



# Analysis of EU Legislated Compounds for Assessing Chemical Status: Main Challenges and Inconsistencies

Josep Caixach and Arancha Bartolomé

**Abstract** The list of priority substances from the EU Water Framework Directive (WFD) (2000/60/EC) was recently revised (Directive 2013/39/EU). A total of 12 new priority substances were added, and some EQS values were also modified. For different reasons (toxicity, uses, and environmental fate), the proposed EQS values are extremely low, and it is the need to reach excessively low quantification limits. This chapter considers challenges and limitations of analytical methodologies and, according to literature and the *state of the art* of our laboratory, explains the difficulties for routine laboratories to achieve some EQS values.

**Keywords** Analytical methodologies, Chemical status, EQS, LOQs, Priority substances, WFD

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J. Caixach (✉) and A. Bartolomé  
Laboratory of Mass Spectrometry, Organic Pollutants, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), c/ Jordi Girona, 18-26, 08034 Barcelona, Spain  
e-mail: [josep.caixach@cid.csic.es](mailto:josep.caixach@cid.csic.es)

A. Munné et al. (eds.), *Experiences from Surface Water Quality Monitoring: The EU Water Framework Directive Implementation in the Catalan River Basin District (Part I)*, Hdb Env Chem, DOI 10.1007/698\_2015\_443,  
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## Abbreviations

AA	Annual average
DEHP	Di(2-ethylhexyl)-phthalate
EQS	Environmental quality standard
GC-Q	Gas chromatography-quadrupole
HPLC	High performance liquid chromatography
HRGC	High-resolution gas chromatography
HRMS	High-resolution mass spectrometry
IDMS	Isotope dilution mass spectrometry
JRC	Joint Research Center
LOQ	Limit of quantification
MAC	Maximum allowable concentration
MS/MS	Tandem mass spectrometry
NP	Nonylphenol
OP	Octylphenol
PAH	Polycyclic aromatic hydrocarbons
PBDE	Polybrominated diphenyl ethers
PS	Priority substances
QA	Quality assurance
QC	Quality control
SCCPs	Short-chain chlorinated paraffins
US EPA	United States Environmental Protection Agency
WFD	Water Framework Directive (2000/60/EC)

## 1 Introduction

The Water Framework Directive (WFD) of the European Commission (2000/60/EC) [1] describes the monitoring of priority substances in surface water of the European Union. The daughter directive 2008/105/EC [2] defined the environmental quality standards (EQS) for priority substances (PS) in water, with the aim to protect the aquatic environment. The PS has been defined as substances presenting a significant risk to or via aquatic environment at EU level. In order to assess risk, both hazard and exposure need to be considered. The list of PS was recently revised (Directive 2013/39/EU) [3], a total of 12 new priority substances were added, and some EQS values were also modified. Values are defined as annual averages (AA-EQS) and maximum allowable concentrations (MAC-EQS). Moreover, some additional biota values were included.

For various reasons, such as toxicity, uses, and environmental fate, in some cases or substances, the proposed EQS values are extremely low. In that case, along with the QA/QC parameters of the analytic methods (2009/90/EC) [4], there is the need to reach “excessively” low quantification limits (LOQs). Additionally, remember that compliance monitoring for the PS in the WFD requires the achievement of a

LOQ equal or below a value of 30% of the relevant EQS. The achieved method quantification limits are therefore  $0.3 \times \text{EQS}$ .

The norm does not specify if there are AA or MAC or whether there is a family or individual substance. This is even more critical in coastal waters where the existing precautionary principle requires lower values of EQS. This issue has caused an interesting analytical discussion that involves the overcoming of some analytical challenges – state of art – and it results in some inconsistencies worth mentioning.

This chapter discusses what substances are feasible for routine methods (official control laboratories), which substances require more sophisticated analytical methods, and which ones – despite all the strategies of the sampling and instrumental – remain above the proposed EQS. Therefore, some questions arise in this situation: What should the government do? How to define the chemical status of the affected water bodies? Or why are EQS values proposed when the analytical community or the same technical committees of the EU know that these are difficult to achieve?

We are not going to discuss neither the benefits nor the intentions. We will focus on the analytical results or analytical methodologies that will give valid results or robustness to the analytical determinations required in achieving the EQS and allowing the intercomparison.

## 2 Challenges and Limitations of Analytical Methodology

The application of WFD raises a number of analytical challenges that can be summarized as:

- Work to have the best available methods to obtain the lowest possible LOQs according to EQS.
- Apply the best laboratory practices for a reliable/consistent result (QA/QC).
- Validate methods and results participating in interlaboratory exercises aiming at monitoring data of sufficient quality to ensure harmonization or intercomparison.
- With the purpose of risk assessment for future identification of PS, in particular as regards emerging pollutants, the Directive has introduced what they call watch list [3]. The mechanism will ensure the targeted collection of monitoring data on the concentration of substances in the aquatic environment. The proposed list of substances to be monitored has been subject of numerous meetings and discussions within the Commission. These substances will be monitored in a limited number of representative stations across Europe to gain high-quality information to assess the potential risk posed of emerging pollutants and in consequence set reasonable EQS and help to make a validation of analytical methods used in monitoring and provide suitable analytical protocols with the

aim of shortening the necessary standardization process. The monitoring will be in water, sediments, or biota.

These issues come from some inconsistencies in the implementation of WFD that should be reconsidered:

- The mix of protocols and criteria (toxicological/use/monitoring) and various commissions originates unrealistic EQS and analytically intractable LOQs, resulting in lack of robustness of the method.
- Concerning the determination of LOQ, the Directive 2009/90/EC [4] does not specify from which EQS (AA or MAC) should be done.
- What is the LOQ for each compound in the case where EQS is defined for a sum of substances? Do you have to divide 30% of EQS between the numbers of congeners?
- Monitoring data from literature for the inclusion in the proposals, it is desirable that all are scrutinized according to the same criteria or the comparison with the performance and robustness/reliability of the analytical methods used.
- There is the need of improvements in the sampling and analytical methodological and instrumental capabilities to allow widespread adequate measurements.
- Despite sediment as an important compartment for its ability to bioaccumulate, and the existence of guidance to chemical monitoring [5], nowadays there is not EQS defined for this matrix yet. Member states had the order to set up commissions to work on deriving EQS for sediment [6]; there has not been consensus on this issue. According to Directive 2013/39/UE [3], member states could monitor PS on this matrix applying the relevant EQS. In any case, member states shall take measures aimed at ensuring that concentrations do not significantly increase.

### 3 Discussion

#### 3.1 *Limitations of Analytical Methods and Harmonization Exercises*

Intercomparison exercises are the most practical and operative ones that give validity to the analytical methods applied. It is a good tool to highlight analytical problems and harmonize analytical methods. In this context, the European Commission, through the Joint Research Center (JRC), organized the Chemical Monitoring Activity Exercises (CMA on-site). The main objective was focused on assessing the limitations of analytical methods for some groups of PS. Three exercises were organized: the first one took place on the River Po in October 2006 (CMA on-site 1), the second one on River Danube at Budapest in September 2008 (CMA on-site 2), and the last one in October 2010 on River Meuse at Eijsden (the Netherlands) (CMA on-site 3). Different laboratories that participated were



**Fig. 1** Method performance for PBDEs WFD monitoring. Number of laboratories ready (*green*) or not ready (*red*) for the sensitivity requirements of 30% EQS ( $1/6 \times 30\%$  of 0.5 ng/L sum of BDE congener numbers 28, 47, 99, 100, 153, and 154 equals LOQs of 0.025 ng/L for each single congener) as specified in the proposal for the Commission Directive on technical specifications for chemical analysis and monitoring of water status for WFD chemical monitoring [8]

chosen as representative of member states. The results and conclusions of the three exercises were published [7].

In our opinion, the results of CMA exercises 2 and 3 give an example of the difficulties of harmonizing analytical methods and comparing the results obtained by different laboratories in “conventional” families. The findings are conclusive in this respect.

Figures 1, 2, and 3 show some of the results of CMA on-site 2, in which samples from the River Danube located downstream Budapest city were analyzed with a joint exercise of sampling and a subsequent analysis with methodologies that each laboratory had readied.

The conclusions of the CMA on-site 2 studies are especially relevant [8]:

- Environmental concentrations of PAH, PBDE, and NP/OP can be analyzed in surface waters at concentrations taking into account the set European Environmental Quality Standards values and the proposed performance criteria.
- Among the included analytic groups, PBDE appear to be a major challenge monitoring at sub-ng/L level in water samples.
- Very much differing sampling and analytical methodologies are still in use within Member States.
- Not all among the participating laboratories were able to deliver results at the required concentration levels.
- No proficiency testing scheme or other external quality control possibility, taking into account the problematic of real environmental samples, is available at present for these analyses.

**Fig. 2** Method performance for nonyl-/octylphenol WFD monitoring. Number of laboratories that are ready (*green*) or not ready (*red*) for the sensitivity requirements of 30% EQS as specified in the proposal for the Commission Directive on technical specifications for chemical analysis and monitoring of water status for WFD chemical monitoring [8]



**Fig. 3** Method performance for PAHs WFD monitoring. Number of laboratories ready (*green*) or not ready (*red*) for the sensitivity requirements of 30% EQS as specified in the proposal for the Commission Directive on technical specifications for chemical analysis and monitoring of water status for WFD chemical monitoring [8]



- In vicinity to the proposed EQS concentration levels, high data quality is of importance for compliance checking.
- Blank values in analytical procedures are of crucial importance, as analytical problems can lead also to an overestimation of pollutant content and consequently even noncompliance.
- The occurring variability of contaminants in surface waters is of utmost importance for the selection of the monitoring strategies and needs therefore to be studied.

The 5-year period (2006–2010) on CMA on-site exercises provides a picture of the development of harmonization level of selected monitoring methodologies in EU Member States.

The more relevant conclusions [7] add to the above would be:

- It was evident that not all participating laboratories were able to deliver results at the required concentration levels. Furthermore, we obtained in some cases very high data variability, which represents a problem in compliance checking.
- The reduction of the variability among laboratories should be the most important goal to be achieved for the harmonization of WFD monitoring around Europe.
- Investigating gaps in analytical performance can help to identify needs for further development strategies and methodologies. Examples of such issues are the analysis of whole water and the variability of concentrations in surface water.
- While the requirements can change with the legislative context (e.g., revision of the EQS Directive), there is a clear need to continue harmonization at different organizational levels.

### ***3.2 Need of Most Advanced Instrumentation and Methodologies***

According to Directive 2009/90/EC [4] concerning technical specifications for chemical analysis, the need of most advanced instrumentation is obvious. MS/MS (HRGC or HPLC) methods are regularly used today, we do not see why we should renounce to the most advanced methods based on criteria that is not a routine method, economic high cost, etc. Methods like HRGC-HRMS and HPLC-HRMS are common in many methodologies.

US EPA is innovative using best available analytical methodologies as IDMS and HRMS (methods 1613 [9], 1614 [10], or 1668 [11]) or IDMS and MS/MS (method 1664 [12]). However, currently, the methods MS/MS are coming with a good state of the art and sensibilities almost as good as of HRMS. Therefore, there is no serious argument for not allowing the use of it to reach the fulfillment of lower EQS. Furthermore, there are prescreening strategies available.

New advances have been introduced in the field of instrumentation, HRMS Orbitrap analyzer, and recently GC-Q Orbitrap. This instrumentation is going to allow an important advance toward getting better quantification limits. It is noteworthy that the HRMS gives robustness to analytical methods minimizing the effect of the matrix and also the potential inaccuracies in quantification in the analysis by liquid chromatography tandem to mass spectrometry. HRMS is a good approach for combining the qualitative and quantitative analysis together. Remember that misuse of MS/MS has led to many false-positives or questionable results that have remained described at the literature. In our opinion, many environmental data are questionable for this fact. We would like to highlight again the importance of intercomparison exercises.

Another point to keep in mind is that the use of this instrumentation is not easy or a routine in many cases. Hence, it is very important to have trained personnel.

Nevertheless, with the use of advanced instrumentation, to date, there are many analytical problems with some substances. The works of Vorkamp [13] and Loos [14] give us the exact extent of the limitations of the analytical methods regarding the compliance of the proposed EQS in Directive 2013/39/EC [3]. It will be developed later.

Among others technical requirements, LOQ must be equal or below a value of 30% of the relevant EQS [4]. This is one of the goals of the analytical methods. The LOQs given are linked to a specific methodology and instrumentation and current approach of water volumes [14], and an adequate state of the art could improve it. However, LOQs are not constant values and can change over time. They are dependent on several parameters and hence have to be verified regularly [14].

The blanks of laboratory/method are one of these parameters. The values obtained show the “reality” of LOQs and may invalidate all the effort improving the sensitivity of instrumental methods. One of the PS that present many problems with blanks are PBDEs that are widespread in the laboratory environment. As an example, Table 1 shows levels of PBDEs obtained in pristine waters from a high mountain lake used as blanks of method to calculate LOQs. You have to realize that the concentration obtained for the sum of legislated PBDEs is in the same level of required LOQ for coastal waters (0.06 ng/L) under Directive 2008/105/EC [2]. In the case of PBDEs, the EQS has changed, but we want to highlight this problem that occurs with other PS as DEHP (LOQ required 0.39 µg/L) or naphthalene (0.6 µg/L).

In the improvement of the analytical methods, the use of isotope dilution mass spectrometry (IDMS) is a very good tool. IDMS consists in the use of isotopically labeled analogues as internal standards considering that the natural sample contains negligible amounts of them. The isotopic analogue is added to the sample at the very beginning of the analytical method; it enables exact compensation to be made for errors at all stages of the analysis [15]. IDMS gives accurate, robust, and reliable results [16, 17]. However, the use of IDMS has a number of advantages and disadvantages, which the user should consider [15]. Therefore, the method

**Table 1** Levels of PBDEs in pristine waters used as blanks of laboratory. *Source:* Laboratory of Mass Spectrometry-Organic Pollutants

Sample	Pristine groundwater (ng/L)	Surface water <sup>a</sup> (ng/L)	Deep water <sup>a</sup> (ng/L)
<i>Compound</i>			
BDE#28	0.002	0.002	0.002
BDE#47	0.011	0.023	0.018
BDE#99	0.008	0.014	0.012
BDE#100	0.003	0.005	0.003
BDE#153	n.d	n.d	n.d
BDE#154	n.d	n.d	n.d
BDE#183	n.d	n.d	n.d
BDE#197	n.d	n.d	n.d
BDE#209	n.d	0.037	n.d
ΣLegislated BDEs	0.024	0.044	0.035

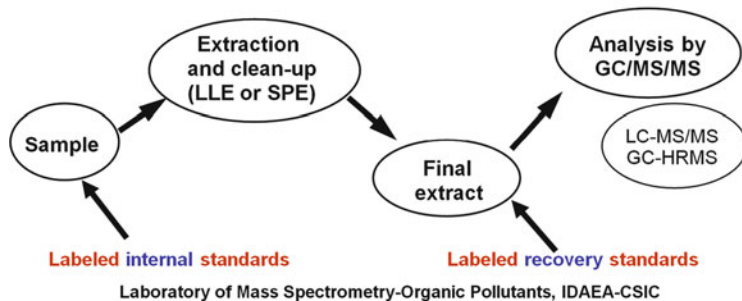
n.d: not detected

<sup>a</sup>Water from high mountain lake

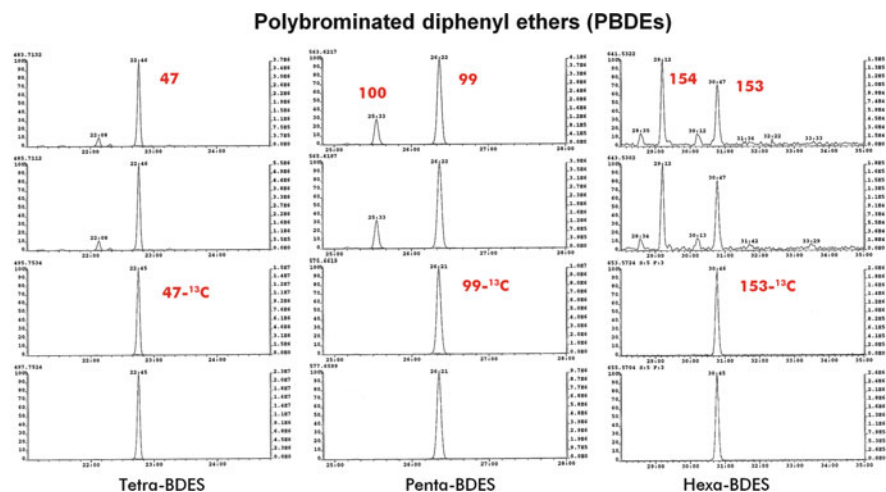


## Analysis of WFD Priority Pollutants in water

### Analytical methodology: Isotope Dilution/MS



**Fig. 4** Scheme of analytical methodology for the analysis of priority pollutants in water. *Source:* Laboratory of Mass Spectrometry-Organic Pollutants



**Fig. 5** Example of use of IDMS for analyzing PBDEs. Profile of a marine sediment obtained by GC/HRMS ( $R = 10,000$ ), with the congeners and its isotope labeled analogous. *Source:* Laboratory of Mass Spectrometry-Organic Pollutants

proposed could follow the scheme shown in Fig. 4, with the addition of labeled standards at the beginning of the method and at the end to check the efficiency of the extraction. Figure 5 shows an HRMS chromatogram obtained working with IDMS, where there are the signals for native and labeled congeners.

### **3.3 Analytical Difficulties for Existing and “New” Priority Substances**

We would like to remark the specific analytical difficulties of some compounds, many of them already described in recent literature.

#### **3.3.1 Polybrominated diphenyl ethers (PBDEs)**

Required LOQs for PBDEs according to EQS on 2008/105/EC [2] are with difficulty achieved in routine laboratory conditions [18], but the new directive [3] has included more acceptable EQS (140 ng/L and 14 ng/L, respectively, for inland and other surface waters). In addition, EQS for biota has been determined (0.0085 µg/Kg).

With all substances that an EQS for biota is established, the Directive [3] recommends the monitoring in this matrix.

#### **3.3.2 Polycyclic Aromatic Hydrocarbons (PAHs)**

The PAHs have focused on the B[a]Pyrene as a marker, with EQS 0.17 ng/L (LOQ required 0.051 ng/L) and 5 µg/kg in biota. The lowest LOQs for water analysis achieved with methods applied by EU Member States are not sufficient of compliance monitoring in waters [14]. Large-volume water sampling is proposed for increasing method sensitivity [18].

#### **3.3.3 Endosulfan**

Although endosulfan is a common analyzed pesticide, the LOQ required, particularly AA-EQS for coastal waters, is not easy to achieve with routine methods [18].

#### **3.3.4 Short-Chain Chlorinated Paraffins (SCCPs)**

The difficulties in the analysis of SCCP reside in the highly complex nature of commercial formulations; the numerous physical, chemical, and biological processes after use; and the lack of certified chemical standards [18]. There is a variety of approaches to analyze SCCPs in environmental samples [18]. A validated procedure for routine monitoring of SCCPs was needed in fulfilling the technical specifications [4]. The ISO/DIS 12010 describes a method using gas chromatography/mass spectrometry (GC-MS) and electron capture negative ionization (ECNI) [19]. The method was validated and allows an analysis of SCCP under routine conditions for laboratories [20].

### 3.3.5 Perfluorinated Compounds (PFC)

In spite of the improvement of the quality in PFC analysis [18], the LOQ achieved with the ISO method 25101 is not sufficient for compliance monitoring in inland and coastal surface waters [14]. To reach LOQs is difficult partly due to blank problems that force to an accurate methodology [21]. However, the EQS for biota is considered more viable.

### 3.3.6 Cypermethrin

One of the most difficult “new” PS is cypermethrin, with an EQS of 80 pg/L (8 pg/L in coastal waters). Although extracting large-volume samples and a strong pre-concentration, sufficiently low LOQs could not be reached [13]. To reach LOQs in the low pg/L concentration range is extremely difficult, if not impossible with current methods [14].

### 3.3.7 Heptachlor/Heptachlor Epoxide

LOQs reported by literature are not sufficient for compliance monitoring (60 fg/L in inland surface waters and 3 fg/L in coastal waters) [14]. These PS can be analyzed in biota (LOQ, 2.01 pg/g) and very difficult to reach even with high-resolution mass spectrometry (HRMS).

Other substances that present problems to reach LOQs required are:

- *Aclonifen*: 36 ng/L (3.6 ng/L coastal waters)
- *Bifenox*: 3.6 ng/L (0.36 ng/L coastal waters)
- *Cybutryne*: 0.75 ng/L
- *Quinoxifen*: 45 ng/L (4.5 ng/L coastal waters)
- *Terbutryn*: 19.5 ng/L (1.95 ng/L coastal waters)
- *Dichlorvos*: 0.18 ng/L (18 pg/L coastal waters)
- *Dicofol*: 0.39 ng/L (9.6 pg/L coastal waters)

## 4 Summary

The implementation of WFD in its entirety is not, in our opinion, an easy work. The requirements in terms of EQS and LOQs require the use of most advanced instrumentation, not available in many cases to all laboratories. It is a necessary exercise, as organized by JRC, to harmonize methods and results that bring to establish adequate and realistic EQS and let intercomparison of results between member states.

The watch list mechanism is a good approach to collect high-quality information of emerging pollutants and in consequence set reasonable EQS for which could be included in future revisions of the Directive. Even today, there are many substances which LOQ is difficult if not impossible to reach. Some strategies have been proposed to achieve lower LOQs, for example, extracting higher volumes of water; however, these methodologies are not very useful for WFD compliance monitoring; they are very work intensive and very costly [14]. Although the LOQs obtained by each laboratory depend on their *state of the art* and its instrumentation, they give us a plausible approximation of the outstanding challenges as well as the inconsistencies in the Directive's proposals.

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