



Publishable Summary for 16ENV01 MercOx Metrology for oxidised mercury

Overview

The overall goal of this project was to develop SI traceable measurements for the monitoring and control of mercury (Hg) and its different species in gas emission sources and in the atmosphere. By achieving this, the project has provided significant improvements in the measurement comparability and uncertainty of Hg measurement results.

Prior to the start of this project, traceable calibration methods only existed for elemental mercury (Hg(0)), however such measurements were also needed for oxidised Hg species, (i.e. Hg(II)) in order to meet the requirements of EU regulation and the implementation of the Minamata Convention. To address these issues, this project developed and validated traceable oxidised Hg standards and methods for sampling and analysing oxidised Hg species in flue gas emissions and in the ambient air.

Need

Mercury is one of the most toxic metals, and as such is regulated by the Industrial Emissions Directive (IED) 2010/75/EU, the Air Quality Directive 2004/107/EC, the Waste Incineration Directive 2000/76/EC and the Minamata Convention (2013) - a global treaty to protect human health and the environment from the adverse effects of Hg. In addition to its elemental form, Hg also exists in oxidised forms, i.e. Hg(II) compounds that are reactive and can be transformed into organic Hg species such as methylmercury (MeHg), the most toxic Hg species and the one most prone to bioaccumulation in aquatic systems. Half of the atmospheric Hg emissions are of natural origin while the remaining half is from anthropogenic sources. The latter is primarily from the burning of fossil fuels and other high temperature industrial processes, such as cement clinker production, waste incineration, ore roasting and steel production.

The development of reliable and direct Hg(II) measurement techniques and reliable and traceable Hg(II) standards has helped to solve the traceability problem that exists in the measurement of total mercury (Hg^{tot}) and oxidised Hg originating from different Hg sources. Prior to the start of this project, traceable calibration methods were only available for Hg(0), but they were also needed for oxidised Hg species to meet EU regulations. Furthermore, methods for measuring oxidised Hg and for accurately comparing the amount of Hg^{tot} in generated elemental and oxidised Hg reference gas standards were needed, as well as improved sampling methods, traceable reference standards, validated methods for online field measurements and for studying interconversion of Hg species.

Knowledge of Hg speciation both in air and in stack gas emissions is critical when validating models for predicting Hg emissions, transport, deposition and fate at the European level as well as on a global scale. In addition, atmospheric Hg isotopic signatures that can be used to trace the origin and fate of atmospheric Hg needed metrological support and development.

Finally, in order to meet future global and European requirements (in relation to the Minamata Convention and European Directives) standardisation bodies have recognised the importance of and need to standardise the method for measuring Hg in industrial flue gases and in the atmosphere. This project helped to meet this need by facilitating the transfer of a measurement infrastructure as developed in the project to standards development organisations such as CEN/TC 264 WG8 and the respective Articles of the Minamata Convention.

Report Status: PU Public

This publication reflects only the author's view and the Commission is not responsible for any use that may be made of the information it contains.



research and innovation programme and the EMPIR Participating States

Publishable Summary



Objectives

The overall goal of this project was to develop traceable online measurement procedures for the monitoring and control of Hg and its different species in gas emission sources and in the atmosphere, and to improve the measurement comparability and uncertainty of Hg measurements. The project's specific objectives were to:

- 1. Develop, establish and implement a traceable calibration methodology for the most important oxidised mercury (Hg) species, especially for mercury chloride (HgCl₂). This includes quantitative confirmation of the output from liquid evaporative HgCl₂ generators and the development of reference gas standards.
- Develop and compare different methods of measuring oxidised Hg and to accurately compare total mercury (Hg^{tot}) concentrations in generated standard gases for elemental mercury (Hg(0)) and oxidised mercury (Hg(II)). This includes methods for bulk and species-specific, e.g. Hg(0) and Hg(II), isotope ratio measurements to determine Hg migration pathways, its origin and species interconversion.
- 3. Optimise sampling methods for gaseous Hg species using traceable reference standards for Hg(0) and Hg(II). The project will look at the different measurement methods available and their long-term efficiency and reliability for sampling different matrices.
- 4. Test and validate new and existing methods for online Hg field measurements using the newly developed gas standards and/or generators. This will include measurement of Hg in stack emissions and in ambient air.
- Facilitate the take up of the technology and measurement infrastructure developed during the project across the measurement supply chain (accredited laboratories) and by standards development organisations (CEN/TC 264 WG8 and those linked to the IED 2010/75/EU, the Air Quality Directive 2004/107/EC and the Waste Incineration Directive 2000/76/EC) and end-users (environmental monitoring programmes, the research community, regional and global programmes).

Progress beyond the state-of-the-art

For the control and assessment of Hg concentrations in the environment it is essential to be able to monitor all Hg species. Unfortunately, prior to the start of this project traceable methods and calibration standards only existed for Hg(0), and even these were based on Hg vapour pressure equations that gave different results. This discrepancy was of great concern and work to improve this situation was done within the previous EMRP project ENV51 MeTra which included work on Hg(0) in air. However, insufficient work was undertaken on oxidised Hg and there was a lack of reference gas standards for HgCl₂ or other oxidised Hg compounds. The main challenge with the evaporative gas generation systems used for measuring Hg was maintaining a high enough temperature during the transfer of the generated standard gas to the detection system.

Prior to the start of this project the direct measurement of gaseous Hg(II) became a major focus of international research programmes for continuous Hg source emission and ambient measurement and monitoring. However, the issue with these measurements was that they were dependent on the availability of reliable Hg(II) gaseous reference standards and materials to assess and verify the quality of data and in most existing methods for Hg measurements, the different oxidised Hg species normally had to be reduced to the detectable elemental form i.e. Hg(0) in order to be quantified. Therefore, reliable Hg(II) reference gases were needed to quantify this conversion and to assess the ability to quantitatively transfer in particular the reactive Hg(II), through the entire measurement system.

The atmosphere contains three forms of Hg: gaseous elemental mercury (GEM), gaseous oxidised mercury (GOM), and particulate bound mercury (PBM). Through a series of photochemically initiated reactions in the atmosphere, involving halogens, GEM is converted to a more reactive species and is subsequently associated to particles in the air and/or deposited, particularly in polar environments. These phenomena are called atmospheric mercury depletion events (AMDE) but prior to the start of this project , only one commercially available instrument had claimed to be able to measure these Hg species, but it was since demonstrated that measurements made with the commercial instrument underestimated GOM concentrations by as much as a factor of 2 to 13. Furthermore, sampling efficiency for GOM is affected by ozone and water vapour and underestimating GOM results in biased values that are too low for modelling dry deposition. The deposition of reactive mercury (RM = GOM + PBM) also produces inorganic Hg complexes that undergo abiotic and biological transformations on surfaces and in water. Thus these knowledge gaps needed comparable and



traceable measurements for GEM, GOM and PBM. This was also true for stable direct Hg isotope ratio measurements of stack gas emissions and atmospheric measurements.

Results

To develop, establish and implement a traceable calibration methodology for the most important oxidised Hg species, especially for HgCl₂.

Traceable calibration methods for oxidised mercury species and a certification protocol for the output of liquid evaporative HgCl₂ have been developed and optimised by the project. A (dual) two-channel direct measurement system based on Zeeman AAS was developed. Several types of liquid evaporative HgCl₂ generators were developed and tested including permeation tubes, salt saturation and liquid evaporators. The output of each type of liquid evaporative HgCl₂ generator was tested using the dual channel Zeeman AAS system which was calibrated with a SI traceable diffusion based gravimetric elemental Hg generator. The SI calibrated dual channel Zeeman AAS measurement system provided an accurate real time measurement of total and elemental Hg which was used to check the species integrity of the developed liquid evaporative HgCl₂ generators. The developed liquid evaporative HgCl₂ generators were capable of generating oxidised mercury reference gases in a wide concentration range, from sub ng/m³ levels typical in ambient measurements to µg/m³ levels typical in continuous process conditions.

Further to this, a new method for calibration of instruments at low ambient concentrations was developed. The new method for calibration is based on the quantitative oxidation of traceable amounts of Hg(0) by cold plasma system in helium/oxygen atmosphere and is convenient for low level Hg concentrations representing ambient Hg levels. Additionally, the performance of the developed liquid evaporative HgCl₂ generators has been validated by direct coupling to species independent detector (Inductively Coupled Plasma Mass Spectrometry (ICP-MS/MS), providing unified sensitivity for both Hg0 and Hg(II), and comparing the generators output signal. The liquid evaporative HgCl₂ generator was also validated using a highly specific ¹⁹⁷Hg tracer, which detected adsorption phenomena on tubing for HgCl₂ and particularly for HgBr₂ species. The results of this contributed to the design of additional validation testing specifically for when the developed liquid evaporative HgCl₂ generators HgCl₂ generators are used for the loading of selective adsorption traps.

A certification protocol for the output of liquid evaporative HgCl₂ generators has been prepared and is available on the project's website for end users such as instrument producers, practitioners, and researchers (<u>http://www.mercox.si/images/D5-Good_practices.pdf</u>)

To develop and compare different methods of measuring oxidised Hg and to accurately compare Hg^{tot} concentrations in generated standard gases for Hg(0) and Hg(II).

Laser ablation (LA) ICP-MS was developed as a method to determine total mercury in activated carbon traps and was fully validated.

Interlaboratory comparisons for accurate determination of total mercury and mercury species in activated carbon materials were also performed. The interlaboratory comparisons used methods based on combustion and acid digestion followed by cold vapour atomic absorption spectrophotometry (CV AAS) and cold vapour atomic fluorescence spectrophotometry (CV AFS). As a reference method k₀-instrumental neutron activation was used (k₀-INAA). The results of the Interlaboratory comparisons showed that acid digestion should be done with care, as it tends to provide lower results due to incomplete digestion of the matrix.

An efficient nanomaterial with a 2D structure and high surface area, that is also low cost and metal-free was successfully prepared by the project. The nanomaterial is based on graphitic carbon nitrite (g-C₃N₄) and graphene oxide (GO) and shows very promising results with selectively trapped Hg(II) in impinger solutions and from the atmosphere. Experiments were also undertaken to implement ID ICP-MS for accurate measurements of Hg(II) and for the testing of Hg species interconversion during preconcentration steps.

Selective trapping systems using KCI loaded traps, denuders and impingers were validated using a 197 Hg tracer. The experiments using a liquid evaporative HgCl₂ generator (from objective 1) resulted in high losses of Hg(II) onto the tubing, especially at low Hg(II) concentrations. Therefore, traceable quantities of mercury loaded onto selective traps and denuders could only be demonstrated by the oxidation of Hg(0) by cold plasma



(using the new calibration method from Objective 1).

The project successfully validated the feasibility of experimental protocols to determine the concentration of Hg species using specific adsorbent techniques, Hg isotopic composition in the gas phase and Particulate Matter (PM) with Multicollector-Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS). A method for the determination of stable isotope ratio of Hg in atmospheric bio-monitors (lichen, moss, needle) was also optimised and subsequently used for the analysis of spruce needle samples from the German specimen bank. In addition, a reference material of urban atmospheric particles from the National Institute for Environmental Studies (NIES) in Japan, has been characterised for Hg isotopic composition in order to provide new reference values for this type of sample. The new Certified Reference Material (CRM) is NIES, CRM No. 28 Urban Aerosols.

A thermal desorption method was developed to separate Hg(0) adsorbed on particles or solid substrates using a quadrupole mass spectrometer (QMS, Pfeiffer QMS 700) for detection. Very clear separation of adsorbed Hg(0) was successfully observed qualitatively, however further optimisation is needed for quantitative determination,. In addition, initial scoping studies using thermal desorption combined with ICP-MS/MS have shown promising results, as accurate species quantification. The ability to account for species conversion was able to be achieved using species-specific Isotope Dilution Mass Spectrometry (ID- MS) with an ICP-MS/MS detector.

A method for the determination of Hg^{tot} in reference Hg solutions using Isotope Dilution Cold Vapor Inductively Coupled Plasma Mass Spectrometry (ID-CV-ICP-MS) was developed for the certification of Hg in a reference material (i.e. bituminous coal CRM 6200625a) for use with proficiency testing. The same method for the determination of Hg^{tot} in reference Hg solutions (with or without cold vapour - CV) can now be used to study interconversion processes during sampling and analysis of Hg(II) and Hg(0).

Finally, a bituminous coal candidate reference material was developed for the determination of total Hg and Hg(II).

To develop optimised sampling methods for gaseous Hg species using traceable reference standards for Hg(0) and Hg(II). Regarding species inter-conversion, different measurement methods and their long-term efficiency and reliability in different matrices will be taken into account.

Both atmospheric chemistry and stack gas emission chemistry were considered by the project. The project's modelling studies focused on updating existing Hg chemistry mechanisms in transport/chemistry models to improve the understanding of the emission, transport and deposition of Hg emitted in industrial plumes. Since the beginning of the project several theoretical studies addressing the chemistry and photolysis of brominated Hg compounds have been published and the results from these studies were included in the chemistry mechanism in the Weather Research and Forecasting (WRF) model coupled with Chemistry (WRF/Chem model). The regional chemistry transport model WRF/Chem has been updated by the project to include the most recent rate constants for BrHg* addition, product reactions and their subsequent photolysis, which yields BrHgO. BrHgO is a radical which reacts in the atmosphere with both inorganic and organic compounds, and these reactions, as far as they are known, have also been included. The WRF/Chem model has undergone comparison with previous versions to understand how the recent changes affect the dynamics of Hg transport and deposition with respect to earlier simulations. Validation was performed using the experimental data obtained within the Mediterranean region.

The project investigated Hg species interconversion during the sampling steps based on pre-concentration on KCl solid traps. The results highlighted the importance of proper preconditioning of solid traps as the sequential thermal heating severely affects the selectivity for Hg(II) trapping. Moreover, selectivity of the KCl trapping solutions used in the ASTM D6784-02 (Ontario Hydro) method showed that elemental Hg can be oxidised due to impurities in the KCl solution and stack gas matrix. This oxidation can then potentially produce a positive and negative bias in the reporting of oxidised and elemental Hg respectively.

The solubility of elemental Hg in KCl solution has been experimentally determined by establishing the dimensionless Henry's law constant. Traces of HgCl₂ were measured in the KCl trapping solution using aqueous phase propylation liquid extraction with Gas Chromatography Atomic Fluorescence Spectrometry (GC-AFS). The influence of stack gas components on the stability of HgCl₂ trapped in the KCl solution was also studied, and in some cases (e.g. e.g. SO₂, N₂O and CO) a reduction of HgCl₂ was observed.



The project studied the stability of Hg species on sorbent traps using conventional techniques based on Chemical Vapour Atomic Fluorescence Spectrometry (CV-AFS) and temperature fractionation analysis using quadrupole MS.

In order to better understand interconversion processes (confirmed by this method) a highly sensitive radiotracer technique was developed using ¹⁹⁷Hg produced from an enriched ¹⁹⁷Hg stable isotope. The highly sensitive radiotracer technique was used to study the outputs of the liquid evaporative HgCl₂ calibrators (from objective 1) as well as the adsorption and desorption of Hg(II) during loading onto traps, denuders and impingers. This unique radiotracer approach indicated severe losses of Hg(II) species in the sampling trains of commonly used methods based on sorbent traps, denuders, and impingers. The importance of these results has been communicated to end users by a publication submitted to Atmospheric Measurement Techniques as well as through direct communication with instrument producer (Tekran, Canada) US EPA and via collaborators the University Nevara-Reno and Utah State University, USA. Detailed results will also be presented to the wider community of users during the project's final Webinar in September 2021.

To test and validate new and existing methods for on-line Hg measurement under field conditions using the developed gas standards or generators.

Coal fired power plants using different flue gas abatement systems (electrostatic precipitators, fabric filters and desulphurisation units) and cement kilns are the major sources of Hg emissions to the atmosphere and were selected for the filed studies. Therefore, a coal fired power plant (in Marl, Germany) and a cement clinker production facility (in Anhovo, Slovenia) were used for the field tests.

The project set-up the logistics for testing and validating new and existing methods for on-line Hg measurement under field conditions. The field testing at the cement clinker production facility in Slovenia included both atmospheric and process gas measurements as well as measurements at air monitoring stations nearby. The testing included active online monitoring of GEM, GOM and PBM with a commercial unit Tekran, collection of mercury from ambient air using epiphytic lichens, passive samplers and wet precipitators, as well as process monitoring with sampling by sorbent traps and the plants continuous emission monitoring system.

Testing at the coal fired power plant in Germany included the collection of samples from different parts of the process using sorbent traps, while in the cement clinker production facility in Slovenia different regimes of operation were tested. The measurement results of standard continuous emission monitoring system (CEM) were also available in both sites.

Atmospheric measurements were organised in the transect from the emission source (at the cement clinker production facility in Slovenia) in order to cover the range of atmospheric concentrations as well as various ratios of Hg(0)/Hg(II) species. The work was also modified/enhanced by adding the validation of commonly used passive samplers of gaseous Hg in the atmosphere as well as the biomonitoring protocols using lichens.

The results from the field testing showed that sorbent traps for on-line Hg monitoring from process stack emissions in coal burning power plants and cement production facilities provided comparable results with continuous emission monitors (CEMs). The evaporative calibrator for oxidized Hg was successfully used in the field trials for emission measurements.

In terms of atmospheric measurements of total gaseous mercury filed testing showed that passive samplers and biomonitoring approaches provide results that are comparable with conventional active measurements and offer a cost-effective approach. In terms of oxidised mercury measurements at ambient levels, the results demonstrated, that the novel approach developed for calibration at low concertation levels, based on quantitative oxidation of elemental mercury (produced from NIST 3133 standard solution) in cold plasma, provides simple and traceable approach.

Impact

Impact on industrial and other user communities

By developing optimised and traceable calibration methods for oxidised Hg species, including HgCl₂, and a certification protocol for the output from liquid evaporative HgCl₂ generators, this project has helped to enable the use of liquid evaporative HgCl₂ generators as reference gas source, particularly relevant for emission



monitoring. Those stakeholders that will benefit directly from this (such as Tekran, the US Envioronmental Protection Agency (EPA), NIST, McGill University, Canada and the University Reno, USA) were contacted and invited to the project's first stakeholder event, which was in October 2017 in Ljubljana.

The MercOx project has been presented at the "Mercury emission from coal - MEC" workshop where representatives from the government, industry and academia were present. As well as at the 3rd Conference of Parties of the Minamata Convention (COP3) where governments and international agencies, non-governmental organisations and other stakeholders met to discuss the implementation of the Minamata Convention and its effectiveness. A need for comparable Hg measurements was strongly agreed at COP3.

During the International Conference on Mercury as a Global Pollutant (ICMGP2019) which is the largest global forum for researchers, industry, policy and other stakeholders, the project partners organised a workshop on "Comparability of mercury measurements in air". At this workshop the latest developments in the area of traceable mercury measurements worldwide were presented by project partners to stakeholders.

The project has engaged with industry and other communities through its stakeholder committee, which includes members from Salonit Anhovo, Slovenia and representatives from CHEMBUREAU (an association of cement producers in Europe), Tekran (Canada), Mercury Instruments (Germany), Lumex Ohio (USA), and Finnsementti (Finland).

Further to this the project has disseminated its results to end users through a range of activities including (i) 4 articles in the popular press, (ii) a virtual corner exhibition at The European Researchers' Night, (iii) training on ID-GC-ICP-QMS and (iv) presentations at the HBM4EU. The HBM4EU is a joint project of 30 countries, plus the European Environment Agency and the EC, with the aim of building bridges between research and policy in order to enhance chemical safety.

The project has demonstrated good examples of uptake by the end user community through:

- the validation of the newly installed continuous measurement system for flue gas stack Hg measurements, at the cement clinker production facility in Anhovo, Slovenia (Objective 4)
- end users NIST and the US EPA using the advances in SI systems of instruments for total gaseous mercury measurements at partner PSA (Objective 2)
- end user the University of Nevada-Reno using the improvements in traceability for low level ambient mercury measurements of commercial Tekran speciation and ion exchange membranes (Objective 1)
- end user the Utah State University using the performance characteristics for commonly available calibration devices at partner JSI (Objective 3)
- The certification of the NIES, CRM No. 28 Urban Aerosols (Objective 2)
- end user Lumex Ohio, USA a separate entity to partner Lumex using the improved sampling for gaseous oxidized mercury at partner Lumex (Objective 2 and 3).

Finally, JSI has submitted a patent for the newly developed calibration method using cold plasma developed as part of objective 1.

Impact on the metrology and scientific communities

The project produced a good practice guide for Hg sample preparation and interspecies conversion correction as well as optimised and validated sampling methods for gaseous Hg species using traceable reference standards for Hg(0) and Hg(II). The good practice guide is available to the scientific community on the project's website http://www.mercox.si/images/D5-Good_practice.pdf Both the good practice guide and the validated methods should help the scientific community to improve Hg speciation both in air and in flue gases, which is vital for the validation of models for predicting Hg emissions, transport, deposition and fate at the regional level (i.e. European level) as well as on a global scale.

The validated bulk and species-specific isotope ratio measurements developed within the project in Objectives 2 and 3 can also be used to determine Hg migration pathways, its origin and the species interconversion of atmospheric Hg. Thus, they will enable the scientific communities working on these issues



to measure Hg(0) and Hg(II) more accurately and to predict Hg species pathways and the Hg biogeochemical cycle.

In total, fifteen scientific papers have been published and one submitted to open access journals. The project has also been presented 37 times (either as posters or presentations) at events including ICP Vegetation, the Mercury Monitoring Workshop: the Korean Society for Environmental Analysis, the National Association for Clear Air (NACA), Gas 2019, Pittcon and PEFTEC. At the ICMGP 2019 MercOx partners organised a special session on: "Metrological traceability for mercury analysis and speciation" and post conference publications include two special issues produced by the project in: Atmospheric Chemistry and Physics and the journal Sensors.

It should also be highlighted that the coordinator of the project M. Horvat received the Life Achievement Award for mercury research at the ICMGP 2019. This award was established in 2011 to celebrate and recognise individuals who have made extraordinary lifetime achievements in mercury research, mentoring, or contributions to governmental policy and public outreach.

The project has provided 10 training sessions for scientists during its lifetime. These have included topics such as (i) the use of MC-ICP-MS and the use of ID-GC-ICP-QMS (ii) calibration of solid trapping systems (iii) installation and use of the Lumex analytical system and of the Optoseven and VTT calibrators, (iv) optimisation for GC-ICP-MS, and for PSA CavKit calibration coupled to ICP-QMS, and (v) Hg(II) measurement methods with GC-ICP-MS. Further to this, 5 PhD students and 1 master student have taken part in the MercOx project of which 1 has already defended their PhD.

The project consortium has established good contact with the European ERA PLANET project (the European network for observing our changing planet, <u>http://www.era-planet.eu/</u>) that collaborates closely with the Global Earth Observation network (GEO) during events in 2018 and 2019. The MercOx project directly contributes to the activities within GEO Global Observation System for mercury (GOS4M) and thus the Effectiveness Evaluation of the Minamata Convention (Article 22) as well as the UNEP's partnership programme in the following domains: (i) Mercury air transport and fate research (ii) Artisanal and small-scale gold mining (ASGM), (iii) Mercury releases from coal combustion, and (iv) Mercury releases from the cement industry (https://web.unep.org/globalmercurypartnership/).

Finally, the project has provided input to 2 new metrological projects: (i) Horizon2020 EU funded MSCA ITN GMOS-Train: "Global Mercury Observation and Training network in support to the Minamata Convention", and (ii) EMPIR project 19NRM03 SI-Hg "Metrology for traceable protocols for elemental and oxidised mercury concentrations".

Impact on relevant standards

The project's validation of field testing of new and existing methods for online and sorbent-based Hg measurements in stack emissions and in the atmosphere (Objective 4) will support stakeholders such as industry, standardisation bodies and policy makers. In Europe, industrial Hg emissions are covered by the IED 2010/75/EU, whereas Directives 2004/107/EC and 2000/76/EC are concerned with air quality and the incineration of waste, respectively. By developing traceable online measurement procedures for the monitoring and control of Hg in gas emission sources and in the atmosphere including oxidised Hg species, this project will make it possible to meet the levels of control in this legislation.

In particular, this project has provided input to standardisation bodies CEN/TC 264 Air quality Working Groups 8, 9 & 10 and ISO/TC 146 Air Quality WG32. As part of which it has provided input to normative documents such as EN 13211, EN 14884, WI 264161, CD 21741 and ISO/DIS 21741.

CEN/TC 264 WG8 are developing standard methods for the measurement of Hg in emissions and how to expand this to cover oxidised Hg emissions in the future. At the last CEN/TC 264 WG8 meeting in Delft in 2018 the project presented evidence for the need and recommendations for an elemental and HgCl₂ calibration gas protocol. Then in 2019 CEN/TC 264 agreed on the adoption of new work items of WG 8: prEN xxxxx "Stationary source emissions — Calibration of elemental and oxidised mercury gas generators for SI-traceable mercury concentration measurements in air". This represents a very important impact on standardisation for the MercOx project.



Longer-term economic, social and environmental impacts

In the long-term the outputs of this project will help to improve Hg measurements and the monitoring capabilities necessary for a reliable and consistent basis for reporting Hg emissions. This is particularly important for the implementation of Minamata Convention on Mercury, signed in 2013, which requires controls and reductions of Hg across a range of products, processes and industries where Hg is used, released or emitted. The results of this project are also of interest to the Global Mercury Partnership of the Minamata Convention, especially the Partnership on Mercury Emissions from Coal and the Fate and Transport partnership.

The long-term and wide impact of this project is demonstrated by the fact that the secretariat of the Minamata Convention at the United Nations Environment Programme (UNEP) convened two meetings during which atmospheric Hg measurements were selected as one of the metrics for effectiveness evaluation of the Convention. Further to this, at the Integrated Global Observing Systems for Persistent Pollutants (IGOSP) meeting for the EU ERA-NET project on satellite measurements of Hg and persistent organic pollutants and at the UNEP//World Health Organisation (WHO) meeting on Global Environmental Facilities, it was agreed that this project has a key role in supporting improved Hg measurement comparability. This was also highlighted at the UNEP second and third meetings of the Conference of the Parties to the Minamata Convention on Mercury (COP2 and COP3 in 2018 and 2019, respectively).

Publications

- [1]. Majda Pavlin, Arkadij Popovič, Radojko Jaćimović, Milena Horvat: Mercury fractionation in gypsum using temperature desorption and mass spectrometric detection, Open Chemistry, 2018; 16: 544–555; <u>https://doi.org/10.1515/chem-2018-0046</u>
- [2]. Majda Pavlin, Radojko Jaćimović, Andrej Stergaršek, Peter Frkal, Maja Koblar, Milena Horvat: Distribution and accumulation of major and trace elements in gypsum samples from lignite combustion power plant, American Journal of Analytical Chemistry, 2018, 9/12 <u>https://doi.org/10.4236/ajac.2018.912044</u>
- [3]. Saxholm Sari , Rajamäki Timo, Hämäläinen Jussi and Hildén Panu, Dynamic calibration method for reactive gases, Measurements Science ad Technology, 2020, 31, 034001, https://dx.doi.org/10.1088/1361-6501/ab4d68
- [4]. Živković, I.; Berisha, S.; Kotnik, J.; Jagodic, M.; Horvat, M. Traceable Determination of Atmospheric Mercury Using Iodinated Activated Carbon Traps. *Atmosphere* 2020, 11, 780. <u>https://doi.org/10.3390/atmos11080780</u>
- [5]. Iris de Krom, Wijnand Bavius, Ruben Ziel, Elizabeth A. McGhee, Richard J. C. Brown, Igor Živković, Jan Gačnik, Vesna Fajon, Jože Kotnik, Milena Horvat and Hugo Ent, Comparability of calibration strategies for measuring mercury concentrations in gas emission sources and the atmosphere, Atmos. Meas. Tech. Discuss. Atmos. Meas. Tech., 14, 2317–2326, 2021. <u>https://doi.org/10.5194/amt-14-2317-2021</u>
- [6]. Iris de Krom, Wijnand Bavius, Ruben Ziel, Evtim Efremov, Davina van Meer, Peter van Otterloo, Inge van Andel, Deborah van Osselen, Maurice Heemskerk, Adriaan M.H. van der Veen, Matthew A. Dexter, Warren T. Corns, Hugo Ent, Primary mercury gas standard for the calibration of mercury measurements, Measurement, Volume 169, 2021, <u>https://doi.org/10.1016/j.measurement.2020.108351</u>
- [7]. Chouhan R. Singh, Ivan Jerman, David Heath, Sivasambu Bohm, Sonu Gandhi, Veera Sadhu, Syed Baker, M. Horvat. Emerging tri-s-triazine-based graphitic carbon nitride: A potential signal-transducing nanostructured material for sensor applications, Nano Sense, 2021, https://doi.org/10.1002/nano.202000228
- [8]. Gačnik J, Živković I, Ribeiro Guevara S, Jaćimović R, Kotnik J, Horvat M. Validating an Evaporative Calibrator for Gaseous Oxidized Mercury. *Sensors*. 2021; 21(7):2501. <u>https://doi.org/10.3390/s21072501</u>
- [9]. Attilio Naccarato, Antonella Tassone, Maria Martino, Sacha Moretti, Antonella Macagnano, Emiliano Zampetti, Paolo Papa, Joshua Avossa, Nicola Pirrone, Michelle Nerentorp, John Munthe, Ingvar Wängberg, Geoff W. Stupple, Carl P. J. Mitchell, Adam R. Martin, Alexandra Steffen, Diana Babi, Eric M.



Prestbo, Francesca Sprovieri, and Frank Wania. A field intercomparison of three passive air samplers for gaseous mercury in ambient air. Atmospheric Measurement Techniques, <u>https://doi.org/10.5194/amt-2020-455</u>

- [10]. Julien P. G. Barre, Silvia Queipo-Abad, Cristina Sola-Larrañaga, Gaëlle Deletraz, Sylvain Bérail, Emmanuel Tessier1, David Elustondo Valencia, Jesús Miguel Santamaría, Alberto de Diego and David Amouroux. Comparison of the Isotopic Composition of Hg and Pb in Two Atmospheric Bioaccumulators in a Pyrenean Beech Forest (Iraty Forest, Western Pyrenees, France/Spain), Frontiers in Environmetal Chemistry, <u>https://doi.org/10.3389/fenvc.2020.582001</u>
- [11]. Panayot Petrov, Timo Rajamäki, Warren T. Corns, Heidi Goenaga-Infante, Evaluating the performance of oxidized Hg reference gas generators in the range ng m-3 to μg m-3 by improved coupling with ICP-MS. Atmospheric Environment, <u>https://doi.org/10.1016/j.aeaoa.2020.100090</u>
- [12]. A. Yamakawa, S. Berail, D. Amouroux, E. Tessier, J. Barre, T. Sano, K. Nagano, S. Kanwal, J. Yoshigawa, O.F.X. Donard. Hg isotopic composition and total Hg mass fraction in NIES Certified Reference Material No. 28 Urban Aerosol, Analytical and Bioanalytical Chemistry, https://doi.org/10.1007/s00216-020-02691-9
- [13]. A. Yamakawa, D. Amouroux, E. Tessier, S. Berail, I. Fettig, J. Koschorreck, O.F.X. Donard, Hg isotopic composition of one-year-old spruce shoots: Application to long-term Hg atmospheric monitoring in Germany. Chemosphere, 2021, <u>https://doi.org/10.1016/j.chemosphere.2021.130631</u>
- [14]. Tassone A., Moretti S., Martino M., Pirrone N., Sprovieri F., Naccarato A.*, Modification of the EPA method 1631E for the quantification of total mercury in natural waters, Methods, <u>https://doi.org/10.1016/j.mex.2020.100987</u>
- [15]. Chouhan, R.S.; Žitko, G.; Fajon, V.; Živković, I.; Pavlin, M.; Berisha, S.; Jerman, I.; Vesel, A.; Horvat, M. A Unique Interactive Nanostructure Knitting based Passive Sampler Adsorbent for Monitoring of Hg²⁺ in Water. *Sensors* **2019**, *19*, 3432. <u>https://doi.org/10.3390/s19153432</u>

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:		01 October 2017, 42 months	
Coordinator: Milena Horvat, JSI, Project website address: <u>http://www.m</u>	Tel: +38 61588 5287 ercox.si/		E-mail: <u>milena.horvat@ijs.si</u>
Internal Funded Partners: 1 JSI, Slovenia 2 LGC, United Kingdom 3 TUBITAK, Turkey 4 UBA, Germany 5 VSL, Netherlands 6 VTT, Finland	External Funded Partners: 7 CNR, Italy 8 Lumex, Germany 9 Optoseven, Finland 10 PSA, United Kingdom 11 UPPA, France		Unfunded Partners: 12 CENAM, Mexico
RMG: -			