Publishable Summary for 14RPT03 ENVCRM
Matrix reference materials for environmental analysis

Overview

This project aimed to develop capacity to produce certified reference materials (CRMs) for environmental analysis by transferring know-how between the partners and combining their skills to focus on environmental CRM production. The production process included good manufacturing practices for processing materials, method development, the validation and application of homogeneity, stability and characterisation tests, the calculation of individual uncertainties (between-unit inhomogeneity, long term stability, characterisation) and combination of uncertainties to determine overall uncertainty of the matrix reference materials. An interlaboratory comparison registered as a EURAMET project was set as the ultimate project outcome, confirming the partners' capabilities in applying newly acquired skills. As a result of the project, new CRMs are available and the partners have developed strategies for long term research capabilities for environmental CRMs.

Need

The need for quality assessment of anthropogenic impact on environmental pollution is increasing due to discharge from various industries, the use of chemicals in agriculture, and the consumption of fossil fuels. Diminishing resources such as drinking water, soil used for the cultivation of agricultural products, and plant and animal habitats are under severe pollution pressure and are at constant risk. The EU has stipulated the maximum allowable concentration of priority pollutants in different classes of surface water under the Water Framework Directive in Directive 2008/105/EC Annex I "Environmental quality standards for priority substances and certain other pollutants", and for the purpose of assessing the quality of river and marine sediment, Canadian and Dutch guidelines are used. Prescribed limits for pollutants are adopted and adapted by regulations at the local level. In addition to ISO 17034, prescribing the general requirements for the competence of reference material producers, standardised methods such as ISO and EN standards for sampling, homogenisation and testing of the pollutants in water,sediment and soil samples are available.

In order to establish a quality system in the testing of environmental samples conducted by dedicated laboratories, it is necessary to provide appropriate quality control materials i.e. matrix CRMs. The term "appropriate" relates to the unique sample matrices representing typical samples in the geomorphological and anthropological sense. In addition to that, bearing in mind the complexity, variability and instability of environmental samples, it is very difficult to obtain appropriate reference materials with no local providers. Dedicated laboratories require strong support from the metrology system for proving competence in performing quantitative tests. Laboratories operating under the watershed, environment and health sectors are recognised as the main stakeholders of this project. Matrix reference materials produced within the project will serve stakeholders locally through the corresponding National Metrology Institutes (NMIs) and Designated Institutes (DIs).

Objectives

The overall objective of this project was to develop research capability for the production of environmental reference materials. The specific objectives were:

1. **Production of CRM Candidates –** through design and production of two inorganic (heavy metal) and one organic pollutant candidate CRMs at NMIs having production facilities for developing traceability to SI units of the measurements performed by environmental analysis laboratories.
2. **Homogeneity and Stability Tests of CRM Candidates –** by designing and carrying out tests to measure the analyte composition of a calculated number of randomly selected units covering the

whole production batch for each candidate CRM and determining the effect of storage and transport temperature and time on the uncertainties.

3. **Characterisation of the CRM Candidates –** via certification campaigns among NMIs, DIs and university research laboratories with comparable measurement capabilities by employing reference analyte measurement techniques such as IDMS (isotope dilution mass spectrometry) for high accuracy and low uncertainty (target uncertainties will depend on the analytes selected and will be in the range of 10 % to 20 %).
4. **Certification of the CRMs –** by drafting and reviewing certification reports with all the information collected throughout the investigation of the materials.
5. **Long term research capability for environmental CRMs –** via development of individual and/or consortium strategies for each partner with discussions within the consortium in collaboration with the communities of each country to determine the priorities and draw up a road map for quality schemes and develop plans to offer services and products from the established capacities.
6. **Contribution to impact –** via contribution to regional and international standards and committees and dissemination of outputs of the project to the end users (e.g. providing the developed CRMs for use by environmental analysis laboratories).

Progress beyond the state of the art

The progress beyond the state of the art was measured on a local level (at NMIs) in terms of matrix CRM production capability, thus fulfilling preconditions for providing suitable matrix CRMs and proficiency test services to stakeholders. At the end of the project, all the NMIs involved have the capacity to carry out all aspects of CRM development and certification including material sampling, preliminary measurements, production of candidate materials (including spiking/blending, homogenisation, bottling and storage), homogeneity and stability testing, development of reference methods (including methods for homogeneity and stability tests, instrument-based methods and standardised technical methods), sample preparation and characterisation, calculation of the results and uncertainties and drafting of certificates. Each partner will benefit from an individual plan for further research and development of CRMs based on stakeholder needs and the results achieved in the project.

Additionally, as a direct result of this project new CRMs are available that differ in matrix, analyte(s) and concentration from those on the market prior to the start of the project. Uncertainty values for the analytes are comparable to commercially available CRMs (e.g. 7 % to 11 % for Cd and Pb in contaminated soil). The mix of analytes and the matrix composition of the new CRMs are appropriate to the region in which the partner NMIs are located. The stability and transportation conditions of the CRMs was analysed as part of the certification process, allowing uptake by industry.

Results

Production of CRM Candidates:

Two inorganic (As, Cd, Hg, Ni, Pb and Se in river water and As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, V, Zn in soil) and one organic pollutant (PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid) in ground water) candidate CRMs were produced at TUBITAK UME, Turkey, using state-of-the-art production facilities for developing traceability of the measurements to the SI and supporting quality assurance/control (QA/QC) activities performed by environmental analysis laboratories. All raw materials were collected from locations in Turkey to ensure representation of the samples that the environmental analysis and monitoring laboratories routinely analyse. River water was collected from a creek which is feeding a reservoir supplying water to İstanbul. Soil was collected from a coal burning power plant area at the district of Ankara. Ground water was collected from a well operating in İstanbul supplying water for the swimming pools and irrigation of gardens. After bottling, CRM candidates were gamma sterilised to further enhance their stability and extend their shelf-lives.

This objective has been achieved.

Homogeneity and Stability Tests of CRM Candidates:

Tests were performed by TUBITAK, SYKE and JSI to measure the analyte composition of a calculated number of randomly selected units covering the whole production batch for each candidate CRM and determining the effect of storage and transport temperature and time on the uncertainties. Results confirmed by other partners showed that the candidate materials are homogenous and stable enough (except Hg in river water) to proceed with the characterisation study.

This objective has been achieved.

Characterisation of the CRM Candidates:

Certification campaigns were organised among NMIs, DIs and university research laboratories with comparable measurement capabilities by employing reference analyte measurement techniques such as IDMS and INAA (instrumental neutron activation analysis) for high accuracy and low uncertainty. For the elements in river water candidate material a EURAMET supplementary comparison study (EURAMET.QM-S11/EURAMET 1424) was organised. Candidate reference material samples were measured by 22 laboratories from 17 countries and initial evaluation of results has been completed. Seven project partners contributed to this characterisation of soil candidate material. A BIPM CCQM comparison study (CCQM-K156 / P198) using “PFOS and PFOA in Ground Water” candidate reference material is scheduled to be completed in May 2019.

This objective has been partially achieved and characterisation of the organic candidate material will be completed in May 2019.

Certification of the CRMs:

Certification reports have been prepared for the river water and soil materials by drafting and reviewing with all the information collected throughout the investigation of the materials.

This objective has been partially achieved and certification of the organic candidate material will be completed following the end of the comparison in May 2019.

Long term research capability for environmental CRMs:

Individual strategies have been developed for each partner. These are based upon discussions within the consortium in collaboration with the communities of each country to determine the priorities and draw up a road map for quality schemes and develop plans to offer services and products from the established capacities.

This objective has been achieved

Impact

Summary of dissemination activities

The work carried out in the project has reached a wider scientific audience at scientific conferences such as International Symposium on Biological and Environmental Reference Materials (BERM 14-USA), 9th and 10th Intrumental Methods of Analysis-Modern Trends and Applications (IMA 2015 and IMA 2017-Greece), ECOBALT Conference (2016-Estonia).

In total 23 oral and poster presentations have been given at international and national conferences and workshops by the partners during the project lifetime.

Two workshops were held in Kocaeli, Turkey in June 2015 and in May 2018, where the needs of environmental analysis laboratories in the partnering countries were shared and discussed among the attendees in the first workshop. In both workshops, research activities of the project partners in the field of environmental analysis were presented. Attendees also benefited from informative presentations on the use of reference materials, reference material search databases, software for uncertainty calculations, primary measurement techniques such as IDMS and INAA and evaluation of standard methods for soil analysis.

Impact on the metrological and scientific communities

The main impact of this project has been to build the capacity and capability in the partner institutes for producing and certifying environmental reference materials. This in turn will have an impact on environmental monitoring in those countries and on the scientific community, who will use the newly developed reference

materials. Furthermore, the NMIs/DIs have developed strategies for producing new CRM either on their own or in cooperation with partner institutes. This will lead to regional CRM programmes serving scientific and official laboratories. Further collaboration for the production of sea water and fish candidate reference materials has already been initiated among the project partners.

The NMIs/DIs participating in this project will apply for new Calibration and Measurement Capabilities (CMCs) statements recorded in the BIPM Key Comparison Database (KCDB). The CMCs focus on the determination of inorganic and organic analytes in environmental matrices and on the reference materials certified within this project. An international comparison study will be proposed at BIPM CCQM on rare earth elements with the use of the soil CRM produced within the EnvCRM project.

Additionally the partners have contributed to the EURAMET Technical Committee for Metrology in Chemistry (EURAMET TC-MC) and kept them informed at its annual meetings about the progress achieved in the project.

A possible collaboration with EU COST Action TD1407 (www.costnotice.net) has been initiated for an unforeseen use of the candidate reference materials. This COST Action aims for better characterisation of 'technology-critical elements' (e.g. platinum group elements, rare earth elements, Ga, Ge, In, Te, Nb, Ta, Tl) in the environment. One of the objectives is the improvement of analytical methods for the determination of the aforementioned metals in environmental samples.

One of the important problems associated with this is defined as the lack of suitable environmental certified reference materials for these metals; as a consequence the COST action will test the candidate reference materials produced in this project for suitability for an interlaboratory comparison of platinum group elements. Inorganic candidate reference material samples were supplied to laboratories in Spain and France to be tested for suitability.

Impact on industrial and other user communities

The project outputs will have substantial impact on NMIs dealing with the production and certification of matrix reference materials, on the water quality monitoring networks, in particular the National Reference Laboratories (NRLs) involved in QA/QC activities, and with industry dealing with water quality.

Impact is being created by making available:

- Robust and comparable analytical data, based on homogeneity and stability of selected organic and inorganic analytes,
- Improved knowledge and good practice of production and certification of matrix reference materials,
- Better understanding of influencing matrix components and impurities,
- Newly gained and improved traceability in production and certification of matrix reference materials.

The project goal was to achieve data quality objectives set by EU regulation and implement them in participant countries. By doing this, measurements of water pollution will achieve better comparability with European regulations and will have improved traceability in each participant country.

Impact on relevant standards

There are several EC & EU directives and position papers which deal with contaminants in the environment, in food, and in water, and related directives and regulations ensuring environmental and health protection, such as those listed below:

- Water Framework Directive (2000/60/EC, amended by Decision 2455/2001/EC and Directives 2008/32/EC, 2008/105/EC and 2009/31/EC);
- Registration, Evaluation, Authorisation and Restriction of Chemicals, Regulation (EC) No 1907/2006;
- Waste Electrical and Electronic Equipment Directive 2012/19/EU;
- Restriction of the use of certain hazardous substances, directive 2011/65/EU.

All these directives and papers have an underpinning need for more reliable measurement data of environmental contaminants to support their implementation, which in turn requires a larger number of reliable CRMs. Particularly with regard to upcoming new legal limits for contaminants, there is a pressing need for

more CRMs. Current reference material institutes are at their limits and therefore it is necessary to introduce or increase the capability and capacity of new upcoming institutes to produce CRMs, which is the primary objective of this project. Institutes producing CRMs automatically contribute to and influence standardisation working groups and technical committees. In light of the findings of the soil characterisation study in this project, information has been shared with ISO technical committees for improvement of relevant standards (ISO 14869-2:2002 and ISO 14869-3:2017) on analysis of soil.

Longer-term economic, social and environmental impacts

The project will result in long term public benefit by providing tools for the reliable analysis of environmental pollutants.

The EU water quality directive 2000/60/EC with corresponding directives (Environmental Quality Standards Directive 2008/105/EC etc.) aims at adequate control of water resources. By conducting specific measures against pollution of water by individual pollutants or groups of pollutants presenting a significant risk to or via the aquatic environment, long-term deterioration of freshwater quality and quantity can be avoided, therefore achieving sustainable management and protection of freshwater resources.

The impact of the project will be to reduce the risk of exceeding the maximum allowable data quality objectives set by EU directive. This will be achieved by preparing each country for the production and/or certification of matrix CRMs needed for adequate QA/QC activities, and improvement of the services offered by calibration laboratories to end-users by achieving full traceability for CRMs developed in this project. Ultimately, the outcome of this project will contribute to a more reliable and robust water monitoring network incorporating a harmonised approach able to fulfil EU regulation.

<table>
<tr><td colspan="2">Project start date and duration:</td><td>01 June 2015, 36 Months</td></tr>
<tr><td colspan="3">Coordinator:
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<tr><td>Internal Funded Partners:
1 TUBITAK, Turkey
2 BAM, Germany
3 GUM, Poland
4 JSI, Slovenia
5 IMBiH, Bosnia and Herzegovina
6 DMDM, Serbia
7 SYKE, Finland</td><td>External Funded Partners:
8 NTUA, Greece
9 UW, Poland</td><td>Unfunded Partners:</td></tr>
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