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THE METROLOGICAL STAKES OF THE EUROPEAN WATER FRAMEWORK DIRECTIVE

M. Coquery, B. Lepot and A. Morin

INERIS, Institut national de l'environnement industriel et des risques, BP 2, F-60550 Verneuil-en-Halatte, France

Résumé

L'Union européenne a introduit, avec la nouvelle réglementation sur l'eau, une dimension nouvelle dans le domaine de la surveillance de l'environnement. Il ne s'agit plus seulement de mesurer un état de contamination mais de suivre et rendre compte de l'état de qualité écologique et chimique des eaux. Cet état doit s'améliorer avec un objectif exigeant de « bon état » dès 2015 pour tous les états membres. Une telle mesure, qui doit se traduire notamment par une intensification du contrôle des contaminants chimiques, a des conséquences importantes en termes de métrologie. Afin d'assurer la comparabilité des données au niveau européen, il apparaît indispensable de développer des méthodes de mesures appropriées et validées au plan international et d'organiser des exercices d'intercomparaison.

Abstract

With the new Water Directive the European Union has given a new dimension to environmental monitoring. It is now necessary to follow and account for the ecological and chemical status of aquatic ecosystems. This status should improve with the objective of "good status" in 2015 for all waters of Member States. Such a regulation will lead to an intensification of chemical contaminants control and has important metrological implications. In order to ensure the comparability of data, it appears necessary to develop internationally validated standard methods and to organise intercomparison exercises for analytical laboratories.

Introduction

The European Water Framework Directive (WFD, 2000/60) [1] is probably the most significant legislative instrument in the water field to be introduced on an international basis for many years. The Directive takes a broad view of water management and has as its key objectives the prevention of any further deterioration of water bodies, and the protection and enhancement of the status of aquatic ecosystems. Its implementation should result in an intensification of monitoring aquatic ecosystems with an increase of contaminants control. The overriding objective of the policy is the achievement of "good status" in all waters.

Article 16 of the WFD sets out the Community strategy against pollution of water by chemical substances. According to the provisions of this article, a list of priority substances shall be established which represent a significant risk to or via the aquatic environment at Community level. Following the proposals of the European Commission in February 2000 and January 2001 and the first Parliament's reading, Council and European Parliament finally agreed to a list of 33 substances [2].

Control of chemical substances is targeted on toxic effect on ecosystems. Good chemical status for a water body is reached when pollutant concentrations are less that the Environmental Quality Standards (EQS). The EQS have been elaborated throughout discussion between experts from Member States using the risk assessment approach described in the Technical Guidance Document [3, 4]. A daughter directive will list the EQS for the priority substances. In order to reach the "good status" for all European surface waters, Member States will have to implement river basin management plans, including water monitoring programmes and take measures when results do not comply with the EQS.

In order to implement appropriate water quality monitoring programmes and to ensure the comparability of data on the state of contamination of the aquatic environment, it appears necessary to develop internationally validated standard methods, to define and organise quality assurance and control, and to set targets for uncertainties of results.

This implies:

- To define new analytical methods for chemical substances regulated by the WFD in water, suspended matter, sediment and biota ;
- To attain detection limits for the analyses of priority substances that are compatible with the EQS ;
- To define at the European level, data quality criteria in order to attain the desired degree of environmental protection ;
- To ensure the traceability of results by developing new certified reference materials ;
- To ensure the comparability of analytical results on water pollution in the aquatic environment on a national and European level by organising inter-laboratory trials.

Analytical challenges for the measure of priority substances

The Water Framework Directive requires the monitoring of water quality to be performed by methods

which are conform to CEN/ISO Standards or National/International Standards which ensure the provision of data of an equivalent scientific quality and comparability. For a large number of priority substances European harmonised methods for sampling and analysis are already available through CEN/TC230. However, some of the methods will have to be revised in order to fit requirements of the WFD.

For instance, lower limits of detection and better precision at low environmental levels would be needed for a number of substances according to the proposed EQS [4]. Existing methods have indeed insufficient sensitivity for the measurement of cadmium, chlorpyrifos and tributyltin compounds in water.

Also the methods are still under development and no routine methodologies are available yet to Member States for several other substances: alkylphenols, pentabromo-diphenylethers and C10-C13 chloroalkanes.

Finally, CEN/ISO standard methods are available for the determination of a majority of the priority substances in water, but a number of these methods are not applicable to transitional and coastal waters (e.g., for metals), and standard methods practically do not exist for suspended matter, sediment and biota samples. In general the standard methods for water samples may be applied to the analysis of sediment without dramatic changes of procedures. However, the pre-treatment step needs to be elaborated or in some cases adjusted to the distinct need. None of the standards has been validated for investigations of biota including fish. For sediment samples, national standards exist in some cases, but most routine laboratories use internal methods for the pre-treatment step, which are usually derived from standard methods on soils or sludge. We will also detail below the specific difficulty of analysing organic substances in water samples containing large amount of suspended matter.

Need for the development of reference methods for new priority substances

Four priority substances, namely brominated diphenylethers, C_{10}-C_{13}-chloralkanes, nonylphenols and octylpenols comprise rather poorly defined groups of chemicals consisting partially of a large number of isomers. For this reason, monitoring data which are available for these groups of substances often relate to different individual chemicals or have been gained by quantification methods which are not comparable. It is, therefore suggested, that strong efforts should be made first to identify indicator substances and standard materials, whenever possible, or to define a reference method for each of these priority substances. For the time being, an ISO committee draft exists regarding the determination of alkylphenols in surface waters and the determination of brominated diphenylethers in sediment and sludge.

Part 1 of an ISO committee draft for the determination of selected alkyphenols in unfiltered waters is available [5]. The method proposed for nonylphenols is also suitable for octylphenol.

For the determination polybrominated diphenyl ethers, seven individual congeners are most frequently detected and therefore are proposed as indicator substances in the ISO draft method [6]. This list of congeners is currently under discussion within the drafting group.

For the chloralkanes, neither an agreed analytical reference method is available nor does a well-defined set of indicator substances exist as for other pollutants e.g. PAH or PCB. C10-C13 chloralkanes are the most challenging group of substances with respect to analyses and quantification. This group comprises a mixture of a large number of individual congeners (C10, C11, C12, C13 with varying number of chlorine atoms and varying chlorine atom positions). Analytical standard methods do not permit the identification and quantification of single isomers. In practice commercial mixtures are characterised by their chlorine content expressed as a percentage by weight. Neither single congeners nor defined pure mixtures are available as standard material commercially at present. Only technical mixtures with known chlorine content are available. The use of technical products from different manufacturers as external standard material for quantification has shown discrepancies in the results of an interlaboratory study [7]. One explanation given was that the amount of additives and impurities is different from one manufacturer to the other. According to the forementioned properties of commercial chloroalkane mixtures it seems impossible to select indicator substances. In this case the only way to gain comparability of results would be to clearly define an analytical methodology which has to be used by all laboratories participating in a common monitoring programme.

Reference methods for suspended matter and sediments ?

Under the WFD, EQS for sediment will be derived for the priority substances with sediment-partition coefficient (log Kp) ≥3 for organic contaminants or metals. When no data are available for Kp, the octanol-water partition coefficient Kow will be used (log Kow ≥3) for organic substances. In that case, contaminant concentrations in suspended matter or in settled sediment should be measured preferably than in the water phase, and compared with EQS values. Several questions arise concerning the monitoring of suspended matter. First as we have briefly discussed above, ISO/CEN standard analytical methods for the sediment and suspended matter need to be urgently developed in order to ensure the quality of data produced. Secondly, methods for suspended matter sampling also need to be developed and harmonised. Sampling methods are generally based on continuous centrifugation or large volume filtration, as sufficient amount of material is needed for the extraction steps (in particular for organic contaminants). These methods are relatively complex and costly to implement in routine laboratories (e.g. risk of sample contamination or adsorption), and the comparability of methods should be verified (e.g. different size of particles selected by centrifugation and filtration).

Also, the case of water samples with high suspended particulate matter (SPM) loads should be specifically

considered and discussed. Proposed EQS for organic substances are established on total concentration (dissolved + particulate) [4]. Thus monitoring of organic priority substances should aim at the total concentration of these contaminants in water. However, standard methods for organic contaminants do not offer any clear advice for waters with elevated SPM levels. For instance, the standards for organochlorine insecticides, PCBs and chlorobenzenes (NF ISO 6468, 1996) and for organic and phosphorous compounds (EN ISO 10695, 2000) indicate that the method is only applicable for waters with SPM below 50 mg/L and specify that interferences are higher above this level. However no recommendation is given for the treatment of waters with SPM above this limit. The standard for chlorophenols (EN 12673, 1998) simply mentions the possibility of interferences in presence of SPM that can lower extraction recoveries. The French standard for 6 PAHs (NF T 90-115, 1988) is more precise: it advises to repeat several times the extraction procedure (at least 3 times) in presence of high SPM, and recommend to filter the sample above 200 mg/l of SPM and to extract the 2 phases separately.

It is clear that solvent extraction of bulk water samples with high SPM concentrations, will be much less efficient for substances with logKp ≥3 (e.g. PCBs, PAHs, trichlorobenzenes, pentachlorophenol, endosulfan, etc.) than if performed on the SPM themselves, using extraction methods designed for solids phases such as sediment or soil. Analyses performed on unfiltered samples will provide underestimated and poor quality data.

In order to ensure comparability of results for high SPM water bodies, such as large rivers and estuaries, a thorough examination of standard methods should be taking place aiming at homogenising the recommendations for SPM treatment.

Measurement uncertainties targets

Compliance with EQS requires that the concentrations of the priority substances in water, sediment or biota be shown to be within set limits. Measurement uncertainty clearly has implications for the interpretation of analytical results in this context.

ENV ISO 13530 proposes guidelines for the definition of analytical requirements for water analysis including defining the relevant concentration range, required accuracy (or maximal tolerable error) and reporting of results. Therein is described as common practise the lowest relevant concentration being 10% of a limit value (e.g., EQS) and the maximal tolerable error being 20 to 25% of that concentration.

The "Analysis and Monitoring of Priority Substances" expert group (AMPS) of the EC for the WFD has proposed target value for measurement uncertainty on a European scale (i.e. combined standard uncertainty of 25% for all substances). The proposition is derived from information on actual laboratory uncertainties obtained from 10 European countries. The AMPS noted however that for some of the priority substances, there is currently no available data for measurement uncertainty (e.g., chloroalkanes, PBDE, TBT) and in any case, for most of them, the challenge is to decrease the uncertainty range in order to fulfill European recommendations. In addition, methodologies for uncertainties determination have to be homogenised all over Europe.

Comparability of analytical results in Europe

According to the WFD, besides ecological parameters, classification of water bodies is based on EQS set for priority substances. In order to ensure comparability of the classification schemes between different Member States and River basins, the analytical results have to be comparable. The organisation of intercomparison campaigns for analytical laboratories on a European scale would ensure progress towards such a goal.

Development of inter-laboratory trials for priority substances

In order to obtain a satisfactory comparability of monitoring results on the chemical quality of water bodies at a national and European scale, analytical performance should be improved. Efforts should focus on organic substances for which the situation appears to be the most problematic as we will show below. Within some Member States, Regions and River basins, quality assurance via proficiency testing is currently applied but does not include all priority substances. Moreover, it will be necessary to investigate how these approaches can be linked in order to achieve a European-wide comparability of analytical results. Specific intercomparison exercises for priority substances of the WFD will need to be organised on a European scale.

Since 1999, INERIS has been organising nation-wide intercomparison exercises for French analytical laboratories. This has allowed us to complete a detailed examination of past exercises, in particular concerning the priority substances that have been tested. A new set of intercomparison exercises is now being organised and it is aimed at improving performances for families of organic contaminants for which difficulties have been identified. It will also include some of the priority substances that have not been tested previously on a national level.

Interlaboratory exercises : an essential tool for quality assurance/control

Participation of analytical laboratories in intercomparison exercises constitutes an essential element of quality assurance for environmental analysis. It is the only procedure which allow a regular and reliable external test of analytical results for a given laboratory. The laboratory can compare its results to that of other laboratories and follow its performance over time for a given test. It is also the best approach to ensure the accuracy of results in the absence of appropriate certified reference materials, which are still badly lacking for organic contaminants in natural waters.

The aims of intercomparison exercises for analytical laboratories should be clearly defined and can include the following:

- to measure the quality and performance of a laboratory and obtain official accreditation and agreements from ministries ;
- to demonstrate the value of the analytical results to administration, local authorities, industries, etc. ;
- to discuss analytical problems encountered for analyses in complex matrices (marine waters, sediment, waste waters, sewage sludge, etc.) and improve the quality of a laboratory in collaborative work ;
- to evaluate the uncertainties of the results that can be linked to the methodologies (repeatability, reproducibility) ;
- to evaluate the performance of a newly developed method.

Main findings of intercomparison testing schemes in France

The objective of the study carried out by INERIS was to assess the results of 4 years of intercomparison testing (1999-2002) for the analyses of chemical contaminants in water [8]. These exercises have been organised within the framework of the provision of the official agreements for analytical laboratories by the French Ministry of the Environment. All results of intercomparison tests on natural and wastewaters obtained from participants for the 3 intercomparison schemes existing in France (i.e., organised by INERIS, BIPEA and AGLAE) were scrutinised. In general, laboratories used French (NF) or international (ISO, EN) standardized analytical methods. Results show clear tendencies for the reproducibility of results for the different water quality parameters and also clearly show areas were progress is needed. "Between laboratory" reproducibility (CVR) for a given test is the relative standard deviation calculated from all laboratory results (except outliers).

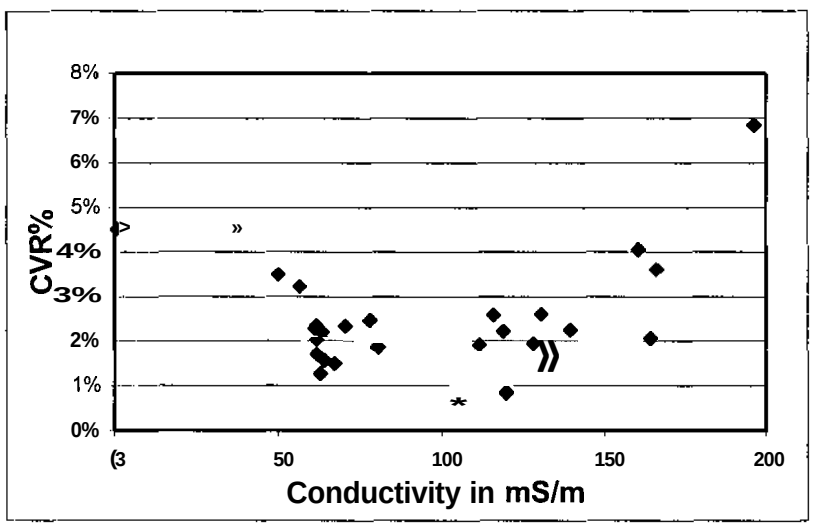


Figure 1: Reproducibility of intercomparison tests for conductivity as a function of concentration level

An average CVR for a given concentration range could be obtained for a parameter when sufficient tests had been performed (see example in Fig.1). Generally the reproducibility increased at lower concentrations.

Most results were satisfactory for general water quality parameters (e.g., pH, conductivity, alkalinity, hardness, SPM, chlorides, sulfates, nitrogen, phosphorus, potassium, calcium, etc.). For these parameters, the average reproducibility between laboratories is less than 15%, or even less than 5-10%, for a wide range of concentrations.

Reproducibility was also satisfactory (<20%) for the priority metals (i.e., Cd, Hg, Ni, Pb,) at the mg/l level, typical for contaminated wastewaters. It was much more variable and could be significantly higher for concentrations at the µg/l level (or ng/l for mercury), more representative of concentrations in natural waters and closer to the EQS levels.

For most organic contaminants, the intercomparison exercises showed that there are recurrent problems of reproducibility between laboratories. The organic substances tested were the following: polychlorinated biphenyls (PCBs, 7 individual congeners), 6 halogenated volatile organics (HVO), benzene/toluene/xylene (BTX), 15 pesticides, 9 polycyclic aromatic hydrocarbons (PAHs) and 3 chlorophenols. Several of the individual compounds tested belong to the list of priority substances of the WFD.

- For many of the organic substances tested, there are not an adequate amount of results (i.e., not enough intercomparison tests performed for a given substance), or the results are too dispersed in order to establish a trend of the reproducibility between laboratories.
- CVR are around 35% for chloroforme, tetracholoethylene and trichloroethylene for concentrations between 1-20 µg/l.
- CVR are between 30-40% for most pesticides (15-3000 ng/l) and PAH (15-2000 ng/1).
- CVR are above 40% for 16 substances. These are the PCBs (40-50%), benzene and toluene (50-56%), two pesticides (43-45 %), and chlorophenols (57-100%).

Clearly the performance of laboratories for the determination of organic contaminants in water samples needs to be improved. For this purpose, the INERIS is currently organising a specific intercomparison exercise for two families of priority substances: OHVs and PAHs. 35 laboratories in France have expressed their interest to participate in this exercise.

In order the test the capacity of laboratories to measure contaminants in water with high SPM content, the exercise will include a specific task on this matter. For the determination of PAHs, a water sample with a significant amount of SPM will be distributed. Participants will be asked to analyse PAHs in the bulk water sample and also to report results from the determination of PAHs in the dissolved and the particulate fractions separately. These exercises should enable the laboratories to improve their performances for the determination of priority pollutants and increase the reliability of results from water monitoring programmes.

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