Overview of Atmospheric Mercury Measurement Uncertainties

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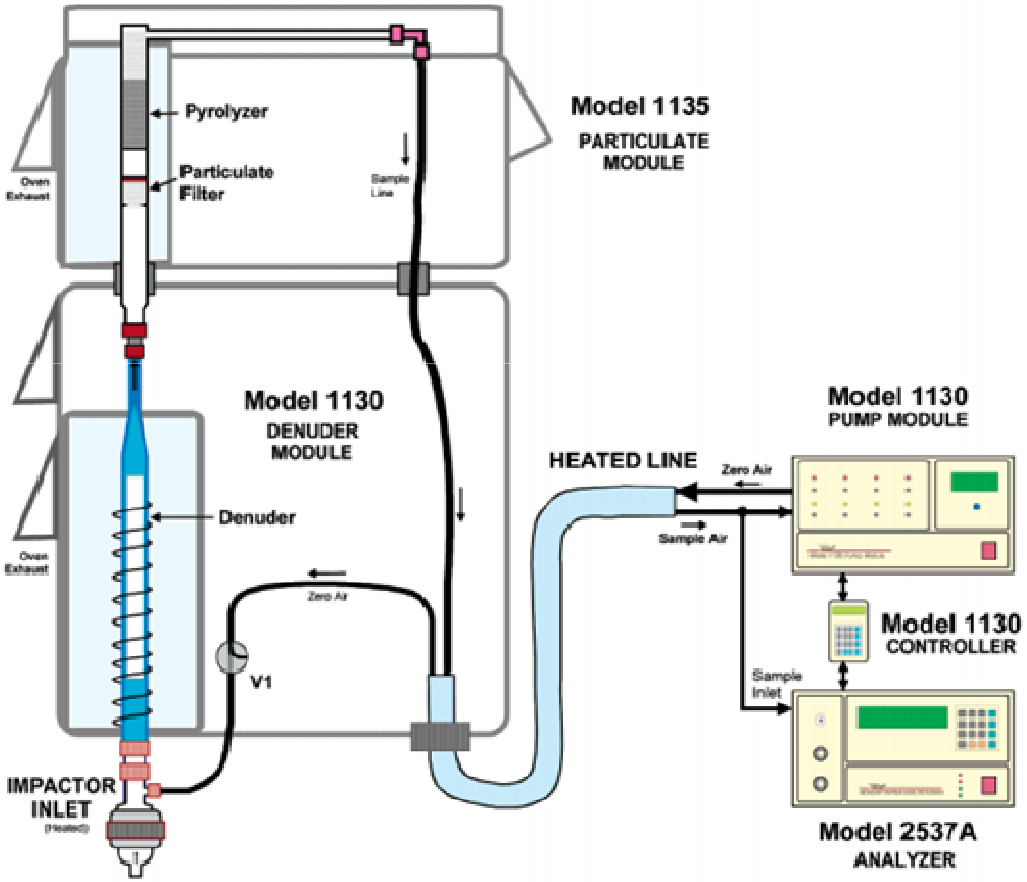
Progress on Understanding Atmospheric Mercury Hampered by Uncertain Measurements

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- "at present there is no consensus on what the chemical form(s) of GOM is(are),nor any reliable method to identify the chemical form(s) in the atmosphere. It is likely that more than one form of Hg(II) exists in the atmosphere, depending on its source." and the oxidants in the air.
- "protocols do not provide a way to calibrate for GOM or PBM, quantify collection efficiency or quantify measurement interferences."
- "There is some uncertainty as to whether current unspeciated measurements capture total gaseous mercury (TGM) or GEM."

EST, 2014

Tekran system



-Has been useful for making progress for understanding atmospheric Hg

-Being used in networks world wide

--KCl-coated denuder and particulate filter not calibrated or checked for interferences

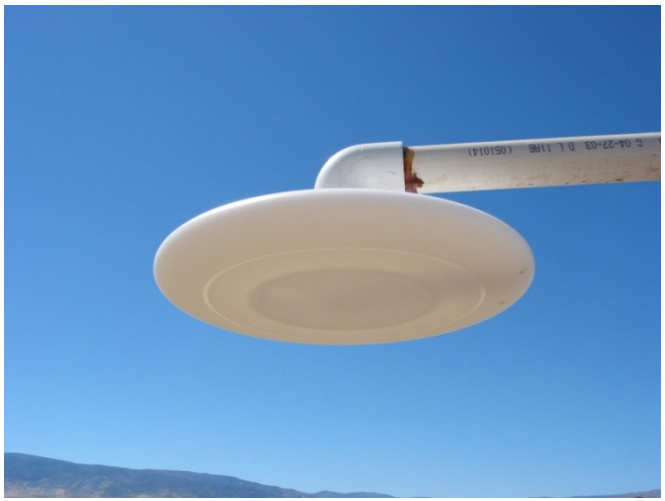
Talk outline

- Focus on GOM uncertainties
- Brief summary of methods
- Chronological discussion of investigation of GOM uncertainties
- Note on PBM-
  - instrument demonstrated to not collect all PBM (Talbot et al., 2011)
  - PBM likely measures GOM not collected by the denuder (Gustin et al., 2013)

GOM Passive samplers



Easily deployed by regular people



Dry deposition



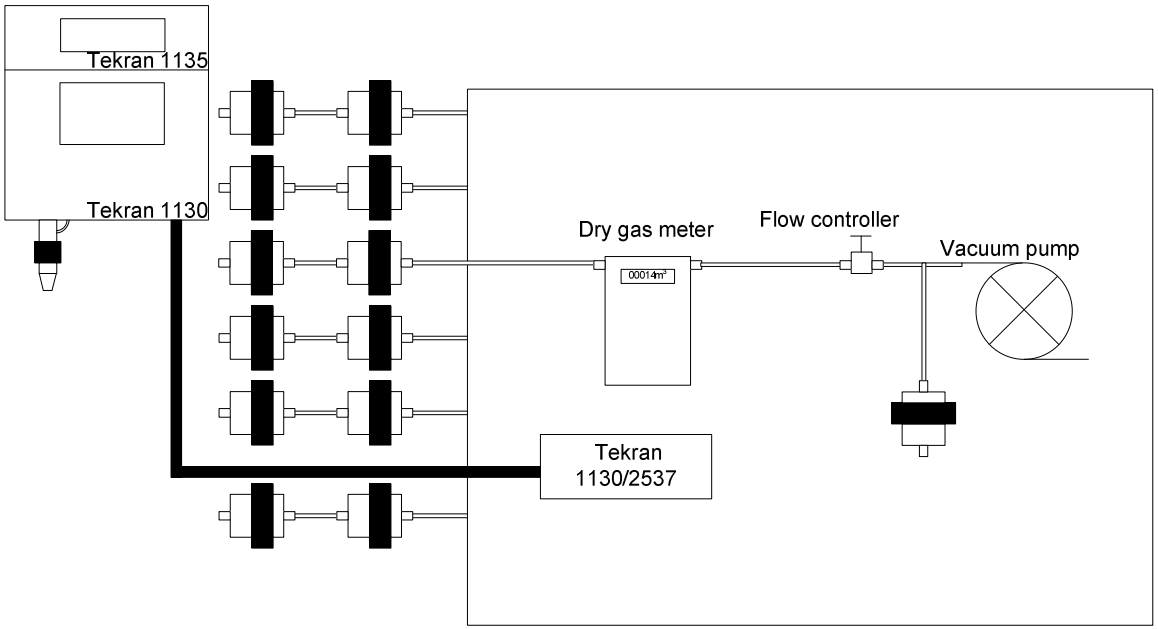
Concentrations

No electricity needed

Demonstrated use in Florida, California, Nevada, New Mexico, Oklahoma, Texas…….Maryland

Lyman et al., 2009 and 2010 EST AE
Huang et al., 2014 Environ. Sci.: Processes Impacts

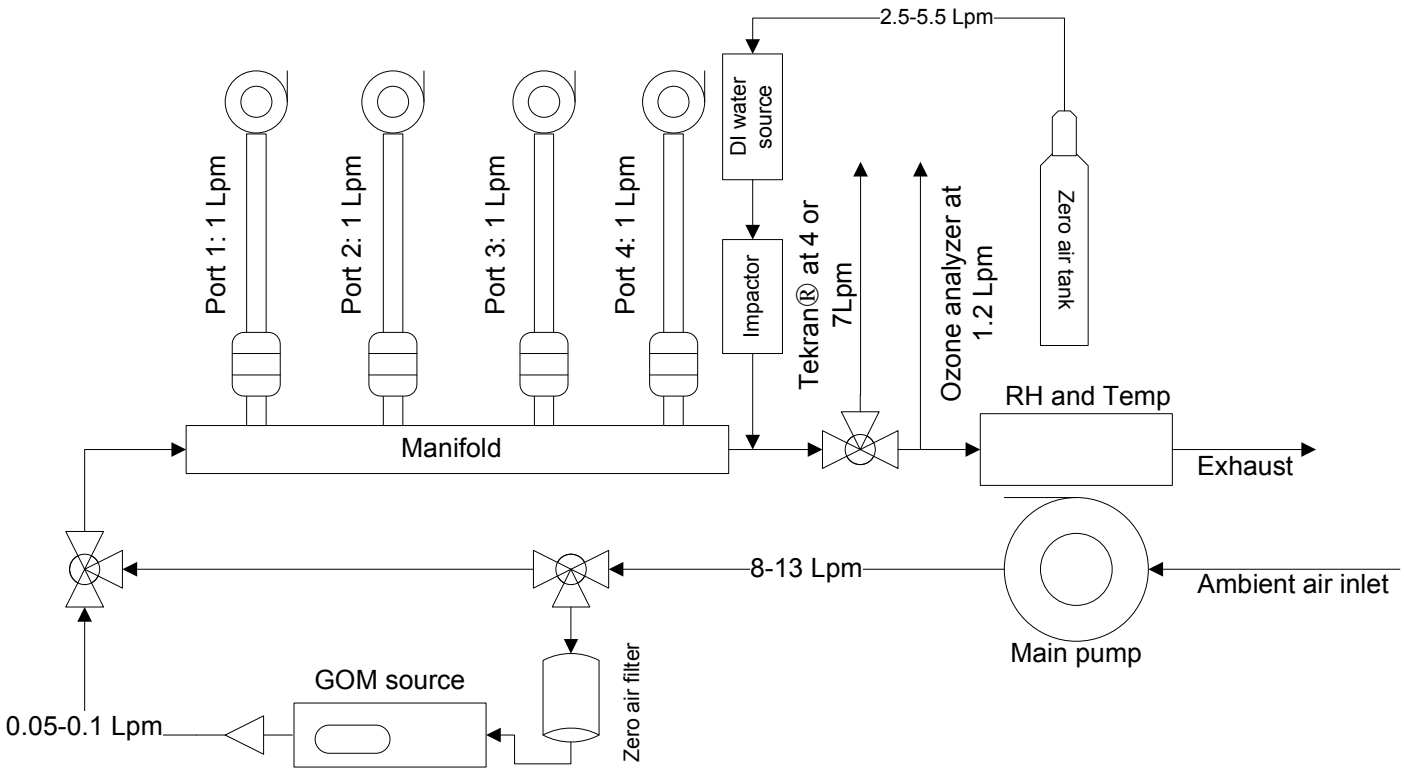
UNR active system



Developed for measurement of GOM concentrations and chemistry

Huang et al. 2013

UNR laboratory manifold

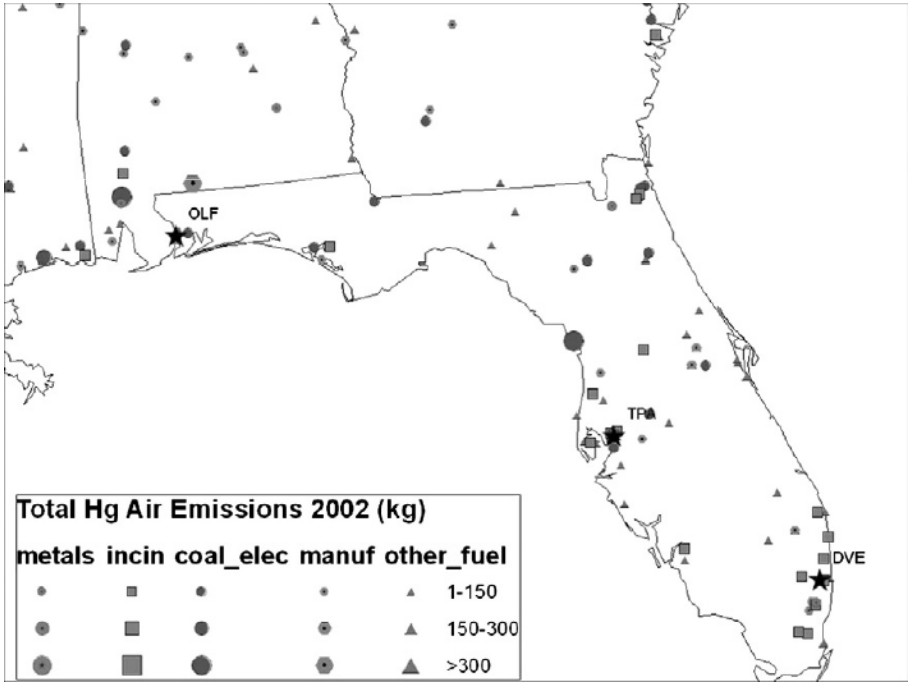


Developed for loading and calibrating membranes and calibrating the denuder

Huang et al., 2013

Florida TMDL Study

Assume the passive sampler data are correct and the Tekran data are wrong





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

Passive samplers in Florida-GOM

SS data corrected should be higher by 0.2 ng m^{-2} h^{-1}

Recent work suggests CEC reflects natural surfaces (Huang and Gustin 2014)

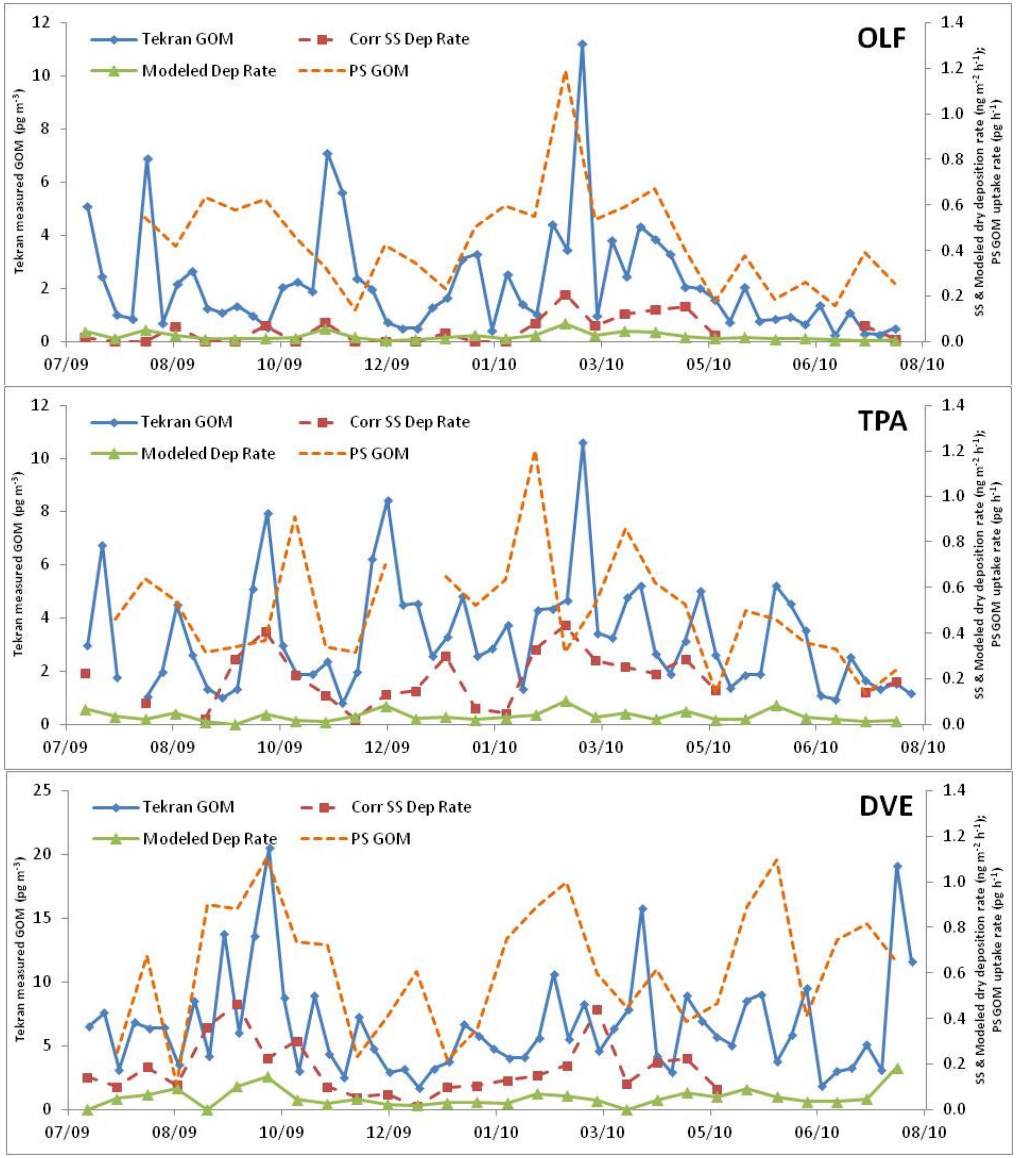
Measured deposition always higher than modeled

Passive samplers and Tekran not always correlated

Passive sampler uptake and SS deposition not always correlated

Different deposition velocity of the different forms will influence uptake

Peterson et al., 2012 STOTEN



Conclusions

- **Peterson et al. 2012 Investigate the utility of passive sampling systems to record spatial and temporal patterns of atmospheric Hg**
  - Samplers do record spatial and temporal variation
  - Variation does not match that measured with the Tekran
  - Data suggests different forms of GOM across space and time

- **Gustin et al. 2012 based on combining criteria air pollutant data and meteorology**
- At OLF
  - natural background dry deposition 0.03 ng m^{-2} hr^{-1}
  - no significant influence of the EGP
  - LRT 0.11 ng m^{-2} hr^{-1} GOM dry deposition derived from N-NW
- At Tampa
  - Mobile sources 0.2 ng m^{-2} hr^{-1}
  - LRT in the spring 0.08 ng m^{-2} hr^{-1}
- Davie
  - Local point sources 0.1 ng m^{-2} hr^{-1}
  - LRT in the fall and spring 0.1 ng m^{-2} hr^{-1}

    Remember the dry deposition values were corrected and should be higher by 0.2 ng m^{-2} hr^{-1}

-Limitations of current methods to measure atmospheric Hg need to be systematically addressed

Reno Atmospheric Mercury eXperiment – RAMIX
August to September 2011





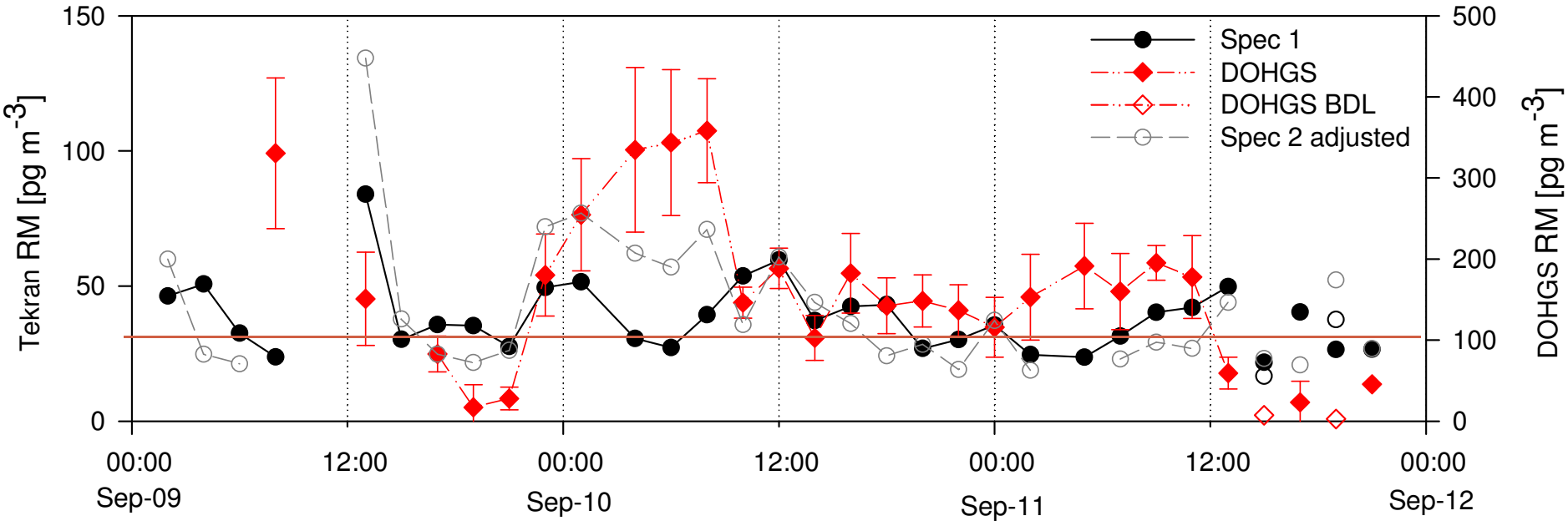
Tekran Uncertainties Field-RAMIX

In manifold	Spike Concentration	Response/Recovery (%) mean	std dev	max	min	Instrument	r^2	n hourly
GEM/TGM Response Weeks 1 to 3 [ng m^{-3}]	5 to 25	72	13	93	40	Spec 1	0.88	20
		55	6	62	43	Spec 2	0.92	16
		76	9	86	60	Spec 2 adjusted	0.92	16
		76	12	97	35	UNR 2537	0.96	47
RM Response Week 3 [pg m^{-3}]	~660	23	13	48	9	Spec 1		16
		24	15	61	9	Spec 2		16
		33	22	85	13	Spec 2 adjusted		16
Estimated GEM Recovery Week 4 [ng m^{-3}]	6 to 8	76	7	-	-	Spec 1 – Spec 2 adjusted		3
Estimated RM Recovery Week 4 [pg m^{-3}]	340 to 780	17	3	24	11	Spec 1 – Spec 2 adjusted		18

Gustin et al., 2013 EST

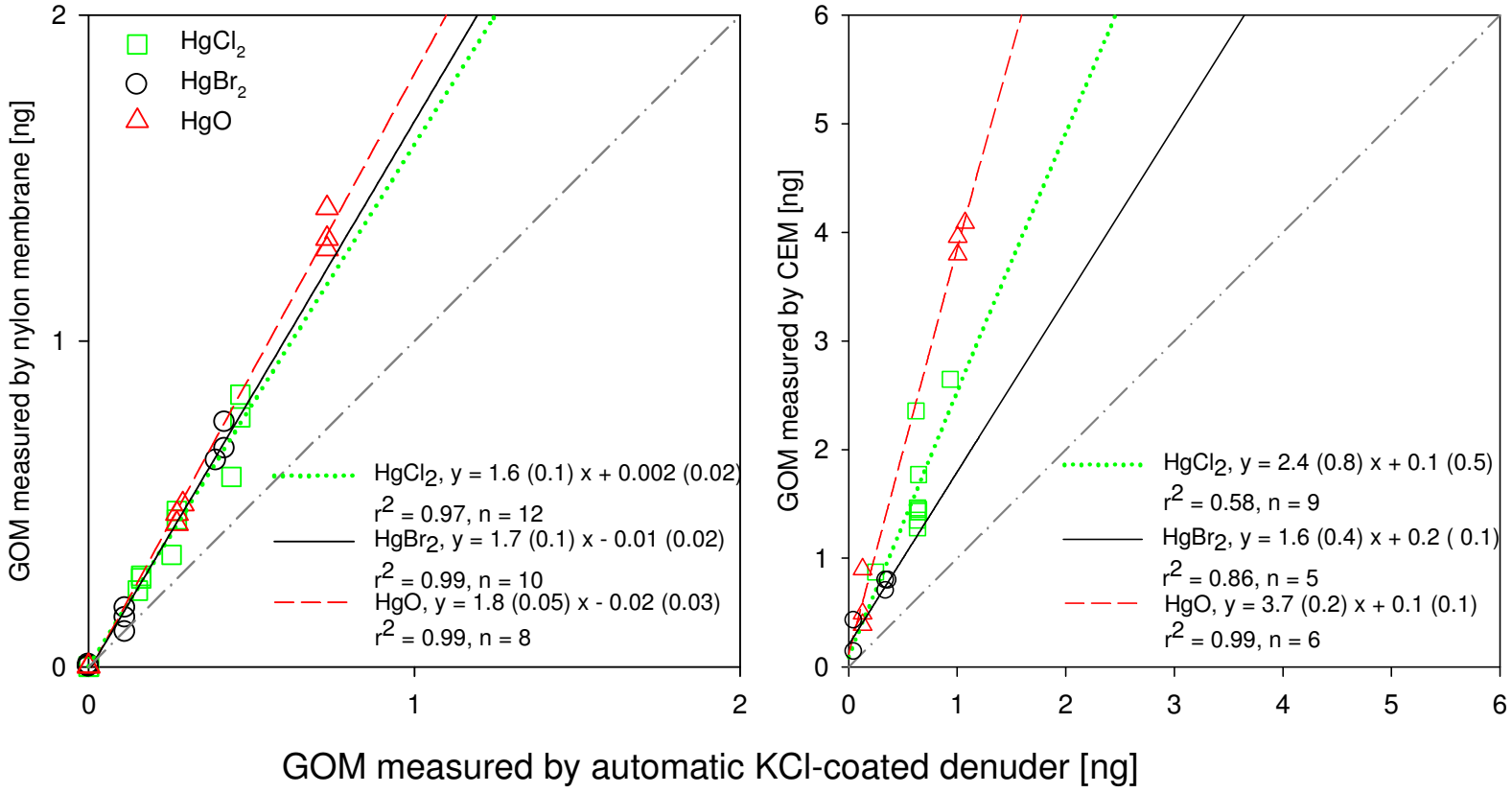
RM comparison between Tekran and DOHGS instruments

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



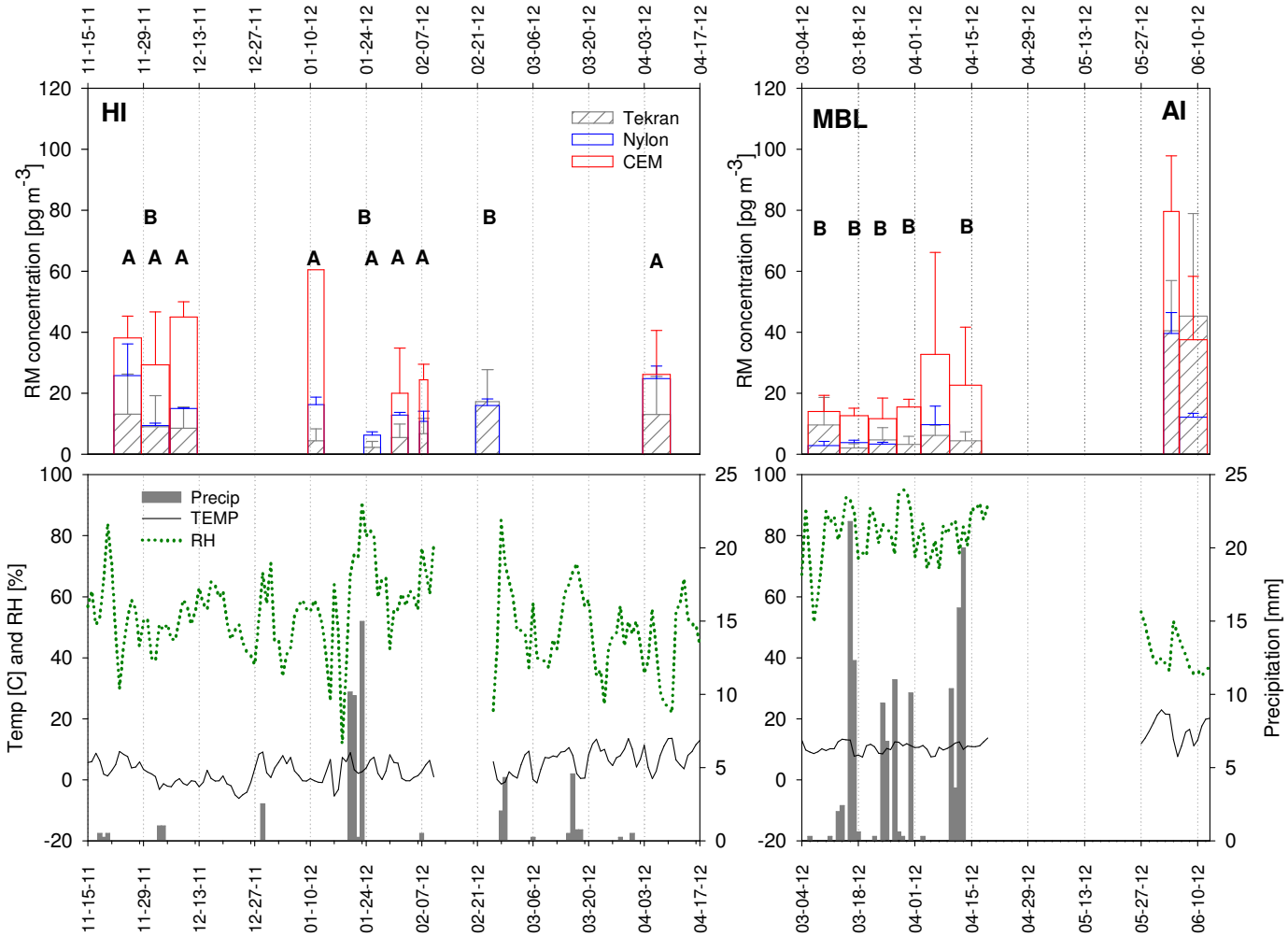
Environmental Science and Technology v 47 Issue 13
Environmental Measurement Methods
Finley et al. Ambrose et al. Gustin et al. 2013

Tekran Uncertainties
Laboratory manifold



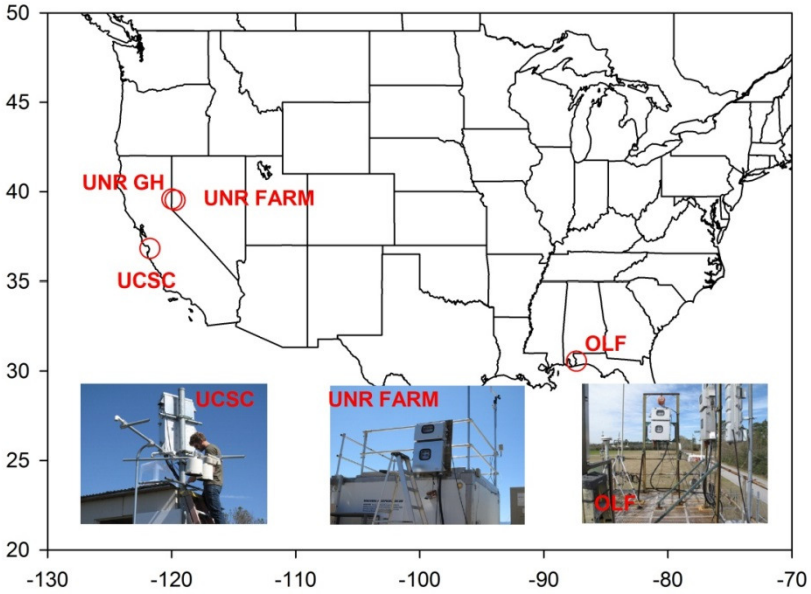
Huang et al., 2013 EST

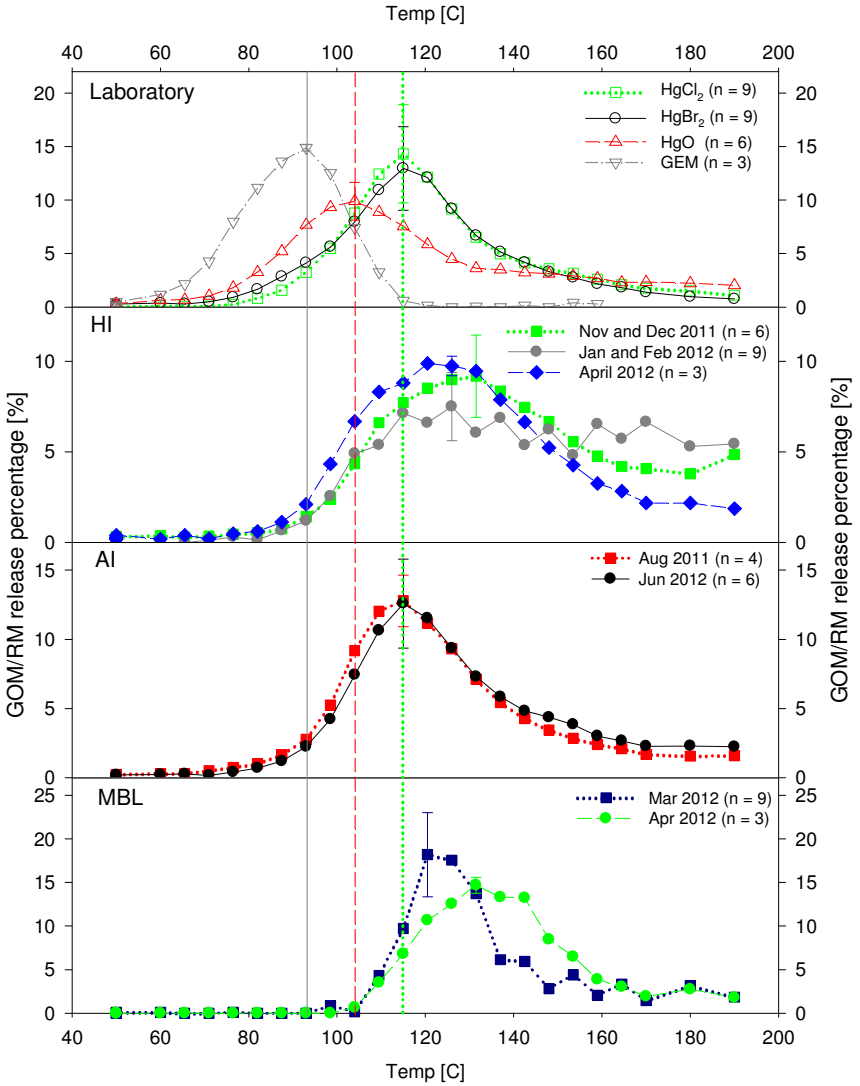
Field measurements



Huang et al., 2013 EST

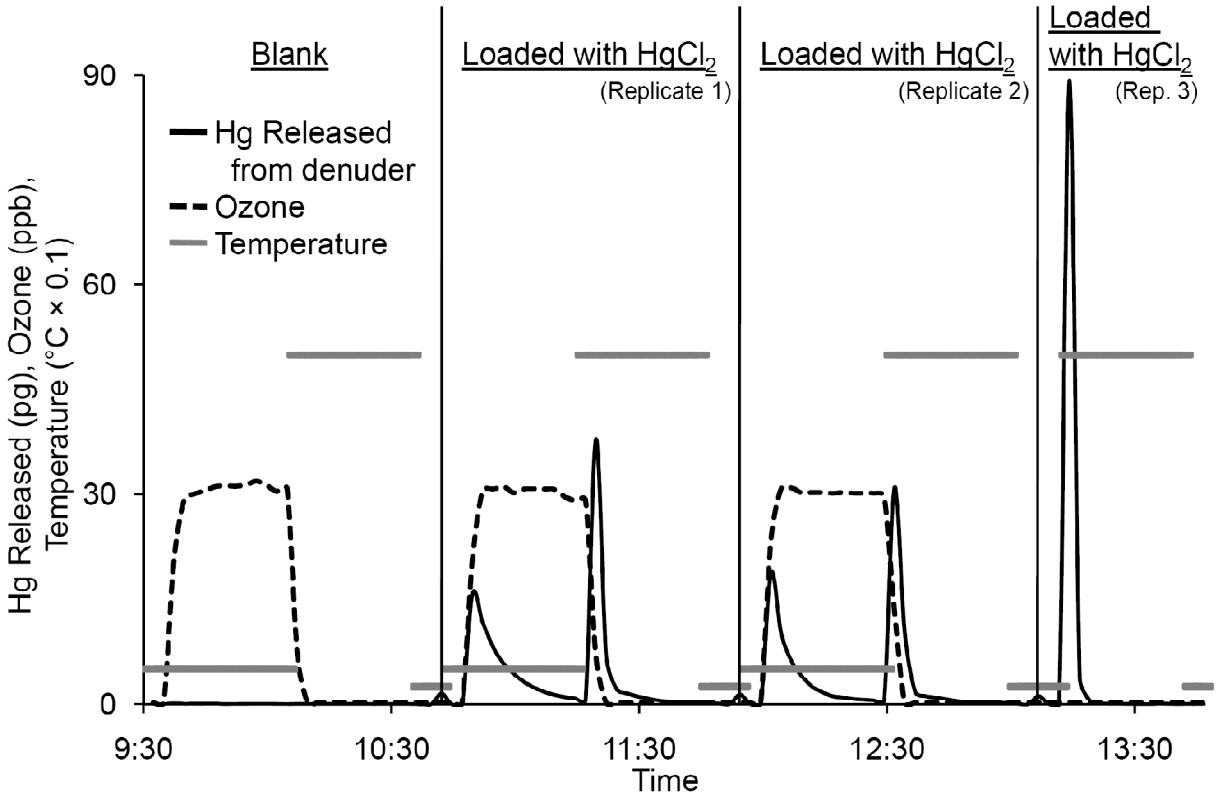
GOM compounds





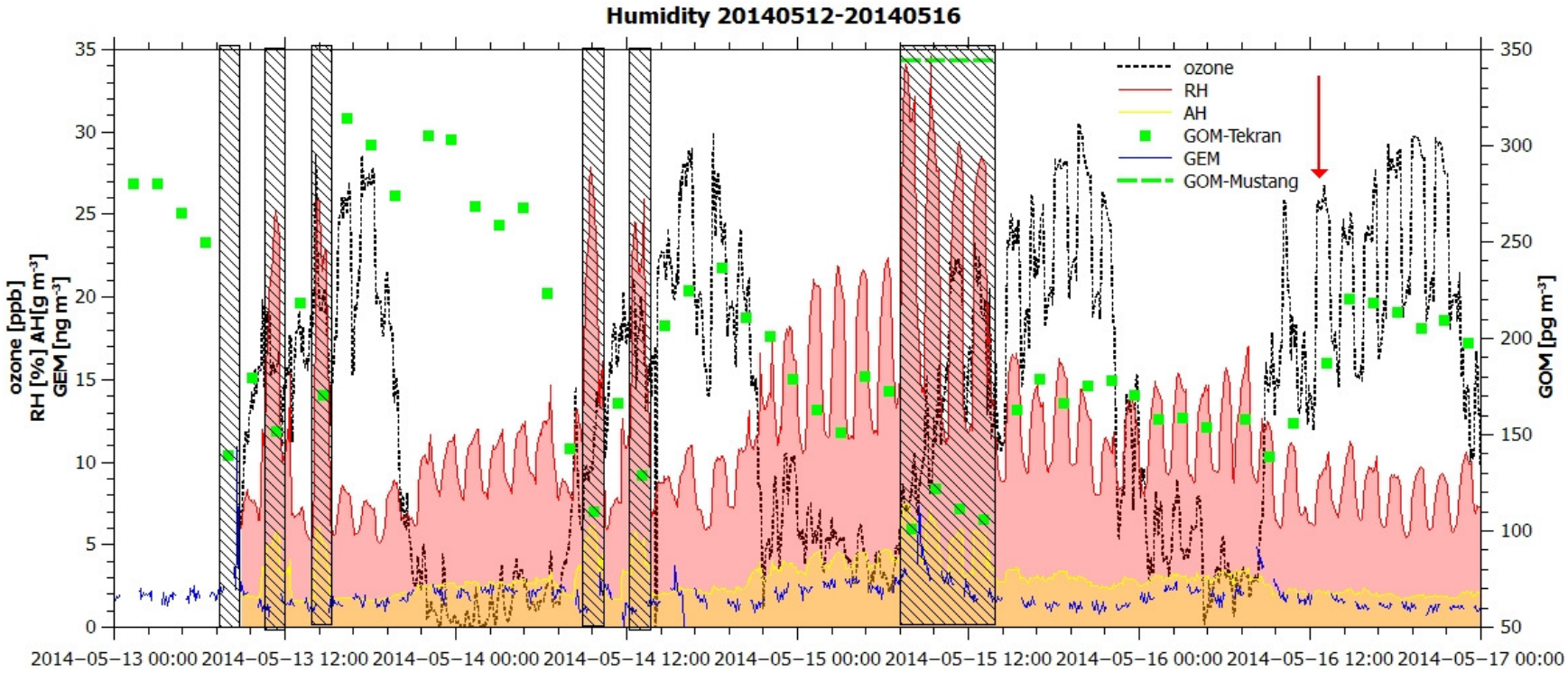
Huang et al., 2013 EST

Laboratory study- Ozone impacts the denuder



Lyman et al. 2010

Laboratory study-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

TGM versus GEM

- Inlet configuration will significantly influence result
- RAMIX insight- covered line and temperature drops results in RM deposition
- Uncovered line results in better transmission of TGM
- Some systematic tests are needed to better understand this

Conclusions

- KCl denuder does not collect different forms of GOM with equal efficiency
- The measurement is biased low and varies as a function of the different forms in air.
- There are interferences with water vapor and ozone that result in GOM being biased low.

Conclusions

- Surrogate surfaces are useful for understanding potential dry deposition
- Passive samplers are useful for understanding relative concentrations
- These samplers may be applied across broad spatial and temporal scales
- The passive sampler method needs to be refined
- Additional laboratory tests are needed to understand and calibrate
- Huang et al 2014 Critical Review Environ. Sci.: Processes Impacts, 16, 374-392.

Conclusions

- GOM compounds vary across space and time
- Source of Hg are global it's the oxidants present that will influence the production of GOM and the GOM chemistry

What are current issues?

- Determine limitations of the denuder so we can interpret data collected in the past
- Additional tests needed for passive samplers
- Unknown GOM compounds in air
- Address uncertainties of PBM measurements
- Lack of world-wide measurement of long term spatial and temporal variation in Hg

How to move forward

- Active system appears to work well for quantifying GOM collected on CEM
- Thermodesorption is a first step at trying to understand presence of different forms in air
- Passive samplers are useful for measuring deposition and assessing concentrations across space and time

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
B dx.doi.org/10.1021/es5026432