

The future development of chemical monitoring of priority substances in the context of the Water Framework Directive

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Abstract Article 16 of the EU Water Framework Directive (WFD) is the legal basis for the identification and review of the European priority substances that should be reduced or eliminated from all emissions, discharges, releases and losses in surface water bodies. Directive 2008/105/EC has defined environmental quality standards (EQS) for 33 priority substances and eight additional pollutants. In 2012, the European Commission published a proposal Directive (COM (2011) 876) with a revised list of priority substances and the derivation of EQS in the water column and biota: 15 new substances were selected through a procedure of prioritization based on a risk assessment methodology with the use of monitoring and modelling data collected over a period of four years. In the list of the new substances, there are several pesticides widely used across Europe, as well as biocides, pharmaceuticals, flame retardants, industrial chemicals and also POP (persistent organic pollutants) such as dioxins and heptachlor. The control of the existing and future priority substances requires substantial effort from all the Member States with respect to the monitoring strategies and, in particular, for the selection of analytical methods that must comply with the legal obligations imposed by Directive 2009/90/EC. For this reason, and in the context of the Working Group E on chemical aspects of the WFD, an expert group, CMEP (Chemical Monitoring and Emerging Pollutants), chaired by Italy and the European Commission (DG JRC) has been established with the aim of supporting all the Member States in the implementation of chemical monitoring for European surface water bodies.

Key words priority substances; chemical monitoring; Water Framework Directive; environmental quality standard

INTRODUCTION – CHEMICAL STATUS

The Water Framework Directive (WFD) 2000/60/EC (European Union, 2000) requires an integrated approach for the monitoring and assessment of the environmental quality status of surface water bodies. A key objective of the WFD is the achievement of “good surface water chemical status” in all bodies of surface water in the 27 Member States of the European Union (EU) by 2015.

The good chemical status of the WFD is defined in terms of compliance with the EQS, legally binding thresholds that aim to protect aquatic ecosystems and human health, established for the European priority substances. Directive 2008/105/EC (European Union, 2008) in the field of water policy (EQS Directive) sets EQS for the priority substances (PS) and certain other pollutants that were already regulated as mentioned in Annex IX of the WFD. Directive 2008/105/EC sets EQS for the water column and for three substances (mercury and compounds, hexachlorobenzene and hexachlorobutadiene) in biota due to their high bioaccumulation properties. In addition, the Directive allows Member States to establish EQS for sediment and/or biota at the national level and to apply those EQS instead of the EQS for water established at the European Community (EC) level. There are two types of EQS in the directive: annual average (AA), based mainly on chronic/long-term risk; and maximum allowable concentrations (MAC), based mainly on acute risk for the aquatic organisms. Article 16 of the WFD gives the legal basis for the identification and review of the European priority substances that should be reduced or eliminated from all emissions, discharges and losses to surface water bodies.

For legal compliance, the EQS Directive obliges Member States to monitor the substances with a monthly frequency in the water column, and with a minimum annual frequency if the matrix is sediment or biota.

PRIORITY SUBSTANCES-RECENT DEVELOPMENTS

The European Commission has recently proposed a review of the list (European Commission, 2011) of priority substances (Com 2011/876) through a prioritization procedure based on a combination of monitoring and modelling of data in compliance with Article 16 of the WFD. This Directive proposal includes a revised (second) list of priority substances, and provisions to improve the functioning of the legislation. This Directive proposal has been elaborated on the basis of four years of work by Working Group (WG) E of the Common Implementation Strategy (CIS) of the WFD. The European Commission coordinates WG E, which is composed of representatives of all Member States and several key stakeholders (industrial and environmental associations).

The Directive proposal, which has been published together with a series of background documents (e.g. impact assessments) and dossiers for the new priority substances, has been developed on the basis of collection of monitoring data from the river basins of all Member States. This database includes 14.6 million analyses from 19 900 stations in 28 countries and covers 1151 substances in total. All five WFD surface water categories (rivers, lakes, transitional, coastal and marine waters) are represented, river stations being predominant as illustrated in Fig. 1.

The data were collected mainly (more than 90%) in the water column, but also in sediment and biota (mainly molluscs). With the aim of identifying newly emerging substances not included in routine monitoring programmes, the European Commission's in-house science service, the Joint Research Centre has lead a prioritization modelling study (European Commission, 2010), taking

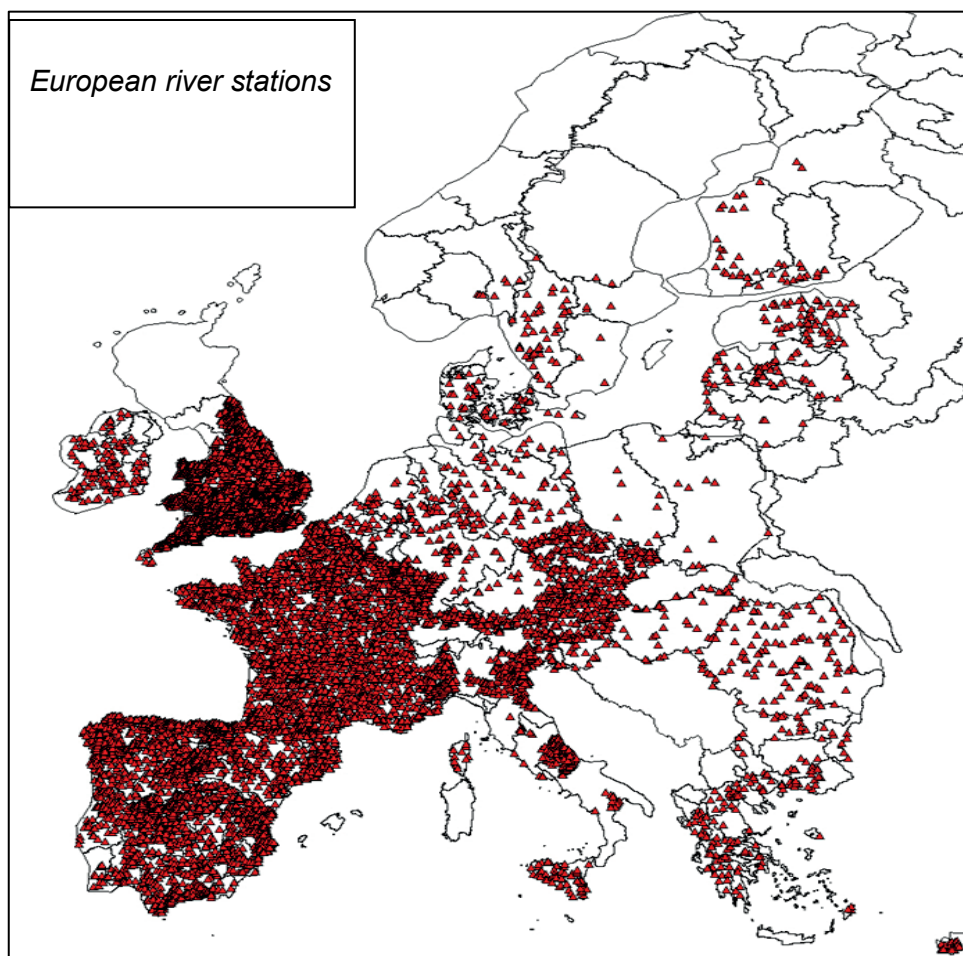


Fig. 1 Monitoring stations reported in the European Union for the review of the priority substances (rivers).

into account the emissions of substances and their physico-chemical properties, to evaluate their potential presence in European water bodies. A final list of 15 substances has been derived from the monitoring and modelling exercise (together with an evaluation of risk assessment report) for which the WG E has derived EQS for protecting environmental and human health. These EQS have been peer-reviewed by the SCHER (Scientific Committee on Health and Environmental Risks) and the procedure for the derivation is based on a methodology that was published by the European Commission (European Commission, 2011).

Table 1 Future possible priority substances and EQS.

Substance	AA-EQS (µg/L) Inland surface waters	AA-EQS (µg/L) Other surface waters	EQS-biota (µg/kg wet weight)
Dicofol	1.3×10^{-3}	3.2×10^{-5}	33
Perfluorooctane sulphonic acid (PFOS)	6.5×10^{-4}	1.3×10^{-4}	9.1
Quinoxifen	0.15	0.015	
Dioxins and dioxin-like compounds			0.008 TEQ*
Aclonifen	0.12	0.012	
Bifenox	0.012	0.0012	
Cybutryne	0.0025	0.0025	
Cypermethrin	8×10^{-5}	8×10^{-6}	
Dichlorvos	6×10^{-4}	6×10^{-5}	
Hexabromocyclododecane (HBCDD)	0.0016	0.0008	167
Heptachlor and heptachlor epoxide	2×10^{-7}	1×10^{-8}	6.7×10^{-3}
Terbutryn	0.065	0.0065	
17 alpha-ethinylestradiol	3.5×10^{-5}	7×10^{-6}	
17 beta-estradiol	4×10^{-4}	8×10^{-5}	
Diclofenac	0.1	0.01	

*Toxicological equivalent.

The main features of the proposal are: 15 additional priority substances, six of them designated as priority hazardous substances; stricter EQS for four existing priority substances and slightly revised EQS for three others; the designation of two existing priority substances as priority hazardous substances; the introduction of biota standards for some substances; provisions to improve the efficiency of monitoring and the clarity of reporting with regard to certain substances behaving as ubiquitous persistent, bioaccumulative and toxic (uPBT); a provision for a watch-list mechanism designed to allow targeted EU-wide monitoring of substances of possible concern to support the prioritization process.

These substances (Table 2) include several pesticides, in particular insecticides and fungicides, historical bioaccumulative substances such as dioxins and Heptachlor, which is a banned pesticide. There are also substances commonly present in surface water bodies on account of their very widespread use (e.g. PFOS) or their use as flame retardants (HBCDD). Furthermore, irgarol has been included, which is a biocide used in the substitution of tributyltin. Three widely used pharmaceuticals (diclofenac, beta-estradiol, 17 alpha ethinyl-estradiol) have also been included in this proposed Directive for the first time. Pharmaceuticals, among the emerging contaminants, are the most relevant group of substances for the possible impact on aquatic ecosystems due to their universal use, to their chemico-physical properties (Oliver *et al.*, 2003) and to their capacity to be reduced poorly after depuration in wastewater treatment plants (Ternes, 1998). The pharmaceuticals issue should be managed through a strategy that takes into account all such products from their source to their final fate in the environment.

This Directive proposal, which is currently in discussion, has also foreseen the application of bioavailability models for the evaluation of EQS for nickel and lead in inland waters. In the case of these substances, the monitoring programmes should also consider physico-chemical parameters.

Table 2 Future Priority Substances and their emission sources.

Substance	Sources / uses	Identified as priority hazardous substance
Dicofol	Organochlorine acaricide	x
Perfluorooctane sulphonic acid (PFOS)	Largely used products (textiles, carpets, coatings)	x
Quinoxifen	Fungicide	x
Dioxins and PCB dioxin - like compounds	Industrial processes, waste dumps, incomplete combustion	x
Aclonifen	Herbicide	
Bifenox	Pesticide-various uses	
Cybutryne	Antifouling Biocide	
Cypermethrin	Insecticide	
Dichlorvos	Insecticide	
Hexabromocyclododecane (HBCDD)	Flame retardant	x
Heptachlor and heptachlor epoxide	Organochlorine insecticide	x
Terbutryn	Herbicide	
17 alpha-ethinylestradiol	Synthetic estrogen (birth control pills)	
17 beta-estradiol	Estrogenic hormone	
Diclofenac	Anti-inflammatory drug	

DEVELOPMENT OF WFD CHEMICAL MONITORING PROGRAMMES

Monitoring programmes are required to establish a coherent and comprehensive overview of chemical surface water status within each River Basin District (RBD) comprising each Member State. A key advantage of measuring chemical concentrations in environmental media such as water, sediment and/or biota, is that these provide evidence of past and/or present exposure to the analysed contaminants. Moreover, when long time-series of data exist, the trends can be used to assess the decrease or increase in risks and the corresponding necessity to regulate emissions of certain individual substances. Chemical data from several trophic levels also provide information on persistence, bioavailability and accumulation in food chains, and thus risks related to human consumption and top predators.

The WFD requires three key types of monitoring programme:

Surveillance monitoring is performed at least every management cycle (usually six years), to assess and design future monitoring programmes and to determine temporal trends. It also has the aim of assessing long-term changes of the natural conditions and changes resulting from anthropogenic activity.

Operational monitoring to establish the status of those water bodies identified as being at risk of failing to meet WFD environmental objectives, and to assess any changes in the status resulting from the Programme of Measures (PoM).

Investigative monitoring to investigate/identify the reasons for failure to comply with the status requirements if unknown, or when accidents occur.

The analysis of pressures and assessment of impacts is needed to determine the WFD operational monitoring needs. In the first step, driving forces, such as land-use patterns, should be described. In the second step, pressures (point and diffuse sources of hazardous substances) with a potential impact on water bodies are identified. The impacts resulting from the pressure are assessed as a third step. Finally, the likelihood of failing to meet the objectives is assessed during the final, fourth step.

The key points of a chemical monitoring programme include: (1) the identification of sampling stations, (2) the selection of chemical parameters, (3) the frequency of monitoring, (4) the standardization of analytical methods, (5) the quality assurance and control procedures, and, (6) the use of effect-based tools as complementary lines of evidence for chemical monitoring programmes.

The EQS derived for the existing priority substances and also the EQS of the future possible priority substances requires a strong analytical effort by all the Member States to achieve a level of compliance appropriate to evaluate the chemical quality status of surface water bodies.

The analysis of priority substances and specific pollutants is restricted to stringent validation requirements, mentioned in the Directive on technical specifications for chemical analysis and monitoring of water status (2009/90/EC). All methods of analysis applied by Member States for the purposes of chemical monitoring programmes of water status have to meet certain minimum performance criteria, including rules on the uncertainty of the measurements and on the limits of quantification-provided by the methods:

- Member States shall ensure that all methods of analysis, including laboratory, field and on-line methods, used for the purposes of chemical monitoring programmes carried out under Directive 2000/60/EC are validated and documented in accordance with EN ISO/IEC-17025 or other equivalent standards accepted at international level.
- Member States shall ensure that the minimum performance criteria for all methods of analysis applied are based on a limit of quantification equal to or below a value of 30% of the relevant EQS.

However, it is important to note that for some priority substances, current or proposed EQS values are lower than the Levels of Quantification (LOQ) currently possible using available laboratory technologies.

The European Commission, with the aim of improving the application and implementation of chemical monitoring programmes by the Member States has established an expert group; the so-called Chemical Monitoring and Emerging Pollutants (CMEP) group. This provides guidance (e.g. European Commission, 2010) on sampling, monitoring and analysis of chemicals, including quality assurance and control issues. The group, chaired jointly by Italy and the European Commission's Joint Research Centre, is composed by experts of all the Member States, key stakeholders and the research community, and operates under the umbrella of the CIS (Common Implementation Strategy). CMEP deals also with topics related to emerging pollutants (Loos *et al.*, 2008) including analytical methods, hazard information, levels in the environment and usage patterns. The activity of CMEP (Quevauviller *et al.*, 2012) focuses on the provision of EU-wide information about the levels and occurrences of emerging environmental pollutants to eventually support the identification of new designated priority substances.

The most recent activities of CMEP have focused on case studies of statistical methods for assessing compliance, an update on the progress of implementation of Directive 2009/90/EC, and comparison of monitoring approaches among EU Member State Laboratories.

The CMEP has also performed a survey on available water, biota and sediment matrix Certified Reference Materials (CRMs) for the 33 WFD Priority Substances (and the eight "other certain pollutants"); the results of this activity has been compiled in tables and presented together with a critical overview of gaps and possible directions for improvement in CRMs, in the form of a published peer-reviewed paper (Ricci *et al.*, 2012).

A report on analytical methods for the new proposed Priority Substances of the WFD has been also finalized by JRC with the support of CMEP members (Loos, 2012) and also a guidance on sediment and biota monitoring has been published in the context of the CIS; in particular, the monitoring of aquatic biota taxa will become more important because most of the current and future priority substances have properties of bioaccumulation, and it is known that climate changes can alter and enhance the bioavailability of these substances (Carere *et al.*, 2011)

Another aim of the current activity is to produce a technical report on the use of effect-based monitoring tools within the context of the WFD. The aim of the report, chaired by Sweden, is to identify potential effect-based tools (e.g. biomarkers, bioassays) that could be used in the context of the three fundamental types of monitoring programmes (surveillance, operational and investigative). It is envisaged, that in general, effect-based tools (e.g. bioassays *in vitro* and *in vivo*, biomarkers) will have different uses, for example linking chemical and ecological status to identify early warning effects and detect the effects caused by mixtures of pollutants difficult to discover

with only chemical analysis. The use of bioanalytical tools will always be more important in combination with the chemical analyses, both for monitoring and for the assessment of the quality status of surface waters.

It is also necessary to link with the Marine Strategy Framework Directive (European Union, 2008) because the chemical status of the WFD also covers the territorial waters and a strong link has been foreseen in the context of the future activities of the group.

CONCLUSIONS

The implementation and revision of chemical monitoring programmes will provide the basis for better knowledge of the status of European water bodies (Brils *et al.*, 2010) and be part of the revision of the next river basin management plans. The Directive proposal, with its future list of priority substances, represents a highly relevant European legislative milestone and it is hoped that Member States, the European Council and European Parliament will achieve a strategic agreement for improving the protection of European water bodies from chemical pollution. For these reasons, the efforts of the WG E on chemical aspects and the CMEP group continue to provide a great deal of support to Member States and all stakeholders involved in the strategic implementation of the WFD.

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