D7: Report on the dissemination of scientific outcomes from this project through guidance documents for accurate field measurement and uncertainty assessment to support the development of a suitable calibration system for mercury measurements in the atmosphere, as part of the global mercury observation system used to measure the effectiveness of the implementation of the Minamata Convention

19NRM03 SI-Hg

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Executive summary

The overall goal of this project was to develop protocols for SI-traceable calibration, evaluation and certification of elemental mercury (Hg^0) and oxidised mercury (Hg^{II}) gas generators used in the field. This research will feed into the standardisation committee CEN/TC264/WG8. The specific objectives of the project were (1) to develop and validate a protocol for the SI-traceable certification of elemental mercury (Hg^0) gas generators used in the field; (2) to validate a certification protocol for the certification of oxidised mercury (Hg^{II}) gas generators used in the field; (3) to organise a performance evaluation to gather data on the characteristics of at least three Hg^0 and three Hg^{II} gas generators on the market; (4) to support the development of a suitable calibration system for mercury measurements in the atmosphere, as part of the global mercury observation system used to measure the effectiveness of the implementation of the Minamata Convention; and (5) to facilitate the take up of protocols, methods, technology and measurement infrastructure developed in the project by the standards developing organisations and end-users.

Deliverable 7 describes activities related to the of scientific outcomes from this project through guidance documents for accurate field measurement and uncertainty assessment to support the development of a suitable calibration system for mercury measurements in the atmosphere, as part of the global mercury observation system used to measure the effectiveness of the implementation of the Minamata Convention, as defined in the Annex 1 of the 19NRM03 SI-Hg project. Deliverable 7 supports project objective 4.

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1. Introduction

Although great efforts have been made in developing primary mercury standards and SI-traceable calibration methods for different mercury species, there are still no standardised procedures that ensures dissemination and the uptake of the developed metrological traceability by calibration and testing laboratories and in the field. This SI-Hg project was developed to improve metrological capabilities in Hg measurements in air and emission sources, thus allowing larger community of users to improve the comparability of measurement results. Metrologically sound certification protocols, to determine the output of elemental mercury (Hg^0) and oxidised mercury (Hg^{II}) gas generators, developed and validated in this project, in the form of documentary standards, will be of fundamental importance to guarantee the accuracy and comparability of the mercury measurement data. Furthermore, gas generators certified using SI-traceable standards will provide the traceability and uncertainty needed by calibration and testing laboratories under ISO/IEC 17025:2017 accreditation to show their conformity assessment.

Deliverable 7 describes activities that created impact related to objective 4 of the project as defined in the Activity A4.1.9 of the Annex 1 of the 19NRM03 SI-Hg project though dissemination, publication, and exploitation of the project results, including knowledge transfer. This also includes the impact of the scientific work delivered by the project through a combination of interaction with stakeholders and end-users, contribution to international standards, engagement with scientists dealing with Hg analysis and speciation, international organisations, and policy makers in the area of environmental issues. Results obtained within this project are described in depth in the corresponding peer reviewed publications. Details can also be found in the SI-Hg deliverables that will be available on the project webpage (http://si-hg.eu/).

2. Dissemination of scientific outcomes

2.1 Stakeholder Committee

Within the Activity A4.1.1, a Stakeholder Committee (SC) was established and managed by VSL. The role of the Stakeholder Committee (SC) was to advise and agree upon the needs of interested parties and to help oversee the direction of the project, and to ensure that outputs have impact and publicity within the stakeholder communities. The SC includes representatives from academia, international organizations, industry associations and instrument producers.

The SC included members from the following SME/NMI/DI/organizations: Uniper (Chief stakeholder), Finnsementti, Salonit Anhovo, Ilmatieteen Laitos, Helen Ltd, IVL, Fortum, Tauw, Linde, UK Environment Agency, NPL, IEA Clean Coal Centre, NEN ISO/TC 158, NIST, UBA, US EPA, French CNRS, Envico, SilcoTek, IAS, Mercury instruments, Optoseven, Tekran, CENAM, Tubitak, Shell, HSL, Verein Deutscher Zementwerke eV, Bringham Research Center Utha State University, Markes International, Anton Paar, INERIS, University of Nevada - Reno, SUEZ, DURAG GmbH, Universidad Nicional de Colombia, JEMAI, Gasmet Technologies Oy, Uniphos Envirotronic Pvt Ltd and National institute of metrology (NIM) China.

Two SC meetings were organised by the project consortium. On 4th March 2022 a webinar was organised to inform the stakeholder about the project and the first results obtained, the presentations can be found on the project website (SI-Hg M18 stakeholder webinar presentations – SI-HG). During the Conference on Emission Monitoring in Barcelona, Spain the final SI-Hg workshop was organised on 19 September 2023. During the final meeting the project results were presented to 20 stakeholders from all over the world (Presentations of the SI-HG workshops and CEM conference – SI-HG).

2.2 Project web page

Within the Activity A4.1.2, a project webpage (http://si-hg.eu/) was created by the JSI website with public access. The webpage has been regularly updated with information from partners such as project reports, progress updates, news regarding sampling campaign, papers published by the partners, and details of project meetings. A part of the website is dedicated to exchange information, data, papers and reports between partners.

Figure 1. Home of the SI-Hg web page

2.3 Contributions at conferences and meetings

As a part of the Activity A4.1.2, project partners were to present at least 8 papers at the international conferences. So far, the partners presented 17 presentations (10 oral presentations and 7 posters) at 6 scientific meetings/conferences: CEM 2022, CEM 2023, GAS analysis 2022, EWCPS 2023, RAP 2023 and ICMGP 2022.

The most important event where SI-Hg project was presented was the 15th International Conference on Mercury as a Global Pollutant (ICMGP 2022; 24–29 July 2022, virtual) which was attended by over 1000 participants. This is an event where science community meets with industry, standardisation bodies and policy makers. This forum has become an event organized (almost) every second year and it is truly an event of global importance in the field of mercury research. At the conference, the SI-Hg project had a special session with an estimated 150 attendees.

Another important event was the CEM conference 2023 (19–22 September 2023, Barcelona, Spain) at which the SI-Hg project organized a pre-conference workshop (https://www.ilmexhibitions.com/cem/workshops/) about calibration of mercury measurements for atmospheric and emission purposes. During the workshop SI-Hg project partners presented development and validation of mercury gas generators, calibration methods and standardisation for mercury monitoring in the atmosphere and emission sources:

- Opening (Iris de Krom, VSL)
- SI-traceable measurement results and standardisation for mercury emission monitoring (Iris de Krom, VSL)
- Development of low-level elemental and oxidized mercury calibrators for atmospheric mercury measurements (Warren Corns, PSA)
- Calibration methods for atmospheric mercury concentrations (Igor Živković, JSI)
- Determining converter efficiency for oxidized mercury measurements (Sophie Page, LGC)

- Validation results of the calibration of mercury gas generators (Timo Rajamäki, VTT)

In March 2022, Milena Horvat (JSI) and Iris de Krom (VSL) gave a presentation for Minamata stakeholders about atmospheric mercury monitoring (https://www.mercuryconvention.org/en/news/save-date-minamata-online-season-2), the recordings are available online: Minamata online recordings – SI-HG.

2.4 Open access peer-reviewed papers

As a part of the Activity A4.1.4, project partners were to submit at least three papers to open access peer-reviewed journals during the project. The expectations are that most of the open access publications would be the result of a collaborative effort from partners from different countries. Indeed, most of the publications are from at least two project partners.

So far, the project partners have published 4 open access peer-reviewed papers, while three are under review in high impact journals and 3 are in draft. From these 10 publications 4 are co-authored by more than 1 partner form organizations in different countries.

- 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. Atmospheric Measurement Techniques, 14(3), 2021, 2317–2326. https://doi.org/10.5194/amt-14-2317-2021.
- Domenico Amico, Antonella Tassone, Nicola Pirrone, Francesca Sprovieri, and Attilio Naccarato. Recent applications and novel strategies for mercury determination in environmental samples using microextraction-based approaches: A review. Journal of Hazardous Materials, 433, 2022, 128823. https://doi.org/10.1016/j.jhazmat.2022.128823.
- Jan Gačnik, Igor Živković, Jože Kotnik, Dominik Božič, Antonella Tassone, Attilio Naccarato, Nicola Pirrone, Francesca Sprovieri, Alexandra Steffen, and Milena Horvat. Comparison of active measurements, lichen biomonitoring, and passive sampling for atmospheric mercury monitoring. Environmental Science and Pollution Research, submitted.
- Maria Martino, Antonella Tassone, Lorenzo Angiuli, Attilio Naccarato, Paolo Rosario Dambruoso, Fiorella Mazzone, Livia Trizio, Cristina Leonardi, Francesco Petracchini, Francesca Sprovieri, Nicola Pirrone, Francesco D'Amore, Mariantonia Bencardino. First atmospheric mercury measurements at a coastal site in the Apulia region: seasonal variability and source analysis: Environmental Science and Pollution Research, 29, 2022, 68460 – 68475. DOI: https://doi.org/10.1007/s11356-022-20505-6
- Antonella Tassone, Olivier Magand, Attilio Naccarato, Maria Martino, Domenico Amico, Francesca Sprovieri, Hippolyte Leuridan, Yann Bertrand, Michel Ramonet, Nicola Pirrone, and Aurelien Dommergue. Seven-year monitoring of mercury in wet precipitation and atmosphere at the Amsterdam Island GMOS station: Heliyon, 9, E14608 (2023) DOI: https://doi.org/10.1016/j.heliyon.2023.e14608
- Teodor D. Andron, Warren T. Corns, Igor Živković, Saeed W. Ali, Sreekanth Vijayakumaran Nair, and Milena Horvat. Traceable and continuous flow calibration method for gaseous elemental mercury at low ambient concentrations. Atmospheric Measurement Techniques, submitted.
- Sreekanth Vijayakumaran Nair, Jan Gačnik, Igor Živković, Teodor-Daniel Andron, Saeed Waqar Ali, Jože Kotnik, and Milena Horvat. Traceable calibration for ambient air GOM measurements using non-thermal plasma oxidation of elemental mercury. Analytica Chimica Acta, submitted.
- Teodor D. Andron. SI traceable calibration for gaseous elemental mercury measurements in air and water, drafted

- Sreekanth V. Nair. Stability of standard preconcentration methods for gaseous oxidized mercury in air, drafted
- Sophie Page. An isotope dilution approach for validating mercury gas generators for mercury pollution monitoring, drafted

2.5 Popular press / trade journals

To help inform the wider community about the project, the project partners were to submit two articles to the popular press or trade journals, as part of the Activity A4.1.5.

In April 2021, we published an article in International Environmental Technology about SI-traceable mercury measurement results with the VSL primary mercury gas standard (https://www.envirotech-online.com/news/air-monitoring/6/vsl-dutch-metrology-institute/si-traceable-mercury-measurement-results-with-the-vsl-primary-mercury-gas-standard/55093). In February 2022, we published an announcement for the SI-Hg webinar "Metrology for traceable protocols for elemental and oxidised mercury concentrations" (https://www.envirotech-online.com/news/environmental-laboratory/7/vsl-dutch-metrology-institute/metrology-for-traceable-protocols-for-elemental-and-oxidised-mercury-concentrations/57231).

Furthermore, the project coordinator was invited for an interview about the ICMGP conference and the special session Dr. Iris de Krom: ICMGP 2022 Will Advance Metrology for Mercury Monitoring on Vimeo.

2.6 Good Practice Guide

LGC with support from Lumex, TÜV Rheinland and VTT documented the conclusions of Activity A2.2.4 in the form of a Good Practice Guide regarding storage and Hg^{II} solutions stability. Within the project, a method for chromatographic purity determination of Hg^{II} was developed and applied to the Hg^{II} stock and working solutions ($HgCl_2$ at ng/g and µg/g levels) and salts used for Hg^{II} gas generators. Using the obtained methods, mercury total mass fraction analysis of the salts used in one dry based Hg^{II} gas generator can be performed. Additionally, the Hg^{II} solution stability was monitored over a period of six months. The monitoring included the effects of the different storage conditions on the mass fraction of mercury and species distribution. The main conclusions from this study of $HgCl_2$ solution stability were:

- FLPE bottles and 0.125 µg/g HNO_3/HCl storage solutions should not be used to store $HgCl_2$ solutions at ambient temperatures or up to 60°C for 24 hours;
- FEP and borosilicate bottles are suitable for storing $HgCl_2$ solutions with 0.1% HCl, 0.125 µg/g HNO_3/HCl and 0.024% v/v HNO_3 + 0.0144% v/v HCl at ambient temperatures and up to 60°C for 24 hours;
- 0.125 µg/g HNO_3/HCl should not be used at all to store $HgCl_2$ solutions at fridge temperatures;
- Higher storage concentrations typically result in less Hg loss.

The knowledge obtained in this study and published as a Good Practice Guide will provide valuable information to other researchers and industry representatives on how to properly store their Hg^{II} solutions used for calibration of their analytical instrumentation for Hg^{II} measurements in the atmosphere and stack emissions. This Good Practice Guide will enable better comparison of measurement results by ensuring best possible procedures for the preservation of Hg^{II} solutions, which otherwise could lead to large discrepancies between measurements. The guide can be

downloaded online: [Good Practice Guide on the Storage and Stability of HgCl2 Solutions and Salts (zenodo.org)](zenodo.org).

2.7 Intercalibration report

Within the Activity A4.1.7 of the SI-Hg project, CNR and JSI prepared a report for Task 1.4: Comparison at the Climatic-Environmental Observatory. Due to technical difficulties, the intercalibration campaign was performed at the monitoring station located in Rende, Italy. The aim of this task was to determine the consistent quality of mercury measurements during a field campaign. This campaign consisted in the comparison of the performances of multiple Hg analysers produced by different producers, each calibrated with SI-traceable certified gas generators. Participants were invited to perform measurements using elemental gas generators and oxidized mercury generators for the determination of the mercury concentration at the monitoring station in Rende.

The gas generators involved in the intercomparison included:

- Bell-jar 2505 Tekran Calibration Unit;
- Liquid evaporative Hovacal gas generator;
- Non-thermal plasma oxidation of GEM on KCl-coated denuders.

The active analysers involved in the intercomparison included:

- Mercury speciation system Tekran 2537X/1135/1130;
- Mercury Ultratracer UT-3000;
- RA-915M Lumex;
- 10.525 Sir Galahad II.

The goal of the inter-calibration campaign was to evaluate the comparability of calibrations conducted using multiple gas generators on Hg analysers from different companies. Specifically, the calibrations were conducted according to the following Scheme. The Tekran 2505 bell-jar gas generator was used to calibrate all the involved analysers while the non-thermal plasma gas generator and Hovacal were used to calibrate Tekran Integrated system. Calibrations with NIST SRM 3133 were performed on all the analysers, except for Lumex.

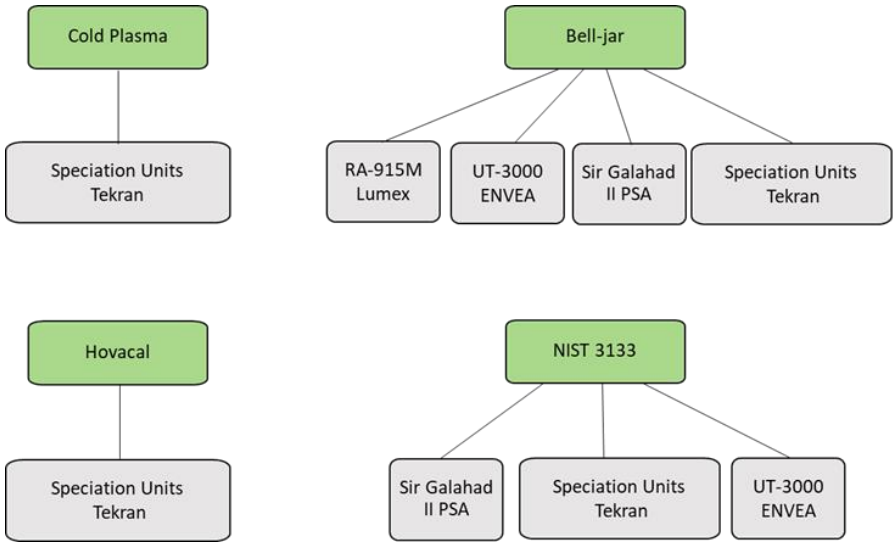

Figure 2. Calibration scenario adopted during the campaign

Although the Hovacal system demonstrated bias when calibrating Tekran speciation unit, our results indicate a promising calibrator unit for further studies of low-level calibrations. Calibration of Tekran denuders using non-thermal plasma oxidation of Hg^0 revealed that GOM can be readily desorbed from the denuder during the full sampling/measurement cycle of the Tekran unit, thus confirming previous findings of Tekran's underestimation of GOM concentrations in ambient air.

All calibration curves obtained in the intercalibration campaign showed good linearity, including those performed through the whole sampling system, which is a requirement of the EN 14181:2014 standard: 6.2.3 Linearity test. However, the observed differences in the calibration slopes were not successfully explained; therefore, further tests are required to address these issues and to explain the observations. The best alignment of calibration slopes is obtained using bell-jar and NIST SRM 3133 calibration under same experimental conditions (Tekran's sampling inlet).

Results from the intercalibration campaign are presented in the **Report: Results of an intercalibration Hg campaign**.

2.8 Dissemination to standards bodies and committees

As a part of the Activity A4.1.8, information on the progress and results from the project (D1 – D6) was disseminated to a range of standards bodies and committees and feedback sought. The committees expect the outcomes of the project to be key inputs to the standards all of which will be adopted as reference methods.

The partners in the previous project (MercOx) were deeply involved in CEN/TC264/WG8 "Measurement of total mercury emissions". During the MercOx project, based on the results of WP1 "Traceable calibration of oxidized Hg", VSL and PSA have set up a preliminary work item proposal in WG8. Conformation on the adoption of the preliminary work item was issued by the secretary of CEN/TC264 in December 2019. JSI joined the WG8 in 2020 and has since further enforced contribution of the SI-Hg project towards the standardisation. The project reports and deliverables are fundamental to support the Preliminary Work Item (PWI) intended to prepare new documentary standards that cover the calibration of elemental and oxidised mercury gas generators underpinning SI-traceable mercury concentration measurements in air. The PWI is currently on hold, but the intention is to re-activate this PWI at the January meeting of CEN/TC 264/WG 8 in 2024.

Other standardisation bodies and committees are also being considered: 390030 – Emissiemetingen en Algemene Aspecten, UK BSI committee EH/2/1 on stationary source emissions, ISO TC146 SC1 (Stationary Source Emissions), VDI/DIN Kommission Reinhaltung der Luft, Fachbereich IV, International Monitoring Programs (Global Monitoring Plan of the Minamata Convention GMP-MC, EMEP, 4°Air Quality Directive), Parties of the Minamata Convention (COP), Expert group for Efficiency evaluation of the Minamata Convention, EURAMET TC-MC, Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) Working Group on Gas Analysis (GAWG), CCQM Working Group on Inorganic Analysis (IAWG), and ISO/REMCO (Reference materials).

3. SI-Hg project, Minamata Convention and international networking

Atmospheric mercury is primarily deposited to ecosystems as oxidised mercury (Hg^{II}) either via dry deposition or in precipitation. The important exception is the uptake of elemental mercury (Hg^0) by foliage. Although this is already well known and has been 'common knowledge' since the last century, exactly which compounds make up atmospheric Hg^{II} continues to elude the scientific community. In the light of recent research efforts focussing on theoretical chemical kinetics of possible Hg^{II} compounds in the atmosphere it has become clear that the atmospheric chemistry of Hg is not as simple as was once thought.

To support the Minamata Convention it is necessary to provide policy makers with evidence of the benefits that measures to reduce anthropogenic Hg emissions provide, and also to be able to model estimates of how much and where emission reductions will lead to reduced ecosystem impacts, and hence health benefits to wildlife and mankind. However, to perform proper measurements of Hg^0 and Hg^{II} in the atmosphere and emission sources, it is imperative to have proper instrumental calibration. The results from the SI-Hg project are fundamental in this regard, as they feed directly into ongoing projects and initiatives both within Europe and globally. A related previous EU project, GMOS (Global Mercury Observation System, http://www.iia.cnr.it/en/project/the-gmos-showcase/) contributed to the Group on Earth Observations (GEO, https://www.earthobservations.org/index.php) and was included in the 2010-2015 work plan as part (C1) of the Task HE-02 "Tracking Pollutants". GMOS supported the achievement of goals of the UNEP Mercury Programme, the GEO (2012-2015) Work Plan, and the Task Force of the Hemispheric Transport of Air Pollutants (HTAP) of the UNECE-LRTAP convention. When this project ended the initiative however continued and is now the GEO Flagship GOS^4M (http://www.gos4m.org/), whose express aim is to lend support to the Minamata Convention Secretariat, the UN Environment and all Nations in the implementation of the Convention. GOS4M activities are particularly related to the Effectiveness Evaluation framework, and it is here that the work of SI-Hg makes a significant contribution.

The conference of the parties is the governing body of the Minamata Convention, responsible for the effectiveness evaluation of the Minamata Convention implementations, that are mandated under Article 22. The protocols developed in the SI-Hg project will support the effectiveness evaluation by providing SI-traceable measurement results of elemental and oxidised mercury concentrations. As these protocols will improve the quality and comparability and uncertainty of mercury measurements in the future, monitoring data may be able to provide a more direct gauge of effectiveness of the Minamata Convention. In this endeavour, JSI, represented by Professor Horvat, assumes a vital role as a member of the Open-Ended Science Group (OESG), contributing to the assessment of the convention's implementation effectiveness. Throughout the 2021-2024 period, Professor Horvat actively participated in several meetings, offering valuable insights to the involved parties. Notably, she emphasized the importance of comparable calibration of mercury measurements in the air during the Knowledge Lab exhibition at the Conference of Parties 5 in Geneva, Switzerland, on November 3, 2023. It's noteworthy that this Knowledge Lab was organized by the EU MSCA ITN project GMOS-Train, specifically addressing metrological aspects of atmospheric mercury measurements in its work package 4.