Advances in our Understanding of the Chemical Forms and Concentrations of GOM in the Atmosphere

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Acknowledgements

- NSF
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- Dr. Seth Lyman

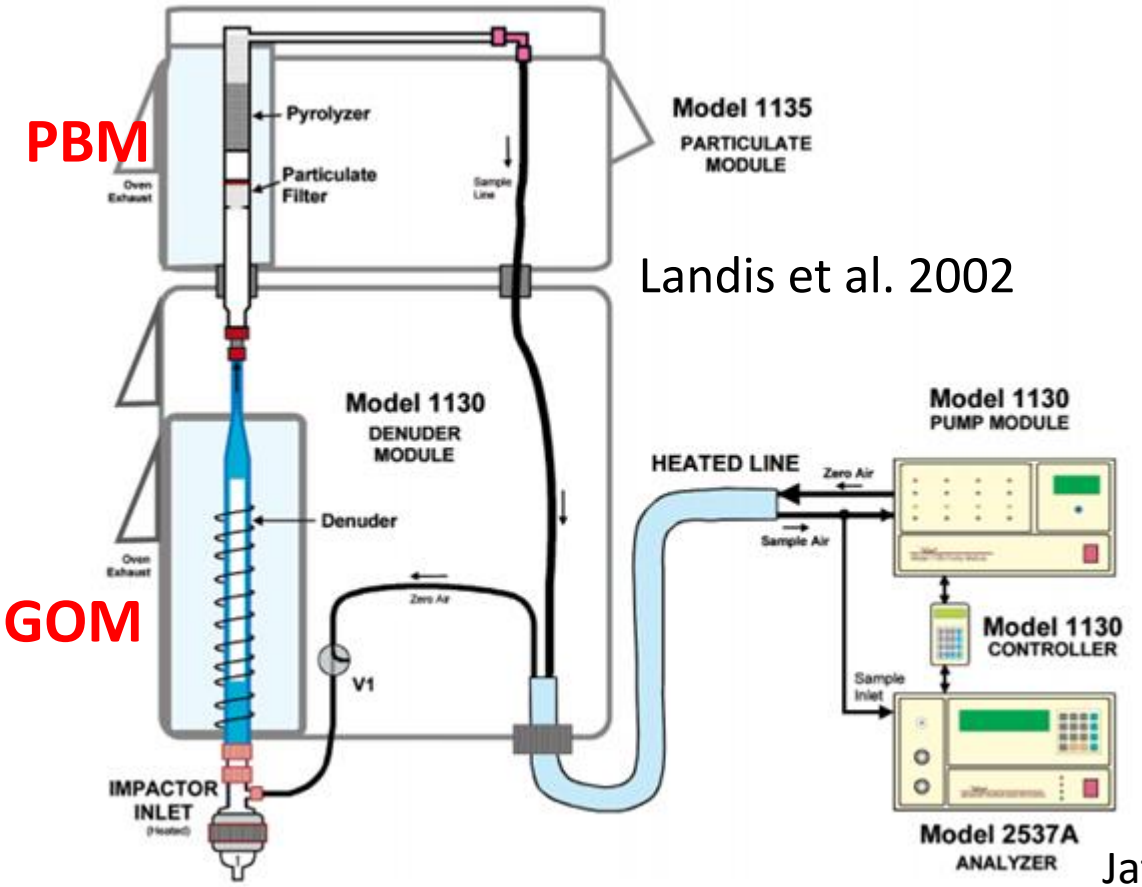
Outline

- Major conclusions regarding Tekran system
- How we got to this place in time-brief history
- Where we are now with UNR methods for measurement of GOM
- Ongoing and future work

Mercury in the atmosphere

- Currently 3 operationally (measurement) defined forms
  - Gaseous elemental Hg (GEM)
  - Gaseous oxidized Hg (GOM previously called RGM)
  - Particulate bound Hg (PBM)

Tekran system



Landis et al. 2002

-Being used in networks world wide
-No field calibration for RM
-Unclear ambient air interferences
-High uncertainty associated with the RM measurement

GEM

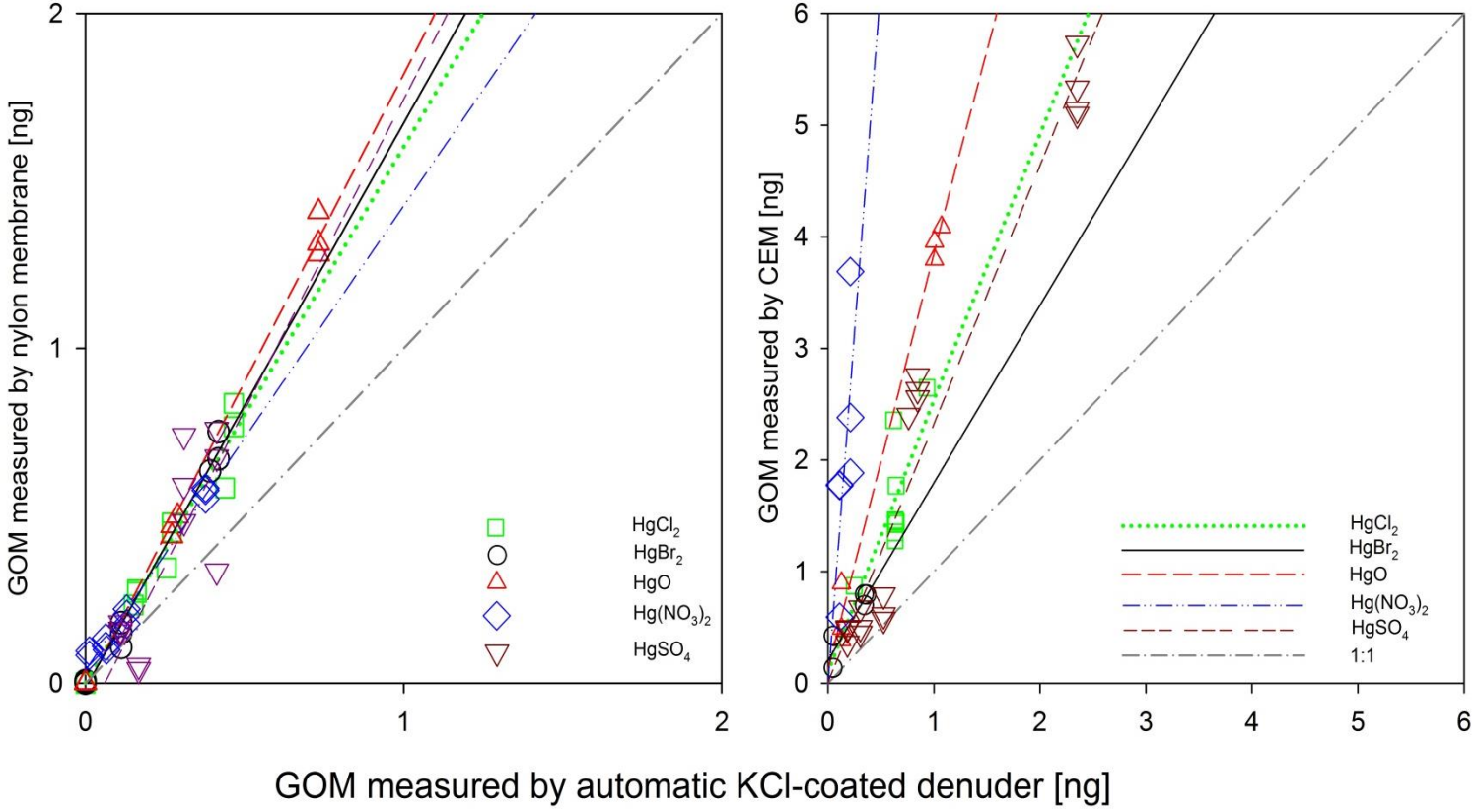
Jaffe et al., 2014 (EST)/Gustin et al., 2015 (ACP)

GOM+ PBM =RM

Conclusions regarding

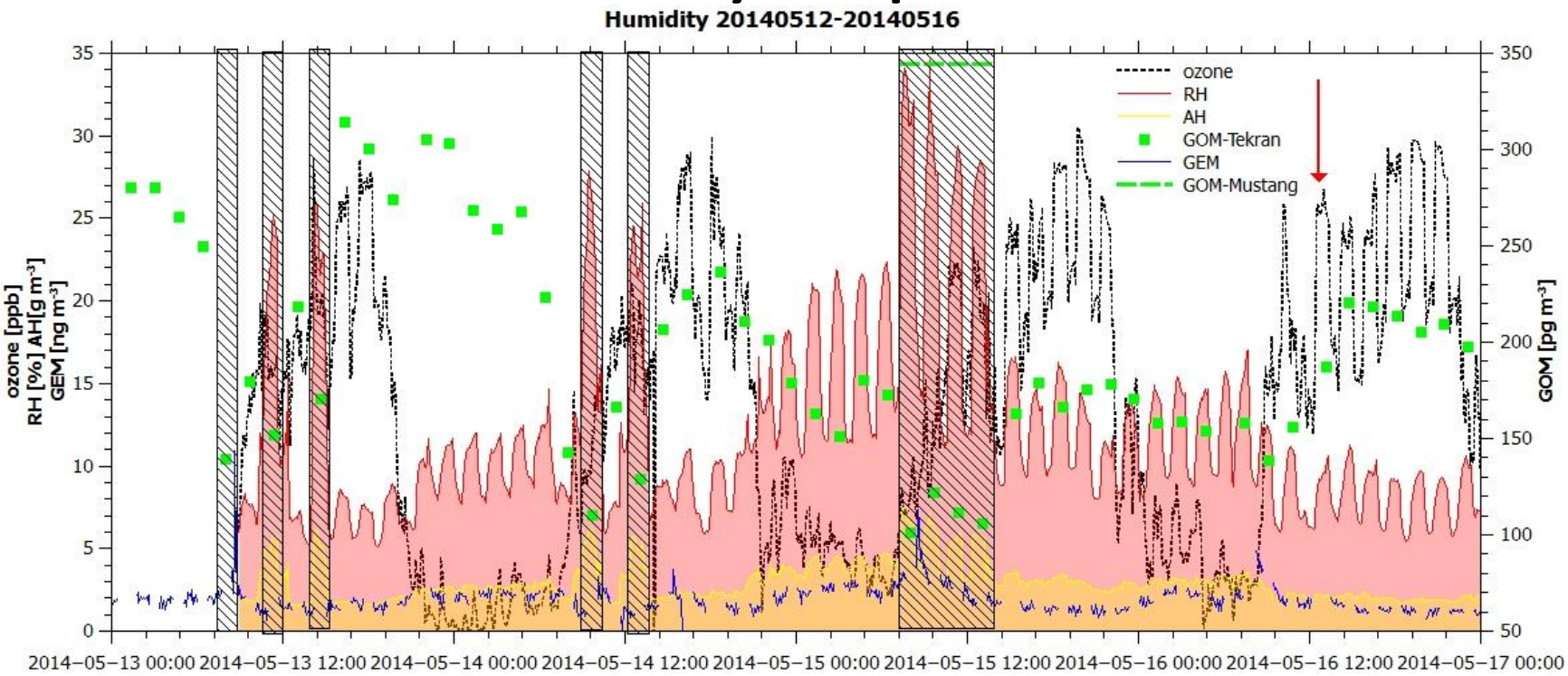
- KCl denuder does not collect different forms of GOM with equal efficiency (Huang et al. EST 2013, Gustin et al. ACP 2015)
- KCl measurement is biased low and varies as a function of the different compounds in air.
- There are denuder interferences with water vapor and ozone (Lyman et al., ACP, 2010 Huang and Gustin, EST 2015; McClure et al., EST 2014)
- The chemical compounds of GOM vary across space and time, and some can get lost within the Tekran system as operated (Gustin et al., 2013 RAMIX EST)

Efficiency of collection of different chemical forms



$HgBr_2$ (1.6)>$HgSO_4$ (2.3)=$HgCl_2$ (2.4)>HgO (3.7) >$Hg(NO_3)_2$ (12.6)

Relative humidity impacts the denuder

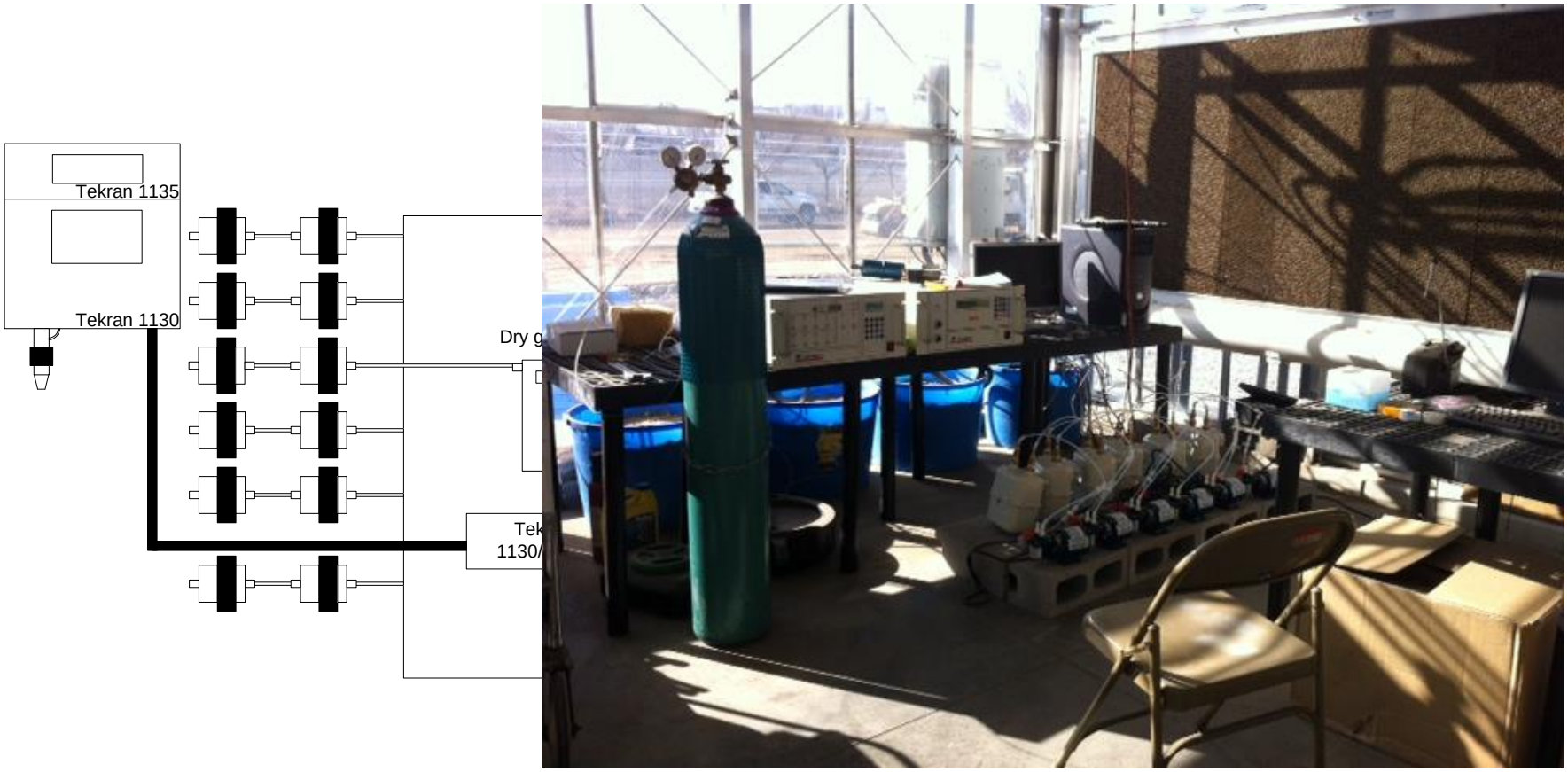


RH <35% collection efficiency is 21 ± 9% lower n=8

RH > 35% collection efficiency is 35 ± 18 % lower n=9

Huang and Gustin, EST, 2015

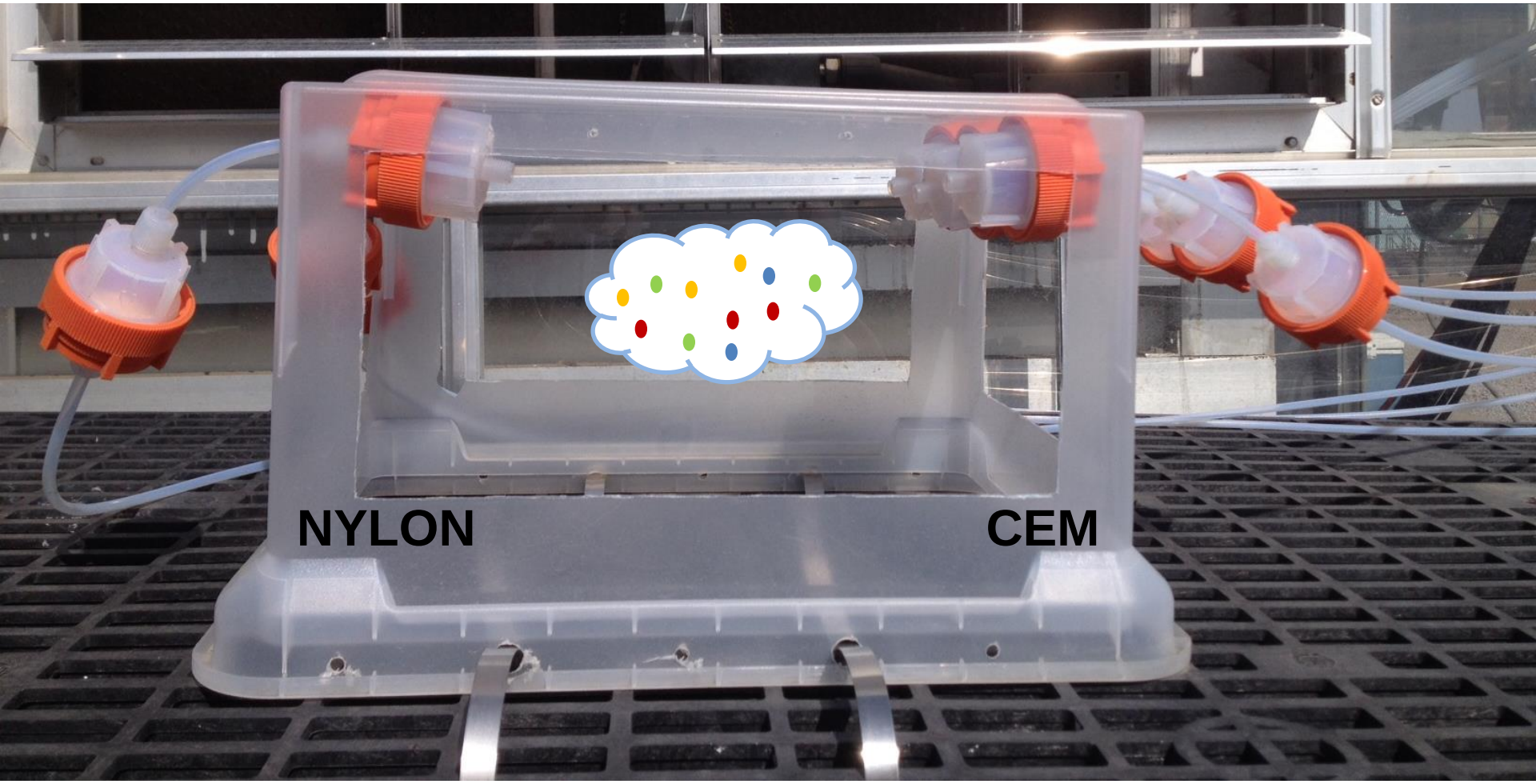
University of Reno Active System for collection of GOM- UNRASGOM



Developed for measurement of GOM concentrations and chemistry-Nylon membranes and cation-exchange membranes

Huang et al. 2013

Methods-UNR Active System



Membranes

Cation Exchange

-Used to quantify GOM

-Does not take up GEM

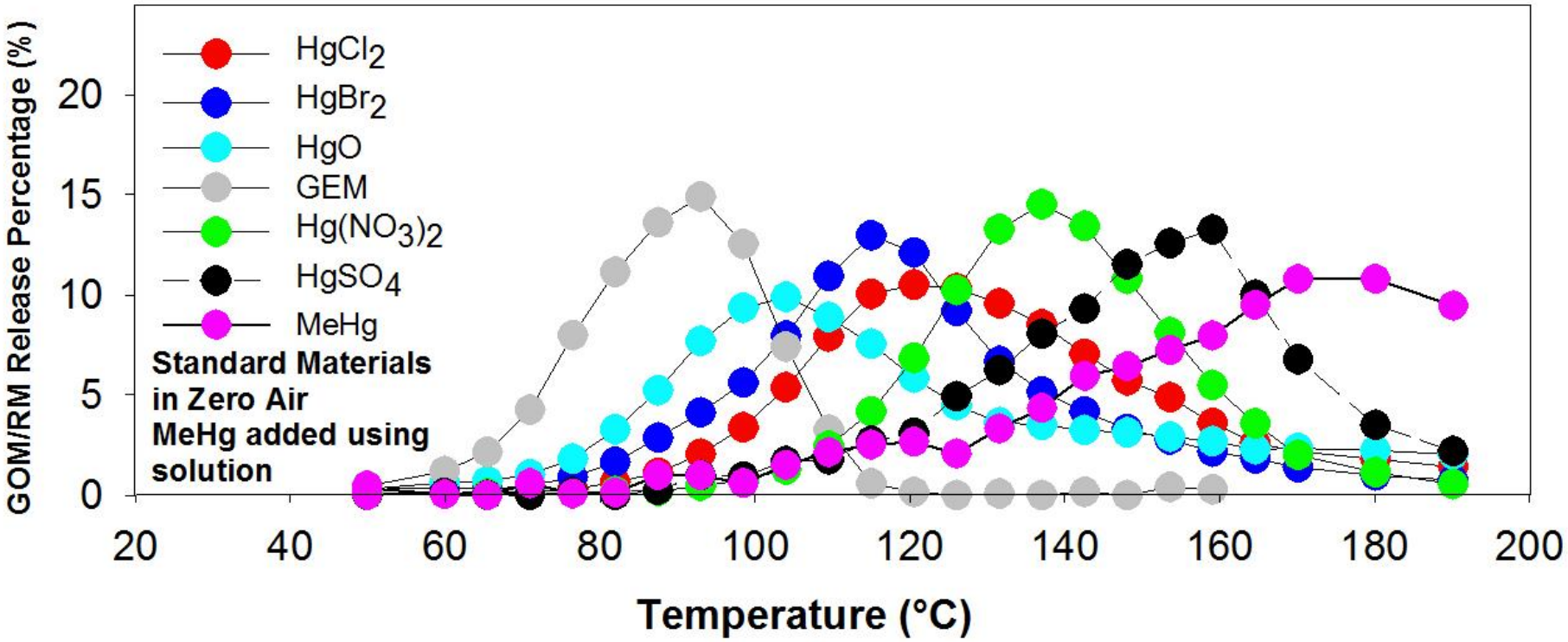
Nylon

-Used for identifying potential GOM compounds

-Does not take up GEM

Huang and Gustin, 2015

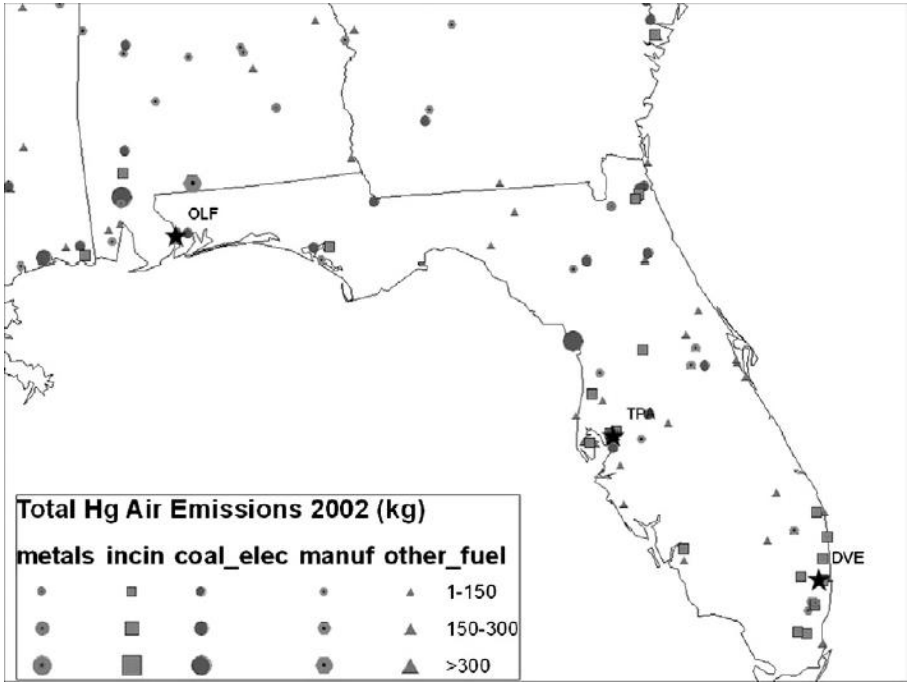
UNR developed desorption profiles for nylon membranes



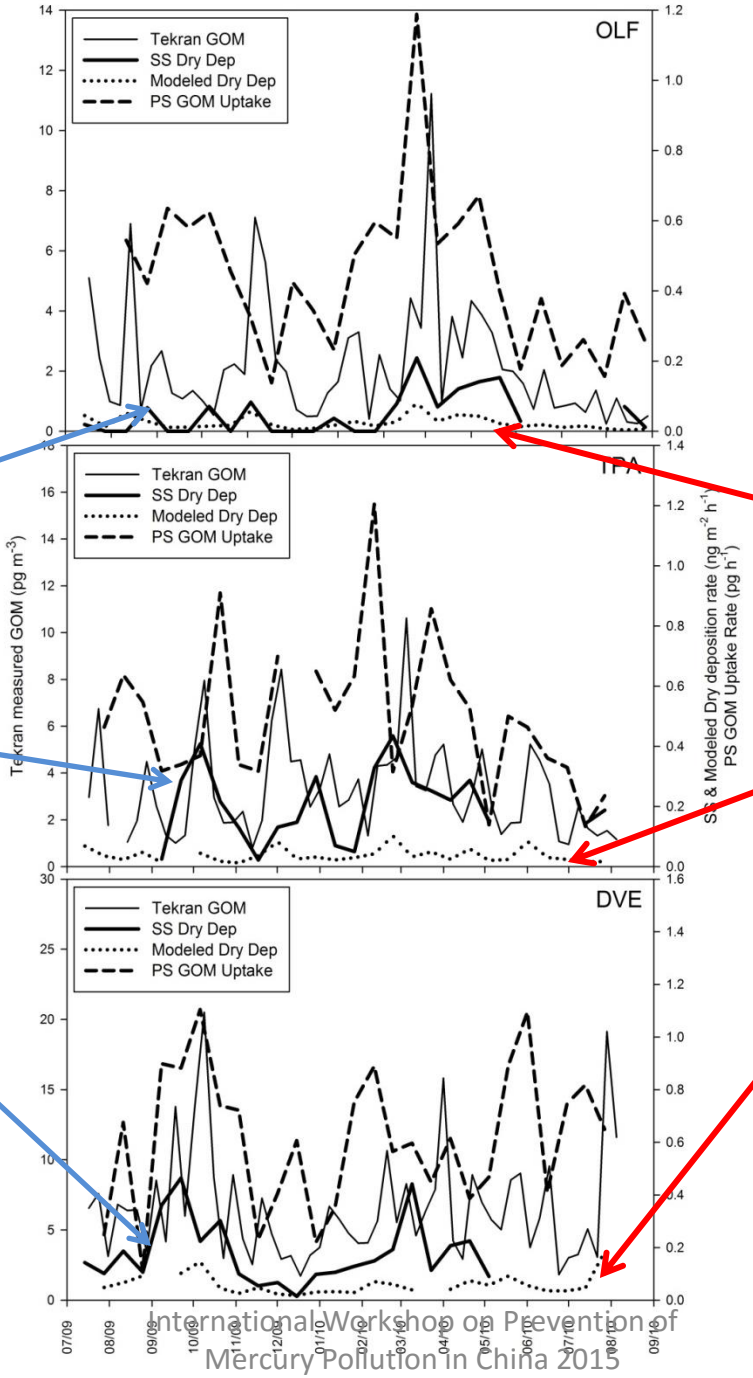
History -Case study-Data collected in Florida, USA

Florida TMDL Study

Data just did not make sense so assumed the passive sampler data are correct and the Tekran data were not accurate



Gustin et al. 2013 ACP
Peterson et al. 2012 STOTEN



Passive sampler trends do not match Tekran concentrations

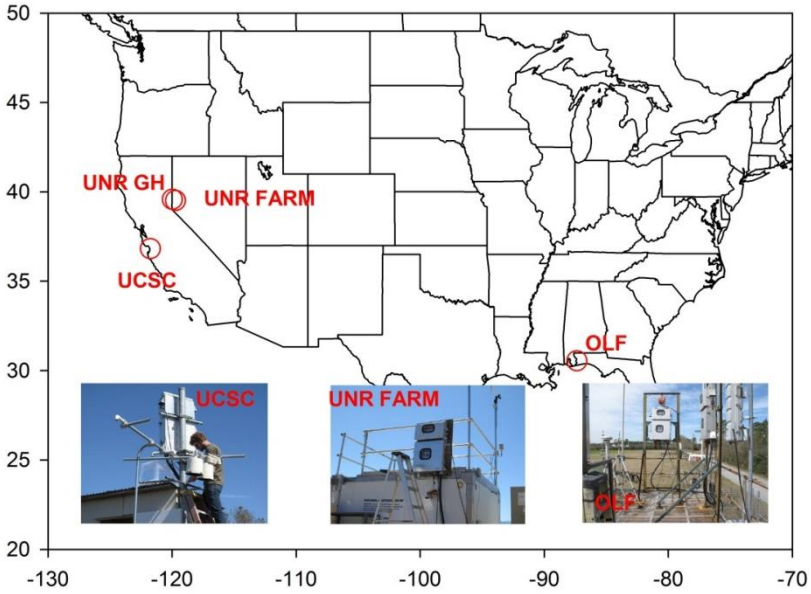
Measured

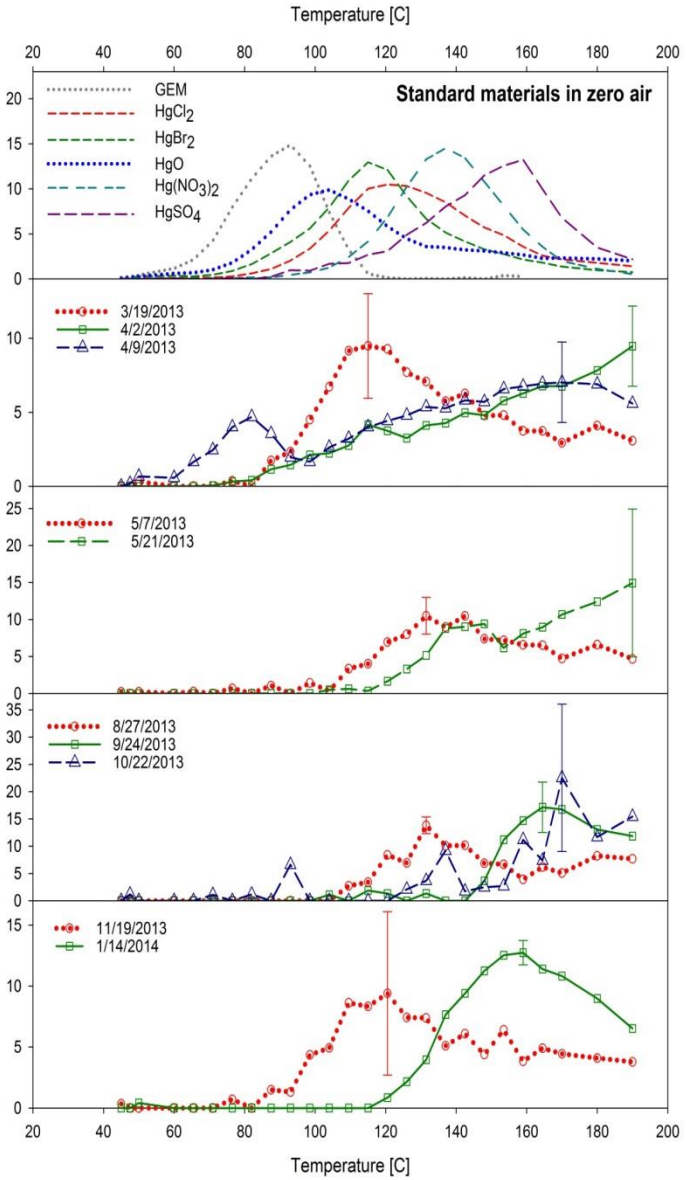
Modeled dry deposition using Tekran GOM

Dry deposition sampler-

- Information gained
  - Different forms of GOM across space and time and these will have different dry deposition velocities
  - GOM concentrations in air are higher than previously realized

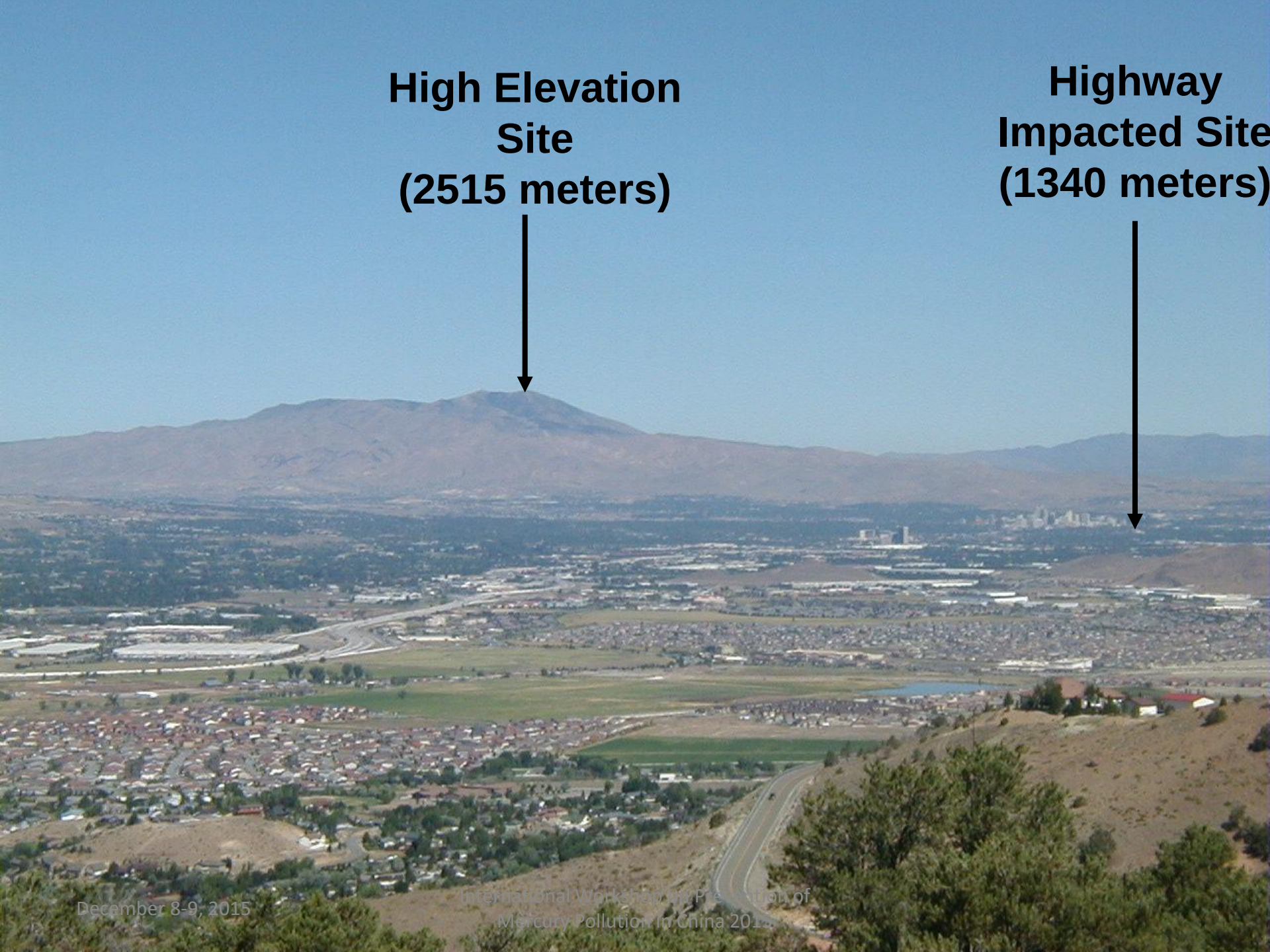
GOM chemistry



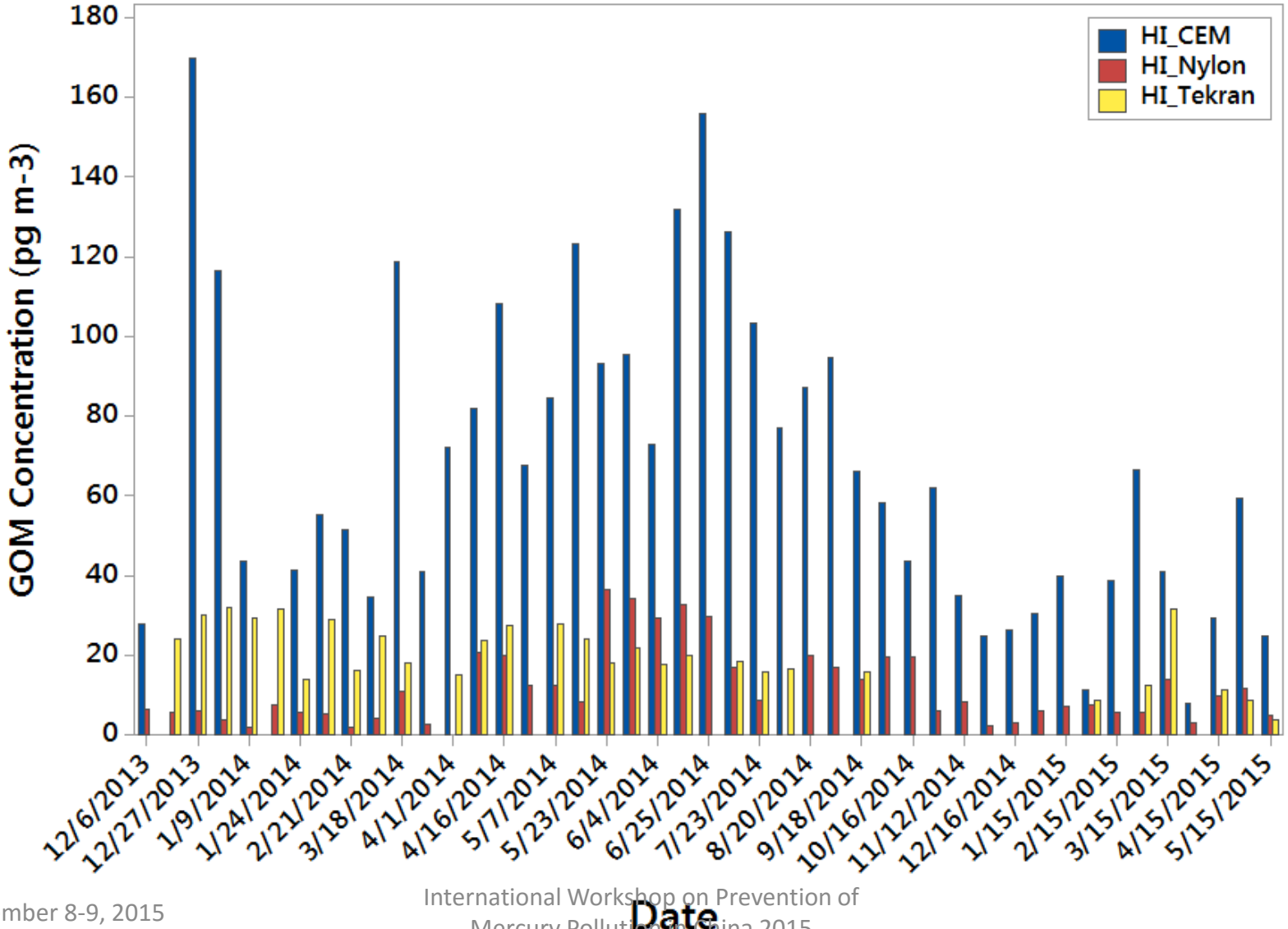


Huang et al., 2015 ACPD

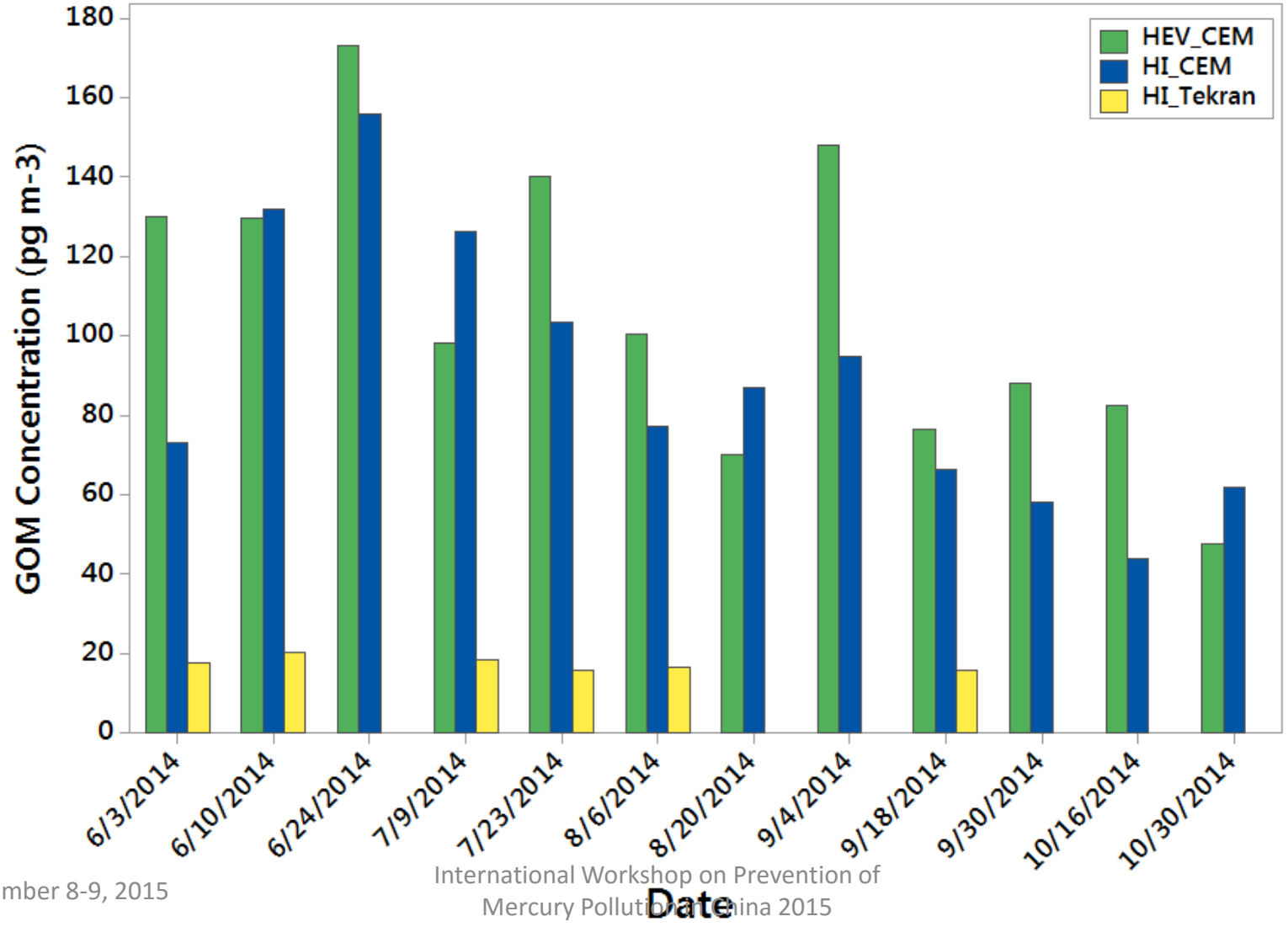
Case study- Nevada USA data


High Elevation Site (2515 meters)
Highway Impacted Site (1340 meters)

GOM Concentrations at Highway Impacted Site

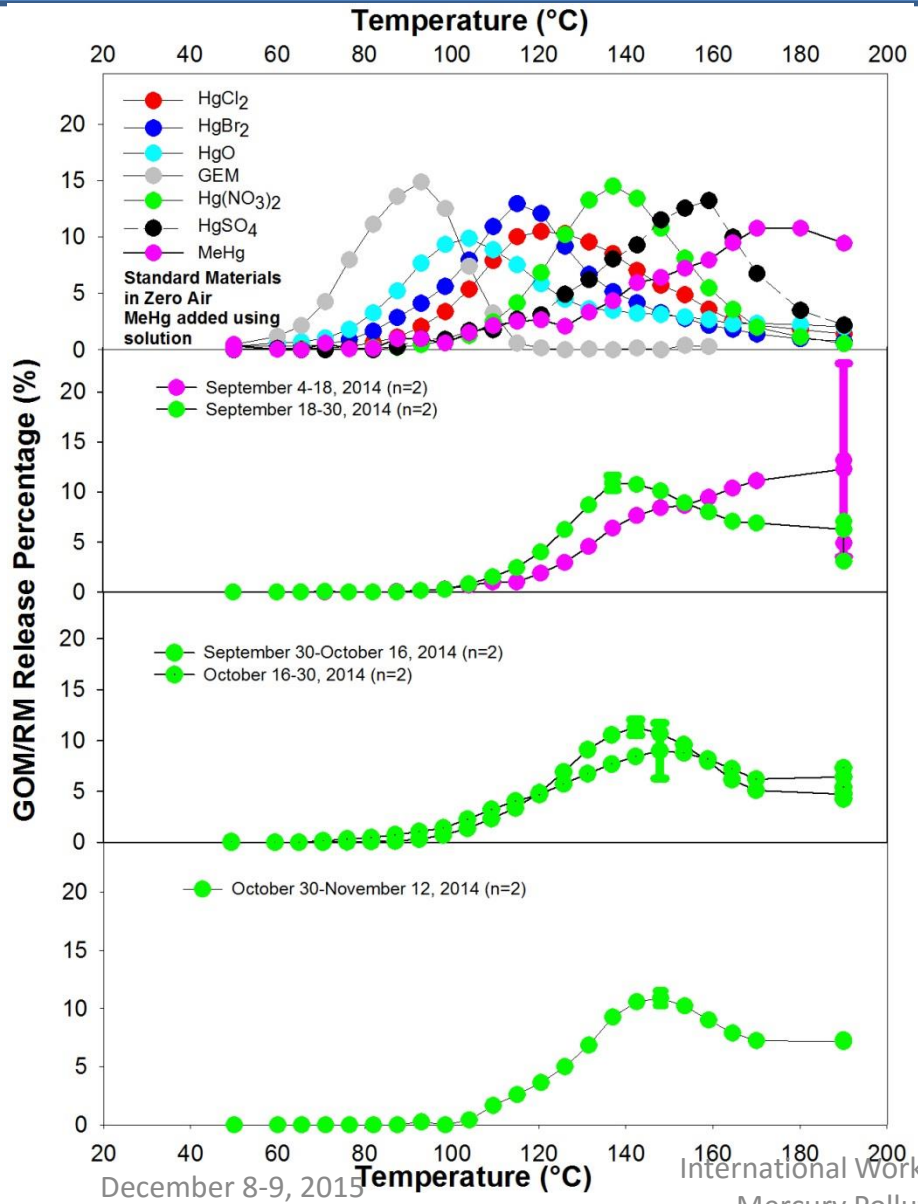


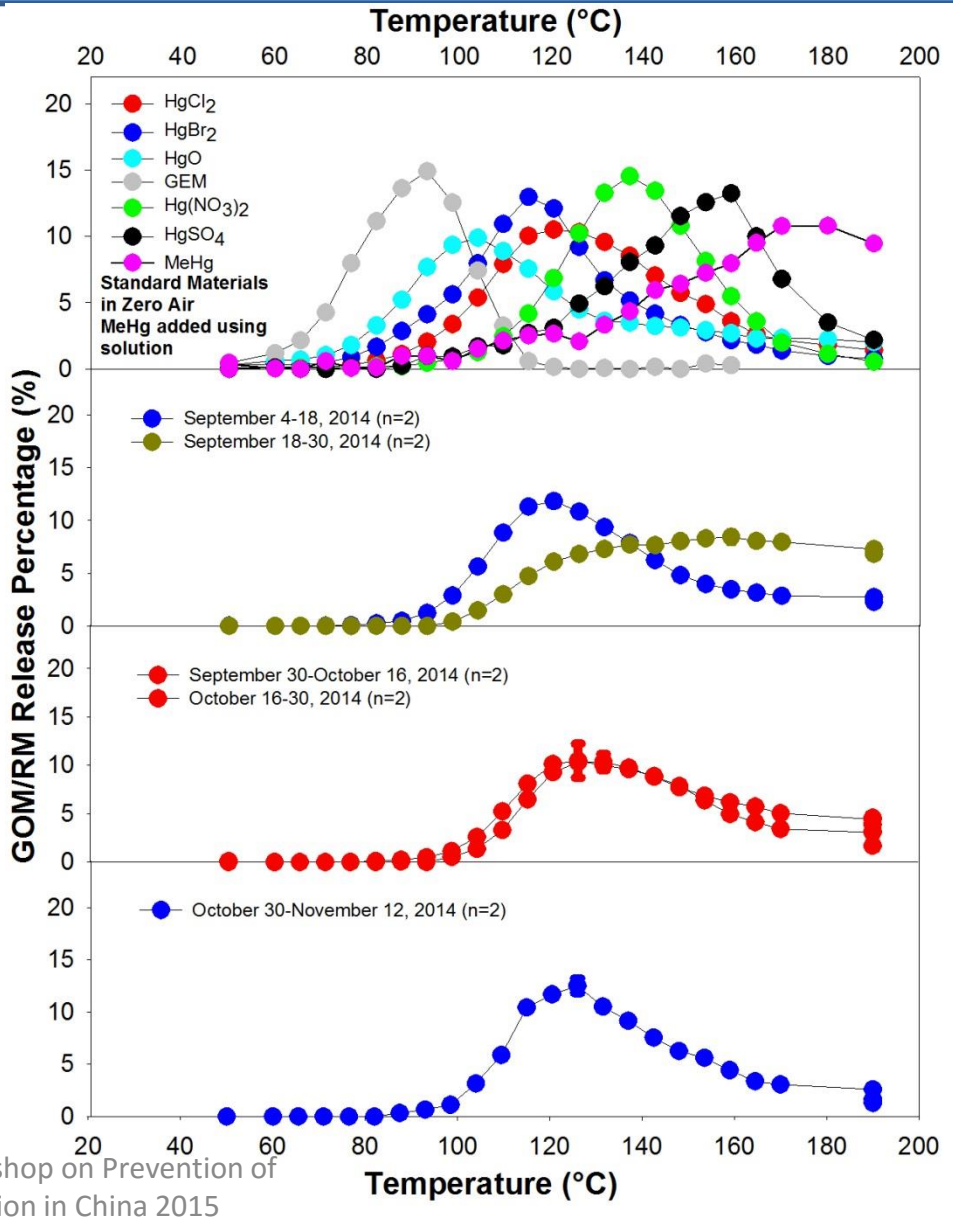
Comparison of GOM Concentrations



Highway Impacted Site:

High Elevation Site:

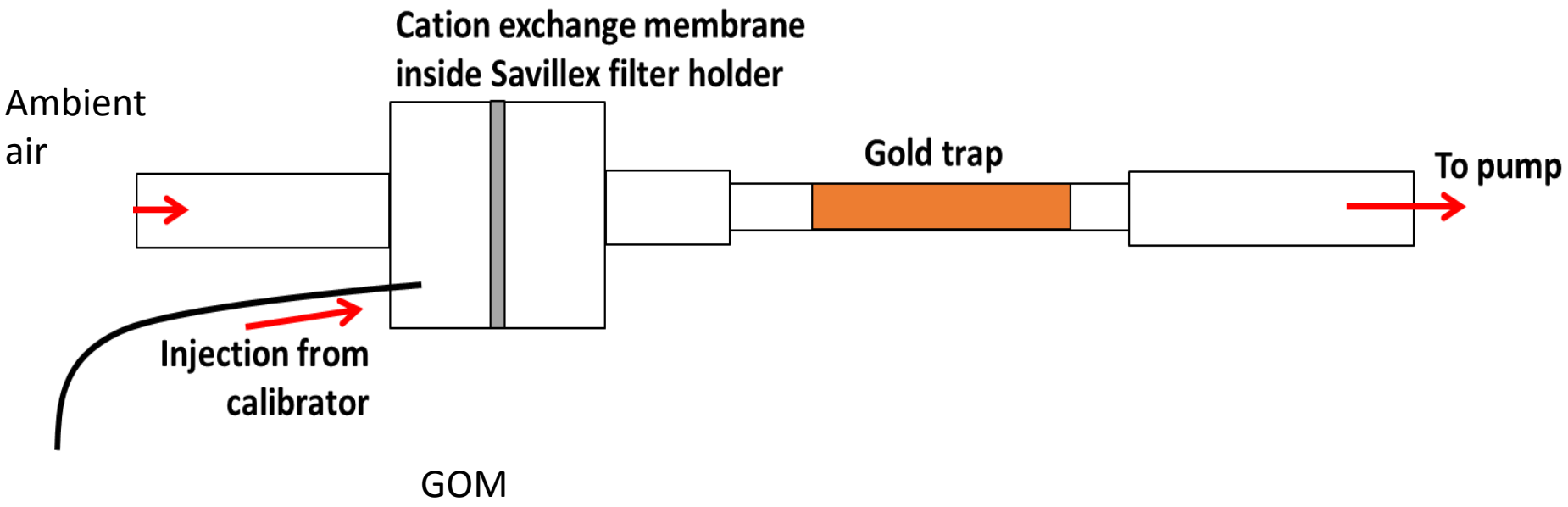




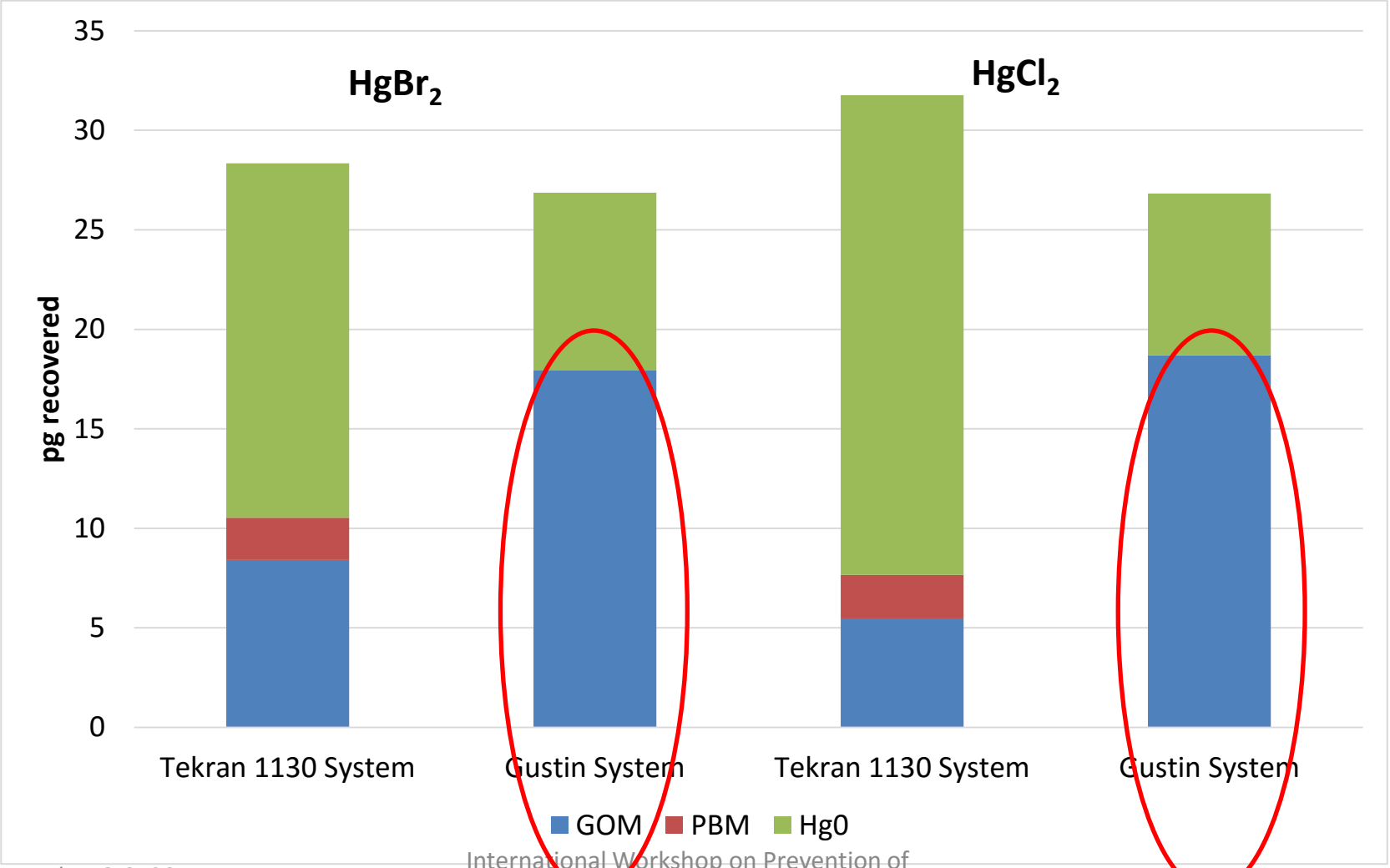
Highway impacted site with co-located GOM calibrator of Lyman

Dr. Seth Lyman and student Trevor O'Neil

Gustin collection method (UNR Active)



Comparison of membrane-based system with Tekran speciation system



Major conclusions

- Lyman et al., 2007 and 2009-Tekran data do not make sense
- Lyman et al., 2010-Interferences of ozone with the GOM measurement
- Peterson et al., 2011-Evidence for different deposition velocities (thus different chemical forms) using Aerohead dry deposition measurements
- Gustin et al., 2012-Evidence for different compounds across space and time in Florida using Aerohead sampler and passive sampler measurements that did not agree with Tekran data

Major conclusions-RAMIX

Reno Atmospheric Mercury eXperiment

August to September 2011

Tekran biased low and different forms being measured in the atmosphere

Gustin et al. 2013

Major conclusions-continued

- Gustin et al., 2013 Denuder becomes passivated over time suggested due to relative humidity
- McClure et al 2014– Impact of relative humidity on the denuder demonstrated in the field
- Huang et al. 2015-laboratory manifold – greater impact of relative humidity than ozone

UNR Active System

- Utility
  - Provides a means of determining GOM concentrations and identifying the potential forms in the air.

UNR active system concerns

- Are there reactions occurring on the membrane-needs to be tested.
- Do they capture all forms?
- Other compounds need to be tested.
- Long deployment time as currently configured

Because we are seeing variation across different areas, it is likely the differences are not an artifact of sample collection, but are real.

UNR Active System

- Information gained
  - Concentrations of GOM are 1.6 to 13 times higher than expected
  - Up to 25% of Hg in atmosphere can be GOM
  - Different forms exist across space and time
  - It will be difficult to calibrate past measurements
  - However , deployment of the active system with the Tekran system for now is useful as we are developing the calibrator with Dr. Seth Lyman

Conclusions

- Surrogate surfaces are useful for understanding GOM dry deposition
- Passive samplers are useful for understanding relative levels (needs a new design)
- These samplers may be applied across broad spatial and temporal scales

Conclusions

- Active system appears to work well for quantifying GOM collected on CEM
- Thermal desorption is a first step at trying to understand presence of different forms in air
- Source of Hg are global it's the oxidants present that will influence the production of GOM and the GOM chemistry

Needs

- “Develop calibration methods for GOM and provide routine calibrations for field instrumentation;
- Conduct detailed investigations to quantify interferences in the existing GOM methods and develop new methodologies to measure it; and
- Conduct fundamental research on the chemistry, reaction kinetics and chemical identity of the compounds that makeup GOM and PBM in the atmosphere.
- We believe these items should be given high priority by the mercury scientific community. To do otherwise impedes scientific progress and environmental monitoring efforts.”

Exact words from Environmental Science & Technology Viewpoint Jaffe et al. 2014
B dx.doi.org/10.1021/es5026432

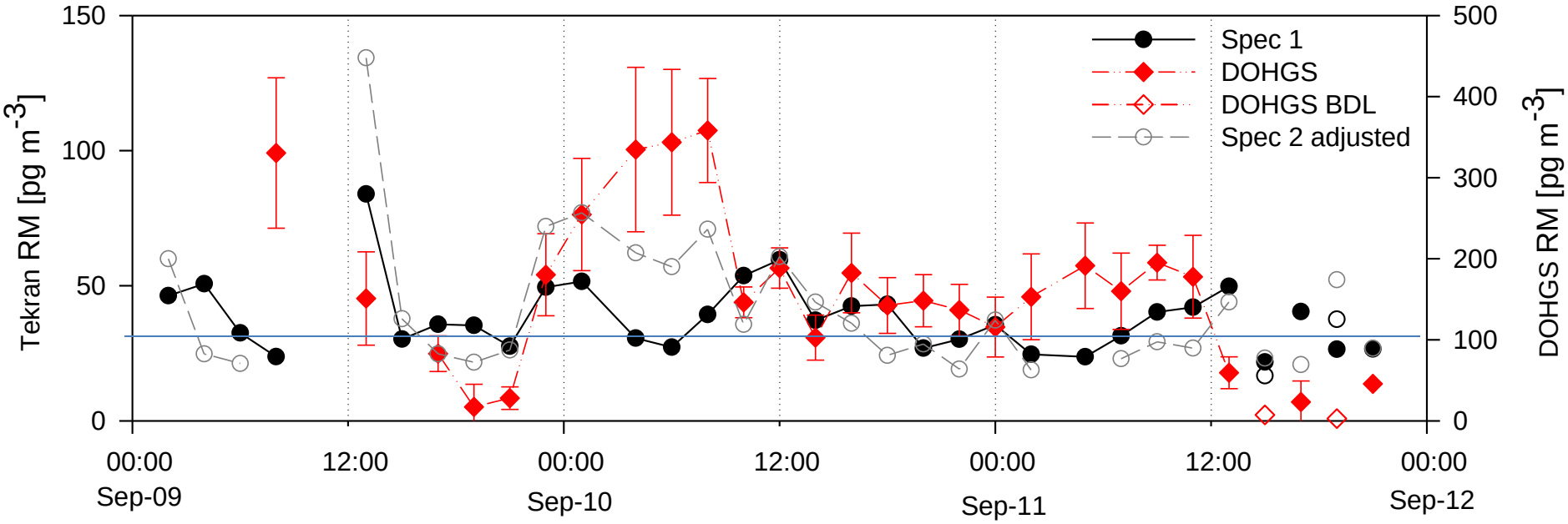
Ongoing and Future work

- Testing of an additional method for measuring GOM
- Deployment of Lyman calibrator
- Write papers
- Submit proposals for better understanding and refining measurements

Thanks for listening
感谢收听

RM comparison between Tekran and DOHGS instruments

DOHGS system higher RM concentration and measured form(s) of RM not detected by Tekran



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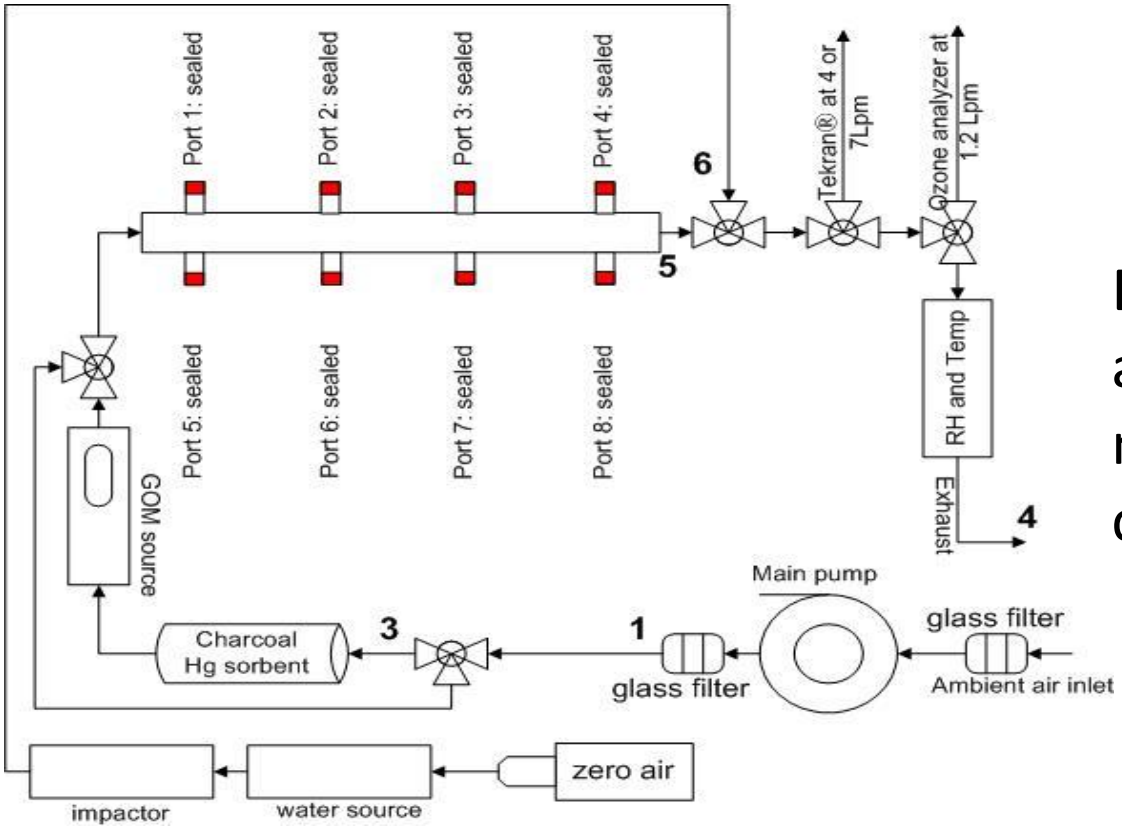
Environmental Measurement Methods

Finley et al. Ambrose et al. Gustin et al. 2013

UNR laboratory manifold



Developed for loading and calibrating membranes and calibrating the denuder

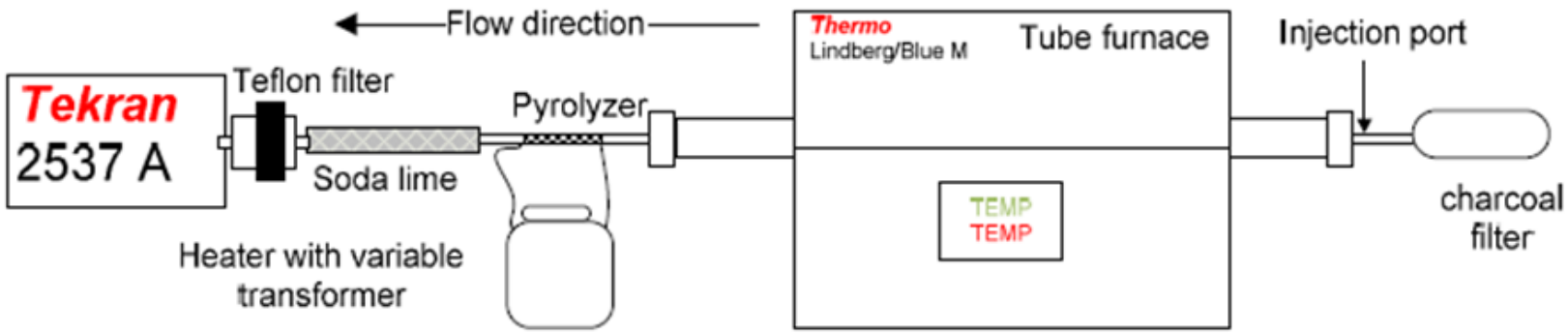
Huang et al., 2013; Huang and Gustin, 2015

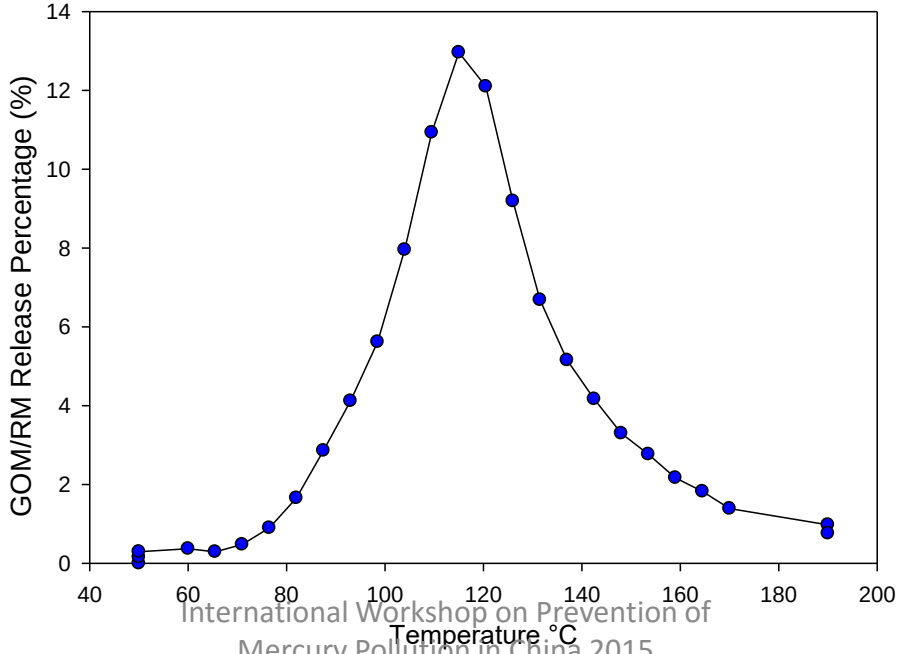
Membrane Analysis

- Cation Exchange Membranes
  - Total Hg analyses using Tekran 2600 (EPA Method 1631E)

- Nylon Membranes
  - Thermal desorption Analyses followed by Tekran 2600(EPA Method 1631E)

Understanding GOM Chemistry





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