Final 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. It occurs naturally in the environment, and in addition human activity has increased mercury levels over the last 100 years.

In order to prevent the global environmental pollution and damage to health caused by mercury, a new global and legally binding convention aimed at reducing global mercury emissions, the Minamata Convention, was signed and agreed by 185 countries in 2013.

European Directives on mercury require the enforcement of target values for mercury in the environment.

This project developed new traceable measurements and the measurement infrastructure needed to support EU legislation and the global convention aimed at reducing global mercury emissions.

Need for the project

Mercury is very toxic even in low concentrations. It can cause damage to human health such as cancer and cardiac disease, and affects the health of unborn children. Mercury enters the food chain, and is a bio-accumulative substance, meaning that living organisms absorb it at a rate faster than that at which they can excrete it.

Mercury's ability to accumulate in terrestrial and aquatic biosystems makes it an insidious threat to environmental sustainability. Its long lifetime and ability to be transported in air over long distances means that it is ubiquitous to all environmental compartments (such as water, sediment, fish and other living creatures) and is a pollutant of global concern. The increase in the presence of mercury in the environment is 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.

The EU Directives relating to the control of mercury in the environment are:

- EU Directive 2002/95/EC: Restriction of the use of hazardous substances in electrical & electronic equipment
- EU Directive 2000/60/EC: Water framework directive
- EU Directive 2013/39/EC: Environmental quality standards
- EU Directives 2004/107/EC, 2010/75/EU and written standards EN15852 & EN15853 & EN13211 & EN14884: Measurement of emissions and concentrations in air

The EU Directives classify Mercury as a Priority Hazardous Substance due to its persistent, bio-accumulative and toxic properties. For these substances, European Member States are legally obliged to progressively reduce discharges, emissions and losses to zero within the next 20 years.

Prior to this project, the infrastructure needed to provide traceable measurements of mercury and to underpin advanced analytical techniques to support the next generation of environmental mercury measurement was absent in Europe, and globally. This meant that it was not possible to compare measurement results obtained by different laboratories.

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Therefore, the European Directives were awaiting a solid metrological infrastructure that would provide traceability and reduced uncertainties for mercury measurements thus enabling the introduction and subsequent enforcement of target values for mercury, and to ensure the reliability and comparability of measurement results.

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.

Unfortunately mercury is still entering the European environment in large amounts and with large uncertainties.

Natural sources of mercury include volcanoes, forest fires, the Earth's crust, earthquakes and cinnabar rock. Manmade sources include gold mining, fossil fuels such as oil and petroleum, hydroelectric mining, compact fluorescent lamps, paper and other industries.

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.

Mercury is reactive, difficult to store and handle, and extremely difficult to measure accurately as it easily volatilises or adsorbs onto surrounding media (such as the surfaces of sample containers) prior to analysis. These effects impinge on measurements of mercury in ambient air and also in emissions from stationary sources. The state of the art at the start of this project had not fully quantified such losses or developed strategies to minimise these effects.

This project builds on some of the outputs of project *ENV02 Emerging requirements for measuring pollutants from automotive exhaust emissions,* in particular preliminary proof of principle measurements linking the mercury traceability chain to gravimetry rather than previously used mercury vapour concentration equations.

This JRP will establish 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.

Scientific and technical objectives

The project addresses the following objectives:

1. 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 observing system.
2. 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.
3. 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.
4. To develop primary measurement procedures for mercury speciation (separates and measures the different forms / species of mercury) 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.
5. To develop and accurately perform bulk and compound specific isotope signature measurement methods for Hg(0) and Hg species
6. 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.

Results and conclusions

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 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.

1. Traceable primary standard for mercury in air

Research and outputs in this objective focussed on the development and implementation of a new primary measurement standard to link the mercury (Hg(0)) traceability chain to gravimetry instead of the currently used mercury vapour concentration equations. To ensure robustness and comparability of this innovative new primary gravimetric mercury vapour standard it was also crucial to compare the new standard with currently used calibration techniques to gain the confidence needed for full implementation. Key to this is the demonstration of coherence of the calibrator when compared against measurements of mercury in the particulate phase – since the ratio of particulate and vapour phase mercury concentrations is a key parameter in understanding source apportionment, atmospheric processes, and long-range transport. This coherence was assessed by a comparison against two types of ICP-MS measurement of mercury in particulate, which showed good agreement of the results, showing that the objective was achieved.

2. In-line measurement method

Research was done in order to determine the most efficient method for the cleaning of gold traps, used for the collection and measurement of vapour-phase mercury in ambient air for analysis in the PS Analytical Sir Galahad instrument. A recommended cleaning procedure for these gold traps has been produced and the detection limits for traps cleaned using this procedure have been evaluated.

Moreover, a revision of the EN13211 standard “Air quality — Stationary source emissions — Manual method of determination of the concentration of total mercury” was conducted. A new HF-free digestion method to be used for the measurement has been introduced as informative annex within the standard.
Finally a low-cost prototype passive sensor based on nanostructured sensing materials with the advantage of robustness, traceability, sensitivity, reaching ultra-trace levels, and not requiring power supply and gas carrier, as well as highly qualified technical expertise was developed.

3. Emerging requirements in indoor air

An easy, on-line, sensitive and traceable method for the determination of released Hg from a broken CFL bulb was developed. The procedure is based on a gas tight plexiglass box with bulb crushing system, heated gold amalgamation trap coupled to a CV AAS mercury analyser with Zeeman background correction. The data on mercury releases indicate that breakage of CFLs will result in releases that are near levels of health concern. Real life conditions vary from the experimental design used to develop these results, such as room size, room temperature, age of lamps, use of lamps, and type of floor covering. However, this variability is unlikely to result in higher hazard quotients, because the scenarios used in this study maximised exposures and risk values were calculated with the maximum hourly exposures, rather than the average exposures.

4. Mercury speciation in water and biota

Measurement procedures for Hg species in water and biota were developed and are now available to be used for comparison with results obtained in routine laboratories and to ensure their traceability.
For water, the challenge is mainly the low concentrations of various species. To handle samples with very low Hg concentration, the principal challenge is to minimise the influence of the blank, i.e. the impact that impurities present in the reagents can have on the analysis, especially for Hg(II) measurements. Hence, the following critical parameters were optimised: sampling volume, pre-concentration factor, container material and cleaning procedures.

A method for the continuous measurement of different Hg species such as Dissolved Elemental Hg (DEM) and inorganic Hg Hg(II) in aqueous samples was developed within the project.
In animal and plant life, the main challenge is the complete extraction of the Hg species from the matrix without changing the species composition. To develop and validate measurement procedures for Hg species in fish, four different fish materials were prepared within the project. Different methods to quantify total Hg and MeHg in fish samples were developed and compared. These methods were successfully applied to the characterisation of three fish samples collected in collaboration with the German Environmental Specimen Bank, which stores high quality samples from the environment and human populations in support of chemicals management and innovative research for a better environmental quality. The robustness of the methods were proven and complete uncertainty budgets were established.

5. Bulk and compound specific isotope signature measurement methods

Key challenges in obtaining accurate and precise Hg isotope ratio data at environmentally relevant concentration levels include measurements at low Hg concentration, significant potential for artificial Hg isotope fractionation of analyte due to its non-quantitative conversion during sample preparation steps, matrix interferences and bias induced by instrumental mass discrimination.
A thorough investigation of instrumental operating parameters provided a deeper insight into the causes of instrumental mass bias of Hg isotopes. It was shown that data reduction strategy based on normalisation to the internal standard provided the best means of minimising the drift in the magnitude of instrumental mass discrimination over a measurement session.
For the first time, an on-line pre-concentration method was developed to determine Hg isotopic composition at ng L^{-1} (nanogram per litre) concentration level in liquid samples. This method opens up the unique possibility of metrologically traceable Hg isotopic analysis in seawater and atmospheric precipitation.
Also for the first time, a methodology for species-specific Hg isotope ratio measurements in fish tissues by HPLC-CVG-MC-ICPMS (a spectrometry technique) was developed. It was shown that Hg isotopic data can be useful in identifying sources and transformation of Hg when applied to robust sample archives such as fish tissues from environmental specimen bank of Federal Environmental Agency of Germany.

6. Ratio measurement for light isotopes in organo-Hg species

Measurement of light element isotope ratios in organo-mercury species was investigated using the carbon isotope ratio in methyl Mercury (MeHg) as an example. A limit of sensitivity inherent to the analysis of MeHg was found. While the carbon isotope ratio of MeHg can be determined using the methods developed during this objective, the amounts of sample material required greatly limit the practical application of the methods. Nonetheless in cases where there is significant mercury pollution in the natural environment, there may be instances where the methods developed can be used to glean additional information about the MeHg in environmental samples.

Actual and potential impact

This JRP put in place an underpinning traceability framework for the measurement of mercury in all environmental compartments, which will have a global impact on the quality and comparability of measurement results, providing SI traceability for all Hg measurements required to be measured by current European and international legislation.

Dissemination

Twenty articles were published in peer-reviewed journals including Atmospheric Environment, Metrologia, and American Journal of Analytical Chemistry. Seven of these were joint papers.

43 presentations (oral and poster) describing the work of the project were given at international conferences. This included two special sessions at the International Conference on mercury as a Global Pollutant: the first one, entitled "traceability for mercury measurements" was held in Korea, in July 2014, and the second one, entitled "Comparable measurement results for mercury analysis and speciation", was held in Rhode Island, USA, in July 2017.

The following training courses and workshops were run for external audiences:

- Training workshop for national coordinators and laboratory analysts involved in the United Nations Environment Programme / World Health Organisation project "Development of a Plan for Global Monitoring of Human Exposure to and Environmental Concentrations of Mercury"
- On-line training course: 3rd Advances in Environmental Analysis (http://blog.sepscience.com/environmental/advances-in-environmental-analysis-eseminar)
- Microwave digestion of fish samples, integrated data management system approaches to quantification, measurement of isotope ratios on MC-ICPMS (multicollector inductively coupled plasma mass spectrometry)
- Hyphenated techniques to MC-ICPMS
- Issues and solutions: Quality Assurance in laboratory measurements
- Mercury monitoring and regulation, attended by public bodies and agancies
- Traceability of mercury measurements
- Comparable measurement results for mercury analysis and speciation

Early impact

Examples of early impact from the project are:

- GMOS: The standard operating procedures developed in the project have been adopted by the Global Mercury Observation System to use as a quick reference guide when starting up Hg measurements in ambient air. The novel low-cost prototype passive samplers developed for measuring the most abundant Hg form in ambient air have been employed across 5 selected GMOS monitoring sites at different latitude and altitude and thus in different conditions. (Objective 2)
- A patent has been submitted for a device for continuous sampling of dissolved elemental mercury from aqueous solutions or suspensions, and the procedure for its use.
- IAEA: The primary measurement procedures developed within the project for the Hg and Hg speciation in biota matrices were used for the characterisation of an IAEA certified reference material. Once this material is available, it will be used by analysis laboratories in their QA and QC prodedures.
- United States Environmental Protection Agency and NIST: throughout the project USEPA and NIST have worked with the partners, in order to achieve an international consensus for Hg standards and with the aim of providing traceable Hg gas standards.

Contribution to standards

The work of this project has contributed to the following documentary standards:

- Annex of the revised EN13211 “reference method for the analysis of mercury in stationary source emissions” - a new digestion method developed within the project for mercury in particulate matter based on an *aqua regia* digest. This will allow analysis of mercury in stationary source emissions across Europe to be safer and be performed with a lower uncertainty.
- Revision of the ISO 17852 standard “Water quality - Determination of mercury - Method using atomic fluorescence spectrometry” - novel information from the project about the stability of total Hg in water samples with different Total Organic Carbon will be taken into account

Potential future impact

One of the main metrological achievements of this project was the development and implementation of a new primary measurement standard to enable traceability for mercury vapour measurement based upon gravimetry. This will ensure the comparability of measurement across Europe and globally, the ability to accurately assess changes over time with small uncertainties, and assure measurement coherence between different environmental compartments and between the different measurement methods used.

The outcome of this JRP will provide end users with the underpinning infrastructure for producing primary calibration standards and traceable measurement results. Quantitative determination of Hg is of the utmost importance to a variety of applications, such as ambient air and water quality monitoring programmes as well as industrial sectors such as energy production and refineries.

Traceable measurements will:

- aid the increased understanding of human and environmental exposure to mercury, thereby working towards improving environmental sustainability and the health of the EU citizen, especially those more susceptible to mercury.
- help to demonstrate trends in mercury concentrations, its speciation in different media, and its movement between environmental compartments.
- help European industry meet the requirements of mercury abatement and emissions legislations with greater confidence and at low cost, resulting in huge overall savings across the EU, whilst making EU industry cleaner and more competitive globally.

List of publications

1. Richard J.C. Brown, Sharon L. Goddard, David M. Butterfield, Andrew S. Brown, Chris Robins, Chantal L. Mustoe, Elizabeth A. McGhee; Ten years of mercury measurement at urban and industrial air quality monitoring stations in the UK; Atmospheric Environment; 2015, 109, 1-8
2. Teemu Näykkia, Timo Sara-Aho, Tero Väisänen & Ivo Leito; Application of enriched stable 196Hg isotope for monitoring the stability of total mercury in water samples; Int J Environ Anal Chem; 2015, 95 (1): 1-15.
3. Richard J C Brown, Paul J Brewer, Hugo Ent, Paola Fisicaro, Milena Horvat, Ki-Hyun Kim, Christophe R Quétel; Who should take responsibility for decisions on internationally recommended datasets? The case of the mass concentration of mercury in air at saturation Metrologia; 2015, 52, L25–L30
4. Sharon L Goddard and Richard JC Brown; Investigation into Alternative Sample Preparation Techniques for the Determination of Heavy Metals in Stationary Source for the Determination of Heavy Metals in Stationary Source Emission Samples Collected on Quartz Filters; Sensors; 2014, 14, 21676-21692
5. SEDLAR, Matej, PAVLIN, Majda, JAĆIMOVIĆ, Radojko, STERGARŠEK, Andrej, FRKAL, Peter, HORVAT, Milena. Fractionation (TF) of Hg compounds in gypsum from wet flue gas desulfurization system of the coal fired Thermal Power Plant (TPP); American journal of analytical chemistry; 2015, vol. 6, no. 12, str. 939-956,
6. KOTNIK, Jože, HORVAT, Milena, OGRINC, Nives, FAJON, Vesna, ŽAGAR, Dušan, COSSA, Daniel, SPROVIERI, Francesca, PIRRONE, Nicola. Mercury speciation in the Adriatic Sea. Marine pollution bulletin. vol. 96, vol. 1/2, str. 136-148, 2015
7. SPROVIERI, Francesca, PIRRONE, Nicola, HORVAT, Milena, KOTNIK, Joze, et al. Atmospheric Mercury Concentrations observed at ground-based monitoring sites globally distributed in the framework of the GMOS network; Atmospheric Chemistry and Physics (ACP); Atmos. Chem. Phys., 16, 1–21, 2016
8. SPROVIERI, Francesca, PIRRONE, Nicola, HORVAT, Milena, KOTNIK, Joze, *et al*. Five-year records of Total Mercury Deposition flux at GMOS sites in the Northern and Southern Hemispheres Atmospheric Chemistry and Physics Discussion (ACPD); Atmos. Chem. Phys. Discuss., 2016
9. Dmitriy Malinovskiy and Ellie Gadd; Battle to control Hg; Chemistry & Industry Magazine; 2015, 5, 41-42

10. A. Macagnano, E. Zampetti,V. Perri, A. Bearzotti, F. Sprovieri, N. Pirrone, G. Esposito, F. De Cesare Photocatalytically decorated Au-nanoclusters TiO2 nanofibres for elemental mercury vapor detection; Procedia Engineering; Procedia Engineering 120 (2015), pp. 422 – 426
11. A. Macagnano, V. Perri, E. Zampetti, A. Bearzotti, A.M. Ferretti, F. Sprovieri, G. Esposito , N. Pirrone, F. De Cesare Elemental Mercury Vapour Chemoresistors Employing TIO2 Nanofibres Photocatalytically decorated with AU-Nanoparticles; Sensors & Actuators: B. Chemical; DOI:10.1016/j.snb.2017.03.037, 2017
12. A. Macagnano, V. Perri, E. Zampetti, A. Bearzotti, F. De Cesare, F. Sprovieri, and N. Pirrone A Smart Nanofibrous Material for Adsorbing and Real-Time Detecting Elemental Mercury in Air Atmospheric Chemistry and Physics (ACP); doi:10.5194/acp-17-6883-2017
13. F. De Simone, P. Artaxo, M. Bencardino, S. Cinnirella, F. Carbone, F. D'Amore, A. Dommergue, X.B. Feng, C. N. Gencarelli, I. M. Hedgecock, M. Landis, F. Sprovieri, N. Suzuki, I. Wangberg and N. Pirrone Particulate-Phase Mercury Emissions during Biomass Burning and Impact on Resulting Deposition: a Modelling Assessment; Atmos. Chem. Phys., 17, 1–19, 2017, doi: 10.5194/acp-17-1-2017.
14. Brown, R J C; Braysher, E C; McGhee, E A; Goddard, S L; Ent, H; Kim, K-H; Nielsen, J Characterising and reducing the blank response for measurements of mercury vapour Analytical Methods; 2017, 9, 2654-2659.
15. Quétel, C R; Zampella, M; Brown, R J C Temperature dependence of Hg vapour mass concentration at saturation in air: new SI traceable results between 15 and 30°C; Trends in Analytical Chemistry, 2016, 85B, 81–88
16. BERAIL Sylvain, CAVALHEIRO Joana, TESSIER Emmanuel, BARRE Julien P.G., PEDRERO Zoyne, DONARD Olivier F.X and AMOUROUX David. Determination of total Hg isotopic composition at ultra-trace levels by on line cold vapor generation and dual gold-amalgamation coupled to MC-ICP-MS ; Journal of Analytical Atomic Spectrometry (JAAS); 2017, 32, 373-384
17. Živković, Igor, Fajon, Vesna, Tulasi, Delali, Obu, Kristina, Horvat, Milena. Optimization and measurement uncertainty estimation of hydride generation-cryogenic trapping-gas chromatography-cold vapor atomic fluorescence spectrometry for the determination of methylmercury in seawater. Marine Chemistry, ISSN 0304-4203. 2017, 10 str., doi: 10.1016/j.marchem.2017.03.003.
18. Kotnik, Jože, Horvat, Milena, Begu, Ermira, Shlyapnikov, Yaroslav, Sprovieri, Francesca, Pirrone, Nicola. Dissolved gaseous mercury (DGM) in the Mediterranean Sea: spatial and temporal trends. Marine Chemistry, 2017, 193, 8, doi: /10.1016/j.marchem.2017.03.002

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