Final Publishable JRP Summary for ENV08 WFD
Traceable measurements for monitoring critical pollutants under the European Water Framework Directive (WFD-2000/60/EC)

Overview

The project developed primary reference methods for selected water pollutants as well as concepts for whole water reference materials and test materials that can meet the requirements of the European Water Framework Directive (WFD) and related Directives. The project also helped to improve the quality and comparability of monitoring data obtained by laboratories under the WFD.

Need for the project

The project was undertaken to support the implementation of the WFD and related directives 2008/105/EC: (Directive on Environmental Quality Standards (EQS) in the field of water policy) and 2009/90/EC (Directive on technical specifications for chemical analysis and monitoring of water status). These directives establish a legal framework to protect and restore clean water across Europe and ensure its long-term sustainable use. Directive 2008/105/EC specifies a list of priority water pollutants which present a significant risk to or via the aquatic environment. For these substances EQS values, equivalent to the maximum allowable concentrations, have been defined. EU member states are then obliged to implement monitoring programs to control compliance of their water bodies with the defined EQS.

The priority substances are toxic, persistent and liable to bioaccumulate within the food chain and can endanger a wide range of living organisms. Therefore the EQS for several pollutants are very low, e.g.

- Tributyltin (TBT): 0.2 ng/L
- ∑ Polybrominated diphenylether (PBDE): 0.5 ng/L
- Selected Polycyclic Aromatic Hydrocarbons (PAH), e.g. ∑ Benzo(g,h,i)perylene, Indeno (1,2,3-cd)pyrene: 2 ng/L

EQS values refer to whole water and include contaminants associated with suspended solids or colloids. For reliable measurement of pollutants at EQS levels analytical methods are required that have a limit of quantification (LOQ) equal or lower than 30% of the EQS with a relative expanded uncertainty ≤ 50 % at the EQS (Directive 2009/90/EC). Therefore primary reference methods (i.e. at National Metrology Institute (NMI) level) are necessary to underpin these requirements. Besides the very low LOQs the presence of colloids and suspended matter in natural waters represent a particular challenge for the analysis. Very often organic contaminants are strongly bound to colloids and particles which hampers exhaustive extraction. Therefore knowledge about the distribution, interaction and partitioning of the target analytes in whole water are important for method development..

In 2008 an inventory by CEN Technical Committee 230 'Water Analyses' identified a lack of standardised, analytical methods able to meet the WFD requirements for substances such as TBT, PBDE and some PAH. In particular primary reference methods (i.e. at National Metrology Institutes (NMIs)) that provide accurate and traceable determination of these pollutants at EQS levels did not exist. While the European Commission tasked CEN via Mandate 424 to develop and improve standards for routine test laboratories it required the input of the metrology community to develop the primary measurement capabilities.

In addition well characterised reference materials that represent real water samples with contaminants at EQS levels were needed for intercomparisons and proficiency testing schemes. Furthermore, field

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laboratories undertaking water monitoring under the WFD need such materials for the validation of their in-house methods and for the establishment of reliable quality assurance and quality control (QA/QC) systems.

Scientific and technical objectives

The central aims of the project were the development of primary reference methods and materials in support of the WFD. The work also focused on three analytes; TBT, PBDE and PAH. The project addressed the following scientific and technical objectives:

1. Validated primary reference methods based on isotope dilution for the analysis of selected priority contaminants (TBT, PBDE, PAH) in whole water samples at EQS levels. Methods will have specific LOQs and a measurement uncertainty of ≤ 50 % at the EQS. Methods will be traceable to the International System of Units (SI).
2. Systematic study of the interaction and partitioning of pollutants (PBDE, TBT) in environmental aquatic compartments by field flow fractionation techniques; mass balance data for the size based distribution of pollutants in whole water samples.
3. Development of preparation methods for aqueous reference materials with proven homogeneity, short and long time stability, which are as close as possible to real water samples, i.e. including suspended particulate and colloidal matter.
4. An intercomparison and workshop for stakeholders to disseminate the methods and materials developed in the project.

Results

Validated primary reference methods for the analysis of selected priority contaminants (TBT, PBDE, PAH) in whole water samples at EQS levels.

Reference method for TBT
Two measurement procedures based on gas chromatography in combination with inductively coupled plasma mass spectrometry and tandem mass spectrometry were developed and validated for the quantitative determination of TBT in whole water samples containing organic and suspended particulate matter. Preconcentration and extraction techniques (liquid/liquid extraction, solid phase extraction, solid phase microextraction, large volume injection) as well as the derivatisation conditions were optimised and compared; and liquid/liquid extraction was found to be the most suitable extraction procedure. Quantification was based on isotope dilution using a tin labeled TBT standard. In addition, a Tributyltin Chloride (TBTCl) calibration standard was assessed for purity by ^{13}C and ^{1}H quantitative nuclear resonance spectroscopy in order to establish traceability. Objective 1 of the project was achieved for TBT. Both methods are traceable and meet the requirements of the WFD with respect to LOQ and uncertainty at EQS. They can be used by NMIs, proficiency testing providers or reference materials producers to provide benchmarks for testing laboratories

Reference method for PBDE
Methods such as liquid-liquid extraction and solid phase extraction using discs or cartridges were tested and compared for measuring PBDE in surface and coastal waters. The goal was to extract and analyse whole water without separation of the suspended particulate matter. The PBDE congeners contained in the penta-PBDE mix were quantified using gas chromatography in combination with inductively coupled plasma mass spectrometry and tandem mass spectrometry, respectively. From the results a complete uncertainty budget was prepared for each method and results were compared regarding the limits of detection, possible interferences and uncertainty.

As there are a large number of bromine-containing organic molecules (artificial and natural), that can interfere with PBDE congeners in real water samples, more than one method was developed by the project in order to achieve accurate results. No one particular method developed by the project had a clear advantage for measurements of PBDE, therefore the conclusion was that the choice of the method may vary depending on the complexity and contamination level of the samples as well as the accuracy required. All

methods developed for PBDE measurements meet the requirements of the WFD with respect to LOQ and uncertainty at EQS. Objective 1 of the project was achieved; the methods are now ready for use.

Reference Method for PAH
Liquid/liquid extraction and solid phase extraction with disks and cartridges were optimised and compared for the development of a reference method for PAH in whole water samples. The LOQ required by the WFD were achieved in mineral water spiked with humic acids and in water containing suspended model particulate matter for all WFD regulated PAH except indeno(123-cd)pyrene and benzo(ghi)perylene. The relative expanded uncertainties obtained at EQS were also lower than 50 % for all target analytes. The project also compared a one step solid phase disk extraction of PAH from whole water samples with a two-step extraction method (filtration, liquid/liquid extraction of the dissolved part, pressurised liquid extraction of the filter) and found that both methods gave comparable results. Objective 1 of the project was achieved for six out of the eight PAH regulated under the WFD.

Systematic study of the interaction and partitioning of pollutants (PBDE, TBT) in environmental aquatic compartments by field flow fractionation techniques; mass balance data for the size based distribution of pollutants in whole water samples.

The project developed and tested methods for the interaction and partitioning of pollutants (PBDE, TBT) in environmental aquatic compartments, methods included field-flow fractionation and classical (ultrafiltration and centrifugation) techniques applicable for the separation of environmentally relevant colloids in natural waters. The optimised methods were applied to natural and synthetic samples containing PBDEs and TBT. Mass balances were established for the distribution of TBT in water containing humic acids in order to provide data on the size based distribution of pollutants in whole water samples. These new measurement capabilities provide better elucidation and understanding of the interaction of critical environmental pollutants with natural colloids present in water.

For PBDE low recoveries were observed in the field-flow fractionation experiments due to adsorption of the target analytes on the membrane and other parts of the equipment. Furthermore significant contribution of other endogenous Br-containing compounds hampered the measurements. These problems could not be fully resolved despite of extensive efforts to optimize the field-flow fractionation conditions. It was therefore not possible to establish sound mass balances for PBDE. Objective 2 of the project was fully achieved for TBT but only partly for PBDE.

Development of preparation methods for aqueous reference materials with proven homogeneity, short and long time stability, which are as close as possible to real water samples, i.e. including suspended particulate or colloidal matter.

Three types of aqueous reference materials were successfully developed by the project for PAHs, PBDEs and TBT at ng/L levels. These materials contain dissolved humic acids and suspended particulate matter (SPM) and were a major step towards producing aqueous reference materials that mimic whole water.

Jet milling of soils and sediments with known or certified pollutant concentrations has been proven by the project, as an alternative method for the production of model-SPM for the preparation of aqueous reference materials. Furthermore, the small particle size obtained by the method provides a realistic simulation of the particulate phase in water.

In addition, the project found that aliquot sampling from continuously stirred slurries was both a reproducible and reliable method of adding the model-SPM to pre-filled water bottles. This method also has the possibility of being automated. Using this method, the project produced ready-to-use aqueous reference materials with low between-unit heterogeneity, which were validated by measurements at the ng L^{-1} level. The method also allowed the preparation of a larger number of water samples within one campaign and was therefore suitable for producing water samples for proficiency testing schemes.

The only issue unresolved is the long term stability of aqueous reference materials. From the conditions tested in the project gamma-irradiation (the typical method used to stop degradation over time) was found to be unsuitable for the preservation of prepared samples. However, sufficient evidence of stability was gathered for samples kept at 4 °C in the dark for at least 4 weeks. This period of time was chosen as it is

sufficiently long to conduct a proficiency testing intercomparison. Future developments may include the supply of SPM and the associated water matrix separately (i.e. distributed as a kit) for field labs to assemble themselves or the determination of gamma-irradiation conditions that do not cause major analyte break-down.

Nonetheless, the results of the project constitute a significant improvement with respect to the production of aqueous reference materials at sub ng/L levels and that are more realistic water samples at sub ng/L levels. Objective 3 of the project was achieved.

An intercomparison and workshop for stakeholders to disseminate the methods and materials developed in the project.

An interlaboratory comparison was conducted for field laboratories. Thirteen external laboratories from 8 European countries participated in the intercomparison together with 11 project partners, thereby testing the in-house methods of field laboratories with the aqueous reference materials developed in the project as well as the reference methods developed for NMIs. Six different types of water samples were distributed in triplicate, two types each for TBT, PBDE and PAH. In total approximately 250 1-L sample units were prepared and shipped to participants. The samples contained organic colloids (humic acids) and/or suspended particulate matter and therefore met the requirement of the WFD for whole water samples.
Results of the intercomparison were discussed at a final stakeholder workshop held in September 2014 in Berlin. They demonstrated that most parameters could be successfully measured with reasonable agreement between the laboratories. This constitutes a significant achievement as no such intercomparsion has been performed before on whole water samples with analyte concentrations well below ng/L (for some of the parameters). In addition the project partners tested their newly developed reference methods in the intercomparison successfully. Objective 4 of the project was achieved.

Actual and potential impact

The reference methods and materials developed in the project enable National Metrology Institutes, reference materials producers or proficiency testing providers to deliver metrological services for the testing labs that conduct tests of real water samples under the WFD (e.g. services such as production and certification of reference materials, characterization of proficiency testing samples, estimation of reference values for proficiency testing schemes, calibration services). Using these services testing labs can benchmark their routine methods against NMIs by via reference materials and/or regular participation in proficiency testing schemes and so maintain and validate an appropriate QA/QC system in order to perform water monitoring services more accurately, efficiently and economically. As a result, water testing and monitoring results are linked to the International System of Units (SI) and the comparability between testing labs is improved. This ensures long-term reliability and global comparability of water monitoring data obtained under the WFD and supports better decision-making in the field of water management.

All the contaminants investigated in this project accumulate within the food chain and thus endanger humans. The uptake of them via the food is a serious health and social problem. By providing validated reference (primary) methods and materials for TBT, PBDE and PAH the project is helping to reduce the presence of these compounds, according to the requirements of the WFD, to a level considered not harmful.

To ensure the increased of accurate and comparable measurements of water quality the results of the project were widely disseminated to the key user communities;

- Four peer-reviewed papers in the scientific literature. Eleven more publications have been submitted/are under preparation.
- Approximately 40 oral presentations and posters at international conferences and workshops.
- Input was provided to CEN TC 230 draft analytical standards under Mandate 424 for the analysis of TBT, PBDE and PAH in whole water samples. Results of the project have been forwarded and discussed in several national standardisation bodies such as DIN (German Institute for

Standardisation), Standard Committee for water issues, AFNOR (French standardisation body), Committee T91M "Micropollutants in water" or LAWA (German Working Group on water issues of the Federal States and the Federal Government).

- Presentations of the outcomes of the project have also been given at a number of metrological committees, in particular at working groups' meetings of the European Association of National Metrology Institutes (EURAMET) and the Bureau International des Poids et Mesures (BIPM) and the annual meeting of the European reference materials (ERM) consortium. These presentations ensured that the results reached the wider community of National Metrology Institutes and Designated Institutes. In addition the project supported the Bulgarian Institute for Metrology (BIM) to strengthen their metrological and measurement capabilities.
- Twelve training courses were organised for consortium members and external partners.
- An intercomparison and workshop was organized for stakeholders.

The dissemination activities have ensured that the project outputs have already being used by the wider community;

- Around 300 samples (both water samples and model suspended particulate matter) were supplied to CEN (under CEN Mandate 424) for method development and validation. This has contributed to the development of three standardized routine methods for TBT, PAH and PBDE. These methods are now under approval and will be published in summer 2015. Once approved they will be directly applied by testing labs for the monitoring of water.
- Several of methods developed in the project are being used by testing laboratories:
  - Methods developed for the analysis of organotin compounds have been implemented by a Spanish environmental testing company
  - A method developed for the determination of nanoparticles has been implemented by an Irish public research institute
  - A method has been applied for an interlaboratory performance study: "Detection/quantification of silver nanoparticles in an aqueous matrix" organised by JRC of the European commission to support forthcoming regulations.
  - Methods developed in the project have been used to establish reference values for a French Proficiency testing scheme for organotin compounds. About 15 field laboratories participated. With the reference values they were able to benchmark the performance of their in-house procedures.

Increased use of accurate and comparable measurements is expected to increase with time, driven in particular by the publication of the CEN standards that will outline the measurements to be used. These standards are a key route to uptake of accurate and comparable measurements and therefore the project will have made a significant contribution to the long-term reliability and global comparability of water monitoring data obtained under the WFD.

List of publications

[1] Adriana Gonzalez Gago, Daniel Proefrock and Andreas Prange, *Optimizing GC-ICP-MS for ultra-trace quantification of PBDEs in natural water samples using species specific isotope dilution,* Journal of Analytical Atomic Spectrometry, in press, DOI: 10.1039/C4JA00112E.

[2] Claudia Swart, Fanny Gantois, Panayot Petrov, John Entwisle, Marjaana Nousiainen, Mine Bílsel, Burçu Biniçi, George Sawal and Adriana Gonzalez-Gago, *Comparison of various measurement procedures as potential primary measurement procedures for PBDE in surface water*, Accreditation and Quality Assurance, submitted.

[3] Enrica Alasonati, Barbara Fabbri, Ina Fettig, Catherine Yardin, Maria Estela Del Castillo, Janine Richter, Rosemarie Philipp and Paola Fisicaro, *Experimental design for TBT quantification by isotope dilution*

SPE-GC-ICP-MS under the European Water Framework Directive, Talanta, in press, DOI: 10.1016/j.talanta.2014.11.064.

[4] Saioa Elordui-Zapatarietxe, Ina Fettig, Rosemarie Philipp, Fanny Gantois, Beatrice Lalere, Claudia Swart, Panayot Petrov, Heidi Goenaga-Infante, Guido Vanermen, Gerard Boom and Håkan Emteborg, *Novel concepts for preparation of reference materials as whole water samples for priority substances at ng L^{-1} level using model suspended particulate matter and humic acids*, Analytical and Bioanalytical Chemistry, in press, DOI: 10.1007/s00216-014-8349-8.

[5] Janine Richter, Ina Fettig, Rosemarie Philipp and Norbert Jakubowski, *Tributyltin-Critical pollutant in whole water samples, Development of traceable measurement methods for monitoring under the European Water Framework Directive (WFD) 2000/60/EC*, Journal of Analytical Atomic Spectrometry, submitted.

[6] Janine Richter, Ina Fettig, Christian Piechotta und Norbert Jakubowski, *Tributylzinn in Gesamtwasserproben - Entwicklung eines Referenzverfahrens für die EU-Wasserrahmenrichtlinie*, GIT-Laborfachzeitschrift, **9** (2013) 2-4.

[7] Julie Cabillic, Sebastian Hein, Petra Lehnik-Habrink, Elisa Calabretta, Monica Potalivo, Ahmed Ceyhan Goren, Mine Bilsel, Ileana Nicolescu, Mugurel Georgescu, Beatrice Lalere and Rosemarie Philipp, *Joint Research Project ENV08 "Traceable measurements for monitoring critical pollutants under the European Water Framework Directive (WFD) 2000/60/EC"*, Proceedings of the 16th International Congress of Metrology, Paris, 2013, DOI: 10.1051/metrology/201310001.

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