EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

MercOx project and impact

Milena Horvat on behalf of all partners
Jožef Stefan Institute, Slovenia

Stakeholder Webinar

4. March, 2021

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

EMRP/EMPIR Hg related projects

- EMRP ENV02 PartEmission (2010 – 2013)
- EMRP ENV51 MeTra http://projects.lne.eu/metra/ (2013 – 2016)
  - Development of traceable calibration methods for mercury
- EMPIR 16ENV01 MercOx http://www.mercox.si/ (2017 – 2020)
  - Development of traceable calibration methods for oxidised mercury
- EMPIR 19NRM03 SI-Hg http://si-hg.eu/ (2020 – 2023)
  - Metrology for traceable protocols for elemental and oxidised mercury concentrations

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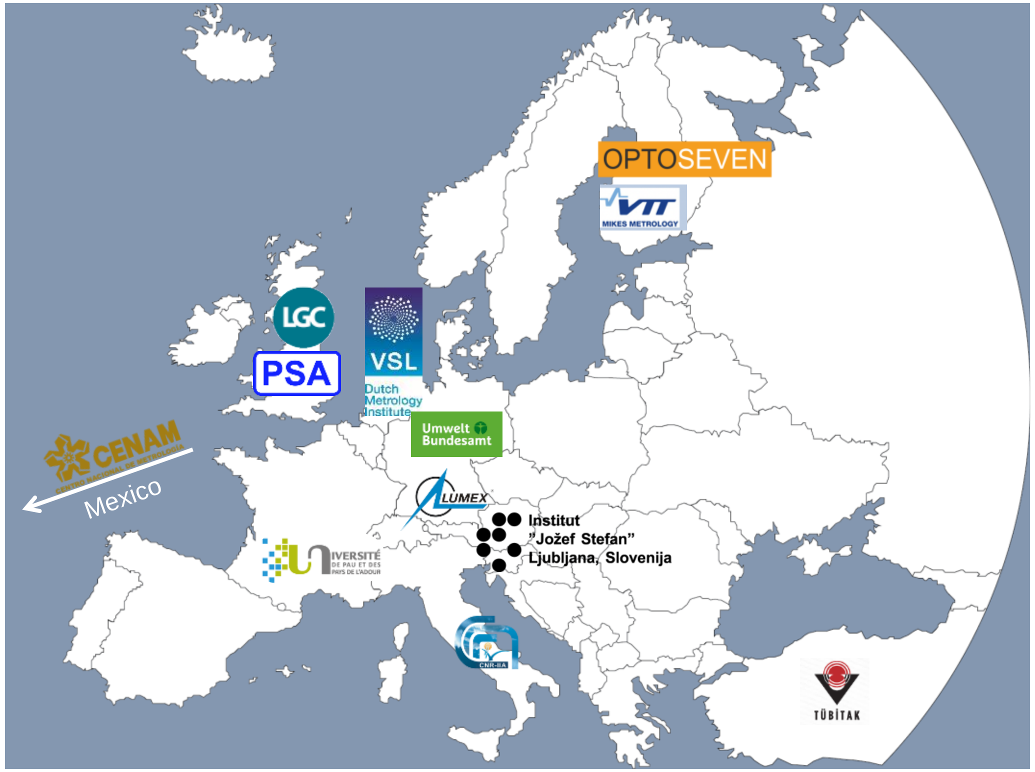
Traceability of oxidised mercury - MercOx project (2017-2020)

Starting date: 1. October, 2017
Total costs: 1,96 Mio EUR, EU: 1,80 Mio EUR



Coordinator: Milena Horvat
Jožef Stefan Institute,
Ljubljana, Slovenia

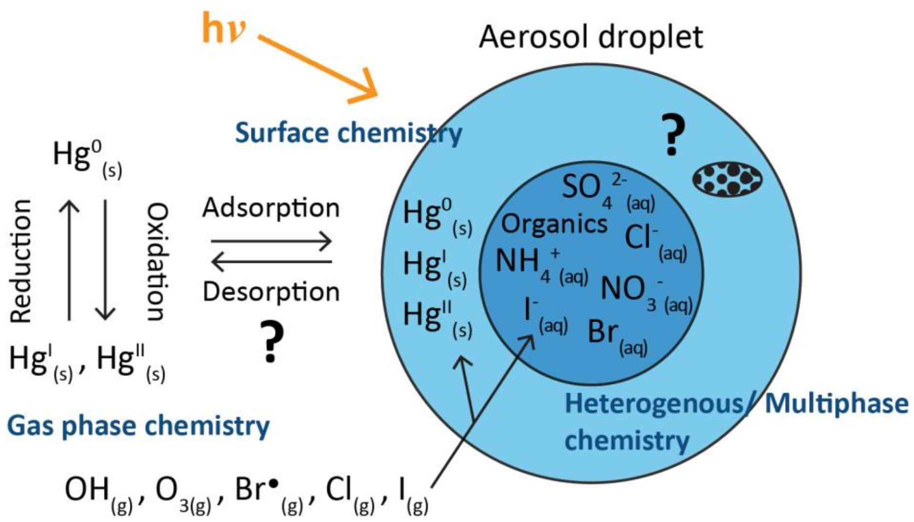
and the MercOx consortium:
Ina Fettig, Timo Rajamäki, Panayot Petrov, Iris deKrom, David Amouraux, Maria del Rocio Arvizu, Jarkko Makkonen, Warren Corns, Ian Hangecock, Reinhold Moeseler, Can Suleyman, Jan Gačnik, Igor Živković, Jože Kotnik, N. Pirrone, F. Sprovieri, A. Naccarato, A. Tassone, R. Chouhan Singh, M. Pavlin, S. Berisha, etc…

Hg-ox

Aims of the MercOx project

- MercOx aims to **validate and develop traceable oxidised Hg standards** and methods for **sampling and analysing oxidised Hg species** in **flue gas** emissions and in **the atmosphere**. This will result in significant improvement in measurement **uncertainty and comparability** of measurement results.
- MercOx will introduce **comparability of measurement** results to enable legislation and support Europe’s international obligations to reduce Hg emissions. Europe and the NMIs involved will be able to take a leading role in the future of metrology for mercury measurements.

Analytical challenges

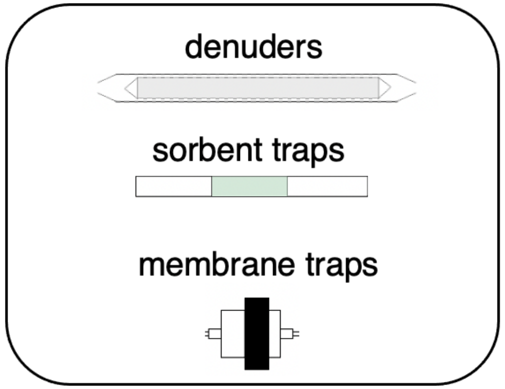


Real-time air monitoring not possible for individual mercury chemical species without preconcentration

Need to collect mercury halides from large volume of air without losing chemical identity (i.e. no reactions allowed!)

Assuring Global Comparability for GOM

Sampling	+	**Processing**	+	**Measurement**	=	**Result**
Representative Appropriate Contamination-free Stability Handling		Selective trapping of GOM		Comparison to SI units or conventional scale		± uncertainty



Selective nanomaterials for GOM

GEM generators:

- Saturated air in a bell-jar
- Hg(0)diffusion
- (Hg(0) permeation
- Liquid standards

GOM generators:

- Permeation tubes
- Diffusion
- Liquid standards
- Cold plasma

MercOx Project structure

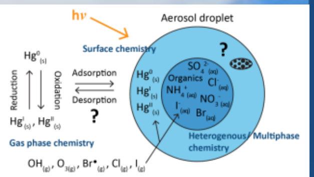
Management and coordination

Traceable calibration

Validated methodology for **calibration** and corresponding **uncertainty** budget for **stack gas** emissions and **atmospheric** Hg measurements

Measurements

Validated measurement techniques for oxidised mercury of both gaseous Hg(II) and Hg(0), as well as Hg(II) on particulates



Sampling, storage and processing

Mercury chemistry in the atmosphere and stack gas emissions

Sampling of Hg(II) and Hg(0) in the atmosphere and stack gas emissions

Accurate bulk and species specific isotope ratio measurements & the origin discrimination/migration, pathways and species interconversion

Field applications: on-line and sorbent based oxidised mercury measurements in stack gas emissions and atmospheric measurements

Creating impact

Procedures & reference methods

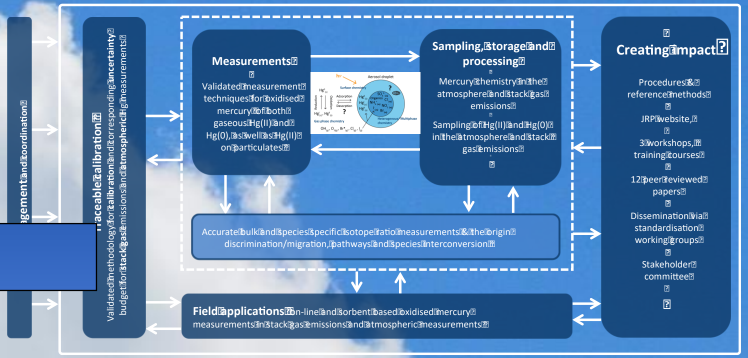
JRP website,

3 workshops, training courses

12 peer reviewed papers

Dissemination via standardisation working groups

Stakeholder committee



VSL Dutch Metrology Institute

WP 1

Traceable calibration

Traceable calibration method for the most important Hg (II) species, including $HgCl_2$, based on a validated method to accurately compare the Hg concentration in generated standard gases for Hg(0) and $HgCl_2$.

Traceable generation of $HgCl_2$ at **µg/m³** levels for **stack gas emission measurements**, including a certification protocol for confirming the output of liquid evaporative $HgCl_2$ generators

Transfer reference gas standards for **atmospheric** (oxidised) Hg measurements for the calibration of liquid evaporative $HgCl_2$ generators at **sub-ng/m³** levels

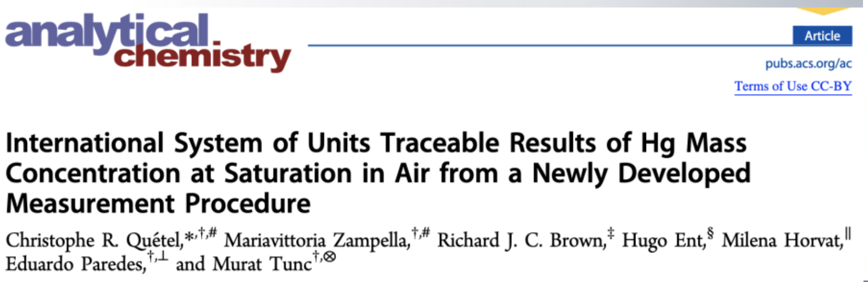
Deliverables:

D1 Optimised and traceable calibration methods for oxidised mercury (Hg) species, including mercury chloride ($HgCl_2$)

D2 Certification protocol for the output of liquid evaporative $HgCl_2$ generators

Primary Mercury Gas Standards

- Traceable to SI-units
- Uncertainty


Article
pubs.acs.org/ac
Terms of Use CC-BY

International System of Units Traceable Results of Hg Mass Concentration at Saturation in Air from a Newly Developed Measurement Procedure

Christophe R. Quétel,*,†,# Mariavittoria Zampella,†,# Richard J. C. Brown,‡ Hugo Ent,§ Milena Horvat,∥ Eduardo Paredes,†,⊥ and Murat Tunc†,⊗


IOP Publishing — Measurement Science and Technology
Meas. Sci. Technol. 25 (2014) 115801 (11pp) — doi:10.1088/0957-0233/25/11/115801

A gravimetric approach to providing SI traceability for concentration measurement results of mercury vapor at ambient air levels

Hugo Ent[1], Inge van Andel[1], Maurice Heemskerk[1], Peter van Otterloo[1], Wijnand Bavius[1], Annarita Baldan[1], Milena Horvat[2], Richard J C Brown[3] and Christophe R Quétel[4]

[1] VSL, Thijsseweg 11, 2629JA Delft, The Netherlands
[2] Jožef Stefan Institute, Jamova 39, Ljubljana, Slovenia
[3] Analytical Science Division, National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK
[4] European Commission—Joint Research Centre—Institute for Reference Materials and Measurements, Retieseweg 111-2440 Geel, Belgium

- VSL – diffusion method

de Krom et al. Measurement 169 (**2021**) 108351

doi: https://doi.org/10.1016/j.measurement.2020.108351

de Krom et al. Atmos. Meas. Tech., 14 (**2021**) 2317

doi: https://doi.org/10.5194/amt-14-2317-2021




- NIST – HR LA spectroscopy

Srivastava et al. Anal. Chem. 90 (2018) 6781

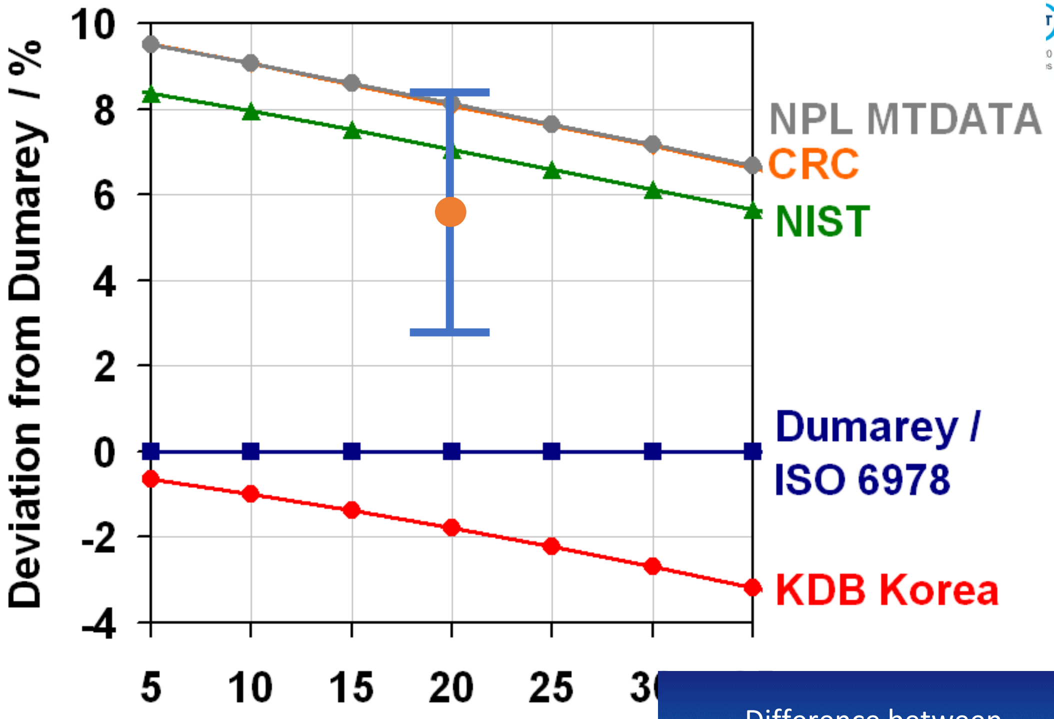
Doi: https://doi.org/10.1021/acs.analchem.8b00757

Srivastava et al. Anal. Chem. 93 (2020) 1050

Doi: https://doi.org/10.1021/acs.analchem.0c04002

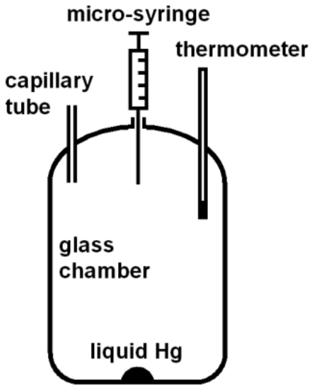
Calibration of GEM

- **CRMs- calibration solutions**
  - SRM 3133 - Mercury (Hg) Standard Solution
  - SRM 3177 - Mercuric Chloride Standard Solution
    - Reduction to Hg(0) by $SnCl_2$ or $NaBH_4$ and preconcentration on Au gold

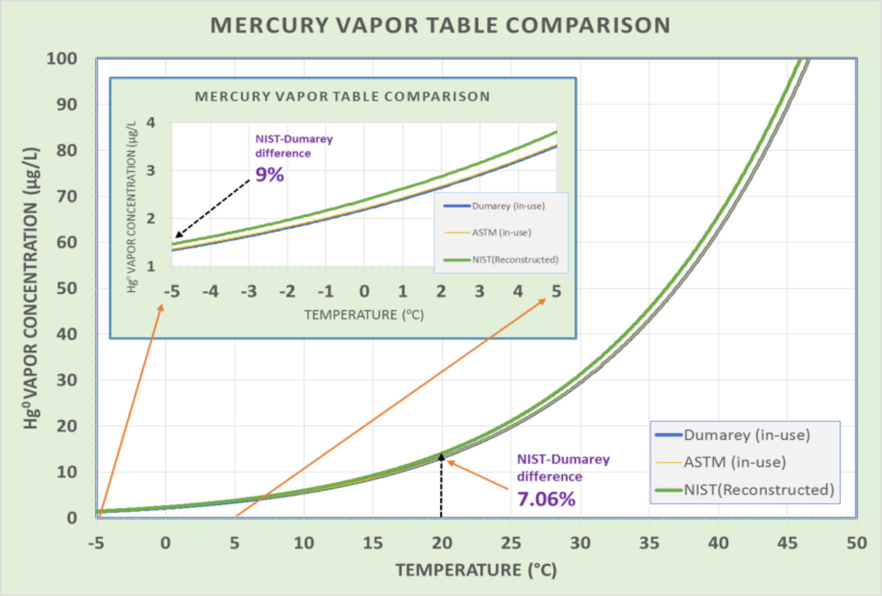


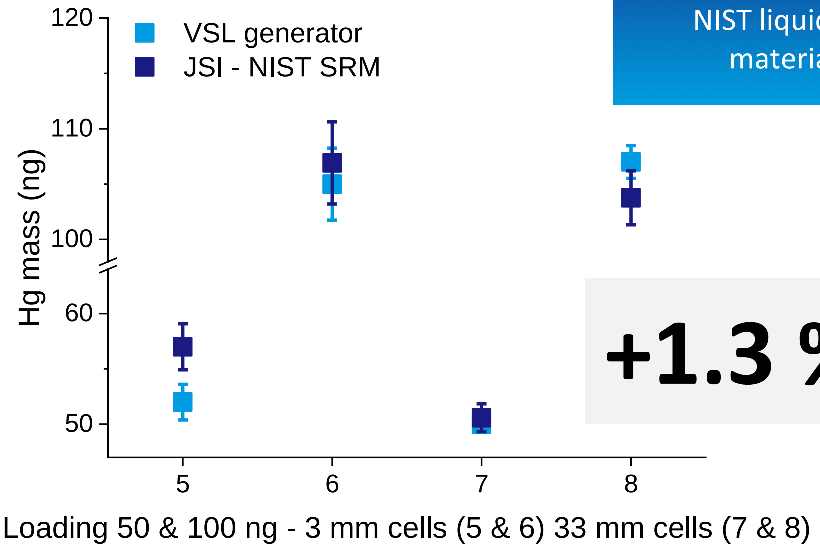
Difference between VSL generator and NIST liquid reference material (3133)

- **Hg gas standards:**



Current situation
- Bell-jar
- Permeation device
- Gas mixtures
- IDMS

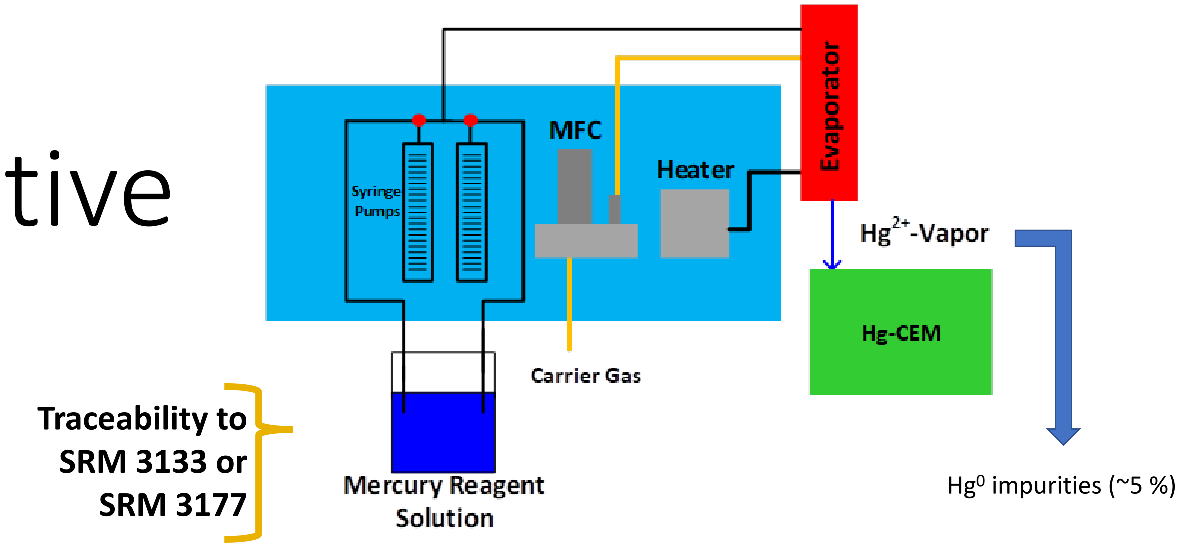


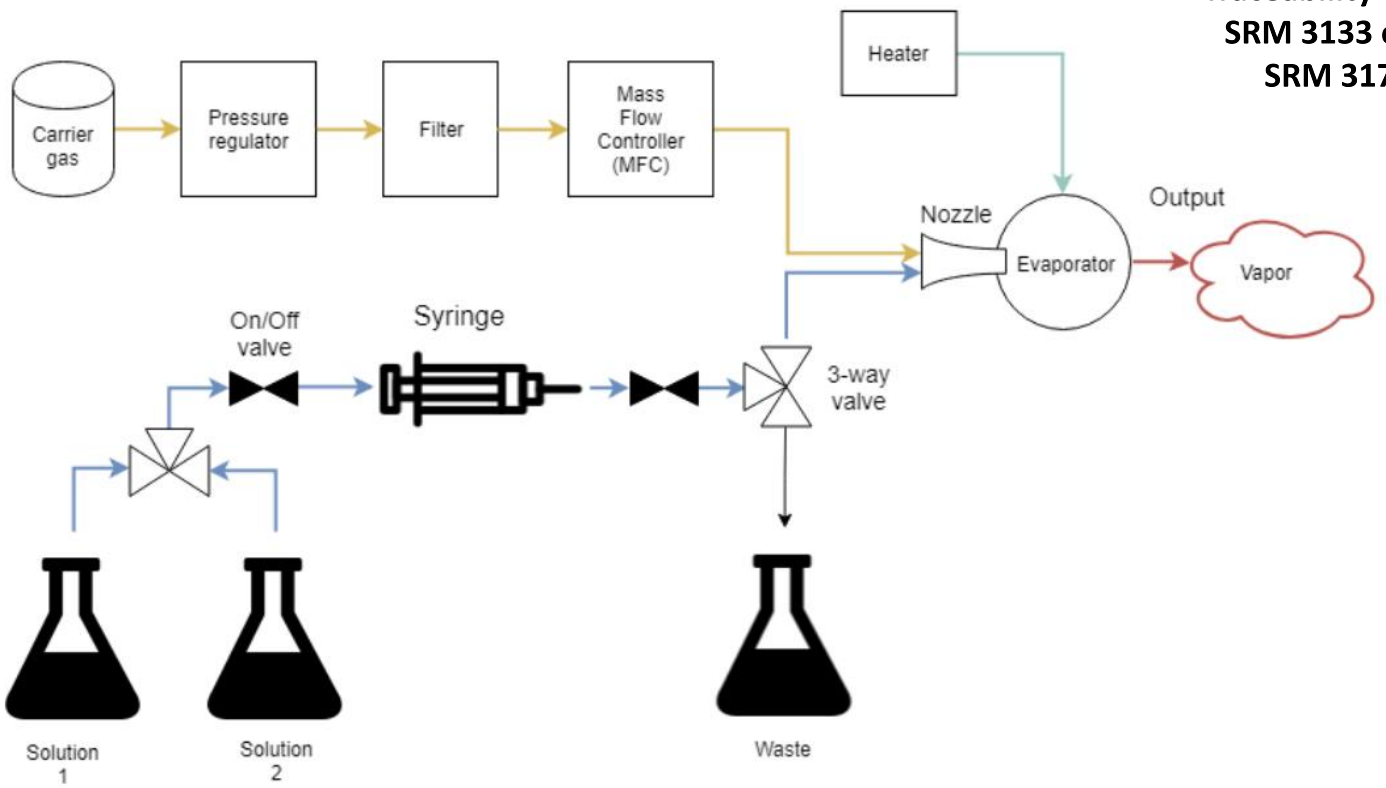


+1.3 %

Mercury vapour concentration *dependent* upon equation use

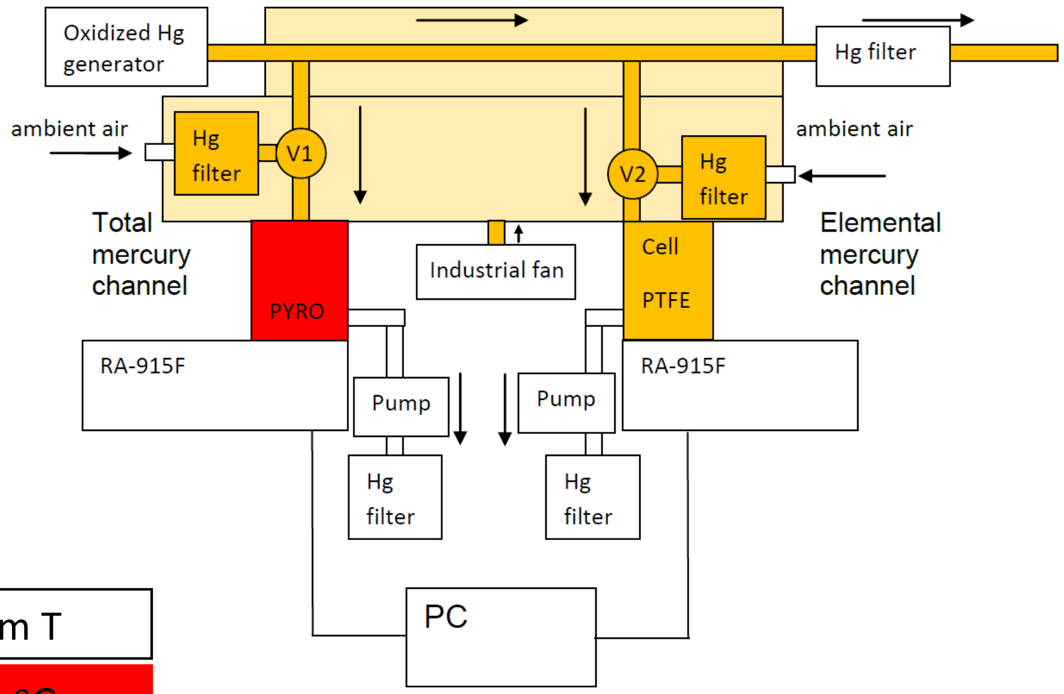
Optoseven Liquid Evaporative GOM Calibrator

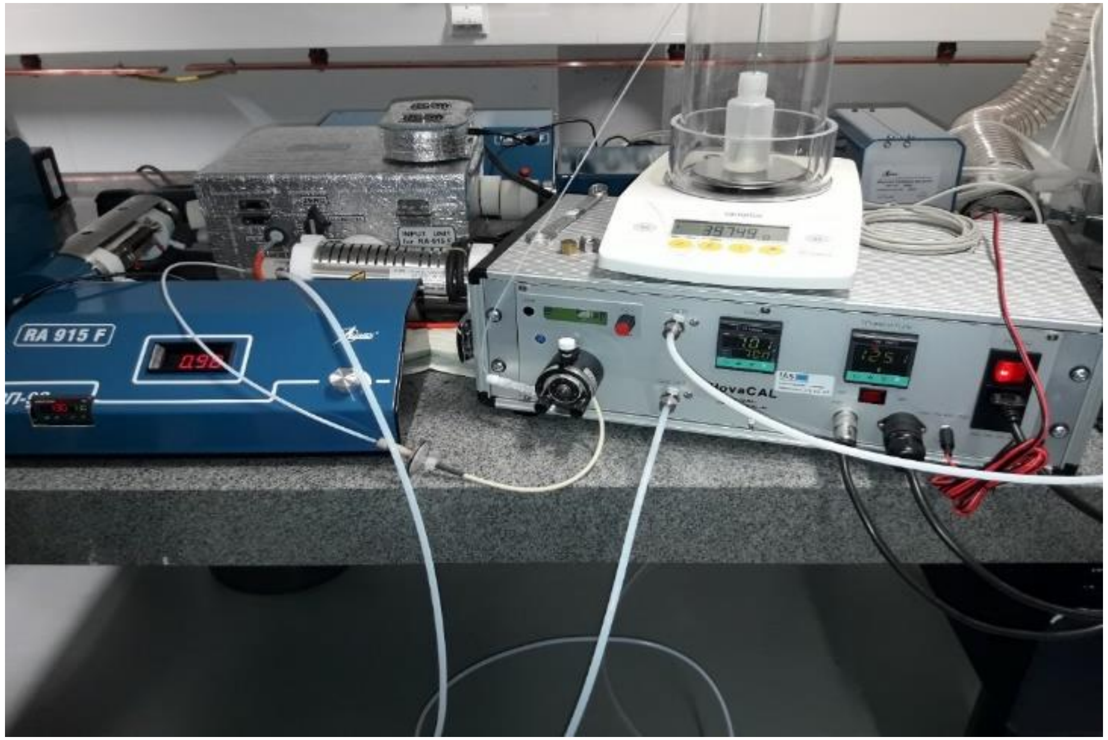




Saxholm Sari , Rajamäki Timo, Hämäläinen Jussi and Hildén Panu, Dynamic calibration method for reactive gases, ***Measurements Science ad Technology,*** *2020, 31, 034001, https://dx.doi.org/10.1088/1361-6501/ab4d68*

Lumex MercOx two-channel analytical set-up



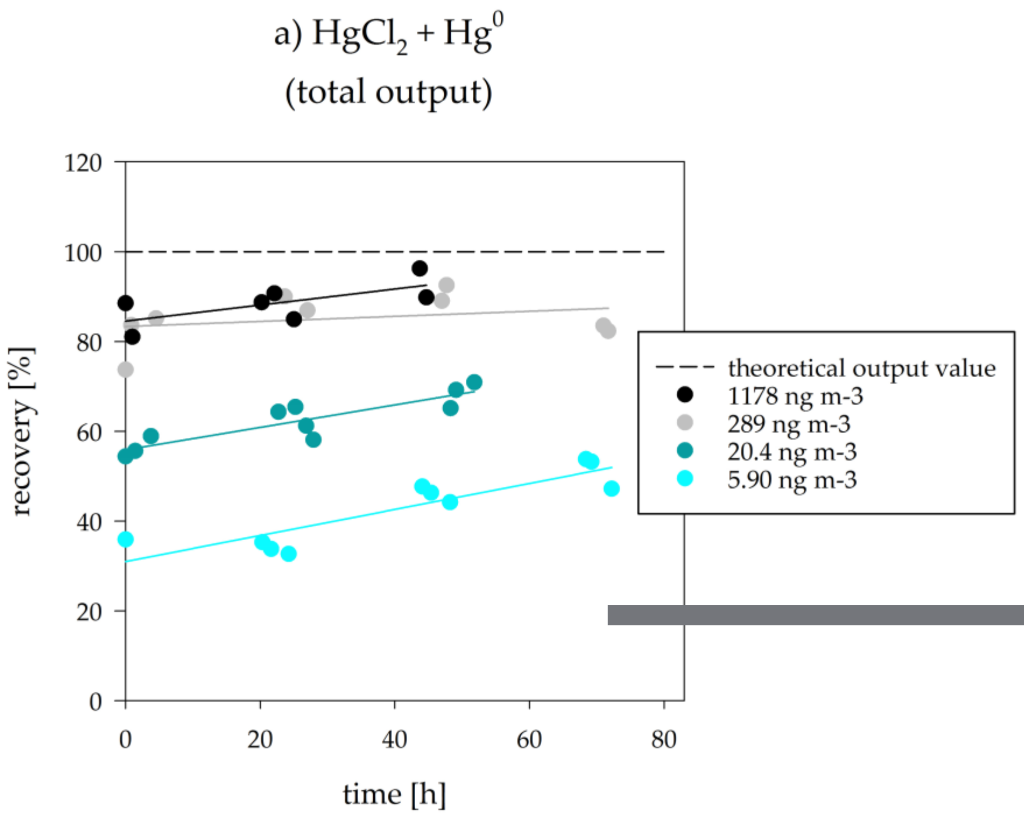


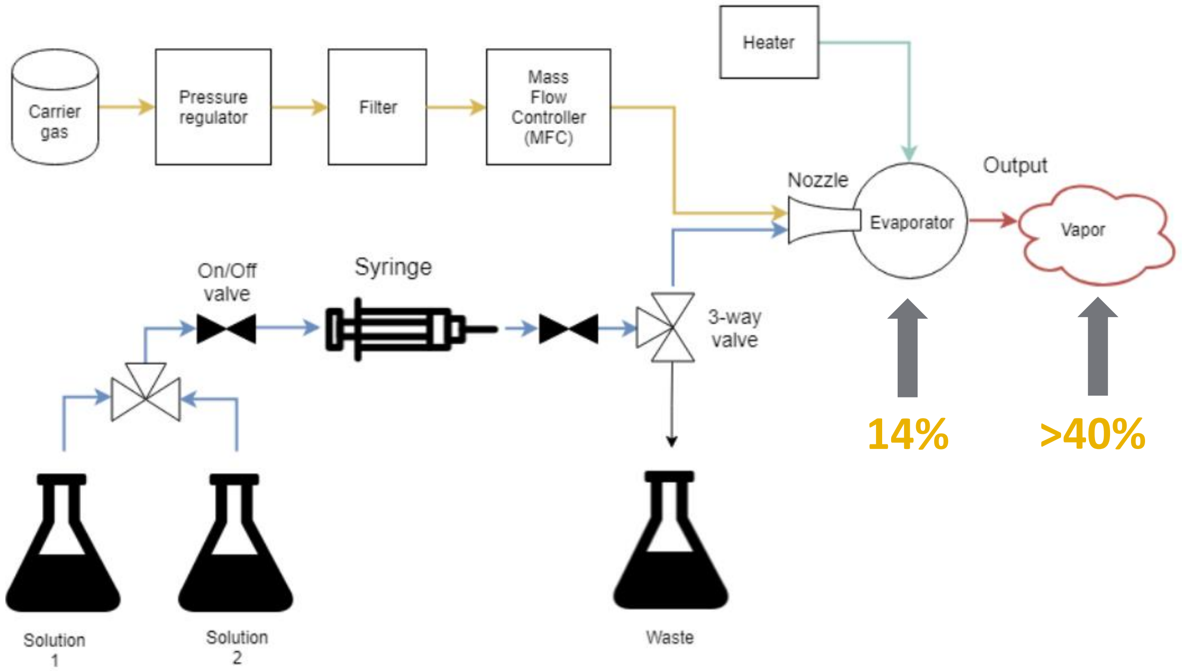
Room T
750 °C
150-180 °C

Total Hg – Hg^0 = GOM

Hg-ox/Optoseven calibrator output time-trends over different concentrations ranges

A challenge for low concentrations!



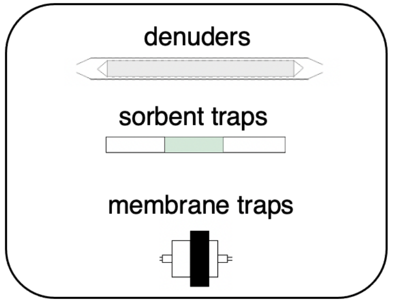


Gačnik, J. Sensors **2021**,

Cold Plasma GOM Calibration

Non-thermal or cold plasma

Atmospheric pressure and ambient T



Traceability to
NIST 3133 and 3177

Traceable quantity of
Hg(0) in He gas

+air, Cl_2, Br_2

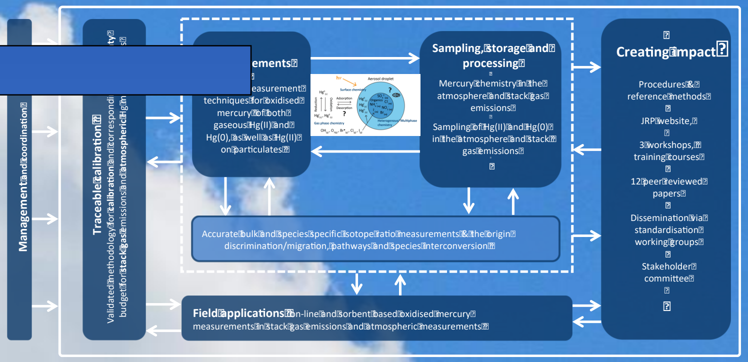
Quantitative conversion

Hg(0) → Hg(II) (HgCl, HgBr, HgO)
and 100% trapping efficiency

No detectable
breakthrough of any
Hg species

Gačnik et al., Anal Chem. 2022, under review

Jožef Stefan Institute, Ljubljana, Slovenia



WP 2
Measurement of Hg(II)

Measurement of gaseous Hg (II)
selectively trapped gaseous Hg (II) at environmentally relevant concentrations

Measurement of Hg (II) on particulate matter (PM)

Deliverables:

D3 Report on the comparison of different methods for measuring oxidised Hg (Hg(II))

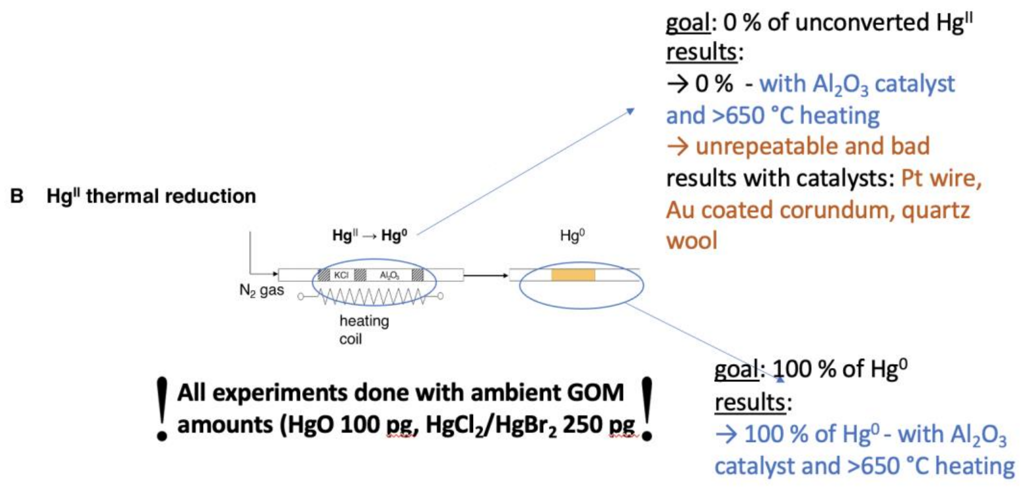
D4 Report on bulk and species specific **isotope ratio measurements** to determine Hg migration pathways, its origin and species interconversion including the use of **biomonitors** as passive monitors for Hg speciation and isotopic signatures representing the origin and fate of atmospheric Hg

Hg-ox

Achievements

WP 2 Measurement of Hg(II)

- **Isotopic composition in gas phase** by pre-concentration techniques coupled to (MC) ICPMS performed
- Testing method for **measuring Hg(II) and Hg0** by GC-ICP-MS/MS using a reference aqueous solution and $HgCl_2$
- **Traceable measurements** performed on Au and AC traps at VSL SI traceable Hg(0) source
- **Comparison of methods :** ASTM D6784-02 (Ontario Hydro) method with commercially available speciation sorbent traps, using elemental and oxidized Hg generators
- Interlaboratory comparisons implemented for the determination of **Hg trapped on activated carbon and PM**
- **Temperature fractionation methodology** was tested for speciation of Hg forms on adsorbent traps.



Gačnik et al., Anal. Chem. 2022, under review

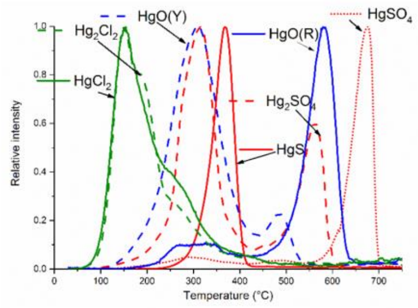


Figure 5: TPD spectra of mercury compounds prepared by dry mixing various Hg-species with pure $CaSO_4 \cdot 2H_2O$.

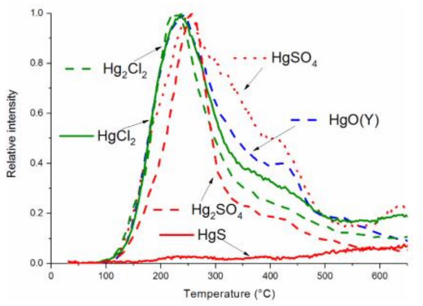
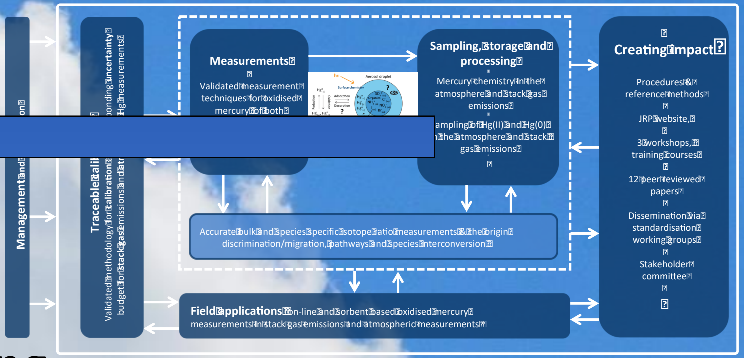


Figure 6: TPD spectra of mercury compounds in precipitates prepared by wet mixing various Hg-compounds in a saturated solution of $CaSO_4 \cdot 2H_2O$. *Note:* The absence of HgS peak is due to its low solubility.

Pavlin et al., Open Chemistry, 2018



Institut "Jožef Stefan" Ljubljana, Slovenia

WP 3

Traceable sampling methods

To investigate how atmospheric and stack gas emissions chemistry influences Hg sampling and measurement

Identify the critical components and parameters, that can alter Hg speciation during sampling and to study these processes using tracer experiments.

Deliverables:

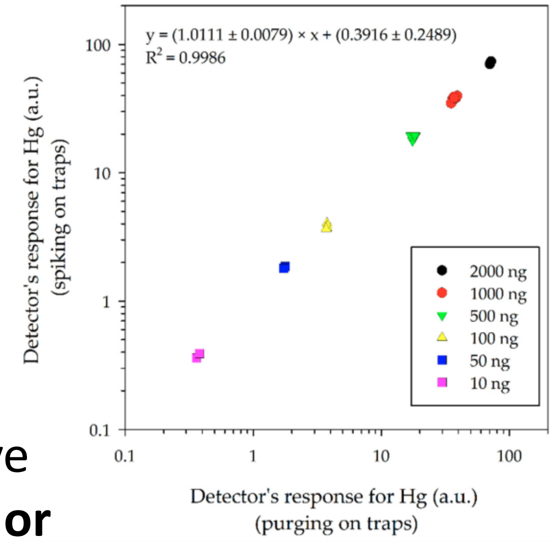
D5 Best practice guide for Hg sample preparation and interspecies conversion correction

D6 Optimised and validated sampling methods for gaseous Hg species using traceable reference standards for Hg(0) and Hg(II))

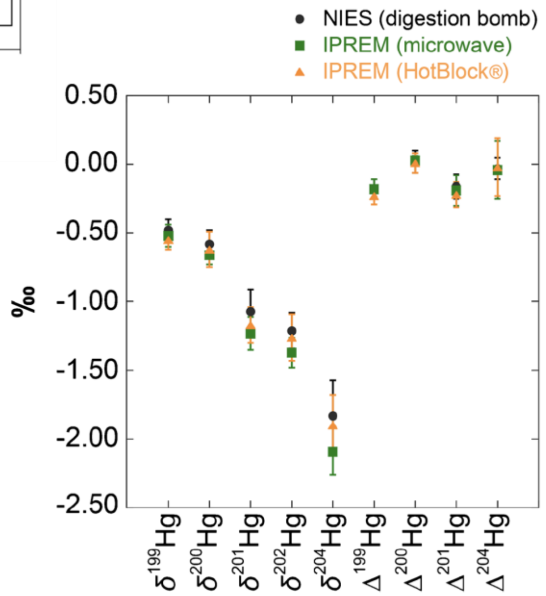
Achievements

WP 3 Traceable sampling methods

- Selective Hg(II) extraction/extraction and complexation have been performed using **CRMs and $HgCl_2$ spiked brominated or iodated carbon materials.**
- Method development for **Hg(II) and Hg(0) interconversion and stability testing using** 197-Hg radiotracer
- An efficient nanomaterials with 2D structure, low cost and metal-free was prepared (g-C3N4) and graphene oxide (GO) **for selective trapping of Hg(II)**
- Samples collected from the German environmental specimen bank for **Hg isotope measurements** in biomonitors –trends analysis
- Specific isotope ratio measurements and use of biomonitors for Hg isotope and atmospheric Hg migration pathways was summarized and published

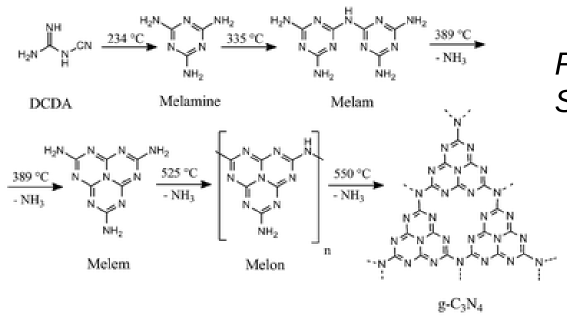


Živković et al., Atmosphere, 2020

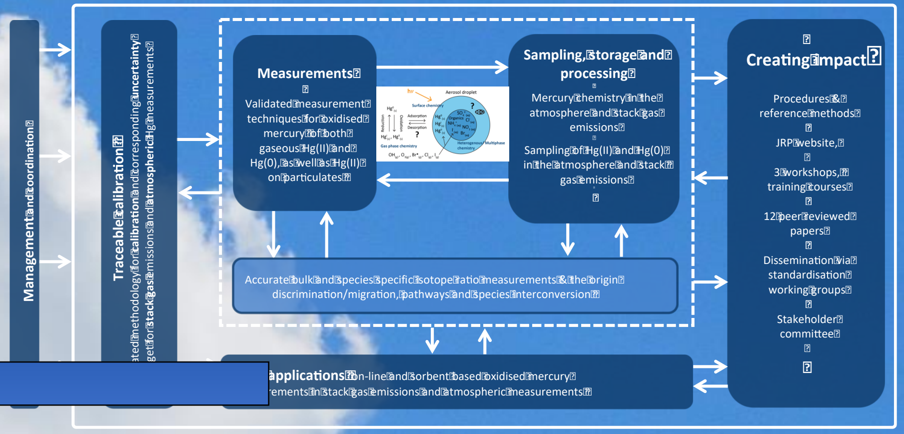


Yamakawa et al. ABC, 2020

Graphitic Carbon Nitride g-C_3N_4



Raghu et al., Sensors, 2019



MIKES METROLOGY

WP 4

Field applications

Test and validate existing methods for on-line Hg monitoring from process stack emissions (coal TPP, cement production)

Test and validate existing methods for on-line Hg monitoring in the atmosphere (GMOS sites)

Deliverables:

D7 Validation report on the field testing of new and existing methods for on-line and sorbent based Hg measurements in stack emissions

D8 Validation report on the field testing of new and existing methods for on-line and sorbent based Hg measurements in the atmosphere

WP4: Field testing

Atmospheric measurements

- *PAS (AC, Au,..)*
- *Automated (selective traps)*
- *Active (Lumex)*
- *Biomonitoring, lichens*

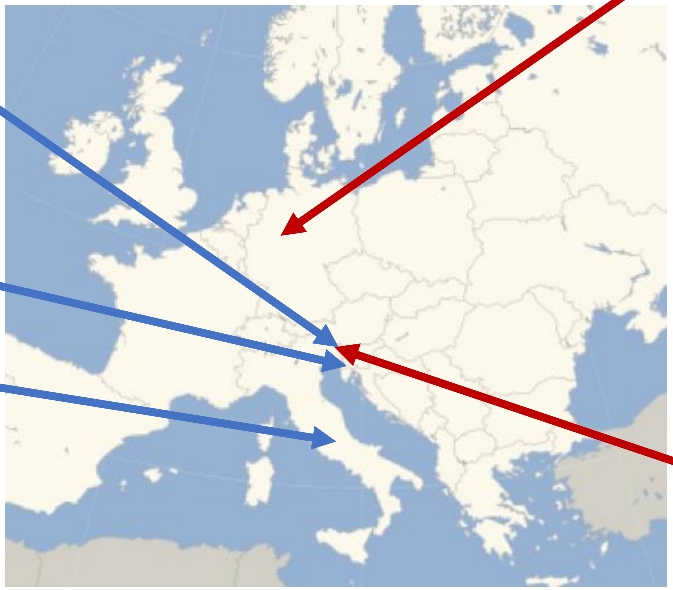
Emission measurements

- *CEM*
- *Sorbent traps*

Down-wind Salonit and Idrija

GMOS-Train, Iskrba, Slovenia

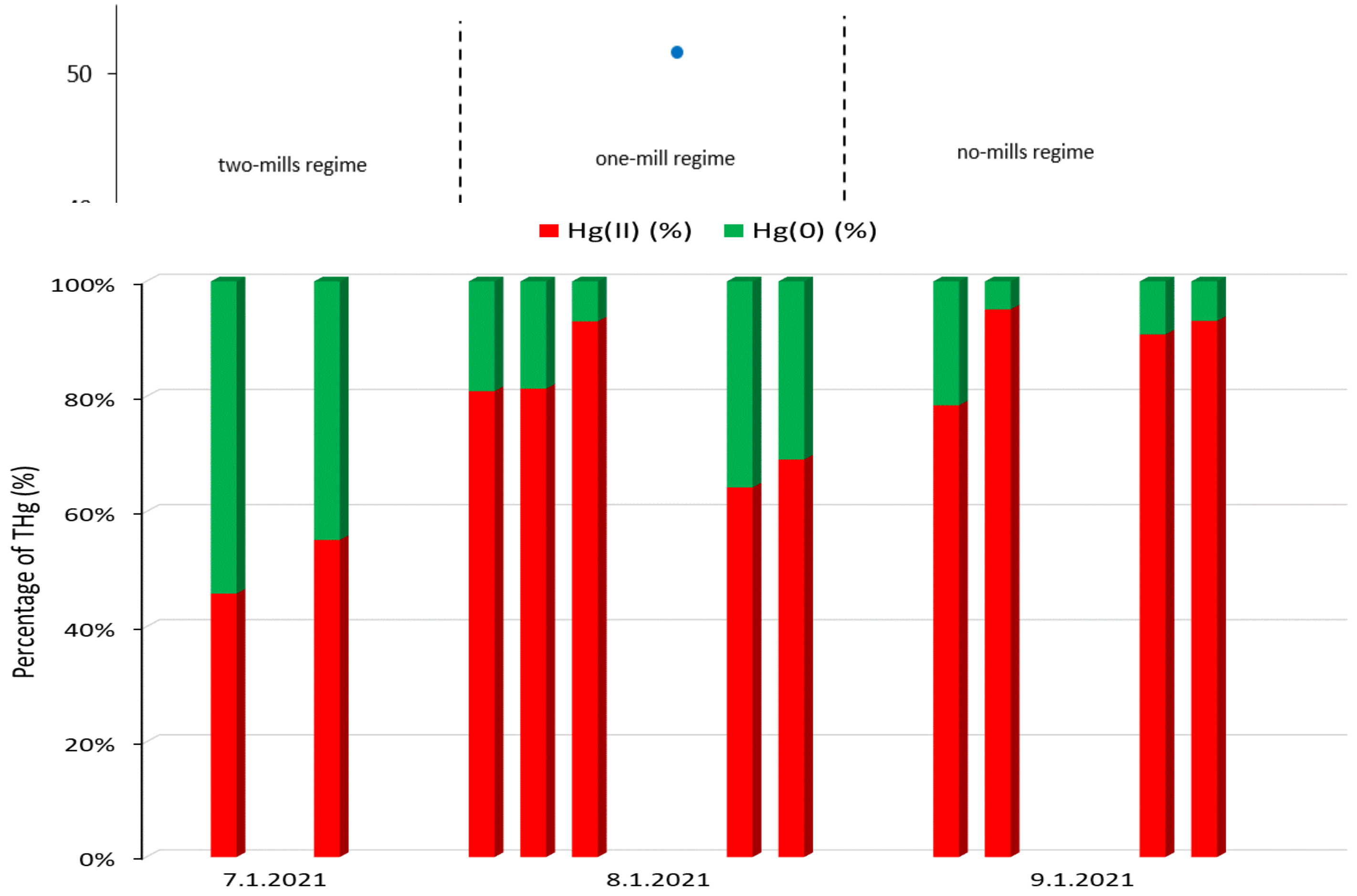
GMOS-site, Mt. Curcio, Italy



Power station, Marl

Cement kiln, Salonit Anhovo

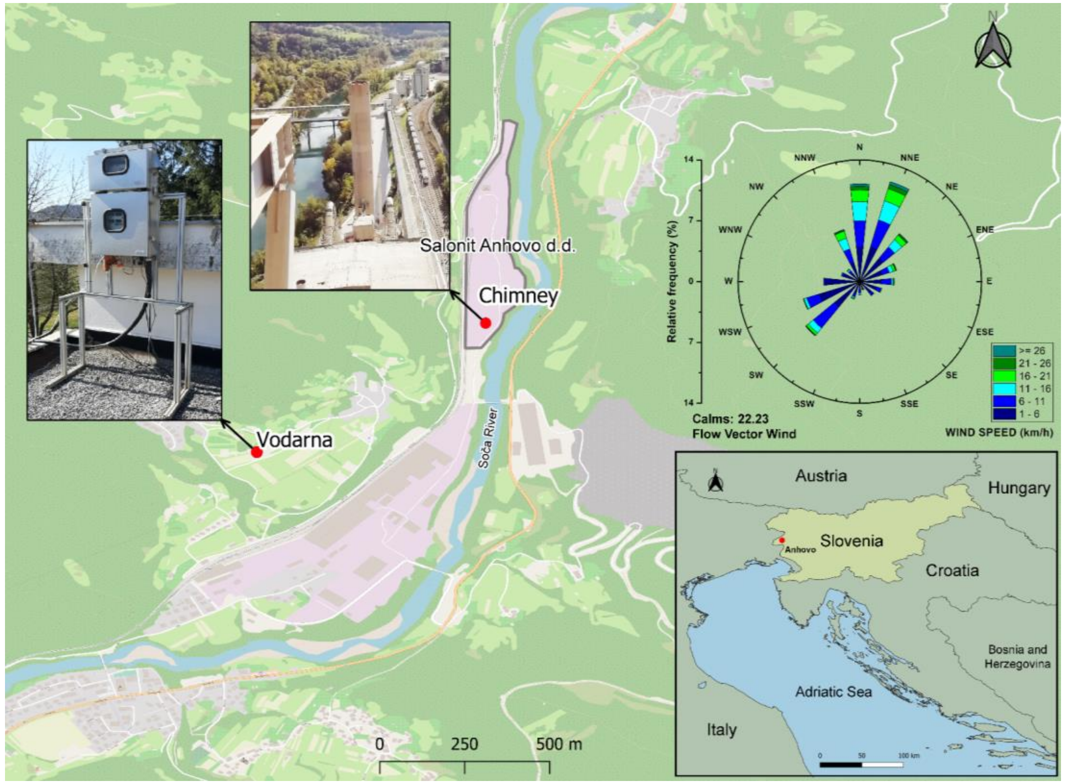
Oxidized, elemental, and total Hg on sorbent traps - Salonit cement plant

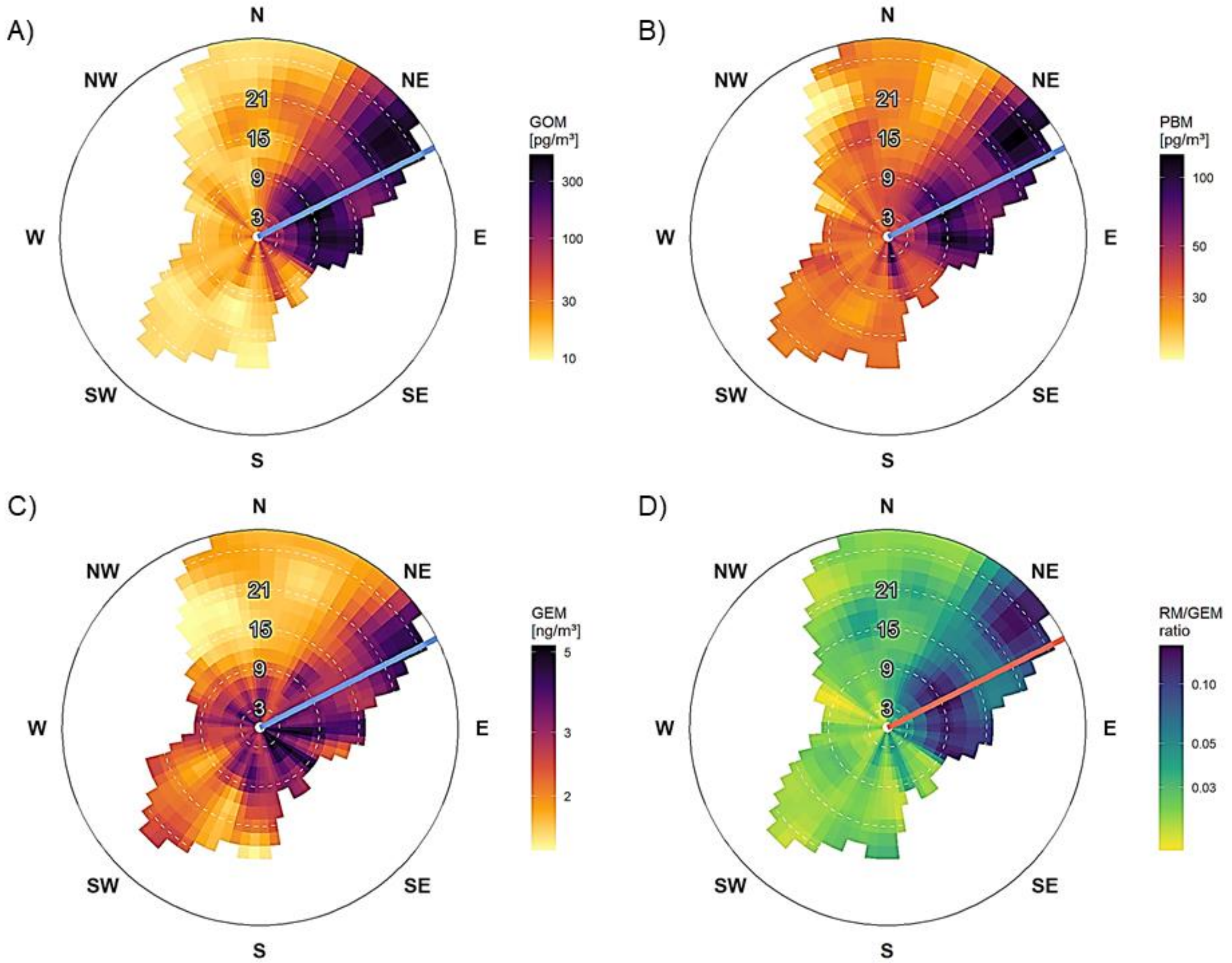


The average concentration in stack gas is calculated as the average of Hg concentrations obtained by two parallel traps in the Ohio Lumex sampler probe. Dotted lines indicate corresponding trendlines

Kotnik et al., JHM, 2022, in preparation

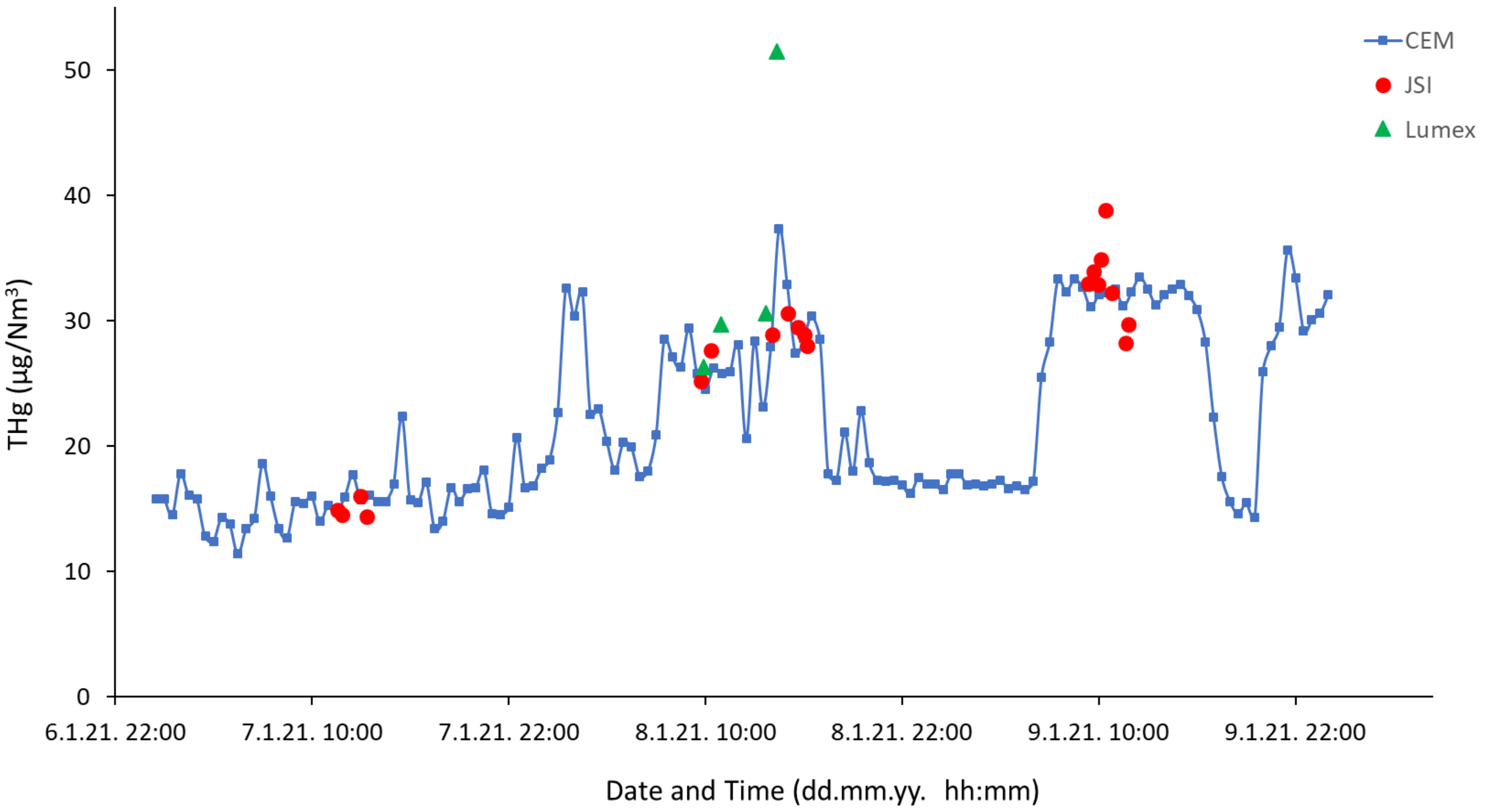
Mercury emissions and speciation from the cement plant Anhovo





Sreekanth et all, 2022, Mercury Emission and Speciation in the Vicinity of Salonit Anhovo Cement Plant in Western Slovenia, *to be submitted*

Comparison between CEM and sorbent trap method



Kotnik et al., JHM, 2022, in preparation

Outputs of the MercOx projects

- **Stakeholder Committee** established, 28 members, two workshops organized
- Project ***web site, flyers, exhibition, professional press release,*** and *presentations at general public and professional events*
- Minamata Conference of the Parties, at ***COP2*** and ***COP3***, in November 2018 and November 2019
- 30 presentations at 18 ***scientific workshops/conferences***; 13 oral and 17 posters. (7 invited)
- ***ICMGP*** *September 2019; Krakow; Special session, preconference workshop*
- *22 peer reviewed* ***journal articles*** *(36 citations, over 12000 views)*

Impact of the MercOx projects

- **Standardisation:** CEN/TC264/WG8/WG9/WG10; CEN/TC146/WG32
- A ***good practice guide*** on Hg sample preparation and interspecies conversion
- ***Certification protocol*** *for confirming the output of liquid evaporative* $HgCl_2$ *generators*
- 8 staff exchange and training; *5 PhD and 1 master degree students*
- *Contribution to:*
  - ***GEO-*** *Global Earth Observation platform,* ***GOS4M*** *– Global Observation System for Mercury*
  - *UNEP's* ***Guidelines for monitoring for effectiveness evaluation***
- ***Metrological uptake*** *in new projects:*
  - *Horizon2020 EU funded MSCA ITN GMOS-Train: "Global Mercury Observation and Training network in support to the Minamata Convention"*
  - *EMPIR project 19NRM03 SI-Hg "Metrology for traceable protocols for elemental and oxidised mercury concentrations"*

Creating impact in SI-Hg project (WP4)

- Web page http://si-hg.eu/
- Special sessions at the ICMGP 2022: dead line for abstracts 15. March 2022

www.ilmexhibitions.com/mercury2022/

Special Sessions

- Artisanal and Small- Scale Gold Mining – challenges and solutions
- Assessing the effectiveness of the Minamata Convention on Mercury under climate uncertainties
- Climate-Driven Perturbations of Arctic Mercury Cycling – a Special Session Coupled to the 2021 AMAP Mercury Assessment
- Global mercury concentrations in biota: their use as a basis for a global monitoring framework
- Impacts of Climate Change on Global Mercury Cycling
- Mercury in the Southern Hemisphere
- Meta-omic and geochemical approaches to linking microbial activity to biogeochemical mercury cycling
- Metrological Traceability for mercury analysis and speciation
- National Action Plans to reduce mercury use in artisanal and small-scale gold mining: translating data into policy responses
- New developments in understanding reactive mercury concentrations and chemistry
- planetGOLD: A Pathway to Reducing Global Mercury Pollution from Artisanal and Small- Scale Gold Mining
- Selenium-mercury interactions in aquatic food webs: The state of the science and future research directions

Week of 18 – 22 July
Pre conference workshops
Reactive Mercury Measurement
Organized by Mae Gustin & Team, SI-HG invited

Minamata on-line series

https://www.mercuryconvention.org/en/events/reactive-mercury-air

Speakers:

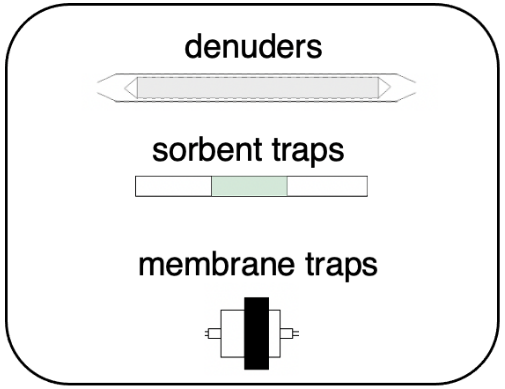
- **Mae Sexauer Gustin**, University of Nevada, Reno
- **Milena Horvat**, Jožef Stefan Institute, Slovenia
- **Seth Lyman**, Utah State University
- **Sarrah Dunham-Cheatham**, University of Nevada, Reno
- **Lynwill Martin**, International Conference on Mercury as a Global Pollutant
- **Iris de Krom**, National Metrology Institute, the Netherlands
- **Eisaku Toda**, Minamata Convention on Mercury

Conclusions from the joint Minamata on-line

- Research teams are making progress toward development of oxidized Hg measurement and calibration methods
- New measurement methods are demonstrating comparability
- New calibrator method is demonstrating accurate measurements by the RMAS and dual channel systems *(Lyman et al. 2020; Dunham-Cheatham et al., in prep)*
- Next Steps
  - Continued development and testing of accuracy, precision, robustness, and comparability of newly developed measurement and traceable calibration methods
  - Metrological traceability is a key to comparability! Comparing different calibration systems
  - Harmonization of new methods and demonstration of comparability is urgently needed by global community (e.g., field inter-laboratory comparisons)

Assuring Global Comparability for GOM

Sampling	+	Processing	+	Measurement	=	Result
Representative Appropriate Contamination-free Stability Handling		Selective trapping of GOM		Comparison to SI units or conventional scale		± uncertainty



Selective nanomaterials for GOM

GEM generators:

- Saturated air in a bell-jar
- Hg(0)diffusion
- (Hg(0) permeation
- Liquid standards

GOM generators:

- Permeation tubes
- Diffusion
- Liquid standards
- Cold plasma

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