu: Browse Categories -> European Commission - Environment -> WFD CIRCA: "Implementing the Water Framework Directive and the Floods Directive". Many documents can be found in the Library section, including the CIS Guidance Documents. Refer also to the References section of this document for links to the Guidance Documents used and quoted for this document.

2 PRIORITY SUBSTANCES AND CERTAIN OTHER POLLUTANTS

2.1 A brief history

When the WFD came into force in the year 2000, reference was made to priority – hazardous – substances listed in Annex X. At that time, however, Annex X was still empty. The actual first List of Priority Substances in the Field of Water Policy was published in the DECISION No 2455/2001/EC *establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC*, containing 33 substances.

This list of Priority Substances was extended with eight more ‘certain other pollutants’ in the Directive 2008/105/EC *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*. This Directive furthermore provided with environmental quality standards (EQS) for the ‘Priority substances and certain other pollutants’ (PS).

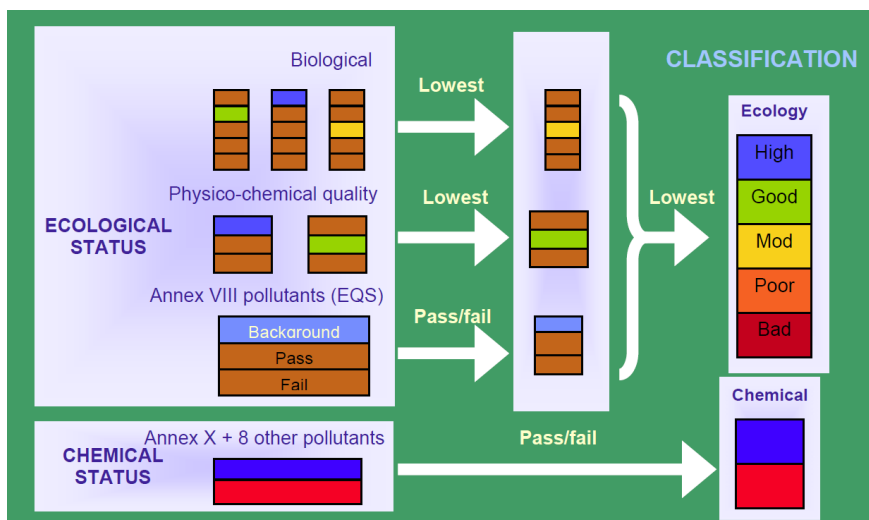
Yet twelve more substances were added in the Directive 2013/39/EU *amending Directives 2000/60/EC and 2008/105/EC as regards Priority substances in the field of water policy*. Some of the EQSs were changed and EQSs for biota were added for more substances. The list of PSs and EQSs of the Directive 2013/39/EU are included in Annex I of this document.

2.2 Good chemical status

The ultimate objective of the WFD is good status in all water bodies. The status of surface water under the WFD consists of the *ecological* status⁴ and the *chemical* status.

⁴ Either *ecological potential* in the case of artificial water bodies and heavily modified water bodies.

Figure 1 Classification of the status of surface water bodies under the WFD (adapted from [GD 27])



Contrary to the ecological status with its five classes for the biological quality elements, there are only two classes of chemical status: “good” and “failing to achieve good”. Good chemical status means compliance with the EQSs stipulated by the corresponding Directive, with the Directive 2013/39/EU currently being the most recent one.⁵

In case the EQSs for one or more PSs are not met, then the corresponding surface water body is failing to achieve good chemical status. Therewith, the surface water body does not meet the criteria for good status, since this requires both good ecological *and* good chemical status.

The Directive 2013/39/EU contains two, complementary, EQSs:

- annual average – environmental quality standard (AA-EQS), and
- maximum allowable concentration – environmental quality standard (MAC-EQS).

The AA-EQS applies to the arithmetic mean of one year of data⁶, whereas the MAC-EQS applies to the maximum concentration of this annual set of data.⁷

More details about assessment are mentioned in Chapter 6.

⁵ WFD Article 16.4 “The Commission shall review the adopted list of priority substances at the latest four years after the date of entry into force of this Directive and at least every four years thereafter, and come forward with proposals as appropriate.”

⁶ WFD Annex V.1.3.4: *Frequencies of monitoring* implies that water samples for analysis on PSs are to be taken monthly.

⁷ Directive 2013/39/EU “... for any given surface water body, applying the MAC-EQS means that the measured concentration at any representative monitoring point within the water body does not exceed the standard.”

2.3 “... being discharged into the body of water”

From WFD Annex V.1 one can infer that the chemical status applies to “*Pollution by all priority substances identified as being discharged into the body of water*”. It is, however, not easy to determine which PSs are indeed discharged into surface water bodies. Complicating factors include:

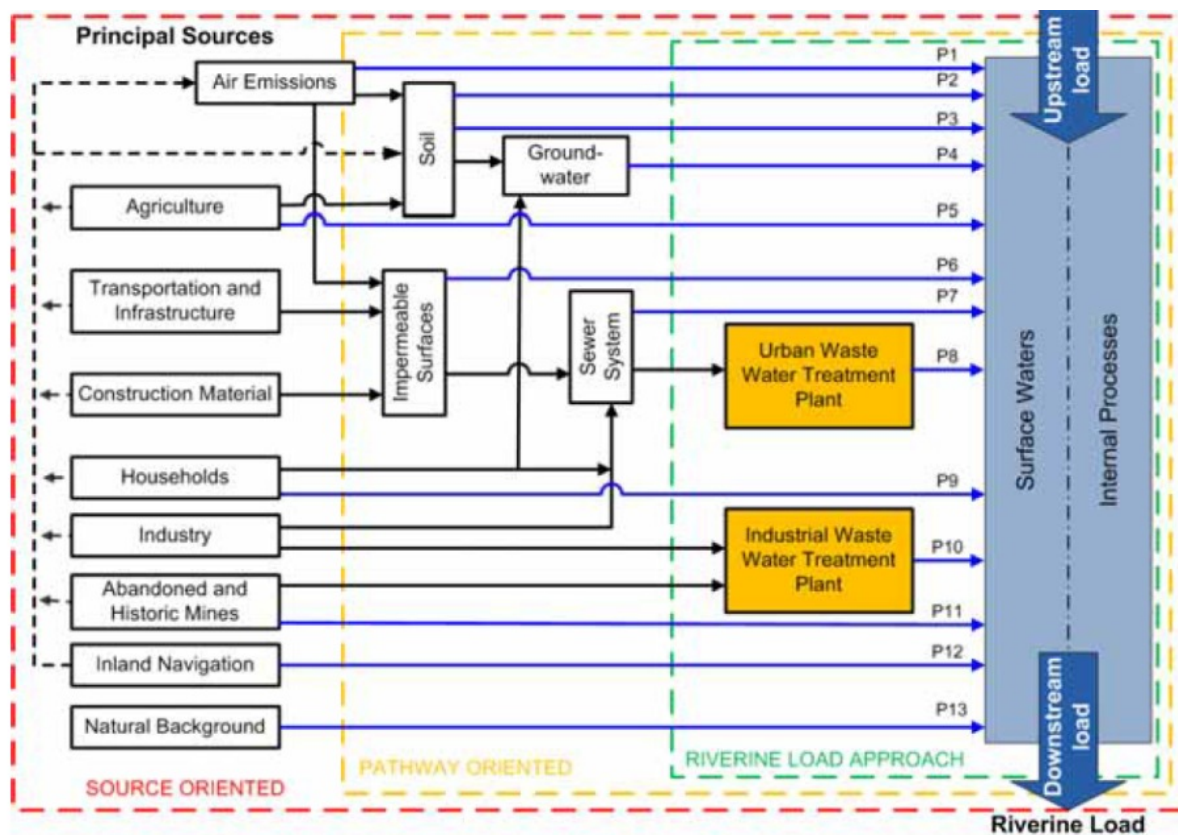
- The PSs are a heterogeneous group of substances, comprising non-synthetic and synthetic substances.⁸
- As a group, they cannot be linked to specific anthropogenic pressures; each PS has its own characteristics. Individual substances can originate from different sources and can arrive in surface water bodies via multiple pathways (compare Figure 2). In the case of transboundary waters, PSs can furthermore be ‘exported’ by upstream countries.
- Analysis of the whole range of PSs requires sophisticated laboratory capacities (refer to Chapter 5 for further details).

Worth reading is the CIS Guidance Document № 28: *Technical Guidance on the Preparation of an Inventory of Emissions, Discharges and Losses of Priority and Priority Hazardous Substances*.

The EPIRB project has furthermore prepared the “*Guidance Document addressing Chemical Status of Surface Water Bodies for a Pressure-Impact Analysis/Risk Assessment according to the EU WFD*” [Buijs, 2014], briefly describing approaches for identifying potentially relevant PSs.

⁸ Non-synthetic substances can be present due to natural conditions, like for example metals and polyaromatic hydrocarbons (PAH). Many trace/heavy metals are actually essential for proper functioning of many organisms, although only up to certain levels; in higher dosages, such metals can start having toxic effects. Anthropogenic activities (pressures) can lead to concentrations in surface waters beyond natural background levels. Synthetic substances, such as ‘biocides’ (pesticides, herbicides, insecticides, fungicides, et cetera) , are solely man-made.

Figure 2 Sources and pathways into surface waters (adopted from [GD № 28])



P1: Atmospheric Deposition directly to Surface Waters

P4 Interflow, Tile Drainage and Groundwater⁴

P7: Storm Water Outlets, Combined Sewer Overflows and Unconnected Sewers

P10 Industrial Waste Water treated

P13 Natural Background

P2: Erosion

P5: Direct Discharges and Drifting

P8: Urban Waste Water Treated

P11: Direct Discharges from Mining Areas⁵

P3: Surface Runoff from Unsealed Areas

P6: Surface Runoff from Sealed Areas

P9: Individual - Treated and Untreated-Household Discharges

P12: Direct Discharges from Navigation⁶

3 CIS GUIDANCE DOCUMENTS

Guidance Documents (GD) have been published as part of the Common Implementation Strategy (CIS) to support the (candidate) EU Member States in interpretation and implementation of the WFD. The GD provide comprehensive information about various topics, including monitoring and assessment. It is not possible to summarise the GD without losing relevant details. Therefore, it is recommended to examine the full text for proper understanding. (Unfortunately, the GD are published in the English language only.) This chapter describes the core ingredients of GD related to monitoring the chemical status of surface water bodies.

3.1 № 7: Monitoring under the Water Framework Directive

This GD was issued in 2003, thus soon after the WFD came into force in the year 2000. The document addresses monitoring of surface water (for all quality elements) and for groundwater. In those years, EU Member States were still trying to get better understanding about the WFD as such, including its implications for monitoring. According to the timetable for then EU Member States, monitoring programmes had to be established by the year 2006.

GD № 7 is a rather generic document, especially useful for getting a better conceptual understanding of WFD's requirements and implications for monitoring.

3.2 № 19: Guidance on Surface Water Chemical Monitoring under the Water Framework Directive

This GD was issued in 2009, when Member States had more practical experience with monitoring design under the WFD. The title already indicates that this document focusses on “... *monitoring of the WFD priority substances, other specific pollutants and all other chemical parameters relevant in the assessment of the ecological or chemical status of a water body or in the assessment of programmes of measures*”.

This GD will not answer all questions that could be raised in conjunction with chemical monitoring of surface water, but provides many practical examples and relevant notices regarding various parts of the monitoring cycle.

Laboratory experts will definitely appreciate the Substance Guidance Sheets in Annex II of this GD. These sheets address several aspects relevant for laboratory analyses of the 33 PSs that were defined in that period.

3.3 № 25: On Chemical Monitoring of Sediment and Biota under the Water Framework Directive

The Directive 2013/39/EU provides mainly EQSs for water, although this is not always the preferred sampling matrix.⁹ So-called hydrophobic substances do not easily dissolve in water and rather adsorb on suspended particulate matter (and through this can accumulate in sediment); also, they can accumulate in tissues of biota. The Directive 2013/39/EU mentions that “*Some very hydrophobic substances accumulate in biota and are hardly detectable in water even using the most advanced analytical techniques.*” Implying that certain PSs can be present in the aquatic environment, but might not be detected via the analysis of water samples. Sediment, suspended particulate matter (SPM) and/or biota would be a better sample matrix for analysis of those hydrophobic substances.

This GD provides much information about the considerations for, as well as the implementation of, monitoring PSs based on sediment, SPM and/or biota samples.

3.4 № 27: Technical Guidance for Deriving Environmental Quality Standards

This GD addresses the derivation of environmental quality standards for water, sediment and biota. It is quite a technical document with many details, addressing a complex matter.

It will not be necessary to read this GD when designing chemical status monitoring programmes. After all, the EQSs for the Priority substances have already been defined (in the Directive 2013/39/EU).

3.5 № 28: Technical Guidance on the Preparation of an Inventory of Emissions, Discharges and Losses of Priority and Priority Hazardous Substances

Reading this GD is definitely recommended in conjunction with the issue about determining which PSs are discharged in the sub-basin. Besides providing pointers to desk-based research, the document also contains useful principles for designing, inter alia, investigative monitoring campaigns (refer also to chapter 7 further below).

There are not many details about PSs themselves in this GD. For this kind of information, the so-called ‘*Substance source screening sheets*’ are more useful. The ‘*Substance source screening sheets*’ are published on the CIRCABC site (refer to footnote 3 in Chapter 1) and also briefly described in “*Guidance Document addressing Chemical Status of Surface Water Bodies for a Pressure-Impact Analysis/Risk Assessment according to the EU WFD*” [Buijs, 2014], briefly describing approaches for identifying potentially relevant PSs.

⁹ “Matrix” means a compartment of the aquatic environment, namely water, sediment or biota

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№ 32 and № 33, Biota Monitoring

Two GDs have been published quite recently on biota monitoring:

- № 32: On Biota Monitoring (the Implementation of EQS_{biota}) under the Water Framework Directive
- № 33: On Analytical Methods for Biota Monitoring under the Water Framework Directive

GD 32 provides useful information for designing surface water monitoring programme with inclusion of biota. GD 32 focuses more on the further chemical laboratory analysis of the biota samples.

4 SAMPLE MATRIX

4.1 Matrix

The EQs in the Directive 2013/39/EU apply mainly to concentrations in water; for some PSs, furthermore EQs in biota are included (refer to Annex 1 for further details). Water is though not the optimal sampling matrix for the so-called hydrophobic micropollutants. Hydrophobic micropollutants do not easily dissolve in water and rather absorb to suspended particulate matter (and via this accumulating in sediment) and/or to accumulate in tissues of biota. The Directive 2013/39/EU mentions that *“Some very hydrophobic substances accumulate in biota and are hardly detectable in water even using the most advanced analytical techniques.”*

Annex 2 of this document provides an overview of the preferred monitoring matrix of the 33 PSs that were included in the Directive 2008/105/EC. Table 1 lists the PSs that are explicitly mentioned in the Directive 2013/39/EU as tending to accumulate in sediment/biota.

Table 1 PSs tending to accumulate in sediment/biota [adapted from the Directive 2013/39/EU]

No	Name of substance	No	Name of substance
2	Anthracene	28	Polyaromatic hydrocarbons (PAH)
5	Brominated diphenylethers		Benzo(a)pyrene
6	Cadmium and its compounds		Benzo(b)fluoranthene
7	C10-13 Chloroalkanes)		Benzo(k)fluoranthene
12	Di(2- ethylhexyl)- phthalate (DEHP)		Benzo(g,h,i)perylene
15	Fluoranthene		Indeno(1,2,3- cd)pyrene
16	Hexachlorobenzene	30	Tributyltin compounds (tributyltin- cation)
17	Hexachlorobutadiene	34	Dicofol
18	Hexachlorocyclohexane	35	Perfluorooctane sulfonic acid and its derivatives (PFOS)
20	Lead and its compounds	36	Quinoxifen
21	Mercury and its compounds	37	Dioxins and dioxin-like compounds
26	Pentachlorobenzene	43	Hexabromocyclododecane (HBCDD)
		44	Heptachlor and heptachlor epoxide

Another advantage of sediment, suspended particulate matter (SPM) or biota samples is that they give a better indication of the overall pollution over time. Water samples are normally taken as ‘grab samples’ with monthly or seasonally frequencies. With such spot samples, there is a risk of not detecting certain pollutants if they are not discharged continuously either concentrations vary significantly over time.

It is important to keep in mind that hydrophobic PSs are not easily determined in water samples, even if they are present in the aquatic environment. Implications are, for example, that monitoring

and surveys solely based on water samples may not provide with sufficient field data for determining the presence of certain PSs.

4.2 Water

While acknowledging the limitations regarding hydrophobic PSs, water remains the most commonly used matrix for sampling and analysis of pollutants. In order to be able to compare the results with the EQSs of the Directive 2013/39/EU, several aspects should be taken into consideration.

4.2.1 Total or dissolved concentration?

The Directive 2013/39/EC mentions the following about the EQS:

“The water EQS laid down in this Annex are expressed as total concentrations in the whole water sample.

By way of derogation from the first subparagraph, in the case of cadmium, lead, mercury and nickel (hereinafter “metals”), the water EQS refer to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0.45 µm filter or any equivalent pre-treatment, or, where specifically indicated, to the bioavailable concentration.”

Thus, depending on whether the water samples are to be analysed for metals either for organic micropollutants, they have to be filtered or not in order to assess the results of the laboratory analysis against the EQSs of the Directive 2013/39/EU.

Water samples for heavy metals are usually put in polyethylene bottles, whereas for organic micropollutants glass bottles are recommended.¹⁰ So, from this point of view this requirement whether or not to filter should not lead to confusion.

Textbox 1: Indicative percentage dissolved concentration of some heavy metals

The table below gives an indication of the percentage of metals dissolved in unfiltered water samples, based on average conditions determined in Dutch surface waters and a suspended solids concentration of 30 mg/l.

Metal	Percentage dissolved
Ni	81%
As	77%
Cu	40%
Zn	23%
Cd	20%
Hg	16%
Cr	10%
Pb	5%

¹⁰ Note though that glass either teflon coated bottles prevail for water samples for mercury analysis. However, normally this will be different bottles from the ones used for analysis on organic micropollutants.

The table indicates that, for example, nickel (Ni) would largely be in the dissolved phase in unfiltered surface water samples, whereas lead (Pb) would mainly be absorbed to the suspended solids (including organic matter). Therewith, the difference between total (unfiltered) and dissolved (filtered) surface water samples would normally be much larger for a metal like lead (Pb) compared to a metal like nickel (Ni).

4.2.2 Filtration and preservation

The recommended pre-treatment of samples to be analysed of the dissolved metal fraction is to:

- 1) Filter the sampled water in the field over a 0.45 μ mesh filter.
- 2) Preserve the filtered water sample with nitric acid (HNO₃).

Filtration in the field requires staff well trained in using the equipment, reagents and method, in order to avoid contamination. A 'false positive' due to contamination can have far reaching impacts, especially with the low concentrations of the EQSs of the Directive 2013/39/EU.

In case of doubt, it could be decided not to filter the sample in the field, but in the laboratory, where conditions are better under control. However, this would only be an option when the samples can be returned to the lab and filtered on a short term (in principle on the same day of sampling). Meanwhile, the samples should be stored in a cool and dark environment.

The preservation agent should only be added after filtration, since HNO₃ can leach metals from the SPM. In case the laboratory has already added HNO₃ in the sample bottles in the laboratory in advance, then filtration in the field is inevitable when dissolved metal concentrations are to be determined.

4.2.3 Supporting Surface Water Quality Parameters

Information about other water quality parameters is required for proper interpretation of the results.

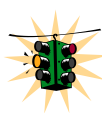
- **Hardness.** The EQSs for 'cadmium and its compounds' vary depending on the hardness of the water (refer to Annex 1 for details). Therefore, the hardness of the sampled water (in mg/l CaCO₃) has to be determined as well.
- **Suspended particulate matter.** The amount of SPM could affect the total concentration of the more hydrophobic micropollutants analysed in unfiltered water samples. After all, with pollutants absorbed to the SPM, their concentration in unfiltered samples can vary simply with the amount of SPM in the sample.

4.2.4 Sampling

In principle, the requirements for taking water samples for the analysis on PSs are not different from the overall requirements, like for example described in ISO 5667-1:2006: *Water quality - Sampling - Part 1: Guidance on the design of sampling programmes and sampling techniques*, and ISO 5667-3:2012: *Water quality - Sampling - Part 3: Preservation and handling of water samples*.

However, avoiding contamination becomes even more important with the generally very low concentrations of the EQSs.

One PS requires some specific attention: di(2-ethylhexyl)phthalate (DEHP). Phthalates are mainly used as plasticizers (substances added to plastics to increase their flexibility, transparency, durability, and longevity). This underlines the importance of using stainless steel buckets for taking water samples to be analysed on organic micropollutants (whereas polyethylene buckets, without artificial colouring, are used for samples to be analysed heavy metals). Obviously, samples to be analysed on phthalates should not be put in polyethylene bottles. As generally recommended for organic micropollutants, glass bottles, either bottles with teflon coating, are to be used. Generally, it is not easy to 'avoid contact with plastic' even in the laboratory.



Refer to Chapter 5: TECHNIQUES FOR SAMPLING in the CIS Guidance Document № 19 Guidance on Surface Water Chemical Monitoring under the Water Framework Directive for more details on sampling.

4.3 Sediment

Sediment is one of the matrices more suitable for sampling and analysis for hydrophobic substances. Generally, it is less complicated to take sediment samples when compared to SPM or biota. Sediment sampling is, however, not without its own peculiarities.

One disadvantage of sediment samples is that neither the Directive 2013/39/EU, nor other EU regulations, provide with EQSs for PSs in sediment. Thus, how to assess the concentrations of PSs detected in a sediment sample?

- a) The absence of hydrophobic PSs in sediment gives at least a reasonable indication about them not being 'discharged' in the connected (sub-)basin. This is important information, for example for the pressure-impact analysis.
- b) Some countries have developed EQSs for substances in sediment, although probably not covering all relevant PSs. Comparison with such EQSs can be helpful in the interpretation of the results, including taking decisions whether follow-up investigations and studies might be needed.

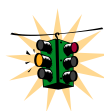
Some general considerations should be taken into account for taking sediment samples.

- Micropollutants adsorb to the smaller suspended particles, with the organic matter/carbon content also being relevant. Therewith, the grain size composition of the sediment sample can already affect the results. In order to obtain more standardised sediment material for laboratory analysis, wet sieving the sediment over a 63 µm mesh sieve is common practise.
- It can be difficult to distinguish 'historic pollution' from 'actual pollution'. Depending on, among other things, the sampling device, the rate of sedimentation and possible disturbance of sediment layers, the sample might contain more recently sedimented SPM, sediment that was formed decades ago, either a mix of both. Several PSs are among the group of

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'persistent organic pollutants' (POP); substances that only slowly degrade after being released into the environment. When for example DDT is found in the sediment sample, then this does not necessarily mean that it is still being (illegally) used. It could well be that the sample contains sediment that was deposited in the 1980-ies.

- Laboratory analysis of pollutants in sediment requires additional (pre-treatment) steps that do not apply for the analysis of water samples.



	Refer to Chapter 5. <i>Monitoring of chemical substances in sediment</i> in the CIS Guidance Document № 25 On Chemical Monitoring of Sediment and Biota under the Water Framework Directive for more details about using sediment as sample matrix.
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4.4 Suspended Particulate Matter

The main advantage of SPM over sediment is that it represents more actual pollution; there are less risks for measuring historic pollution, as can be the case with sediment samples. Thus, detecting certain pollutants in SPM gives a reasonable indication that they are (still) being discharged.

The main problem is to collect sufficient SPM for further laboratory analysis. About 300 – 400 grams (dry weight) of SPM is recommended for analysis of pollutants. For surface waters with SPM concentrations of e.g. 50 mg/l this would be equivalent to a volume of 6 – 7 m³. SPM samples are normally obtained with flow-through centrifuges. Centrifuges are though rather expensive and cannot flexibility be deployed in the field.

Another disadvantage is the lack of EQSs for PSs in suspended particulate matter agreed at a European level (such EQSs are not necessarily equal to those for sediment).

Also the laboratory analysis of pollutants in SPM requires additional (pre-treatment) steps that do not apply for the analysis of water samples.

4.5 Biota

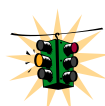
The Directive 2013/39/EU contains EQS for biota for 11 PSs (refer to Annex 1 for further details). The majority concerns EQS_{biota} derived for 'fish', except for the polyaromatic hydrocarbons (PAH), for which crustaceans and molluscs are listed.

Advantages of using biota as matrix for analysis on PSs include, among other things:

- Presence in tissue of biota may indicate pollution at levels too low to be detected in water, sediment or SPM.
- When aiming at protection of aquatic species (with human beings eating some of them) against pollution with PSs, this provides the most direct way of measurements.

Disadvantages include, *inter alia*:

- Monitoring and assessment of biota requires special programmes.
- Analysis of pollutants in biota needs special laboratory techniques, including the pre-treatment of the samples. The overall laboratory requirements are equally demanding as the analysis of PSs in water or sediment samples (compare also Chapter 5).
- With migrating fish it might be difficult to relate the findings to the areas/locations where the substances would be discharged.



For details about using biota as sample matrix, readers are referred to the following CIS Guidance Documents:

- № 25: On Chemical Monitoring of Sediment and Biota under the Water Framework Directive
- № 32: On Biota Monitoring (the Implementation of EQS_{biota}) under the Water Framework Directive
- № 33: On Analytical Methods for Biota Monitoring under the Water Framework Directive

4.6 Passive sampling

The Directive 2013/39/EU mentions “*Novel monitoring methods such as passive sampling and other tools show promise for future application, and their development should therefore be pursued.*” Using semi-permeable membranes is one example of passive sampling techniques. The membrane remains submerged in the water for a certain duration and, due to its characteristics, will absorb certain pollutants, including hydrophobic substances. Advantages are clear: the ‘sampling’ itself requires little effort and a wide range of organic micropollutants – dissolved in water – can be sampled, with the findings reflecting recent pollution. The techniques are not yet sufficiently developed for formulating related EQSs, but can be very useful for identification purposes.

5 LABORATORY ANALYSIS

Laboratory analysis of the PSs requires sophisticated analytical equipment and methods. Their EQSs furthermore challenge the concentration levels that can be analysed with existing techniques. For several PSs it is known that the EQSs defined in the Directive 2013/39/EU are too low concentrations for reliable analysis with existing methods.

5.1 Limit of Detection and Quantification

The Directive 2009/90/EC *laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status*, stipulates various requirements for laboratories and laboratory analysis.

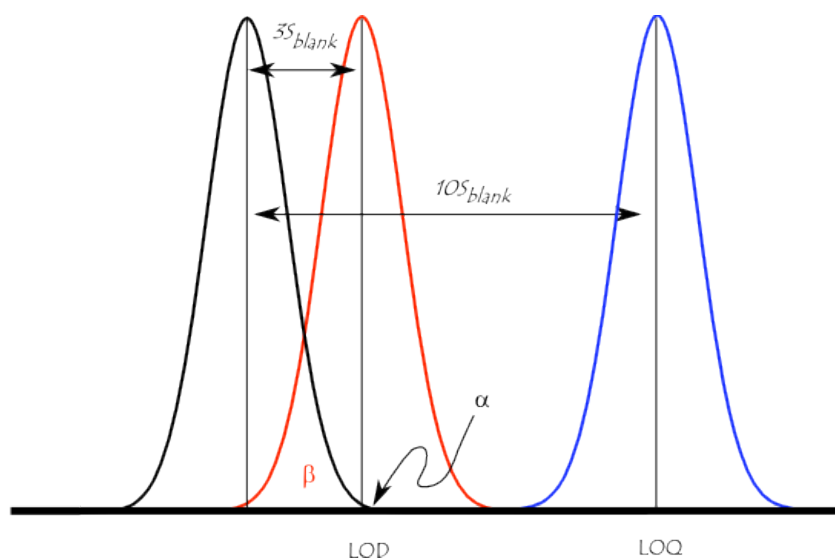
One of these requirements concerns the limit of quantification (LOQ), in the Directive 2009/90/EC defined as *“a stated multiple of the limit of detection at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, excluding the blank”*.

Directive 2009/90/EC, Article 4: Minimum performance criteria for methods of analysis, stipulates that *“Member States shall ensure that the minimum performance criteria for all methods of analysis applied are based on ... a limit of quantification equal or below a value of 30 % of the relevant environmental quality standards.”* For example, the AA-EQS for ‘Lead and its compounds’ is 1.2 µg/l, hence the LOQ should be $1.2 * 0.3 = 0.4$ µg/l or better.

The concept of limit of quantification is not yet widely used in the EPIRB project’s countries. Here, the laboratories are more familiar with the limit of detection (LOD), defined in the Directive 2009/90/EC as *“the output signal or concentration value above which it can be affirmed, with a stated level of confidence that a sample is different from a blank sample containing no determinand of interest”*.

Figure 3 gives an illustration of the concept of detection limit and quantitation limit by showing the theoretical normal distributions associated with blank, detection limit, and quantification limit level samples.¹¹

¹¹ Refer to http://en.wikipedia.org/wiki/Detection_limit for further details.

Figure 3 Illustration of the concept of LOD and LOQ¹²

From Figure 3, one can derive that $LOQ = 10/3 = 3.3 * LOD$. Hence, the requirement of a $LOQ = 0.3 * EQS$ implies a $LOD = 0.09 * EQS$.

In the example of the AA-EQS for 'Lead and its compounds' of $1.2 \mu\text{g/l}$, one can derive that the:

- $LOQ = 0.3 * 1.2 = 0.36 \mu\text{g/l}$;
- $LOD = 0.3 * LOQ = 0.3 * 0.36 = 0.11 \mu\text{g/l}$.

Thus, the required LOD can be approximately estimated as being better than 10% of the EQS. Hence, the required LODs for analysis of the PSs can be derived from the Directive 2013/39/EU (also refer to Annex 1 of this document).

5.2 Equipment and Methods

Table 2 gives an overview of the laboratory equipment used for analysis of the *Priority substances and certain other pollutants*. Additional details can be found in Annex 3, which also enumerates the recommended EN/ISO standards for analysis.

It is though important to notice that this information does not include the PSs that were added with the Directive 2013/39/EU. The recommended methods of analysis for these PSs are still being reviewed. Therefore, it is recommended to visit the EU CIRCABC website (see footnote 3 above for details) regularly for updates.

¹² Adapted from http://en.wikipedia.org/wiki/Detection_limit

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Table 2 Inventory of equipment required for analysis of WFD Priority substances¹³

Group of substances	Analytical equipment
heavy metals	<ul style="list-style-type: none"> • inductively coupled plasma mass spectrometer (ICP-MS), either Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES); • atomic absorption spectrometer (AAS), graphite furnace/flame; • atomic fluorescence spectrometer (AFS); recommended <i>for analysis of mercury (Hg)</i>
organic micropollutants	<ul style="list-style-type: none"> • gas chromatograph (GC) with ^(*) <ul style="list-style-type: none"> ○ atomic emission detector (GC-AED) ○ electron capture detector (GC-ECD) ○ flame ionization detector (GC-FID) ○ mass spectrometer (GC-MS) ○ nitrogen phosphorous detector (GC-NPD) ○ headspace - gas chromatography (headspace - GC) ○ purge-and-trap and thermal desorption - gas chromatography (purge&trap - GC) • high performance liquid chromatograph (HPLC) with: <ul style="list-style-type: none"> ○ ultra-violet detection (HPLC-UV); ○ fluorescence detection (HPLC-FD).

(*) Various detectors and samplers can be combined with one GC, but having two or more GCs prevails; similar considerations apply to HPLC.

¹³ Compiled on the basis of the [GD 19], ANNEX II: Substance Guidance Sheets.

6 ASSESSMENT

The major criteria for assessment of the chemical status were mentioned already in section 2.2. A surface water body is of 'good chemical' status if the concentrations of the PSs are in compliance with the EQSs mentioned in the related Directive in force. In case the concentration of even one PS exceeds the EQSs, then the surface water fails to meet good chemical status, therewith qualifying the surface water body as failing to meet 'good status'.

6.1 Natural background concentrations

The Directive 2013/13/EU mentions that:

Member States may, when assessing the monitoring results against the relevant EQS, take into account:

(a) natural background concentrations for metals and their compounds where such concentrations prevent compliance with the relevant EQS;

In principle, it could happen that natural metal concentrations are already equal to or even higher than the AA-EQS. Since natural background concentrations represent (type-specific) reference conditions, this actually means that this reflects 'high status'. In this situation the concentrations are not caused by anthropogenic pressures, so have basically not to be 'solved' via a programme of measures.

Therefore, it is important to determine the natural background concentrations of the metals, which furthermore can be type/region-specific, and take this into consideration when assessing the monitoring data.

Textbox 2: "Added risk"

One way for dealing with elevated natural background concentrations could be the so-called "added risk" approach that is applied in the Netherlands.

EQSs are often established on the basis of laboratory research in a clean environment with background concentrations being zero. Thus, implicitly, adverse effects are determined (extrapolated) to start happening at a certain concentration, increased compared to zero.

In the "added risk" approach, it is assumed that adverse (toxic) effects can occur when concentration are elevated to a certain level, *on top of the natural background concentration*. It is not the absolute concentration level, but the concentration in addition to the background level, where adverse effects can happen.

Take for example the AA-EQS for lead, which is 1.2 µg/l and let's assume a natural background concentration of 0.5 µg/l. Under the "added risk" approach, the critical level is not 1.2 µg/l, but $0.5 + 1.2 = 1.7$ µg/l.

6.2 Bioavailability

The Directive 2013/13/EU mentions furthermore that:

Member States may, when assessing the monitoring results against the relevant EQS, take into account:

... (b) hardness, pH, dissolved organic carbon or other water quality parameters that affect the bioavailability of metals, the bioavailable concentrations being determined using appropriate bioavailability modelling.'

Also notice footnote 13 for the AA-EQSs for lead and nickel: *"These EQS refer to bioavailable concentrations of the substances."* (refer to Annex 1 of this document).

The AA-EQSs for 'cadmium and its compounds' can be considered as an example where EQSs have been differentiated on the basis of the water hardness.

However, from the Directive itself it becomes not clear how to address such additional conditions for lead and nickel. While using their AA-EQSs for the initial assessments, it might though be important to verify (e.g. via consulting other experts or international platforms) to which extent interpretation of the results might have to be amended.

6.3 MAC-EQS, percentile

In conjunction with the MAC-EQS, the Directive 2013/39/EU mentions that *"... However, in accordance with Section 1.3.4 of Annex V to Directive 2000/60/EC, Member States may introduce statistical methods, such as a percentile calculation, to ensure an acceptable level of confidence and precision for determining compliance with the MAC-EQS ..."*

Using the 90 or 95-percentile value for compliance checking, rather than the maximum concentration, is one way to deal with outliers (extreme deviations from the mean) and false readings. Therefore, applying this option should definitely be taken into consideration.

7 MONITORING DESIGN

Designing programmes for monitoring chemical status of surface water bodies follows largely the general principles and requirements for surface water monitoring programmes under the WFD. Some more specific are highlighted in this chapter.

7.1 Surveillance monitoring

WFD Annex V. 1.3.1: *Design of surveillance monitoring* mentions, among other things, the following regarding the selection of quality elements: "... *priority list pollutants which are discharged into the river basin or sub-basin.*" It can, however, be quite complicated to determine whether or not certain PSs are indeed discharged, as mentioned in section 2.3.

The objectives of surveillance monitoring programmes include:

- supplementing and validating the impact assessment;
- the efficient and effective design of future monitoring programmes.

These objectives could actually be used for obtaining more information about the presence/absence of PSs. Taking samples at strategically chosen locations during one year of surveillance monitoring can provide with valuable data regarding possible pollution with PSs. By taking monthly water samples (indicated by WFD Annex V.1.3.4: Frequency of monitoring), a reasonable picture could be derived for at least those PSs where water is an appropriate sample matrix (refer to section 4.1 and Annex 2).

One or two sediment samples will suffice during one year of surveillance monitoring. Identification of potentially relevant PSs would be the major purpose of this exercise. Even though EQSs for sediment might be lacking, the results can at least give more information about the presence/absence of the more hydrophobic PSs.

7.2 Operational monitoring

The implications of WFD V.1.3.2: *Design of operational monitoring* are that all priority substances discharged into the water bodies concerned have to be monitored, at least those PSs that lead to (the risk of) failing to meet good chemical status. In principles, water samples are to be analysed monthly throughout all six years of the river basin management planning period.

7.3 Investigative monitoring

The surveillance monitoring proposed in section 7.1 could provide a broader picture more systematically, whereas investigative monitoring can be used for obtaining field data in certain areas of specific interest. Of course, not only surface water or sediment samples will be of interest. Also analysing PSs in wastewater discharges is strongly recommended.

8 STRATEGIES FOR INTRODUCTION IN WESTERN EECCA COUNTRIES

One of the key challenges for monitoring the chemical status is establishing the laboratory capacity for analysis of the (whole range of) Priority substances, with limits of detection sufficiently low for a reliable assessment against their EQSs (refer also to Chapter 5). Laboratory requirements for analysis of the *'Priority substances and certain other pollutants'* include:

- modern analytical equipment;
- certified reference material plus many other reagents and consumables;
- EN/ISO standards for analysis methods;
- an operation in accordance with EN ISO/IEC-17025;
- sufficient and experienced staff;
- budgets for operation and maintenance.

Clearly, this implies that countries have access to considerable (financial) resources, which is unfortunately not the case for EPIRB beneficiary countries. The capacity of the laboratories, used for analysis of the samples taken under the routine monitoring programmes, varies among these countries; some laboratories are better equipped than the others. All these laboratories have though an AAS and a GC-MS, equipment that can be used for analysis needed for several PSs (compare also Chapter 5 and Annex 3).

The EPIRB project has prepared a series of documents with strategies for introduction of WFD-compliant monitoring and assessment of water bodies in the beneficiary countries. Enhancing laboratory capacities is one of the topics addressed in those documents, including indicative estimates of the potential financial ramifications. Readers interested in those details are referred to these Monitoring Strategy documents.

Meanwhile, how to continue? Considerations for optimally using existing capacities are briefly discussed in the sections below.

8.1 Regulatory context

It is important to stress that the Directive 2013/39/EU has no mandatory implications yet for any of the beneficiary countries. (Notice though that *"Establishment of programmes for monitoring water quality in accordance with Article 8 of the WFD"* is one of the commitments of the Association Agreements between the EU and Georgia, Moldova, and Ukraine.) Therewith, the list with PSs and their EQSs may be regarded more like benchmarks for further developments.¹⁴

¹⁴ There is nothing 'WFD-specific' about the EQSs as such. The concentrations have been derived from thorough (ecotoxicological) research and are aimed at safeguarding both the aquatic environment, as well as the human beings who are using this environment.

8.2 Limit of detection

During the Joint Field Surveys in the Pilot River Basins, organised under the EPIRB project, surface water samples were analysed for selected number of PSs, including cadmium, lead, mercury, nickel, DDT, hexachlorobenzene and lindane (note that not all substances were analysed in all laboratories). In many cases, the requirement of the LOD being better than 10% of the EQS could not be achieved, notably regarding the AA-EQSs (compare also section 5.1). Generally, the following situations could be distinguished:

- a) *LOD higher than the EQSs.* One batch of samples was analysed for cadmium with a LOD of 5 µg/l. This LOD is simply too high for assessment against the EQSs of the Directive 2013/39/EU and cannot provide with any relevant environmental information.¹⁵
- b) *LOD higher than the AA-EQS, but about 10% of the MAC-EQS.* One of the laboratories reported LOD for lead of 0.5 µg/l. Such a LOD is basically too high for a reliable assessment against the AA-EQS for inland waters of 1.2 µg/l, but definitely adequate for an assessment against the MAC-EQS of 14 µg/l. This can provide with already relevant information, since one concentration over 14 µg/l (in a series of –monthly– data) in principle implies a failure to meet good chemical status.
- c) *LOD near the AA-EQS.* The LOD represents a tricky area. A value just above the LOD indicates the presence of the pollutant, but there is still much (statistical) uncertainty about its concentration. For example, with a LOD of 1 µg/l, readings of 2 - 3 µg/l are not yet very accurate, since they are still in the range of (statistical) uncertainty around LOD levels (compare also Figure 3 in section 15). Some environmentally relevant information might be derived from this kind of results, but generally they are not sufficiently robust for compliance checking.
- d) *LOD closer to 0.1 * AA-EQS.* If, for example, the LOD is something like 20% or 30% of the EQS, is this still insufficient? When referring to the Directive 2009/90/EC, then the answer would be “No” (compare also section 5.1). However, this does not mean that such data are not useful. The basic idea behind the Directive 2009/90/EC requiring a LOQ equal to or better than 30% of the EQS is to better guarantee robust data for compliance checking; the lower the LOD/LOQ, the better. Vice versa, the closer the LOD gets to the EQS, the less strong the conclusions that can be derived from the data.

So, in case the objective of the sampling and analysis is to make comparisons with the EQSs of the Directive 2013/39/EU, then it is recommended to investigate in advance how good the LODs of the laboratory will compare to them. Too high LODs are a decent argument to skip analysis of the substances concerned, thus not only saving money, but also avoiding the risks for receiving inaccurate data.

¹⁵ Actually, such LOD for cadmium is not adequate for ambient water monitoring in general.

8.3 Water sampling frequencies

For PSs, monthly sampling is indicated in WFD Annex V.1.3.4: Frequency of monitoring, both for surveillance as well as operational monitoring. Analysis of micropollutants is quite expensive, so monthly water sampling and analysis of PSs could lead to substantial budgetary demands. Considering that the financial resources in the beneficiary countries are limited, the following might be considered.

- Surveillance monitoring can be used, among other things, for assessing the presence/absence of PSs. In principle, such monitoring would be conducted at a 'limited number' of locations during one year in a planning period (which is six years under the WFD). Monthly water sampling is strongly recommended for obtaining robust series of data; after all, important conclusions are drawn from the results. With lower sampling frequencies, there are furthermore risks of not capturing certain seasonally used PSs (e.g. pesticides). With more data, also possible peak concentrations/outliers can be pinpointed better.
- For operational monitoring, analysis of one water sample per two months might be a reasonable compromise, albeit not ideal.
- Analysis of water samples once per season would be a bare minimum, for both surveillance and operational monitoring.

8.4 Identification of discharged PSs: egg and chicken

The PSs comprise a heterogeneous group of substances that in many cases cannot be linked to single sources (section 2.3). Field data will provide the most solid basis for determining which PSs are indeed being discharged, but this requires sophisticated laboratories, analysis of PSs in various matrices (water, SPM, sediment, biota), and sufficient human and financial resources. Obviously, this is not the case in the project's beneficiary countries.

Meanwhile, much information has been obtained during the preparation and implementation of the WFD.¹⁶ Furthermore, the EPIRB project issued a concise Guidance Document addressing Chemical Status of Surface Water Bodies for a Pressure-Impact Analysis/Risk Assessment according to the EU WFD [Buijs, 2014]. The range of possibly discharged PSs could be narrowed down on the basis of desk studies, but finally verification in the field will still be needed.

The 'egg-and-chicken' situation can be described as follows. The results of the desk study could indicate that certain PSs may or may not be discharged. More desk studies will not help in solving the problem, so field measurements will have to give the decisive answer. But, what to do in case this means that the laboratory would have to purchase a new piece of (expensive) equipment plus the necessary consumables, and to train its staff in new methods of analysis? Quite some investments,

¹⁶ The Library section of the WFD CIRCA: "Implementing the Water Framework Directive and the Floods Directive" one of the places start; refer to footnote 3 in Chapter 1 for details.

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while one is not even sure whether the substance is indeed in the aquatic environment (and at levels exceeding the EQSs).

One option would be to outsource analysis of samples to a competent laboratory, preferably inside the country (if available), or otherwise to a laboratory abroad. This will also not be cheap, but might finally save money in case it turns out that certain PSs are most likely not discharged and therewith do not have to be analysed.

References

- Buijs, Paul (2014) Guidance Document addressing Chemical Status of Surface Water Bodies for a Pressure-Impact Analysis/Risk Assessment according to the EU WFD. *EPIRB project document, July 2014.*
- GD 7 CIS Guidance Document 7 Monitoring under the Water Framework Directive.
[https://circabc.europa.eu/sd/a/63f7715f-0f45-4955-b7cb-58ca305e42a8/Guidance%20No%207%20-%20Monitoring%20\(WG%202.7\).pdf](https://circabc.europa.eu/sd/a/63f7715f-0f45-4955-b7cb-58ca305e42a8/Guidance%20No%207%20-%20Monitoring%20(WG%202.7).pdf)
- GD 19 CIS Guidance Document No. 19 Guidance on Surface Water Chemical Monitoring under the Water Framework Directive
<https://circabc.europa.eu/sd/d/e54e8583-faf5-478f-9b11-41fda9e9c564/Guidance%20No%2019%20-%20Surface%20water%20chemical%20monitoring.pdf>
- GD 25 CIS Guidance Document 25 On Chemical Monitoring of Sediment and Biota under the Water Framework Directive.
<https://circabc.europa.eu/sd/a/7f47ccd9-ce47-4f4a-b4f0-cc61db518b1c/Guidance%20No%2025%20-%20Chemical%20Monitoring%20of%20Sediment%20and%20Biota.pdf>
- GD 27 CIS Guidance Document 27: Technical Guidance for Deriving Environmental Quality Standards
<https://circabc.europa.eu/sd/a/0cc3581b-5f65-4b6f-91c6-433a1e947838/TGD-EQS%20CIS-WFD%2027%20EC%202011.pdf>
- GD 28 CIS Guidance Document 28: Technical Guidance on the Preparation of an Inventory of Emissions, Discharges and Losses of Priority and Priority Hazardous Substances.
<https://circabc.europa.eu/sd/a/6a3fb5a0-4dec-4fde-a69d-5ac93dfbbadd/Guidance%20document%20n28.pdf>
- GD 32 CIS Guidance Document 32: On Biota Monitoring (the Implementation of EQS_{biota}) under the Water Framework Directive.
<https://circabc.europa.eu/sd/a/62343f10-5759-4e7c-ae2b-12677aa57605/Guidance%20No%2032%20-%20Biota%20Monitoring.pdf>
- GD 33 CIS Guidance Document 33: On Analytical Methods for Biota Monitoring under the Water Framework Directive.
<https://circabc.europa.eu/sd/a/9cf535ba-14f2-4f0f-b75e-e334ad506caf/Guidance%20No%2033%20-%20Analytical%20Methods%20for%20Biota%20Monitoring.pdf>

Annex 1 Environmental Quality Standards for Priority Substances and certain other Pollutants

The table below contains the Environmental Quality Standards for Priority Substances and certain other Pollutants included in Annex II of the DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 August 2013 *amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.*

The water EQS laid down in this Annex are expressed as total concentrations in the whole water sample.

In the case of cadmium, lead, mercury and nickel (hereinafter “metals”), the water EQS refer to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0.45 µm filter or any equivalent pre-treatment, or, where specifically indicated, to the bioavailable concentration.

Member States may, when assessing the monitoring results against the relevant EQS, take into account: (a) natural background concentrations for metals and their compounds where such concentrations prevent compliance with the relevant EQS; (b) hardness, pH, dissolved organic carbon or other water quality parameters that affect the bioavailability of metals, the bioavailable concentrations being determined using appropriate bioavailability modelling.’;

ANNEX II

ANNEX I

ENVIRONMENTAL QUALITY STANDARDS FOR PRIORITY SUBSTANCES AND CERTAIN OTHER POLLUTANTS

PART A: ENVIRONMENTAL QUALITY STANDARDS (EQS)

AA: annual average.

MAC: maximum allowable concentration.

Unit: [µg/l] for columns (4) to (7)

[µg/kg wet weight] for column (8)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
No	Name of substance	CAS number ⁽¹⁾	AA-EQS ⁽²⁾ Inland surface waters ⁽³⁾	AA-EQS ⁽²⁾ Other surface waters	MAC-EQS ⁽⁴⁾ Inland surface waters ⁽³⁾	MAC-EQS ⁽⁴⁾ Other surface waters	EQS Biota ⁽¹²⁾
(1)	Alachlor	15972-60-8	0.3	0.3	0.7	0.7	
(2)	Anthracene	120-12-7	0.1	0.1	0.1	0.1	
(3)	Atrazine	1912-24-9	0.6	0.6	2.0	2.0	

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(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
No	Name of substance	CAS number ⁽¹⁾	AA-EQS ⁽²⁾ Inland surface waters ⁽³⁾	AA-EQS ⁽²⁾ Other surface waters	MAC-EQS ⁽⁴⁾ Inland surface waters ⁽³⁾	MAC-EQS ⁽⁴⁾ Other surface waters	EQS Biota ⁽¹²⁾
(4)	Benzene	71-43-2	10	8	50	50	
(5)	Brominated diphenylethers ⁽⁵⁾	32534-81-9			0.14	0.014	0.0085
(6)	Cadmium and its compounds (depending on water hardness classes) ⁽⁶⁾	7440-43-9	≤ 0.08 (Class 1) 0.08 (Class 2) 0.09 (Class 3) 0.15 (Class 4) 0.25 (Class 5)	0.2	≤ 0.45 (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)	≤ 0.45 (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)	
(6a)	Carbontetrachloride ⁽⁷⁾	56-23-5	12	12	not applicable	not applicable	
(7)	C10-13 Chloroalkanes ⁽⁸⁾	85535-84-8	0.4	0.4	1.4	1.4	
(8)	Chlorfenvinphos	470-90-6	0.1	0.1	0.3	0.3	
(9)	Chlorpyrifos (Chlorpyrifos- ethyl)	2921-88-2	0.03	0.03	0.1	0.1	
(9a)	Cyclodiene pesticides: Aldrin ⁽⁷⁾ Dieldrin ⁽⁷⁾ Endrin ⁽⁷⁾ Isodrin ⁽⁷⁾	309-00-2 60-57-1 72-20-8 465-73-6	Σ = 0.01	Σ = 0.005	not applicable	not applicable	
(9b)	DDT total ⁽⁷⁾ , ⁽⁹⁾	not applicable	0.025	0.025	not applicable	not applicable	
	para-para-DDT ⁽⁷⁾	50-29-3	0.01	0.01	not applicable	not applicable	
(10)	1,2-Dichloroethane	107-06-2	10	10	not applicable	not applicable	
(11)	Dichloromethane	75-09-2	20	20	not applicable	not applicable	
(12)	Di(2- ethylhexyl)- phthalate (DEHP)	117-81-7	1.3	1.3	not applicable	not applicable	
(13)	Diuron	330-54-1	0.2	0.2	1.8	1.8	
(14)	Endosulfan	115-29-7	0.005	0.0005	0.01	0.004	
(15)	Fluoranthene	206-44-0	0.0063	0.0063	0.12	0.12	30
(16)	Hexachlorobenzene	118-74-1			0.05	0.05	10
(17)	Hexachlorobutadiene	87-68-3			0.6	0.6	55
(18)	Hexachlorocyclohexane	608-73-1	0.02	0.002	0.04	0.02	
(19)	Isoproturon	34123-59-6	0.3	0.3	1.0	1.0	
(20)	Lead and its compounds	7439-92-1	1.2 ⁽¹³⁾	1.3	14	14	
(21)	Mercury and its compounds	7439-97-6			0.07	0.07	20

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(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
No	Name of substance	CAS number ⁽¹⁾	AA-EQS ⁽²⁾ Inland surface waters ⁽³⁾	AA-EQS ⁽²⁾ Other surface waters	MAC-EQS ⁽⁴⁾ Inland surface waters ⁽³⁾	MAC-EQS ⁽⁴⁾ Other surface waters	EQS Biota ⁽¹²⁾
(22)	Naphthalene	91-20-3	2	2	130	130	
(23)	Nickel and its compounds	7440-02-0	4 ⁽¹³⁾	8.6	34	34	
(24)	Nonylphenols (4-Nonylphenol)	84852-15-3	0.3	0.3	2.0	2.0	
(25)	Octylphenols ((4-(1,1',3,3'-tetramethylbutyl)-phenol))	140-66-9	0.1	0.01	not applicable	not applicable	
(26)	Pentachlorobenzene	608-93-5	0.007	0.0007	not applicable	not applicable	
(27)	Pentachlorophenol	87-86-5	0.4	0.4	1	1	
(28)	Polyaromatic hydrocarbons (PAH) ⁽¹¹⁾	not applicable	not applicable	not applicable	not applicable	not applicable	
	Benzo(a)pyrene	50-32-8	1.7×10^{-4}	1.7×10^{-4}	0.27	0.027	5
	Benzo(b)fluoranthene	205-99-2	see footnote 11	see footnote 11	0.017	0.017	see footnote 11
	Benzo(k)fluoranthene	207-08-9	see footnote 11	see footnote 11	0.017	0.017	see footnote 11
	Benzo(g,h,i)perylene	191-24-2	see footnote 11	see footnote 11	8.2×10^{-3}	8.2×10^{-4}	see footnote 11
	Indeno(1,2,3- cd)pyrene	193-39-5	see footnote 11	see footnote 11	not applicable	not applicable	see footnote 11
(29)	Simazine	122-34-9	1	1	4	4	
(29a)	Tetrachloroethylene ⁽⁷⁾	127-18-4	10	10	not applicable	not applicable	
(29b)	Trichloroethylene ⁽⁷⁾	79-01-6	10	10	not applicable	not applicable	
(30)	Tributyltin compounds (Tributyltin- cation)	36643-28-4	0.0002	0.0002	0.0015	0.0015	
(31)	Trichlorobenzenes	12002-48-1	0.4	0.4	not applicable	not applicable	
(32)	Trichloromethane	67-66-3	2.5	2.5	not applicable	not applicable	
(33)	Trifluralin	1582-09-8	0.03	0.03	not applicable	not applicable	
(34)	Dicofol	115-32-2	1.3×10^{-3}	3.2×10^{-5}	not applicable ⁽¹⁰⁾	not applicable ⁽¹⁰⁾	33
(35)	Perfluorooctane sulfonic acid and its derivatives (PFOS)	1763-23-1	6.5×10^{-4}	1.3×10^{-4}	36	7.2	9.1
(36)	Quinoxifen	124495-18-	0.15	0.015	2.7	0.54	

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(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
No	Name of substance	CAS number ⁽¹⁾	AA-EQS ⁽²⁾ Inland surface waters ⁽³⁾	AA-EQS ⁽²⁾ Other surface waters	MAC-EQS ⁽⁴⁾ Inland surface waters ⁽³⁾	MAC-EQS ⁽⁴⁾ Other surface waters	EQS Biota ⁽¹²⁾
		7					
(37)	Dioxins and dioxin-like compounds	See footnote 10 in Annex X to Directive 2000/60/EC			not applicable	not applicable	Sum of PCDD+PCDF+PCB-DL 0.0065 µg.kg ⁻¹ TEQ ⁽¹⁴⁾
(38)	Aclonifen	74070-46-5	0.12	0.012	0.12	0.012	
(39)	Bifenox	42576-02-3	0.012	0.0012	0.04	0.004	
(40)	Cybutryne	28159-98-0	0.0025	0.0025	0.016	0.016	
(41)	Cypermethrin	52315-07-8	8 × 10 ⁻⁵	8 × 10 ⁻⁶	6 × 10 ⁻⁴	6 × 10 ⁻⁵	
(42)	Dichlorvos	62-73-7	6 × 10 ⁻⁴	6 × 10 ⁻⁵	7 × 10 ⁻⁴	7 × 10 ⁻⁵	
(43)	Hexabromocyclododecane (HBCDD)	See footnote 12 in Annex X to Directive 2000/60/EC	0.0016	0.0008	0.5	0.05	167
(44)	Heptachlor and heptachlor epoxide	76-44-8/1024-57-3	2 × 10 ⁻⁷	1 × 10 ⁻⁸	3 × 10 ⁻⁴	3 × 10 ⁻⁵	6.7 × 10 ⁻³
(45)	Terbutryn	886-50-0	0.065	0.0065	0.34	0.034	

⁽¹⁾ CAS: Chemical Abstracts Service.

⁽²⁾ This parameter is the EQS expressed as an annual average value (AA-EQS). Unless otherwise specified, it applies to the total concentration of all isomers.

⁽³⁾ Inland surface waters encompass rivers and lakes and related artificial or heavily modified water bodies.

⁽⁴⁾ This parameter is the EQS expressed as a maximum allowable concentration (MAC-EQS). Where the MAC-EQS are marked as "not applicable", the AA-EQS values are considered protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute toxicity.

⁽⁵⁾ For the group of priority substances covered by brominated diphenylethers (No 5), the EQS refers to the sum of the concentrations of congener numbers 28, 47, 99, 100, 153 and 154.

⁽⁶⁾ For Cadmium and its compounds (No 6) the EQS values vary depending on the hardness of the water as specified in five class categories (Class 1: <40 mg CaCO₃/l, Class 2: 40 to <50 mg CaCO₃/l, Class 3: 50 to <100 mg CaCO₃/l, Class 4: 100 to <200 mg CaCO₃/l and Class 5: ≥ 200 mg CaCO₃/l).

⁽⁷⁾ This substance is not a priority substance but one of the other pollutants for which the EQS are identical to those laid down in the legislation that applied prior to 13 January 2009.

⁽⁸⁾ No indicative parameter is provided for this group of substances. The indicative parameter(s) must be defined through the analytical method.

⁽⁹⁾ DDT total comprises the sum of the isomers 1,1,1-trichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 50-29-3; EU number 200-024-3); 1,1,1-trichloro-2 (o-chlorophenyl)-2-(p-chlorophenyl) ethane (CAS number 789-02-6; EU Number 212-332-5); 1,1-dichloro-2,2 bis (p-chlorophenyl)

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ethylene (CAS number 72-55-9; EU Number 200-784-6); and 1,1-dichloro-2,2 bis (p-chlorophenyl) ethane (CAS number 72-54-8; EU Number 200-783-0).¹⁷

(¹⁰) There is insufficient information available to set a MAC-EQS for these substances.

(¹¹) For the group of priority substances of polyaromatic hydrocarbons (PAH) (No 28), the biota EQS and corresponding AA-EQS in water refer to the concentration of benzo(a)pyrene, on the toxicity of which they are based. Benzo(a)pyrene can be considered as a marker for the other PAHs, hence only benzo(a)pyrene needs to be monitored for comparison with the biota EQS or the corresponding AA- EQS in water.

(¹²) Unless otherwise indicated, the biota EQS relate to fish. An alternative biota taxon, or another matrix, may be monitored instead, as long as the EQS applied provides an equivalent level of protection. For substances numbered 15 (Fluoranthene) and 28 (PAHs), the biota EQS refers to crustaceans and molluscs. For the purpose of assessing chemical status, monitoring of Fluoranthene and PAHs in fish is not appropriate. For substance number 37 (Dioxins and dioxin-like compounds), the biota EQS relates to fish, crustaceans and molluscs, in line with section 5.3 of the Annex to Commission Regulation (EU) No 1259/2011 of 2 December 2011 amending Regulation (EC) No 1881/2006 as regards maximum levels for dioxins, dioxin-like PCBs and non-dioxin-like PCBs in foodstuffs (OJ L 320, 3.12.2011, p. 18).

(¹³) These EQS refer to bioavailable concentrations of the substances.

(¹⁴) PCDD: polychlorinated dibenzo-p-dioxins; PCDF: polychlorinated dibenzofurans; PCB-DL: dioxin-like polychlorinated biphenyls; TEQ: toxic equivalents according to the World Health Organisation 2005 Toxic Equivalence Factors.'

¹⁷ Author' additions: CAS number 50-29-3: 4,4'-DDT (p,p'-DDT); CAS number 789-02-6: 2,4'-DDT (o,p'-DDT); CAS number 72-55-9: 4,4'-DDE (p,p'-DDE); CAS number 72-54-8: 4,4'-DDD (p,p'-DDD)

Annex 2 Monitoring matrices for the priority substances and certain other pollutants listed by the EQS Directive

Adapted from [GD 25], Table 1.

The substances in red are those suggested by Directive 2008/105/EC for sediment and biota trend monitoring.

P = preferred matrix, O = optional matrix., N = not recommended, n.a. = not applicable

Priority Substance	Water	Sediment/SPM	Biota
<i>Alachlor</i>	<i>P</i>	<i>O</i>	<i>N*</i>
<i>Anthracene</i>	<i>O</i>	<i>O</i>	<i>O</i>
<i>Atrazine</i>	<i>P</i>	<i>N</i>	<i>N</i>
<i>Benzene</i>	<i>P</i>	<i>N</i>	<i>N</i>
<i>Brominated diphenyl ethers^a</i>	<i>N</i>	<i>P</i>	<i>P</i>
<i>Cadmium and its compounds</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>
<i>C10-13-chloroalkanes</i>	<i>N</i>	<i>P</i>	<i>P</i>
<i>Chlorfenvinphos</i>	<i>O</i>	<i>O</i>	<i>O</i>
<i>Chlorpyrifos (-ethyl, -methyl)</i>	<i>O</i>	<i>O</i>	<i>O</i>
<i>1,2-Dichloroethane</i>	<i>P</i>	<i>N</i>	<i>N</i>
<i>Dichloromethane</i>	<i>P</i>	<i>N</i>	<i>N</i>
<i>Di(2-ethylhexyl)phthalate (DEHP)</i>	<i>N</i>	<i>O</i>	<i>O</i>
<i>Diuron</i>	<i>P</i>	<i>N</i>	<i>N</i>
<i>Endosulfan</i>	<i>O</i>	<i>O</i>	<i>O</i>
<i>Fluoranthene</i>	<i>N</i>	<i>P</i>	<i>P</i>
<i>Hexachlorobenzene</i>	<i>N</i>	<i>P</i>	<i>P</i>
<i>Hexachlorobutadiene</i>	<i>O</i>	<i>O</i>	<i>P</i>
<i>Hexachlorocyclohexane^b</i>	<i>O</i>	<i>O</i>	<i>P</i>
<i>Isoproturon</i>	<i>P</i>	<i>N</i>	<i>N</i>
<i>Lead and its compounds</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>
<i>Mercury and compounds^c</i>	<i>N</i>	<i>O</i>	<i>P</i>
<i>Naphthalene</i>	<i>O</i>	<i>O</i>	<i>O</i>
<i>Nickel</i>	<i>n.a.</i>	<i>n.a.</i>	<i>n.a.</i>
<i>Nonylphenols^d</i>	<i>P</i>	<i>P</i>	<i>O</i>
<i>Octylphenol^d</i>	<i>P</i>	<i>P</i>	<i>O</i>
<i>Pentachlorobenzene</i>	<i>N</i>	<i>P</i>	<i>O</i>
<i>Pentachlorophenol</i>	<i>O</i>	<i>O</i>	<i>O</i>
<i>Polyaromatic Hydrocarbons^e</i>	<i>N</i>	<i>P</i>	<i>P</i>

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Priority Substance	Water	Sediment/SPM	Biota
<i>Simazine</i>	P	<i>N</i>	<i>N</i>
<i>Tributyltin compounds</i>	<i>O</i>	<i>O</i>	P
<i>Trichlorobenzenes</i>	<i>O</i>	<i>O</i>	<i>O</i>
<i>Trichloromethane</i>	P	<i>N</i>	<i>N</i>
<i>Trifluralin</i>	<i>N</i>	P	<i>O</i>
<i>DDT (including DDE, DDD)</i>	<i>N</i>	P	P
<i>Aldrin</i>	<i>N</i>	P	P
<i>Endrin</i>	<i>N</i>	P	P
<i>Isodrin</i>	<i>N</i>	P	P
<i>Dieldrin</i>	<i>N</i>	P	P
<i>Tetrachloroethylene</i>	<i>O</i>	<i>O</i>	<i>N</i>
<i>Tetrachloromethane</i>	P	<i>N</i>	<i>N</i>
<i>Trichloroethylene</i>	P	<i>N</i>	<i>N</i>

^a Including Bis(pentabromophenyl)ether, octabromo derivate and pentabromo derivate

^b HCH (all isomers) - BCF (lindane)

^c methylmercury

^d Nonyl- and Octylphenols do not follow the classical K_{ow} partition, because they can establish hydrogen bonds by the phenolic hydroxyl.

^e Including Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)-pyrene. For these compounds the metabolisation in higher trophic levels should be taken into account.

Annex 3: Overview of EN/ISO standards and equipment for analysis of the Priority Substances and certain other pollutants included in the Directive 2008/105/EC

The table below has been compiled on the basis of Guidance Document No. 19 GUIDANCE ON SURFACE WATER CHEMICAL MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE, ANNEX II: Substance Guidance Sheets.

Available Standard Method	Equipment	Parameter
EN ISO 10695:2000 Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods	GC-NPD or GC-MS	<ul style="list-style-type: none"> • Alachlor • Atrazine • Chlorfenvinphos • Chlorpyrifos • Simazine
EN ISO 17993:2003 Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction	HPLC-FD	<ul style="list-style-type: none"> • Anthracene • Fluoranthene • Naphtalene • Benzo[a]pyrene • Benzo[b]fluoroanthene* • Benzo[g,h,i]perylene* • Benzo[k]fluoroanthene* • Indeno[1,2,3-cd]pyrene*
ISO 11423-1:1997 Determination of benzene and some derivatives – Head-space gas chromatographic method	Headspace GC	<ul style="list-style-type: none"> • Benzene
EN ISO 17294-2:2004 Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements	ICP-MS	<ul style="list-style-type: none"> • Cadmium and its compounds** • Lead and its compounds** • Nickel and its compounds**
EN ISO 17852:2008 Determination of mercury by atomic fluorescence spectrometry	AFS	<ul style="list-style-type: none"> • Mercury
EN ISO 6468:1996 Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction	GC-ECD	<ul style="list-style-type: none"> • Aldrin • Dieldrin • Endrin • Isodrin • DDT total • para-para-DDT • Endosulfan (alfa and beta isomer) • Hexachlorobenzene • Hexachlorocyclohexane (HCH) α-, β-, γ- and δ- isomers • Pentachlorobenzene
EN ISO 15680: 2003	purge and- trap GC-	<ul style="list-style-type: none"> • 1,2-Dichloroethane

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Available Standard Method	Equipment	Parameter
Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge and- trap and thermal desorption	MS (EI mode)	<ul style="list-style-type: none"> • Naphtalene • Trichloromethane
EN ISO 18856: 2005 Determination of selected phthalates using gas chromatography/mass spectrometry	GC-MS	<ul style="list-style-type: none"> • Di(2-ethylhexyl)phthalate (DEHP)
EN ISO 11369:1997 Determination of selected plant treatment agents in water by high performance liquid chromatography with UV detection after solid-liquid extraction.	HPLC-UV or LC-MS-MS	<ul style="list-style-type: none"> • Diuron • Isoproturon
EN ISO 18857-1:2006 Determination of selected alkylphenols - Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection	GC-MS	<ul style="list-style-type: none"> • Nonylphenol (4-nonylphenol) • Octylphenol (4-tert-octylphenol)
EN 12673:1998 Gas chromatographic determination of some selected chlorophenols in water	GC-ECD or GC-MSD	<ul style="list-style-type: none"> • Pentachlorophenol
EN ISO 17353:2005 Determination of selected organotin compounds -Gas chromatographic method	GC-MS, FPD, or AED	<ul style="list-style-type: none"> • Tributyltin compounds
EN ISO 10301:1997 Determination of highly volatile halogenated hydrocarbons – Gas-chromatographic methods	GC-MS (liquid/liquid extraction or a static headspace method)	<ul style="list-style-type: none"> • 1,2 Dichloroethane • Dichloromethane • Hexachlorobutadiene • Tetrachloroethylene • Trichloroethylene • Trichloromethane
<i>no methods available yet</i>		<ul style="list-style-type: none"> • Pentabromodiphenylether • C₁₀₋₁₃-Chloroalkanes

* The methods do not attain low enough LOQs and uncertainties for compliance checking with the AA-EQS for the sum of *Benzo[b]fluoranthene* and *Benzo[k]fluoranthene* as well as the sum of *Benzo[g,h,i]perylene* and *Indeno[1,2,3-cd]pyrene*. A new ISO standard for the determination of PAH in water using gas chromatography with mass spectrometry detection is under development (ISO/CD 28540)

** Autor's note: Based on laboratory performance records it might be decided whether AAS (graphite furnace, flame) techniques are able to achieve the required levels of quantification (LOQ) matching the environmental quality standards in the Directive 2008/105/EC.