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## 1 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.

## 2 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.

## 3 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 ( $HgCl_2$ ). This includes quantitative confirmation of the output from liquid evaporative  $HgCl_2$  generators and the development of reference gas standards.

2. 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.
5. 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).

## 4 Results

### 4.1 Objective 1: To develop, establish and implement a traceable calibration methodology for the most important oxidised Hg species, especially for $HgCl_2$ . This includes quantitative confirmation of the output from liquid evaporative $HgCl_2$ generators and the development of reference gas standards.

A primary Hg gas standard was developed at VSL as part of the previous EMPIR project ENV51 MeTra project in order to establish an SI-traceable reference point for mercury concentrations at emission and background levels in the atmosphere. This primary mercury gas standard was used in this project to further develop and improve Hg measurement made in the ENV51 project.

Currently, the majority of Hg concentration measurements are made traceable by using the empirically determined vapour pressure of Hg. The developed primary Hg gas standard can be used for the accurate and precise calibration of analytical systems used for measuring Hg concentrations in air. Indeed it was specifically developed to support measurements related to ambient air monitoring ( $1 \text{ ng m}^{-3}$  –  $2 \text{ ng m}^{-3}$ ), indoor and workplace related Hg concentration levels according to health standards (from  $50 \text{ ng m}^{-3}$  upwards) as well as to stationary source emissions (from  $1 \text{ \mu g m}^{-3}$  upwards).

The primary Hg gas standard is based on diffusion according to ISO 6154-8. Calibration gas mixtures are obtained by combining calibrated mass flows of nitrogen and air through a generator holding diffusion cells, containing Hg(0). This project compared the primary standard with Hg calibration methods maintained by partners NPL and JSI. The calibration methods currently used at NPL and JSI are based on the bell-jar calibration apparatus in combination with the Dumarey equation or a NIST Standard Reference Material (NIST SRM 3133 Hg standard solution). For the comparisons, Hg was sampled on sorbent traps to obtain transfer standards with levels between 2 ng and 1000 ng with an expanded uncertainty not exceeding 3 % ( $k = 2$ ). The comparisons performed showed that the results for the primary Hg gas standard and the NIST SRM 3133 Hg standard solution are comparable, whereas a difference of - 8 % exists between results traceable to the primary gas Hg standard and the Dumarey equation.

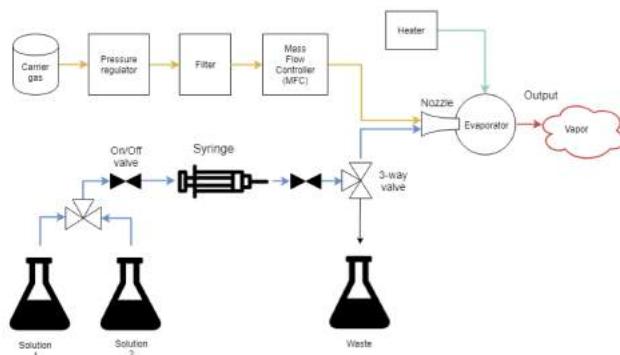


Figure 1. Flow chart of the gas generator developed by Optoseven and VTT. (Published in: Saxholm Sari et al, Measurements Science and Technology, 2020, <https://dx.doi.org/10.1088/1361-6501/ab4d68>)

Two types of conventional  $HgCl_2$  generators were tested including permeation tubes and liquid evaporators. The output of the liquid evaporative  $HgCl_2$  generator developed by partners Optseven and VTT (Figure 1) was then tested using the dual channel Zeeman AAS system developed by partner Lumex (Figure 2). This set up was calibrated with a SI traceable diffusion based gravimetric elemental Hg generator at VSL. This dual channel Zeeman AAS measurement system was shown to provide an accurate real time measurement of  $Hg^{tot}$  and elemental Hg which was then used to check the species integrity of the developed  $HgCl_2$  generators.

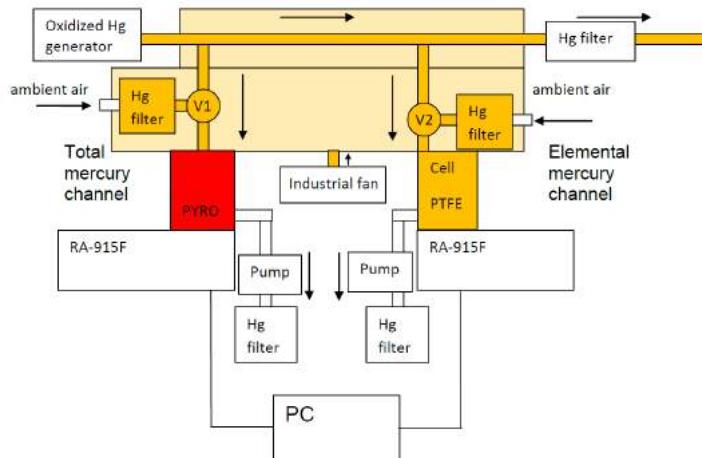


Figure 2. Block diagram of the two-channel analytical system developed by Lumex

The project's developed liquid evaporative  $\text{HgCl}_2$  generator is capable of generating  $\text{Hg(II)}$  reference gases in a wide concentration range above  $\mu\text{g}/\text{m}^3$  levels typical in continuous process industrial conditions. Moreover, a new method for calibration at low ambient concentrations for  $\text{Hg}$  was developed. The new method for calibration was developed by JSI and is based on the quantitative oxidation of traceable amounts of  $\text{Hg(0)}$  by cold plasma systems in helium/oxygen atmosphere and is convenient for low level  $\text{Hg}$  concentrations representing ambient  $\text{Hg}$  levels (Figure 3).



Figure 3. Optical cold plasma for quantitative  $\text{Hg(0)}$  oxidation in denuder developed by JSI

Additionally, the performance of the liquid evaporative  $\text{HgCl}_2$  gas generators has been validated by direct coupling to a species independent inductively coupled plasma mass spectrometry (ICP-MS) detector. The direct coupling to the ICP-MS detector can provide sensitivity for both  $\text{Hg(0)}$  and  $\text{Hg(II)}$  and can compare the liquid evaporative  $\text{HgCl}_2$  gas generators output signal.

Partners LGC, VTT, PSA demonstrated a novel way to introduce a so-called  $\text{Hg}$  reference gas, produced by a gas generator, into an elemental detector, such as ICP MS, and to directly measure gaseous oxidised mercury (GOM as  $\text{HgCl}_2$ ) at a wide range of concentrations, covering 4 orders of magnitude. The approach was tested using two types of generators based on:

1. the dilution of a gas saturated with  $\text{Hg}$  chloride vapours (from dry  $\text{HgCl}_2$  salt) and
2. the evaporation of aqueous  $\text{HgCl}_2$  standards.

The former gas generator (i.e. based on the dilution of a gas saturated with  $\text{Hg}$  chloride vapours) provided reference gas at  $\mu\text{g m}^{-3}$  concentrations, while the latter gas generator (i.e. based on the evaporation of aqueous  $\text{HgCl}_2$  standards) was applicable from low  $\text{ng m}^{-3}$  to  $\mu\text{g m}^{-3}$ . The generation and measurement of gaseous  $\text{Hg}$  was achieved in real time without significant memory effects, and with a response time of less than 5 min. This unique approach of direct measurement (without thermal conversion) of both gaseous

elemental mercury (GEM) and GOM in environmentally relevant and industrial concentrations was shown to offer the potential to significantly improve the reliability of Hg determination from gas generators. Thus, in the longer term, it should significantly improve the accuracy of in-field Hg measurements.

The project's liquid evaporative  $\text{HgCl}_2$  generator was validated by JSI using a highly specific  $^{197}\text{Hg}$  tracer, which detected adsorption phenomena on tubing for  $\text{HgCl}_2$  and particularly for  $\text{HgBr}_2$  species. The work led to the design of additional validation testing specifically for when the liquid evaporative  $\text{HgCl}_2$  generators are used for the loading of selective adsorption traps. A highly specific and sensitive  $^{197}\text{Hg}$  radiotracer prepared by JSI was used for the validation over a wide range of concentrations. As part of this an adsorption isotherm was applied to estimate adsorption enthalpy (DHads); a DHads value of  $-12.33 \text{ kJ mol}^{-1}$  was obtained, suggesting exothermal adsorption. The results of the calibrator performance evaluation suggest that the newly developed calibration unit is only suitable for concentrations of  $\text{HgCl}_2$  higher than  $1 \mu\text{g m}^{-3}$ . This is because the concentration dependence of recoveries prevents the system from being used for the calibration of instruments for ambient GOM measurements. As  $\text{HgBr}_2$  is often used as a proxy for various atmospheric HgBr species, the suitability of the unit for such calibration needs further development. However, this work by the project is a significant step beyond the state of the art.

A certification protocol for the output of liquid evaporative  $\text{HgCl}_2$  generators was prepared by partners VTT, Optoseven, VSL, JSI, PSA and Lumex. The certification protocol is a step by step guide in how to confirm the output of liquid evaporative  $\text{HgCl}_2$  generators (Figure 4). The process consists of two main parts: (1) calibration of a two-channel analyser using a primary  $\text{Hg}(0)$  gas standard and (2) measurement of the output from the generator using the calibrated two-channel analyser.

A follow-on EMPIR project 19NRM03 SI-Hg "Metrology for traceable protocols for elemental and oxidised mercury concentrations" will work on how to convert the protocol into a CEN or ISO standard.

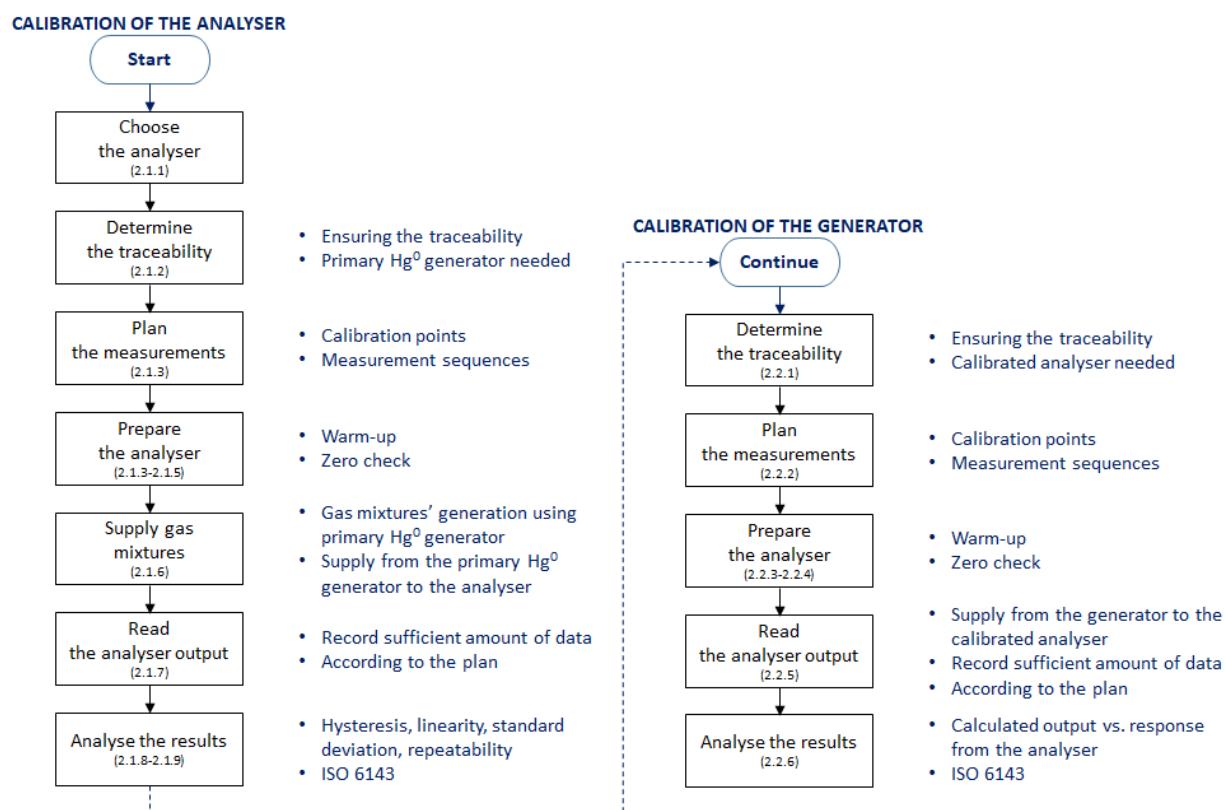


Figure 4. The step by step certification protocol for confirming the output of liquid evaporative  $\text{HgCl}_2$  generators

In order to meet the needs for the calibration of low level GOM in the sub  $\text{ng m}^{-3}$  range (which is typically present in ambient air), JSI developed a novel method using cold plasma for the quantitative oxidation of traceable  $\text{Hg}(0)$ . The new cold plasma method for calibration is based on the quantitative oxidation of traceable amounts of  $\text{Hg}(0)$  (using the NIST SRM 3133) with a cold plasma system in Helium/oxygen atmosphere. The

novel cold plasma method for calibration is convenient for low level Hg concentrations which represent ambient Hg levels: e.g. Hg chlorides, oxide and/or bromides.

### ***Summary***

In summary the project successfully met objective 1 to develop, establish, and implement a traceable calibration methodology for the most important oxidised Hg species, especially for  $\text{HgCl}_2$ . This important work included:

- the validation of a primary Hg gas standard based on diffusion according to ISO 6154-8
- the development of a liquid evaporative  $\text{HgCl}_2$  generator
- the quantitative confirmation of the output from liquid evaporative  $\text{HgCl}_2$  generators
- a certification protocol for the output of liquid evaporative  $\text{HgCl}_2$  generators
- a new method for calibration at low ambient concentrations for Hg
- and a novel method using cold plasma for the quantitative oxidation of traceable Hg(0).

**4.2 Objective 2: To develop and compare different methods of measuring oxidised Hg and to accurately compare Hg<sup>tot</sup> concentrations in generated standard gases for Hg(0) and 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.**

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA ICP-MS) was developed by partner LGC as a method to determine Hg<sup>tot</sup> in activated carbon (AC) traps and was fully validated (Figure 5).

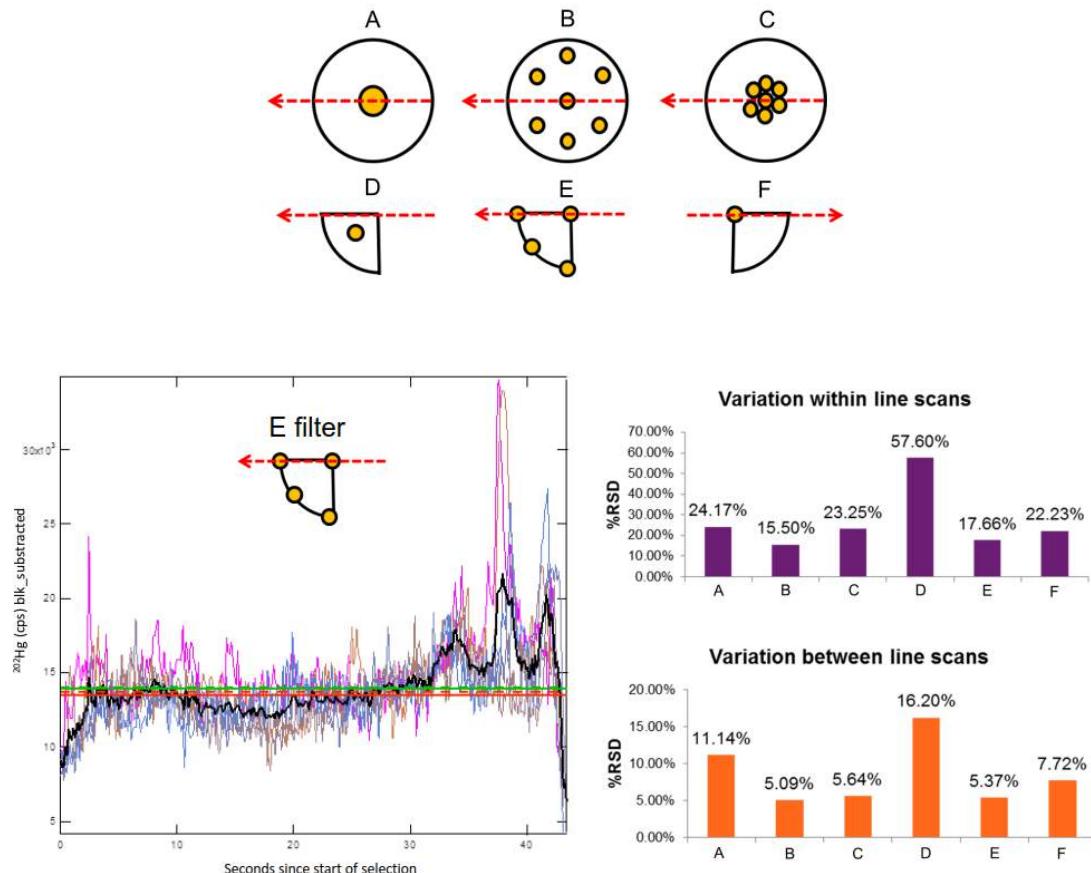


Figure 5. Upper figure represents six investigated spiking methods of the filters. The red arrow shows the laser ablation path. Lower figure represents time-dependent response of the ICP-MS during laser ablation of the filter spiked using the spiking method E (left); the red arrow shows the ablation path. Variations within line scans and between line scans for six investigated spiking methods of the filters (A – F) (right).

A variety of trapping media and conditions were also investigated for selectivity and applicability (potential use) for quantitative trapping of Hg(II) and Hg<sup>0</sup> species in the ambient air and flue gases. The Hg species solubility, stability and trapping efficiency were determined after selective trapping on AC sorbent traps (halogenated and non-halogenated), impinger solutions (as recommended in the current Hg species determination standard methods) and in salts, frequently used for denuder coatings (e.g. KCl). The advantages and disadvantages of each of these media were documented.

In addition to these conventional sorbent trap materials an efficient nanomaterial with a 2D structure and high surface area was developed by JSI. This is a low cost and metal-free material based on graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ) and graphene oxide (GO). This nanomaterial shows very promising results to selectively trap Hg(II) in impinger solutions and from the atmosphere.

Further to this, an Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (ID ICP-MS) for accurate measurements of Hg(II) and testing for interconversions during preconcentration steps was developed by LGC.

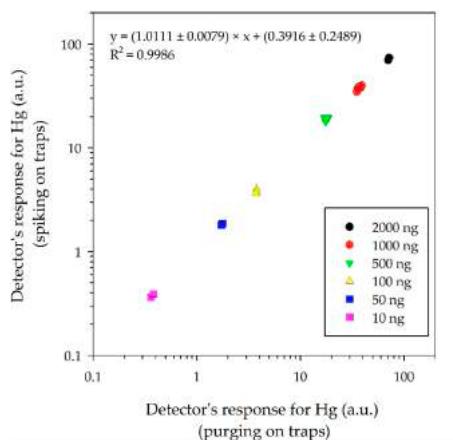
Selective trapping systems using KCl loaded traps, denuders and impingers were validated using a  $^{197}\text{Hg}$

tracer. The experiments using a liquid evaporative HgCl<sub>2</sub> generator (from objective 1) resulted in high losses of Hg(II) onto the tubing, especially at low Hg(II) concentrations. Therefore, traceable quantities of Hg loaded onto selective traps and denuders were only demonstrated by the oxidation of Hg(0) by cold plasma.

Although Hg pre-concentration on AC traps is a simple method for sample collection, Hg determination is difficult due to its complex matrix that cannot be easily digested using wet chemistry. Two approaches for Hg loading on iodinated AC were used to test whether spiking SRM solution on AC can be used for the traceable determination of atmospheric Hg collected as Hg0 (Figure 6). The two approaches were (i) the purging of Hg(0) and (ii) the spiking of a solution of NIST SRM 3133.

Hg on AC was determined using atomic absorption spectrometry after sample combustion. The detector's response for both loading methods was identical in a wide concentration range, indicating that the spiking of NIST SRM 3133 on AC can, indeed, be used for the calibration of analytical systems that are used for the determination of atmospheric Hg. This result was also confirmed by the determination of Hg in a real atmospheric sample collected on an iodinated AC trap and using an SRM spiking calibration.

Different ACs were also compared regarding their ability to quantitatively capture Hg while having the lowest breakthrough. The results showed that the use of a specific impregnating solution probably converted Hg on AC to Millon's iodide, as estimated from the fractionation thermogram.



*Figure 6. Linear dependence of the detector's signal for Hg on activated carbon traps (A/C-500) obtained by two loading methods (purging onto carbon traps and spiking on activated carbon). a.u.—arbitrary units.*  
*(Published in: Živković et al. *Atmosphere* 2020, <https://doi.org/10.3390/atmos11080780>)*

The project successfully validated the feasibility of experimental protocols to determine the concentration of Hg species by specific adsorbent techniques and Hg isotopic composition in gas phase and Particulate Matter (PM) using Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC ICP-MS).

A method for the determination of stable isotope ratios of Hg in atmospheric bio-monitors (lichen, moss, spruce needles) was also optimised and was subsequently used for the analysis of spruce needle samples from the German specimen bank. The Hg isotopic composition of 1-year-old Norway spruce (*Picea abies*) shoots collected from Saarland, Germany, since 1985 by the German Environmental Specimen Bank, were measured for a better understanding of the temporal trends of Hg sources. The isotopic data showed that Hg was mainly taken up as GEM and underwent oxidation in the spruce needles, which then led to a significant decrease in  $\delta^{202}\text{Hg}$  compared with the atmospheric Hg isotopic composition observed for deciduous leaves and epiphytic lichens. Observations of the odd number mass independent isotopic fractionations (MIF) indicated that  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  were close to but slightly lower than the actual values recorded from the atmospheric measurement of the GEM isotopic composition in non-contaminated sites in U.S. and Europe. In contrast observation of the even number MIF indicated almost no differences for  $\Delta^{200}\text{Hg}$ . This confirmed that GEM is a major source of Hg accumulation in spruce shoots.

Interestingly, the Hg isotopic composition in the spruce shoots did not change significantly during the period of > 30 years studied, even though the Hg concentration decreased significantly. In addition, even-MIF ( $\Delta^{200}\text{Hg}$ ) and mass-dependent fractionation (MDF) ( $\delta^{202}\text{Hg}$ ) of the Hg isotopes exhibited a slight decrease with time, whereas odd-MIF did not show any clear trend. These results suggest a close link between the long-

term evolution of GEM isotopic compositions in the air and the isotopic composition of bioaccumulated Hg altered by mass-dependent fraction in the spruce shoots (Figure 7).

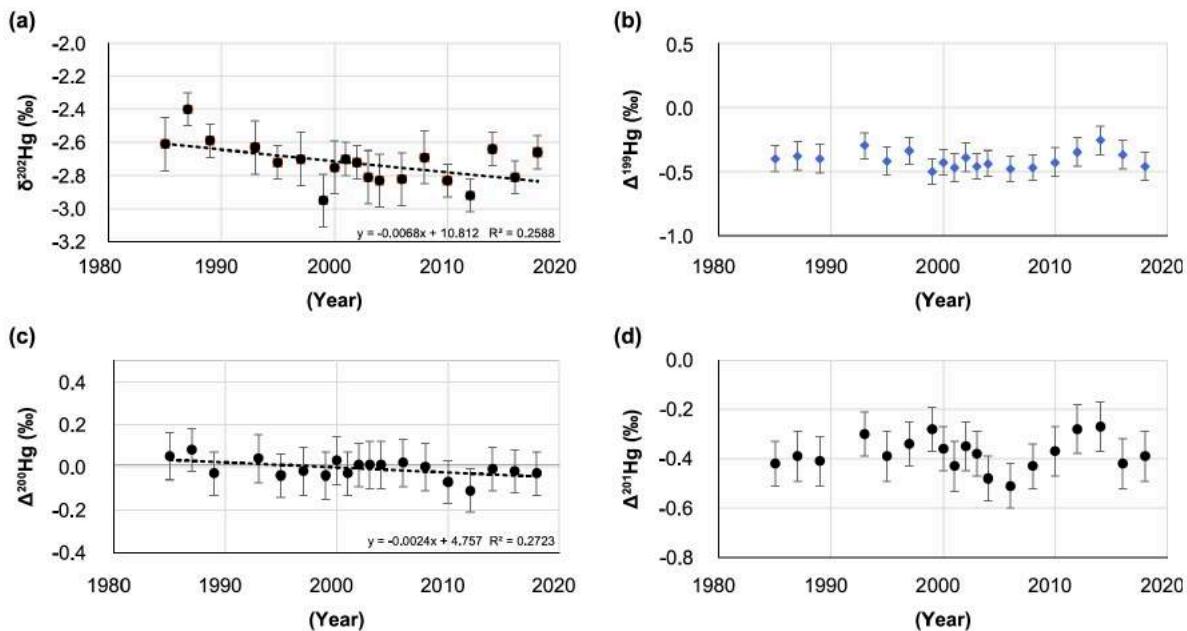


Figure 7. Temporal variations of (a)  $\delta^{202}\text{Hg}$ , (b)  $\Delta^{199}\text{Hg}$ , (c)  $\Delta^{200}\text{Hg}$ , and (d)  $\Delta^{201}\text{Hg}$  in spruce. The uncertainties of each plot represent 2SD of NIST RM 8610. (Published in: Yamakawa et al. Chemosphere, 2021, <https://doi.org/10.1016/j.chemosphere.2021.130631>)

A certified reference material (CRM) of urban atmospheric particles from the National Institute for Environmental Studies (NIES) in Japan, was characterised by partner UPPA for Hg isotopic composition in order to provide new reference values for this type of sample. An interlaboratory study on the NIES CRM No. 28 Urban Aerosols, collected on the filters of a central ventilating system in a building in Beijing city centre, was performed to obtain informative values of Hg isotopic composition and  $\text{Hg}^{\text{tot}}$  mass fraction. The  $\text{Hg}^{\text{tot}}$  mass fraction was determined by partners LGC, TUBITAK, CENAM, PSA and JSI using atomic absorption spectrometry. The results gave a mean value of  $1.19 \pm 0.12 \text{ mg/kg}$  (2SD,  $n = 24$ ).

The Hg isotopic composition of the NIES CRM No. 28 Urban Aerosols was also measured and compared at partners UPPA and JSI by using a cold vapor (CV) generation system coupled to MC ICP- MS. Subsequently, a conventional dissolution Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux (IPREM) method that uses a mixture of  $\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}_2$  in Hotblock® and two different dissolution methods that use a mixture of  $\text{HNO}_3/\text{HCl}$  with a microwave and a digestion bomb were applied. The Hg isotopic compositions were:

- $\delta^{202}\text{Hg} = -1.26 \pm 0.17 \text{ ‰}$
- $\Delta^{199}\text{Hg} = -0.23 \pm 0.06 \text{ ‰}$
- $\Delta^{200}\text{Hg} = 0.01 \pm 0.07 \text{ ‰}$
- $\Delta^{201}\text{Hg} = -0.22 \pm 0.09 \text{ ‰}$

(2SD,  $n = 18$ ) for the conventional IPREM method (that uses a mixture of  $\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}_2$  in Hotblock®). These results agree well with those obtained using the two different dissolution methods with a microwave and digestion bomb. The results indicate that, for the quality control of PM analyses, the NIES CRM No. 28 Urban Aerosols is appropriate for use in environmental and geochemical studies (Figure 8).

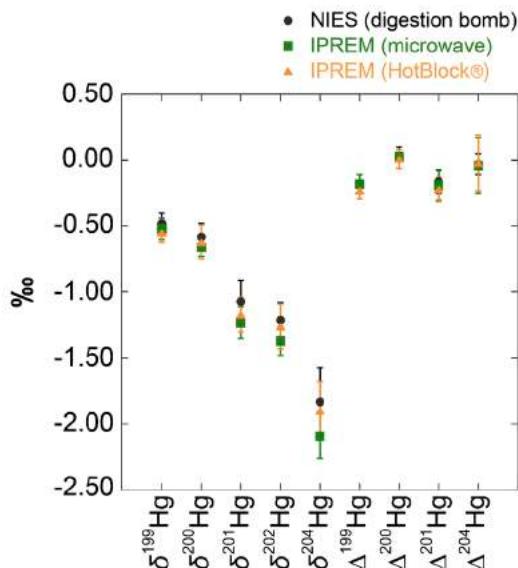


Figure 8. Hg isotopic compositions of NIES CRM No. 28. Three digestion methods were implemented in this study (digestion bomb: black circle; microwave: green square; and HotBlock®: orange triangle). The error bars on the NIES CRM represent 2SD of Hg isotope heterogeneity. IPREM Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux; NIES, National Institute for Environmental Studies (Published in: Yamakawa et al. Analytical and Bioanalytical Chemistry, <https://doi.org/10.1007/s00216-020-02691-9>).

A thermal desorption method was also developed by JSI 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 observed qualitatively, however further optimisation is needed for quantitative determination.

In addition, initial studies using thermal desorption combined with ICP-MS have shown promising results. Accurate species quantification were performed by LGC, accounting for species conversion, can be achieved using species-specific Isotope Dilution Mass Spectrometry (ID-MS) with an ICP-MS detector.

A method for the determination of Hg<sup>tot</sup> in reference Hg solutions using Isotope Dilution Cold Vapor Inductively Coupled Plasma Mass Spectrometry (ID-CV-ICP-MS) was developed at CENAM 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<sup>tot</sup> in reference Hg solutions (with or without cold vapour) can also be used to study interconversion processes during sampling and analysis of Hg(II) and Hg(0).

Finally, the project developed, a bituminous coal candidate reference material for the determination of Hg<sup>tot</sup> and Hg(II).

### Summary

In summary the project successfully met objective 2 to develop and compare different methods of measuring oxidised Hg and to accurately compare Hg<sup>tot</sup> concentrations in generated standard gases for Hg(0) and Hg(II). This work included:

- the development and validation of a LA ICP-MS method to determine Hg<sup>tot</sup> in AC traps
- the validation of thermal decomposition method for total mercury measurements on solid traps
- the development of an efficient nanomaterial with a 2D structure and high surface area
- an ID ICP-MS method for the accurate measurement of Hg(II) and interconversions during preconcentration steps

- the validation of experimental protocols to determine the concentration of Hg species by specific adsorbent techniques and Hg isotopic composition in gas phase and PM using MC ICP- MS.
- an optimised method for the determination of stable isotope ratios of Hg in atmospheric bio-monitors (lichen, moss, spruce needles)
- the validation of the NIES CRM No. 28 Urban Aerosols for the quality control of PM analyses in environmental and geochemical studies
- a thermal desorption method to separate Hg(0) adsorbed on particles or solid substrates using QMS, detection
- a method for the determination of Hg<sup>tot</sup> in reference Hg solutions using ID-CV-ICP-MS
- a bituminous coal candidate reference material for the determination of Hg<sup>tot</sup> and Hg(II).

**4.3 Objective 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.**

Both atmospheric chemistry and stack gas emission chemistry were investigated by the project. The modelling studies at partner CNR focused on updating existing Hg chemistry mechanisms in transport/chemistry models in order to improve the understanding of the emission, transport and deposition of Hg in industrial plumes.

Since the start of this project several theoretical studies addressing the chemistry and photolysis of brominated Hg compounds have been published and the results from these theoretical studies were added by this project to the Weather Research and Forecasting (WRF) model coupled with Chemistry (WRF/Chem model). The regional WRF/Chem was also updated to include (i) the most recent rate constants for BrHg\* addition, (ii) product reactions and (iii) their subsequent photolysis, which yields BrHgO (a radical which reacts in the atmosphere with both inorganic and organic compounds). The project has compared the WRF/Chem model with previous versions in order to understand how 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 has also studied Hg species interconversion during sampling steps based on pre-concentration on KCl solid traps. The results indicated 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. In turn this elemental Hg oxidisation can potentially produce a positive and negative bias in the reporting of oxidised and elemental Hg respectively.

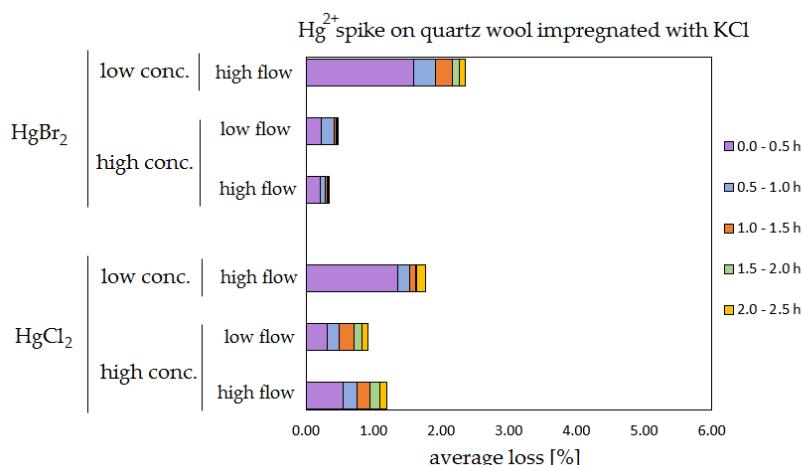
The solubility of elemental Hg in KCl solution has also been experimentally determined by establishing the dimensionless Henry's law constant. At low concentrations this solubility can cause a positive bias as KCl trapping solutions are presumed to be selective for HgCl<sub>2</sub>. Bubbler tests with KCl trapping solution and elemental Hg calibration gas showed mercury oxidation which was enhanced with acid gases such as NO<sub>2</sub>, HCl, NO and N<sub>2</sub>O. Traces of HgCl<sub>2</sub> were measured in the KCl trapping solution using aqueous phase propylation liquid extraction with gas chromatography atomic fluorescence spectrometry (GC-AFS). Further to this, the influence of stack gas components on the stability of HgCl<sub>2</sub> trapped in the KCl trapping solution were studied, and in some cases (e.g. SO<sub>2</sub>, N<sub>2</sub>O and CO) a reduction of HgCl<sub>2</sub> was observed. "This work showed that the KCl trapping solution is not sufficiently selective to offer accurate Hg fractionation results in a flue gas matrix or ambient air.

The results of the project's specificity testing showed that the KCl sorbent traps are very specific when using new (i.e. not reused) traps, however their specificity drops dramatically when the traps are reused. The results of the stability tests showed that the highest Hg<sup>2+</sup> losses (up to 5.5 % of Hg<sup>2+</sup> loss) occur when low amounts of Hg<sup>2+</sup> (< 1 ng) are loaded, due to a reduction of Hg<sup>2+</sup> to Hg<sup>0</sup>. Therefore, GOM losses should be taken into account when using KCl sorbent traps for atmospheric Hg speciation, especially at low ambient GOM concentrations.

KCl trapping solutions have also been proposed as a selective trapping media for GOM in atmospheric samples (Figure 9). A dimensionless Henry's law constant was experimentally derived and was used to calculate the solubility of elemental Hg in KCl solution. The degree of GEM oxidation was then established by purging elemental Hg calibration gas into a KCl solution and determining the GOM trapped using aqueous phase propylation liquid-liquid extraction GC-AFS. A positive GOM bias was observed due to the solubility and oxidation of GEM in KCl trapping solutions, which strongly suggests that this approach is unsuitable for atmospheric Hg speciation measurements.

The project has validated and quantified interconversion processes using a highly sensitive radiotracer technique based on the use of highly sensitive radiotracer <sup>197</sup>Hg produced in the JSI nuclear research reactor from an enriched <sup>197</sup>Hg stable isotope (Objective 1). The highly sensitive radiotracer technique was used to study the outputs of the liquid evaporative HgCl<sub>2</sub> calibrators (from Objective 1) as well as the adsorption and desorption of Hg(II) during loading onto traps, denuders and impingers. This unique highly sensitive radiotracer approach indicated severe losses of Hg(II) species in the sampling of commonly used methods such as Tekran equipped with denuders and commonly used sorbent traps loaded with KCl. 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 Nevada-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.



*Figure 9. Results of the stability test for the  $^{197}\text{Hg}^{2+}$  (radiotracer) spike on quartz wool impregnated with KCl. Low concentrations were loaded with less than 1 ng Hg per time period and high concentrations were loaded with more than 50 ng of Hg per time period. Low air flow experiments were performed with  $100 \text{ mL min}^{-1}$  air flow while high air flow experiments were performed with  $400 \text{ mL min}^{-1}$  flow.*

Studies on the stability of Hg species on sorbent traps using conventional techniques based on cold vapour atomic fluorescence spectrometry (CV AFS) and temperature fractionation analysis using QMS were successfully completed and the results supported the characterisation of Hg (II) compounds loaded by a cold plasma source.

Partners LGC, TUBITAK; UPPA, CENAM, JSI, PSA, VTT and Lumex used the results obtained to produce a good practise guide on Hg sample preparation and interspecies conversion.

The good practice guide was originally designed to be only for Hg sample preparation and interspecies conversion corrections within two specific areas. The first was methods for determining selectively trapped GOM at environmentally relevant concentrations, i.e. in the atmosphere and in the stack emissions. The second was methods for measuring Hg(II) on particulate matter via the determination of Hg<sup>tot</sup> and by species-specific analysis. However, this was expanded to include the most important findings of the project as a whole. The guide now includes how to perform a specific task/measurement/operation and the appropriate application of instrumentation/analysis to specific measurand. In addition, it includes important negative findings that recommend how certain procedures should not be performed.

The good practice guide is available to the scientific community on the project's website [http://www.mercox.si/images/D5-Good\\_practices.pdf](http://www.mercox.si/images/D5-Good_practices.pdf)

## Summary

In summary the project successfully met objective 3 to optimise sampling methods for gaseous Hg species using traceable reference standards for Hg(0) and Hg(II). This work included:

- Modelling of both atmospheric chemistry and stack gas emission chemistry in order to update existing Hg chemistry mechanisms in transport/chemistry models and improve the understanding of the emission, transport and deposition of Hg in industrial plumes
- the updating and comparison of the WRF/Chem model in order to understand how recent changes affect the dynamics of Hg transport and deposition

- a study of Hg species interconversion during sampling steps based on pre-concentration on KCl solid traps
- determination of the influence of stack gas components on the stability of  $\text{HgCl}_2$  trapped in the KCl trapping solution
- calculation of a dimensionless Henry's law constant which was then used to calculate the solubility of elemental Hg in KCl solution.
- validation of a method using a highly sensitive radiotracer technique based  $^{197}\text{Hg}$  for the quantification of interconversion processes
- and a good practise guide on Hg sample preparation and interspecies conversion.

**4.4 Objective 4: To test and validate new and existing methods for on-line Hg measurement under field conditions using the developed gas standards and/or generators. This will include measurement of Hg in stack emissions and in ambient air.**

**Emission measurements:**

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. 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 at both these sites.

The calibration of the Hg continuous emission monitoring system (CEMS) in the coal fired power plant was performed using an evaporative reference gas generator developed by Optoseven and VTT. The response time, signal to noise ratio, and linearity of the CEMS Hg reading were determined in field conditions by flushing the whole system with a reference gas. In general, very good linearity was obtained between reference gas concentration and the CEMS reading. The slope of the calibration curve was 1.035. The calibration curve has a slight positive offset, which is due to a lag in the response time as zero concentration level was not reached between consecutive calibration points.

Samples from the stack gas were collected from the coal fired power plant (in Marl, Germany) and a cement clinker production facility (in Anhovo, Slovenia) using different types of commercial Ohio Lumex sorbent traps. The measurements were carried out using sorbent traps for the determination of  $Hg^{tot}$  in accordance with the new CEN TS 17286 method and the existing US EPA 30B method and with traps for speciation. Sorbent traps were used to collect flue gas for the determination of (i)  $Hg^{tot}$ , (ii) Hg speciation, and (iii) stable isotope ratio analysis. The results of the analyses of using the commercial Ohio Lumex sorbent traps, validated and verified in Objective 3 were in good agreement with the results measured by the CEMs at both sampling sites. The steps identified in the Good Practice Guide (Objective 3) were also used during the field testing.

In order to evaluate the Hg removal efficiency of the flue-gas desulphurisation (FGD) system at the coal fired power plant, sampling was performed simultaneously at two sampling points before and after FGD. These results show that almost 75 % of Hg was effectively removed and transferred to the FGD wastewater.

At the cement clinker plant, three modes of operation were used during the sampling, depending on the number of mills operating. These results showed a clear trend in the concentration of different Hg fractions depending on the plant operation mode.  $Hg^{tot}$  and  $Hg(II)$  were the lowest during the operation of two-mills and at their greatest levels when there was no-mill operation at the plant. The inverse trend was observed for  $Hg(0)$  (Figure 10).

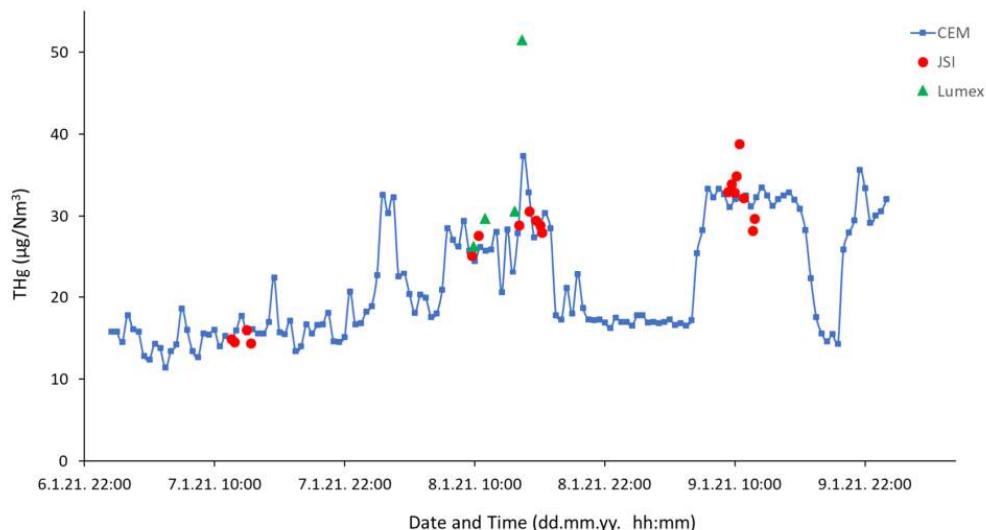


Figure 10. Comparison of  $Hg^{tot}$  concentrations in stack gas as determined by CEM (blue squares) and sorbent traps. Sorbent traps were measured by JSI (red circle) and by Lumex (green triangle).

A CV generator coupled to ICP-MS was used for the quantitative determination of Hg in the sorbent trap samples (from Objective 2). The digestion of the ball-mill homogenised carbon from the carbon-trap sections of the speciation traps and from the Hg<sup>tot</sup> traps was performed with the optimised procedure for total Hg determination on sorbent traps.

In general, as much as 50 % of Hg(II) was found to be trapped on sections of the traps, which are not normally considered as trapping sorbent for Hg(II) (e.g. KCl). Therefore, the data suggested that glass wool and acid gas scrubbers are more efficient trapping media compared to KCl. The results from this work (analysis of field-loaded traps from coal-fired power plant) are in a good agreement with the predictions from the modelling studies performed in Objective 3.

The suitability of a direct thermal decomposition method for the quantification of the Hg<sup>tot</sup> in raw materials used for cement production was evaluated. Two different approaches to calibration were used:

1. using a CRM of the same or comparable matrix to those of the samples and
2. a spiked approach by adding a calibration standard solution to the sample matrix.

The expanded uncertainties of the two methods were estimated and the most appropriate calibration method was found to be using a CRM (supplied by NIST) of the same or comparable matrix to those of the samples. However, the uncertainties in matrix CRMs are relatively large and a cement CRM with appropriate Hg concentration is currently lacking, which led to difficulties in calibration.

Therefore, the second spiked approach was used i.e. the adding of calibration standard solutions to the sample matrix. This second approach was demonstrated to be a suitable as it included the matrix of the considered sample during calibration.

The expanded relative uncertainties were determined at three concentration levels and were below 30 % for calibration with the matrix CRMs. The spiked calibration approach had much lower uncertainties (below 20 %).

Using these 2 calibration methods, Hg concentrations in solid samples from the coal fired power plant and the cement clinker production facility were determined.

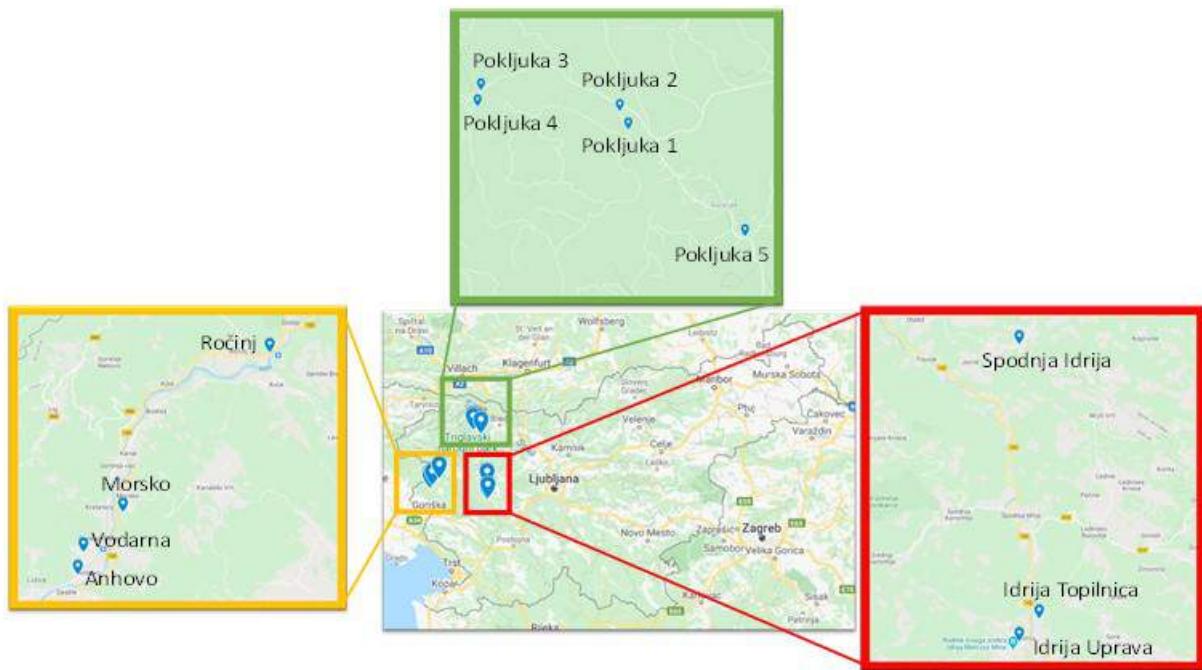
The samples from coal fired power plant included electro-filter dust, and coal and sludge samples. The highest Hg concentrations were found in the sludge, followed by electro-filter dust, indicating good removal efficiency from the flue gas using these abatement systems.

The samples from the cement clinker plant included raw material mixture, corrective material, iron-rich material, sandstone, raw meal from mills and cyclones, filter dust, clinker, and petrol coke. The Hg content in the measured samples was found to be similar to previously measured values.

Finally, a method validation study was completed for sorbent traps in line with the analytical test requirements for CEN TS 17286 and the US EPA 30B sorbent trap methods. The results were in excellent agreement, confirming the validity of both approaches.

#### ***Atmospheric measurements:***

The project's goal was to test and validate existing methods for on-line Hg monitoring, sorbent trap measurement and biomonitoring of Hg in the atmosphere. These tests were conducted at different sites chosen across Europe in order to consider the effect of direct sources of Hg and its short- and long-range transportation. The sites were Monte Curcio, Italy, a cement plant in Anhovo and a former Hg mining area in Idrija) (Figure 11).



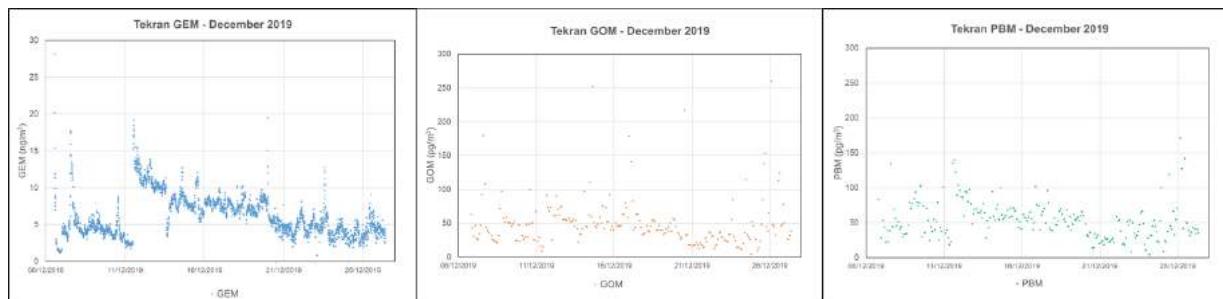
*Figure 11. Geographical locations of stations (relative to Slovenia, the central part of the figure) where in situ lichens were collected, where transplanted lichens and passive air samplers were exposed, and where occasional and continuous active air measurements were performed.*

Active, on-line, Hg measurements were performed near the Anhovo cement plant using three different instruments (analytical systems):

1. Tekran which uses the pre-concentration of Hg on sorbent cartridges and analysis with CV-AFS
2. Sir Galahad which also uses the pre-concentration of Hg on sorbent cartridges and analysis with CV-AFS
3. Lumex's system which directly measures Hg(0) in the air using a Zeeman CV-AAS system.

As the 3 instruments all measured different air Hg species (Tekran – GEM, GOM and Particulate Bound Mercury (PBM); Sir Galahad – total gaseous mercury (TGM); and Lumex – GEM) at different sampling and measurement frequencies direct comparison of the results was very difficult.

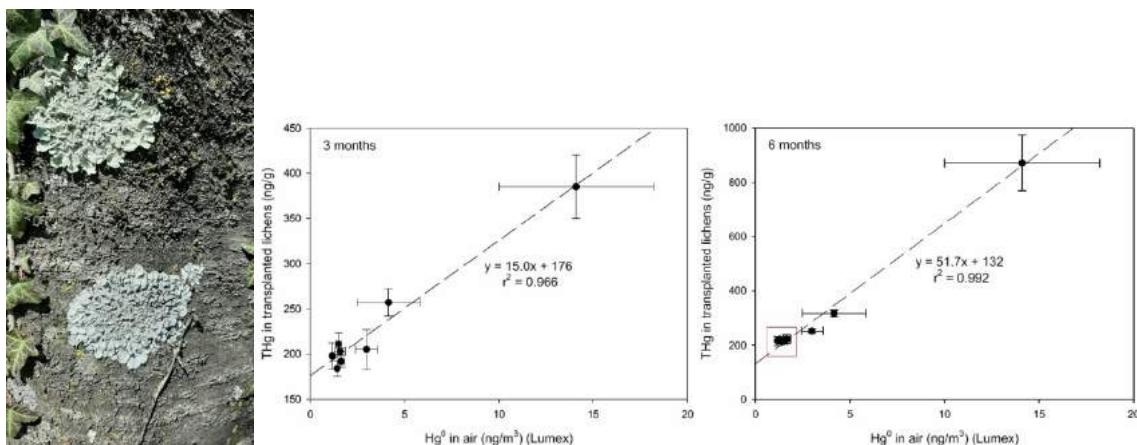
The frequency of the measurements was found to be an important issue when comparing the data (Figure 12). This was due to different frequency of data obtained which meant that the results had different deviations. Therefore, it was very important to obtain proper data averages with standard deviations and measurement uncertainty. Compared to the TGM values recorded at Monte Curcio (background site) those measured at Vodarna with the same active sampling system demonstrated the importance of the anthropogenic impact on the quality of the air surrounding the industrial cement plant complex.



*Figure 12. Typical monthly measurements of GEM, GOM and PTB at the station close to Anhovo cement production facility (Vodarna).*

Several types of passive air samplers (PAS) were exposed and tested at locations near the Anhovo cement plant and the former Hg mine in Idrija. The PAS showed trends between exposure times and air Hg concentrations, and they showed lower variability in the results in Idrija, which had high Hg air concentrations compared to the locations near the Anhovo cement plant where air Hg concentrations were much lower. Thus, the results demonstrate that the PAS have the potential to be used as a cost-effective method for air Hg monitoring.

Linked to the work in Objective 2, an air Hg biomonitoring approach was investigated using transplanted lichens (*Hypogymnia physodes*), and in-situ collected lichens (*Punctelia subrudecta* and *Flavoparmelia caperata*). Lichens were collected at Pokljuka (Slovenia) an area considered to be remote and clean, and then transplanted for different time periods at several locations around the Anhovo cement plant and Idrija Hg mine area. The lichens were highly sensitive to air contamination/pollution. As seen in previous studies, the concentrations of Hg in in-situ and transplanted lichens correlated well with air Hg concentrations and exposure times. The variability of results obtained was low and showed much less measurement uncertainty than that for PAS. Therefore, the use of epiphytic lichens could be a better cost-effective method for the long-term monitoring of Hg in air (Figure 13).



*Figure 13. In-situ lichens *Punctelia subrudecta* and *Flavoparmelia caperata* collected at the Anhovo site. Relation between the amount of Hg<sup>tot</sup> in transplanted lichens following the exposure time of three (left panel) and six months (right panel), and the mean Hg<sup>0</sup> concentration in the air at selected stations. Error bars represent one standard deviation of measurements.*

To ensure accurate results the use of proper metrology principles is necessary for both active or passive measurements, or biomonitoring. However, PAS, that can provide time-averaged concentration of gaseous Hg over the time scale of weeks to months, are promising to fill a gap in the monitoring of atmospheric Hg worldwide (Figure 14). The usefulness of the PAS will depend on their ease-of-use and robustness under field conditions, their availability and affordability, and most notably, their ability to provide accurate results.

Therefore, the project undertook a comparison of three PASs in terms of their ability to record precisely and accurately atmospheric background concentrations at 2 sites in southern Italy and southern Ontario (Canada). The study organised by partner CNR included:

1. CNR's PAS which has gold nanoparticles as a sorbent, developed by the Italian National Research Council
2. , the IVL-PAS which uses an activated carbon-coated disk, developed by the Swedish Environmental Research Institute,
3. and the MerPAS® which uses a sulphur-impregnated activated carbon sorbent, developed at the University of Toronto and commercialised by Tekran.

The detection limits of the PAS were deduced from the variability in the amount of Hg quantified in more than one field blank sample for each PAS. Analytical and sampling precision was quantified using triplicated measurements for each PAS ranging in length from 2 to 12 weeks. Accuracy and bias were assessed through comparison with GEM concentrations recorded by a Tekran 2537 automated Hg analyser operating alongside the PAS at the locations in southern Italy and southern Ontario (Canada). The results showed that the

performance of the PAS was significantly better in southern Italy, with all PAS providing concentrations that were not statistically significantly different from the average of the active sampling results (i.e. recorded by the Tekran 2537 automated Hg analyser). However, in southern Ontario, Canada, where weather conditions were much harsher and more variable during the February-April deployment period, differences were observed amongst the PAS.

In both southern Italy and southern Ontario (Canada), the MerPAS® was the most sensitive, precise and accurate of the PAS. A reason for this is the larger size and the radial configuration of the MerPAS®, which results in blank levels that are lower relative to the sequestered amounts of Hg than in the other two PAS (i.e. CNR-PAS and IVL-PAS), which rely on axial diffusion geometries.

However, as the blank-correction becomes relatively smaller with longer deployment, sampler performance tends to be better during deployments of 8 and 12 weeks for all PAS.



*Figure 14. Installation of passive samplers at Vodarna site.*

### **Summary**

In summary the project successfully met objective 4 to develop, test and validate new and existing methods for on-line Hg measurement under field conditions using the developed gas standards and/or generators. The most important conclusion from the work were:

- sorbent traps for on-line Hg monitoring from process stack emissions in coal burning power plants and cement production facilities provided comparable results with CEMs
- calibration for  $Hg^{tot}$  concentrations by thermal combustion method in solid samples from the coal fired power plant and the cement clinker production were validated and their uncertainties properly assessed
- wet digestion methods were optimised and validated for  $Hg^{tot}$  on sorbent traps using CV ICP-MS
- field testing and validation of new and existing methods for on-line and sorbent-based Hg measurements in the atmosphere
- PAS were compared with conventional methods for time-averaged TGM and demonstrated great potential
- biomonitoring using lichens provided comparable results with both passive and active samplers

## 5 Impact

### *Impact on industrial and other user communities*

By developing optimised and traceable calibration methods for oxidised Hg species, including  $\text{HgCl}_2$ , and a certification protocol for the output from liquid evaporative  $\text{HgCl}_2$  generators, this project has helped to enable the use of liquid evaporative  $\text{HgCl}_2$  generators as reference gas source, particularly relevant for emission monitoring. Those stakeholders that will benefit directly from this (such as Tekran, the US Environmental 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 2<sup>nd</sup> and 3<sup>rd</sup> Conference of Parties of the Minamata Convention (COP2 and COP3, in November 2018 and November 2019 respectively) 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. The measurement of Hg in the atmosphere is recognised as a key indicator for evaluating the effectiveness of the Minamata Convention, a global treaty of the UNEP to protect human health and the environment from the adverse effects of Hg. The UNEP emphasised the significant contributions of EMPIR project MercOx for improving the measurement comparability of Hg on a global scale.

Two workshops for stakeholders were organised to support the acceptance of methods developed within the project; and to ensure that the methods, techniques, and standards developed by the project were widely disseminated. The first workshop was organised held during the first day of the kick-off meeting at JSI, Slovenia (Oct 2017).

The second workshop was on "Comparability of mercury measurements in air" and held in conjunction with the International Conference on Mercury as a Global Pollutant 2019 (ICMGP2019) Krakow, Poland. The ICMGP is the largest global forum for researchers, industry, policy makers, regulatory bodies, representatives of the Minamata Convention and other stakeholders both inside and outside of Europe. At the project's second workshop the latest developments in the area of traceable mercury measurements worldwide were presented by project partners to stakeholders. Over 60 participants attended the workshop.

The project has engaged with industry and other communities through its Stakeholder Committee. The Stakeholder Committee was established at the beginning of the project and was actively involved in project research activities, dissemination, and knowledge transfer. Stakeholder Committee membership include representatives from policy relevant bodies/organisations (UNEP Chemicals and the Secretariat for the implementation of Minamata Convention); International Energy Agency and the Clean Coal Centre that are responsible for the implementation of the UNEP's partnership programme on Hg from Coal; association of Cement Industry in Europe (CEMBUREAU) and local industrial partner; representatives from NIST, USA and from the US EPA who are currently deeply involved in Hg speciation in the gaseous phase; regional and global monitoring programmes: e.g. Group of Earth Observations (GEO) (and the Arctic Monitoring and Assessment Programme (AMAP)), representatives from the research community from the University of Reno, USA and from McGill University, Canada; and representative from Tekran, the instrument producer.

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. The development of ultralight interwoven ultrathin graphitic carbon nitride (g-CN) nanosheets for use as a potential adsorbent in a PAS for binding Hg(II) (Objective 4) also has the potential further IP development.

#### *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 on the project's website [http://www.mercox.si/images/D5-Good\\_practices.pdf](http://www.mercox.si/images/D5-Good_practices.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.



contributions to governmental policy and public outreach.

*Figure 14. MercOx booth at ICMGP2019.*

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, <http://www.era-planet.eu/>) 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 HgCl<sub>2</sub> 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 COP2 and COP3 meetings in 2018 and 2019, respectively.

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