
Title: Traceable measurements for monitoring critical pollutants under the European Water Framework Directive (WFD-2000/60/EC)

Abstract

In Europe, the European Water Framework Directive (WFD-2000/60/EC) was implemented in order to improve and protect water quality (surface water, coastal water, and groundwater) and to prevent further deterioration across Europe by the year 2015. Providing comparable measurement results for the most important water pollutants in Europe is a requirement of the water quality related directives of the EU (e.g., Drinking water directive 98/83/EC, Water Framework Directive (WFD) 2000/60 EC in conjunction with QA/QC Directive 2009/90/EC). This can be achieved by the provision of reference measurement standards, whenever possible traceable to the SI, which serve as reference points for the implementation of a traceability infrastructure supporting a monitoring network in Europe. At present, the lack of suitable reference materials as quality assurance/quality control tool for the determination of organic pollutants in the water matrix is the major obstacle to the establishment of traceability for measurement data of these substances.

The proposed Joint Research Project (JRP) should establish a primary metrological basis for the link of the test laboratories performing control measurements under the European Water Framework Directive (WFD) 2000/60/EC in conjunction with the QA/QC Directive (2009/90/EC).

Conformity with the Work Programme

This Call for JRPs conforms to the EMRP 2008, section on “*Grand Challenges*” related to *Environment* as documented in the EMRP Outline 2008. It directly addresses the need for validated and traceable techniques for “Environment - measuring flow and concentration of species under regulation” (EMRP Outline 2008 p.9) and the need for “improving measurement standards for flow and for the detection of bio and chemical releases into the environment” (EMRP Outline 2008, p.25).

Keywords

European Water Framework Directive (WFD), the QA/QC Directive (2009/90/EC), priority hazardous substance, environmental quality standard (EQS), tributyltin (TBT), pentabromodiphenylether (PBDE), primary method, IDMS, suspended particulate matter, metrological traceability, primary method, ultra trace analysis, pesticides, polycyclic aromatic hydrocarbons (PAHs), reference materials, water pollutants, aquatic biota.

Background to the Metrological Challenges

The European Water Framework Directive (WFD, 2000/60/EC) aims to improve, to protect water quality (surface water, coastal water, and groundwater) and to prevent further deterioration across Europe by the year 2015.

The implementation of the WFD depends on the availability of primary analytical methods and materials for the priority substances specified in the directive. They are indispensable for linking test laboratories with the SI and for assuring EU-wide comparable measurement results for unambiguous assessments of waters as required of the WFD. The WFD requires the monitoring of water quality to be performed by methods that are conform to the CEN/ISO standards or with other national or international standards which will ensure the provision of data of an equivalent scientific quality and comparability.

The WFD specifies a list of 33 priority water pollutants, 13 of them are identified as priority hazardous substances. For these 33 substances, Environmental Quality Standards (EQS), equivalent to the maximum allowable concentrations, had been defined at very low levels, e.g. TBT: 0.2 ng/L and Σ PBDE: 0.5 ng/L. EQS values refer to the whole water body, i.e. include contaminants which are associated to suspended solids or colloids present in the natural water. For reliable measurement of contaminants at EQS level, analytical methods are required for test laboratories which have a limit of quantification (LOQ) equal to or lower than 30 % of EQS. Therefore, primary methods of measurement, which should be the reference for the test laboratories, should have a considerably lower LOQ. Such methods are not available yet. Primary methods for the analysis of selected priority hazardous substances as specified in the WFD are required for NMIs and field laboratories.

European harmonized methods are already available through CEN/TC230 "Water analysis" and ISO/TC147 "Water quality" for a large number of substances but not all are compatible with the WFD.

An inventory by CEN TC 230 identified a lack of applicable methods for five priority hazardous substances including TBT and PBDE. The existing ISO standard 17353:2004 "Water quality – determination of selected organotin compounds – gas chromatographic method" allows quantification of TBT down to a limit of about 10 ng/L only. For analysis of PBDE in water an international standard is missing. The standard ISO 22032:2004 "Water quality – determination of selected polybrominated diphenylethers in sediment and sewage sludge – method using extraction and gas chromatography/mass spectrometry" refers to solid matrices only. Both standards do not address the problem of determining the fraction of analytes which is not dissolved but bound to suspended particulate matter.

In April 2008 CEN received a mandate M/424 "Mandate for standardization addressed to CEN for the development or improvement of standards in support of the Water Framework Directive (WFD-2000/60/EC)" from the European Commission, DG Environment. In September 2008 CEN launched a call under mandate 424 for the development of European standards for the ecological and chemical status monitoring requirements of the WFD. The call included 5 analytical methods for PBDE, TBT, chlorinated pesticides, polycyclic aromatic hydrocarbons and short chain chlorinated paraffins. Mandate 424 shall provide robust analytical methods which enable test laboratories to measure priority hazardous substances under the WFD regulation on a routine basis. However, the objective mandate M424 is to develop European standards in whole water and not the analysis of pollutants in sediments or biota. The WFD states that the Commission shall submit proposals for quality standards applicable to the concentrations of the priority substances in surface water, sediments or biota¹. Reference methods for the determination of contaminants in sediments, suspended particulate matter (SPM) and biota also need to be developed urgently in order to ensure the production of good quality data. Standards for test laboratories will be developed within a project of CEN under mandate M424 but primary analytical methods which are the basis for metrological traceability are relevant to the EMRP.

Several CCQM international intercomparisons (e.g. CCQM-P18 & K28 for tributyltin in marine sediments; P-114 for selected PBDEs in plastics) have proven the measurement capability of National Metrology Institutes for the accurate measurement of the total mass fraction of a range of WFD listed priority pollutants at $\mu\text{g/g}$ levels by IDMS and hyphenated MS techniques in a range of matrices. However the maximum limits of the majority of substances, elements and their compounds in water, as listed in the WFD, are at the ng/l levels. Achieving accurate results for target pollutants, at such low levels in complex water matrices represents a major challenge that cannot be easily tackled using current methods. Therefore, efforts have to be made to develop/validate efficient sample extraction/preconcentration techniques capable to preserve the target pollutants as well as novel sample introduction devices to improve the detection capabilities of current mass spectrometry detection systems. Moreover, there is insufficient knowledge on the stability of the key pollutants at ng/l levels in different compartments of aquatic systems and no reference materials for inorganic toxins element-tagged compounds in water.

Scientific and Technological Objectives

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them, in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the JRP protocol.

¹ WFD, 2000/60, Item 7 article 16

The focus of this topic is the development of a primary metrological basis for the link of the test laboratories performing control measurements under the European Water Framework Directive (WFD) 2000/60/EC in conjunction with the QA/QC Directive (2009/90/EC).

The specific objectives are:

1. Development of a metrology infrastructure for pollutants in aquatic environments, including aqueous soils, sediments and biota media, under the WFD.
2. Development and validation of traceable measurement methods for samples which contain priority substances in concentration as low as required by the WFD. These methods must be applicable in routine laboratories conditions.
3. Development and validation of sample preparation techniques for the quantitative extraction and preconcentration of key analytes from the aquatic compartments.
4. Development of reference materials in respect with the concept of "whole water" defined in the WFD, thus including suspended particulate matter (SPM), sediments and biota.
5. Development of methods for the preparation of sufficiently homogeneous and stable aqueous proficiency testing samples which contain the target analytes in concentration as low as required by the WFD.

Proposers shall give priority to work that meets documented stakeholder needs and may include measures to facilitate the development of European standards and Directives.

Proposers should establish the current state of the art, and explain how their proposed project goes beyond this.

Potential Impact

Proposals must demonstrate adequate and appropriate participation/links with the "end user" community. This may be through the inclusion of unfunded JRP partners or collaborators, or by including links to industrial/policy advisory committees, standards committees or other bodies. Evidence of support from the "end user" community (eg letters of support) is encouraged.

Where a European Directive is referenced in the proposal, the relevant paragraphs of the Directive identifying the need for the project should be quoted and referenced. It is not sufficient to quote the entire Directive per se as the rationale for the metrology need. Proposals must also clearly link the identified need in the Directive with the expected outputs from the project.

In your JRP submission please detail the impact that your proposed JRP will have on the European Water Framework Directive (WFD) 2000/60/EC in conjunction with the QA/QC Directive (2009/90/EC)

You should also detail other impact of your proposed JRP as detailed in the document "Guidance for writing a JRP"

You should detail how your JRP results are going to:

- feed into the development of urgent standards through appropriate standards bodies, such as CEN and ISO.
- transfer knowledge to the calibration and test laboratories, environmental monitoring sector, regulators and policy makers.

You should also detail how your approach to realising the objectives will further the aim of the EMRP to develop a coherent approach at the European level in the field of metrology. Specifically the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of Member States and countries associated with the Seventh Framework Programme whose metrology programmes are at an early stage of development to be increased
- outside researchers & research organisations other than NMIs and DIs to be involved in the work

Time-scale

The project should be of 3 years duration.

Additional information

- [1] 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, <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0060:EN:NOT>