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Workshop Results
Measurement of Atmospheric Mercury: Assessment of new measurement and calibration methods and development of a path forward

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Workshop Participants

Top Row: Jonas Sommar, Geyan Kempkes, Igor Živković, Milena Horvat, Sophie Page, Mae Gustin, Rob Mason, David Gay, Lynwill Martin, Jason Gray, Seth Lyman, Jan Gačnik, Sreekanth Vijayakumaran Nair, Peter Weiss-Penzias, Ly Sy Phu Nguyen

Bottom Row: Lei Zhang, Trevor O'Neil, Sarrah Dunham-Cheatham, Che-Jen Lin, Lynne Gratz, Livia Lown, Alexei Khalizov

Not pictured: Steven Lindberg, Katrina MacSween

Logistics

- Funded by U.S. National Science Foundation
- Webpage developed and participants invited
- Participants provided talk topics
- Participants convened on October 11-13, 2023 at the University of Nevada, Reno campus
- A perspective article summarizing the workshop discussions has been published in *Environmental Science & Technology* (doi: 10.1021/acs.est.4c06011)

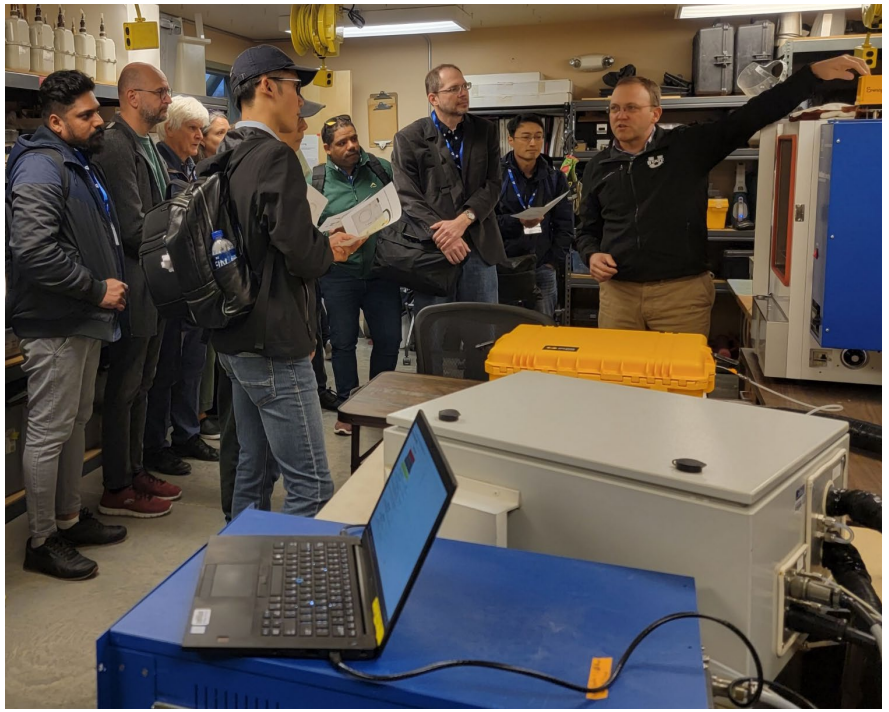
Funding Agency

Workshop Website

Workshop Logo

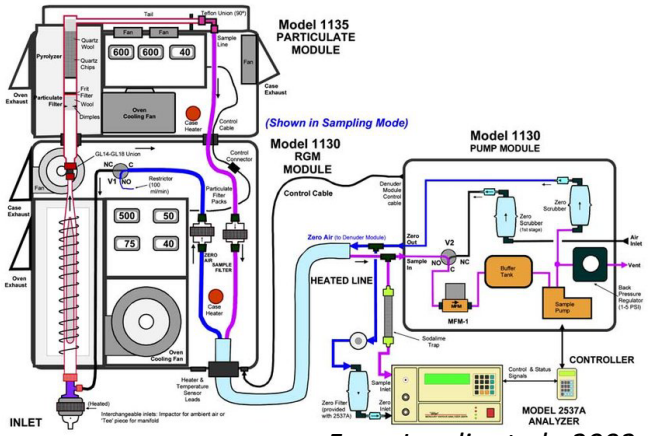
Format

- 26 oral presentations on new and evolving measurement methods and monitoring network needs
- Introduced to methods in 2 laboratories, including:
  - The Reactive Mercury Active System (RMAS)
  - 2 Dual-Channel Systems (DCS)
  - 2 Hg calibrators
  - A gas chromatography mass spectrometer being developed for measurement of Hg^{II} compounds
  - Analytical methods (thermal desorption, 2600, 2700, 2 DMAs)
- Discussion groups tasked with:
  - Summarizing benefits and limitations of current measurements
  - Brainstorming how to improve measurements



GEM & TGM Measurement

- Two **active systems** are primarily used: Tekran 2537 (preconcentration) and Lumex (no preconcentration)
  - Preconcentration typically collects Hg with gold-coated quartz traps
    - TGM: a thermolyzer is needed upstream of the gold trap
    - GEM: a cation exchange membrane should be used upstream of the gold trap *(Gačnik et al., 2024)*



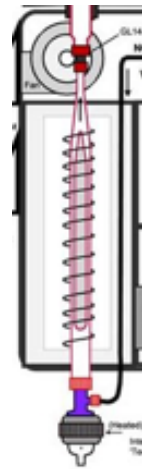
From Landis et al., 2002

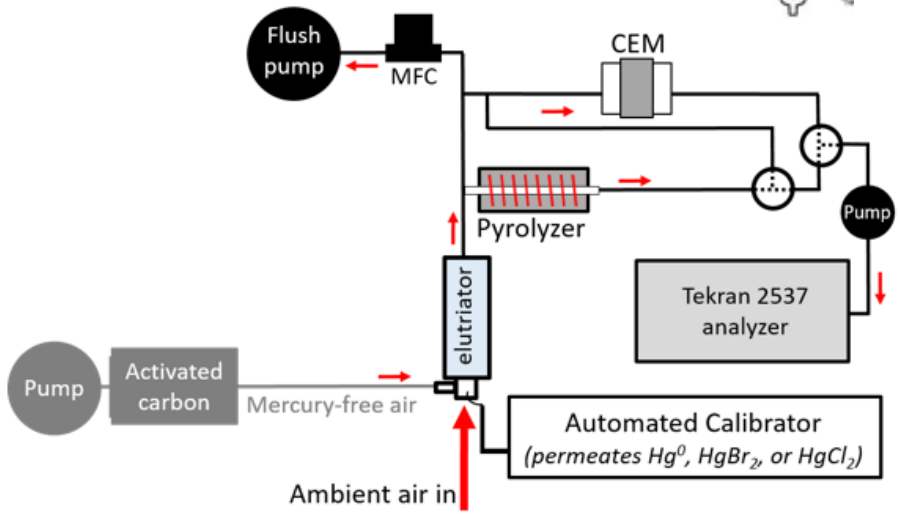
- Variety of **passive materials** have been used
  - Current favorite is the MerPAS® *(McLagan et al., 2016)*
    - Sulfur-impregnated activated carbon in a radiello sampler
    - Long sampling time resolution (1+ month)
    - Sampling rate affected by T, wind speed, and sampler geometry

Oxidized Hg^{II}: Gaseous or Particulate-Bound

Current methods to measure **Gaseous Oxidized Hg (GOM)**

- KCl-coated denuders
  - General consensus: use of this surface should be phased out due to low bias and interferences resulting from humidity, O_3, etc.
  - Continued use may be useful for trends analyses
- Dual-Channel Systems
  - No preconcentration
  - Need a highly precise analyzer
  - Needs regular maintenance
  - Can get negative values when air concentrations are changing rapidly *(Dunham-Cheatham et al., 2023; Elgiar et al., 2024)*





Oxidized Hg^{II}: Gaseous or Particulate-Bound

Current methods to measure **Particulate-Bound Hg (PBM)**

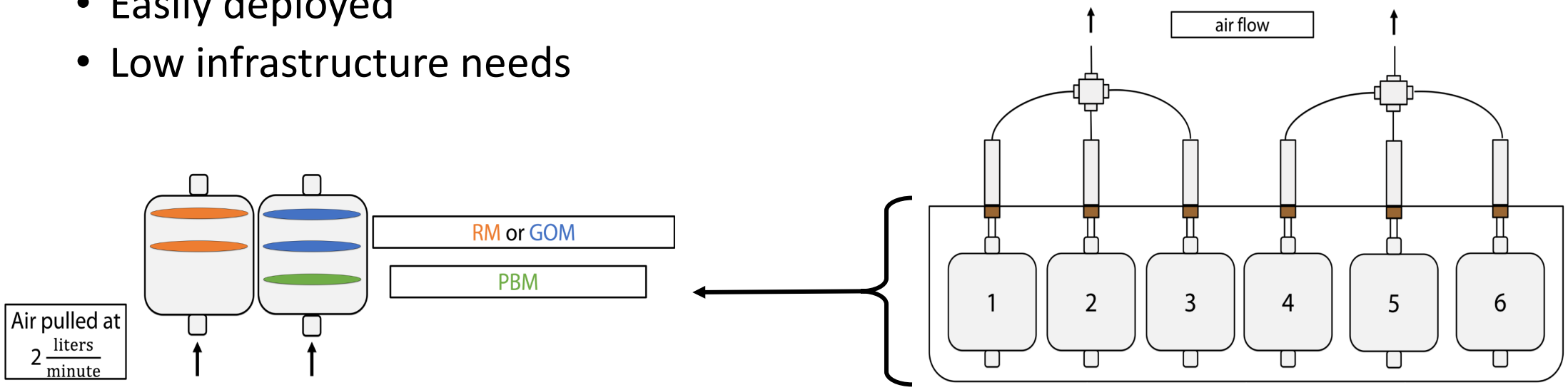
- Permeated $HgBr_2$ is collected on particles collected using PTFE membranes *(Allen et al., 2023)*
  - This puts into question any method that collects PBM on surfaces, because the particles will capture GOM
  - GOM may also be lost from the particles as Hg^0 due to reduction reactions
- <u>General consensus:</u> new methods need to be developed to differentiate between PBM and GOM

Haze covers northern India; NOAA

Oxidized Hg^{II}: Gaseous or Particulate-Bound

Current methods to measure **Reactive Hg (RM)** (= GOM + PBM)

- Cation exchange membranes (Reactive Mercury Active System, RMAS)
  - Preconcentration and digestion
  - Some loss occurs from these membranes in the field
  - Easily deployed
  - Low infrastructure needs



Oxidized Hg^{II}: Calibration Methods

- Currently, no commercially available ambient-level calibrator
- Temperature-controlled calibrated Hg permeation tubes
  - Currently being used in both laboratory and field settings *(Lyman et al., 2020; Dunham-Cheatham et al., 2022)*
  - Both Hg^0 and Hg^{II} can be calibrated
  - Currently uses $HgBr_2$, $HgCl_2$, or Hg^0
- Non-thermal plasma oxidation of Hg^0 → Hg^{II} using ligands
  - Field deployable? *(Vijayakumaran Nair et al., 2024)*
- <u>General consensus:</u> Development of a field-deployable, NIST-traceable calibrator is needed
  - Design is not restricted, to encourage creative solution
  - If permeation tubes are selected, calibrated tubes are required

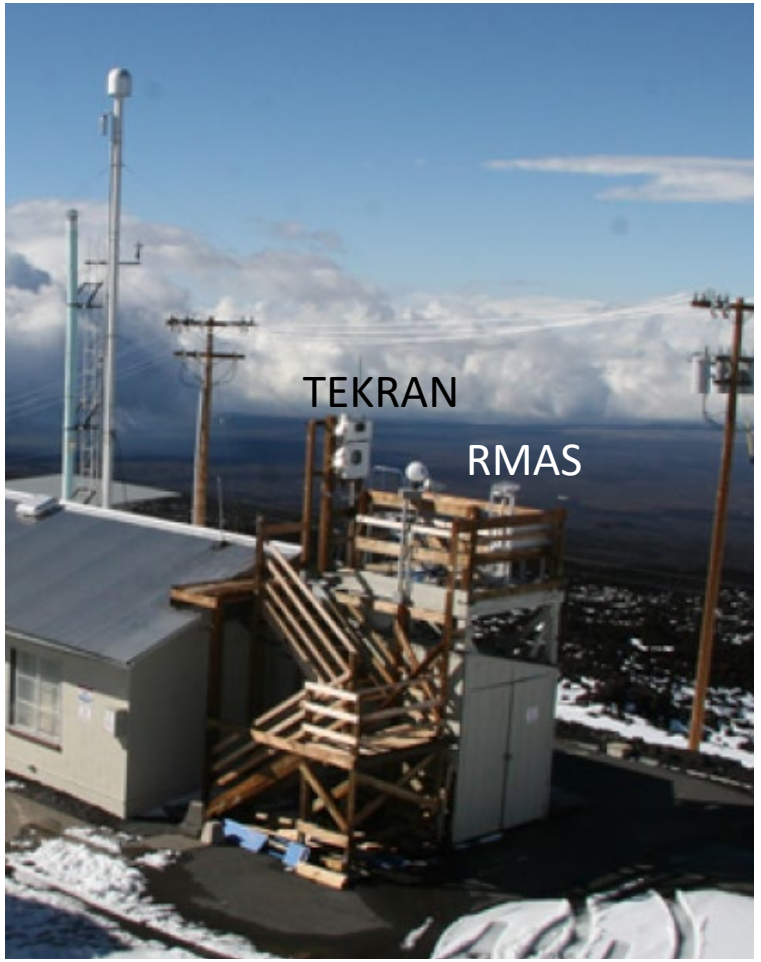
Oxidized Hg^{II}: Chemistry Methods

- Thermal desorption of preconcentrated RM on nylon membranes
  - Compare profiles to those generated using standard compounds
  - Not all Hg^{II} forms are collected with equal efficiency
  - Concentrations lower than those derived with CEM
  - Calibrated forms may not reflect ambient Hg^{II} chemistry
  - Field data show consistent trends *(Gustin et al., 2023)*

- Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS) is a promising potential new method
- <u>General consensus:</u> Direct measurement methods for determining atmospheric chemistry are needed
  - However, chemistry measurements will not provide information on their associated reactions

Network Considerations

- Methods applied must address the research objective(s) of the network
  - Minamata Convention = Long-term monitoring
  - National Atmospheric Deposition Program = Deposition
- Current networks should (re)consider measurement systems in light of new data and measurement limitations
  - Networks with high-time resolution, speciated measurements are needed



Mauna Loa Observatory, Hawaii, USA
AMNet Site

Workshop Outcomes

- Depending on their objectives, researchers and networks should adopt methods that specifically measure Hg^0 or total gaseous Hg
- New methods are needed to separate gaseous oxidized Hg (GOM) and particulate-bound Hg (PBM)
- Methods are needed to determine the chemical composition of RM compounds
- Field-deployable calibrators need to become widely available and adopted
- Monitoring networks (may) need to reassess methods being used

Summary & Path Forward

ES&T Paper

- Hg^{II} measurements are challenging given the low concentration and reactivity of compounds
- All available methods have limitations that need to be acknowledged
- New methods such as RMAS and DCS have provided important information on concentrations and chemistry
- Needs
  - Surfaces that collect GOM and release it without altering GOM chemistry
  - Sampling methods that allow for quantification of both GOM and PBM
  - Methods that identify the chemistry of Hg^{II} compounds
  - NIST-traceable calibration systems
  - Uncertainty analyses for all methods
  - **A global, field-based, calibrated, chemically resolved, direct measurement of ambient Hg^{II} forms and compounds**

Acknowledgements

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Atmospheric Mercury Workshop

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University of Nevada, Reno

Questions?