Publishable JRP Summary Report for ENV51 MeTra Traceability for Mercury Measurements

Background

Mercury in its many chemical forms is highly toxic to human, animal and environmental health. Its ability to accumulate in terrestrial and aquatic biosystems makes it an insidious threat to environmental sustainability. Its long lifetimes and ability to be transported in air over long distances mean that it is ubiquitous to all environmental compartments and is a pollutant of global concern. The increase in the presence of mercury in the environment has been due to human activity over the last hundred years, and whilst legislation is in place to limit human releases, the assessment of the ongoing effect of mercury on humans and the environment is critically dependent on accurate measurements to assess concentrations and trends. This challenge is complicated by the various chemical forms of mercury and its presence in a number of different matrices.

Despite this, the measurement infrastructure to provide traceable measurements of forms of mercury that are currently regulated and to underpin advanced analytical techniques to support the next generation of environmental mercury measurement is absent in Europe, and globally.

In order to prevent global environmental pollution and damage to health caused by mercury, a new convention named the "Minamata Convention on Mercury" has been agreed. The global and legally binding Convention was adopted at the UNEP Diplomatic Conference held in October 2013 in Japan.

European Directives are awaiting the arrival of a solid metrological infrastructure providing traceability and reduced uncertainties for mercury measurements to enable the introduction and subsequent enforcement of target values for mercury, and to ensure the reliability and comparability of measurement results, as is the case for similar toxic elements covered by legislation.

Need for the project

Due to its highly toxic nature, the use of mercury is being phased out for many applications and limited to a mass fraction of mercury in products of less than 1000 mg/kg in current usage or new application. Mercury is classified as a priority hazardous substance (PHS) due to its persistent, bio-accumulative and toxic properties. For PHS, European Member States are legally obliged to progressively reduce discharges, emissions and losses to zero within the next 20 years. Unfortunately mercury is still entering the European environment in large amounts and with large uncertainties. It is also entering via trans-boundary transport from other parts of the world. Because of the global transport of mercury, releases in other parts of the world are as important to Europeans as domestic emissions. In the UNEP 2013 document “Global Mercury Assessment” the global emissions to air from anthropogenic sources were estimated at 1960 tonnes in 2010. Despite recent progress in improving the available knowledge base, these emissions estimates still have large uncertainties, giving a range of between 1010 and 4070 tonnes. Other potentially important sectors identified as emitters, whose effect has not yet been quantified, include the use of mercury in vinylchloride monomer production, secondary metals production and ferro-alloys, oil and gas extraction, and transport.

Overall, indications are that mercury emissions from industrial sectors have increased again since 2005; and without improved pollution controls or other actions to reduce mercury emissions, mercury emissions are likely to be substantially higher in 2050 than they are today.

Scientific and technical objectives

Specifically the project addresses the following objectives:

- To develop a calibration infrastructure enabling the traceable assessment of mercury in air to support European legislation for gaseous emissions and air concentrations and as part of the global mercury

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observing system.

- To develop a metrological in-line measurement method and calibration infrastructure enabling the traceable assessment of mercury thresholds specified in European legislation and as part of the global mercury observing system for continuous and semi-continuous Hg(0) and Hg(II) measurement in (harsh) matrices like stationary source emissions or liquid media, including the use of sensor technology.
- To develop a metrological infrastructure for emerging requirements in mercury science such as the evaluation of mercury concentrations in indoor air from the use of mercury containing compact fluorescent lamps.
- To develop primary measurement procedures for mercury speciation in water and biota in order to improve mercury monitoring through the aquatic ecosystems and support European legislation. This will include the evaluation of transformation artefacts associated with sample collection and preparation, in order to minimise species conversion post-sampling.
- To develop and accurately perform bulk and compound specific isotope signature measurement methods for Hg(0) and Hg species
- To develop and accurately perform ratio measurement for light isotopes (C, N, H, O) in organo-Hg species in order to detect contaminant transformations and migration.

Expected results and potential impact

The project outcomes will provide the required metrological infrastructure for mercury measurements in all environmental media, as required by current and future national and international legislation aimed at controlling mercury emissions and releases. The implementation and assessment of the Minamata Convention on mercury (the global and legally binding treaty aimed at reducing global mercury emissions) will also be supported, together with EC Directives and Member State objectives, to reduce the presence of mercury in the environment.

Specifically, the project aims to provide traceable assessment of mercury concentrations against those specified in European legislation, and as part of the global mercury observing system, in particular through the development of a calibration infrastructure using an innovative primary mercury standard. The impact of this will be the validation of regional and global scale atmospheric mercury models that are used in the evaluation of different policy options for reducing mercury pollution impacts on human health and ecosystems.

Objective 1 - Traceable primary standard for mercury in air

A device was built to automatically trap mercury vapour, produced by the primary calibrator, on sorbent traps. A novel automatic loading device for mercury sorbent traps was also tested for leaks and loadings. Several test runs were already completed to optimise the loading process. This included the preparation of the sorbent traps and some initial measurements to compare the mercury loaded against the Dumarey equation in order to validate the new equipment.

Objective 2 - In-line measurement method

The work on this objective is finished. A study on sampling, storage and analysis of mercury in stack impinger solutions was conducted and clearly demonstrated the stability of mercury in the dichromate stack impinger solutions for periods of up to two months. The solutions were even stable at room temperature which suggests that under refrigeration conditions they would be stable for substantially longer.

Conversely the mercury was not particularly stable in the 0.5 % HCl solutions, of the type used to prepare calibration solutions, and some degradation was observed over very short periods, even upon refrigeration. This suggests that calibration solutions – if prepared in this matrix - should be freshly prepared from (much more concentrated) stock solutions prior to each batch of analysis. Alternatively matrix matched calibration standards could be prepared in dichromate solution to avoid any stability issues.

The results of these studies will be fed into CEN TC264 WG8 who are currently undertaking the revision of EN 13211 'Air quality – Stationary source emissions – Manual method of determination of the concentration of total mercury' to inform the guidelines given on stability periods for samples and calibration standards.

Objective 3- Emerging requirements in indoor air

An experimental set up was developed for testing Hg emitted following CFL breakage. An optimization of the flow and time needed for the quantitative release of Hg at different temperatures was carried out at different ambient temperatures. Calibration of the direct Hg release was tested against the quantitative Hg removal from activated carbon traps followed by either combustion/CV AAS (Cold Vapour Atomic Absorption Spectroscopy) detection or NAA (Neutron activation analysis). CFLs with very variable Hg concentrations were processed, including new and used bulbs.

Objective 4- Mercury speciation in water and biota

A measurement procedure for IHg and MeHg in fish based on liquid-liquid extraction, using ethylation as the derivatisation step and isotope dilution ICPMS was developed. The method has been validated using three CRMs with different origin, fat content and mercury level: IAEA-407 (fish tissues without fat), NIST-1947 (fish fillet, 8% of fat) and NRC-DOLT-4 (dogfish liver). The values found for total Hg and for MeHg were in great agreement with the certified values. Fish samples of roach and pike were collected in collaboration with the German Specimen Bank. Fish was freeze dried, cryo milled, homogenized and sub-sampled and was distributed to the partners. The validated measurement procedure was applied to quantify the total Hg, IHg and MeHg in the 7 different types of fish samples received. 3 samples of each type of fish were analysed. It was observed a good agreement between the sum of IHg and MeHg measured and the total Hg content measured. No heterogeneity among the different samples was observed. Different methods developed by three partners were compared. The results have been presented at the Winter Conference on Plasma in February 2017.

Objective 5- Bulk and compound specific isotope signature measurement methods for Hg(0) and Hg species as well as for light isotopes measurements

A method for the species-specific mercury isotope ratio analysis of fish tissues that can determine isotope ratios of inorganic- and methylmercury with a combined uncertainty of less than 0.5‰ was validated. This method is based upon the offline HPLC separation of the mercury species, quantitative conversion of the methylmercury fraction to inorganic mercury using strong oxidising agents (Fenton reagent and 2 % BrCl) followed by MC-ICPMS analysis. Unfortunately none of the participants have been able to develop a method for the determination of carbon isotope ratios in methylmercury at environmental levels. This is due to the low abundance of MeHg in environmental samples and the even lower carbon content (in terms of mass) of MeHg itself.

After the project start in November 2014, the kick-off meeting was an occasion to gather relevant stakeholders from USEPA (USA), NIST (USA), JRC-IRMM (EC), the Technical University of Braunschweig (Germany), the University of Bremen (Germany) and the Health and Safety Laboratory (UK), who presented the state-of-the-art on the achievements in mercury measurements, in particular relating to the establishment of metrological traceability and quality assessment of the measurement results and highlighted the lack of comparability of measurement results, particularly with respect to mercury measurement in the vapour phase, as well as in elemental and speciation analysis in water.

The project put in place a Stakeholder Committee (SC), which includes 11 members from outside the consortium, including representatives from the industrial sector (energy sector, fluorescent lamp production, cement industry, gas and oil industry), policy making representatives, academic sector, non-European NMIs and instrument manufacturers. Partners are frequently in contact with the SC to discuss project progress and the achievements.

In June 2015, a special session was dedicated to the traceability of mercury measurements at the International Conference on Mercury as Global Pollutant (ICMGP 2015), held in Korea. About 30 people attended the session, where some of the project partners and stakeholders presented activities related to the project.

So far, 29 presentations have been made at European and International conferences and 8 papers have been published in scientific peer-reviewed journals such as Metrologia, Atmospheric Environment and the International Journal of Environmental Analytical Chemistry. The project has also input to a draft documentary CEN standard, and presented the project activities to BSI EH/2/3, on Stationary Source Emissions – Mercury monitoring using sorbent traps.

JRP start date and duration:	01 October 2014, 36 months
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