MELD Meeting Minutes

2022 NADP Spring Meeting
Hybrid – Virtual and Madison, WI
April 19, 2022

Co-chairs: Richard Haeuber & Colleen Flanagan Pritz
Secretary (Interim): Katherine Ko

Objectives

1. Present Hg updates from NADP program office, including methylmercury aliquoting and dry deposition model estimates
2. Convey status on passive Hg network, and intercomparison of active and passive techniques
3. Provide updates on Minamata convention and related activities, including COP-4 and HTAP
4. Highlight tribal-related efforts
5. Share recent related work on Hg science or findings

Key Takeaways

1. **NADP Program Office Updates:** A few new MDN sites starting very soon. Wyatt Sherlock will be new Site Liaison for AMNet. Conversation re: PETG vs. PET bottles will continue in NOS.
2. **MeHg and Aliquoting**: Consider utility of research, and potential reallocation of funds from MeHg in precip to MeHg in litterfall. Will present motion at NOS.
3. **Passive Hg Testing**: Two phases. Phase I – deploy and compare Mer-PAS and NADP passive samplers. Phase II – assuming acceptable results from Phase I, deploy NADP samplers at Beltsville.
4. **Minamata Convention**: At COP-4, all parties agreed on an EE framework, including an Open-Ended Science Group. Stay tuned on how to get on the roster and register for HTAP meeting May 18th on htap.org.
5. **Tribal Connections**: Potential for Hg measurements on Tribal lands to fill data gaps in the West; some talks underway. Successful data compilation project for Bad River Band of Lake Superior Chippewa. DMP pilot on Tribal lands.

Meeting Agenda (April 19, 1-5pm CT)

1pm: Welcome and Introductions
1:15pm: Hg Updates: NADP Program Office
1:30pm: Updates: Methylmercury and Aliquoting
1:45pm: Updates: Mercury Dry Deposition Estimates for NADP
2:05pm: Updates: Intercomparison of Active and Passive Techniques for GEM and Reactive Mercury Measurements
2:20pm: Isotopic Examination of Atmospheric Sources within the Great Lakes: Intercomparison of Active and Passive TGM Collectors
2:35pm: Minamata Convention on Mercury: COP-4.2 Updates and Discussion
3:15pm: Next Steps: Minamata and The Task Force on Hemispheric Transport of Air Pollution (TF HTAP)
3:30pm: BREAK
3:45pm: Tribal Connections: Opening Remarks

3:50pm: An analysis of mercury data from the Bad River Band of Lake Superior Chippewa, northern Wisconsin
4:10pm: Dragonfly Mercury Project: Tribal and EJ-related Updates
4:20pm: Round Robin
4:50pm: Next Steps
5pm: ADJOURN

- Meeting commenced at 1pm CT
- Colleen presented summary of MELD goals and charges since Fall 2021 Meeting, meeting objectives, and overview of agenda.

Hg Program Office Report

David Gay, WSLH

MDN

- MDN site numbers peaked around Jan. 2009, but the decline appears to have slowed
- 2021 Activity:
    - IL 11 (Bondville, ISWS) closed in Aug. 2021
    - WY06 (Pinedale, BLM) opened Nov. 2021
- Expected Changes (*indicates tribal sites):
    - AK02 – starting any day
    - MN97* – started
    - NE25 – expected
    - SC03 – contract complete, starting very soon
    - MNxx* – talking with EPA Region 5
    - ORxx* – purchasing equipment
    - NC08 – may be moving

AMNet

- Similarly, decline in sites appears to have slowed
- 2021 Activity:
    - MS12 became AK95
    - IL69 – short-term site opened and closed
- Two new GEM-only sites"
    - Talking with Dr. Rodolfo Sosa (and Dr. Rocio Garcia) in Southwest Mexico City using NADP equipment. Hope to get an additional 3rd site going in Mining area.
- EEMS (Eric H.) to do AMNet site visits. More details in NOS.
- Wyatt Sherlock will be Site Liaison for AMNet

Litterfall

- Sample prep will start up in August. Current ongoing sites:
    - MO46
    - NY20
    - NY67
    - NY68
    - NY88
    - OH02
    - OH52
    - OK99
    - SC05
    - TN11
    - WI01
    - WI10
    - GA09
    - IN21
    - IN22
    - IN34
    - MD99
    - MI09
    - MI48
    - MN02
    - MN16

- KY10
- TX22

PET vs PETG Bottles

- Polyethylene terephthalate vs Polyethylene terephthalate glycol.
- We can't get PETG bottle (standard), so we are using PET in the short term.
- And we should also consider PET for MDN long term: +$25,000 cost savings and recyclable.
- No plans to test, lit review appears to be sufficient
- Amy Mager is going to cover PETG bottle situation in NOS

Updates: Methylmercury and Aliquoting

Christa Dahman Zaborske, WSLH

Aliquot Testing Presentation

- **Prompted by these questions**:
  - Acid Concentration and Analyte Stability
  - Extended Deployment
  - Bottle Reuse
  - MeHg Compositing/Contamination/Detectability
- **Spike Stability Data**: 30% recovery on first attempt – where did the Hg go? Second attempt yielded 140% recovery. Hg was stuck to the bottle.
- **Pre-Oxidation Sub-Sample**: Aliquots brominated in-vial (to wash and reuse bottle) had up to 80% difference in sample concentration and 30% recovery.
- **MeHg Aliquot Testing – Questions:**
  - Presence or contamination? What qualifies as contamination or debris? Is contamination under-reported?
    - 75% of historical samples have contamination or debris code
  - Absence or conditions?
    - Acid, matrix, sitting in field, compositing?
  - In Spring 2021, we decided to temporarily stop compositing and analyze MeHg as individual aliquots from samples
  - Additional container contact time and acid testing is in progress
- **MeHg Aliquot Testing – Data**:
  - Started testing with surface waters. All samples with over 0.1 ng/L MeHg are contaminated.
  - Next steps: repeat surface water work using lower concentration of acid
  - If a sample starts with low acid, can it be saved by additional acidification?
  - The difference matrix is likely playing a role. More dissolved solids provides more surface to cling to over the container walls.

Q&A

- S. Janssen: why is NADP studying MeHg in rainfall?
  - J. Renfro, Great Smoky Mountains National Park: Around 2006, a few PIs recommended seeing how much of the MeHg was coming from precipitation. Monthly have been anywhere from 1-7%.

- E. Prestbo: None of the uncontaminated samples detected MeHg – this is consistent with previous findings. Seems like the detects are contaminated. We should drop this analyte and save/redirect funding.
- K. Morris: Monitoring dry dep is important and potentially where we could reallocate funds. We should bring up the question of continuing aliquot testing in NOS.
- P. Weiss: we have found MeHg in fog, but that's a bit of a unique situation. Interesting question, but maybe not worth NADP monitoring.

Updates: Mercury Dry Deposition Estimates for NADP

Muge Yasar Kafadar, WSLH

- We have run the model for four pilot AMNet sites for long term
    - Will be running for all AMNet sites
    - Have prepared all pre/post-processing scripts
- Initial data: Seems like NY06 and OH02 had increasing trend. MD08 and NY43 no strong trends.
- Similar to other findings, we found dry dep contributes as much as wet dep.
- Muge is graduating this year and is compiling research so others can replicate or continue.

NADP Field Test – Passive Hg Determination

David Gay, WSLH

- **Phase 1:** Can NADP create a MerPAS-like sampler?
    - Within the NADP Mercury Labs, we must show we can:
        - Do the analytical work with the same accuracy (Test 1)
        - Clean the sampler well enough (good blanks)
        - Pack charcoal/sulfate into sample cleanly (Test 2)
    - **Test 1:** Do we get the same answer as Tekran?
        - June 2022 for 30 sampling days
        - 10 MerPAS units, half analyzed by WSLH and half by Tekran
    - **Test 2**: Can we fill samplers and get same analytical answer as Tekran?
        - August 2022 for 20 sampling days
        - 10 MerPAS units, half analyzed by WSLH and half by Tekran

Phase 1 Budget				4/18/2022
	Price	#	Cost	
Test 1 Raw Samplers	$ 71.00	10	$ 710.00	
Test 1 Analysis	$ 108.00	5	$ 540.00	
Test 2 Raw Samplers	$ 71.00	10	$ 710.00	
Test 2 Analysis	$ 108.00	5	$ 540.00	
extra carbon	$ 50.00	1	$ 50.00	
Test 3 Analysis	$ 108.00	1	$ 108.00	
Incedentals, HAL Lab	$ 1,000.00		$ 1,000.00	
miscellaneous shipping	$ 200.00		$ 200.00	
Total Expected Cost to PO			$ 3,858.00	

- **Phase 2:** Winston and the MELD intercomparison
- **Considerations brought up**: sampling rate and statistical power. S. Steffan has experience doing this with Tekran samplers in Canada. She is happy to contribute and increase statistical power.
- **Suggested reading**: Naccarato et al. 2021 on MerPAS

Minamata Convention on Mercury: COP-4.2 Updates and Discussion

Liz Nichols, Dept. of State; Sandy Steffens, ECCC/Canada

- Going into COP-3, they had presented a conference room paper (CRP) by Canada and Norway, outlining proposed EE framework. They left with little success. Dissent was largely concerning data validation and transparency.
- COP-4 met in Bali, renegotiated these concerns, and all parties agreed on an effectiveness evaluation.
    - EE has officially launched
    - Eight operational paragraphs
    - COP-5 will revisit timing and EE committee (number of regional representatives still up for debate)
    - Open-ended science group will be established
- Each country will nominate one person to officially be on the open-ended science group, to serve as an organizer and funnel for the country. They should be able to pull in additional roster of experts.
    - USA: Terry Keating
    - Canada: Sandy Steffen

Next Steps: Minamata and The Task Force on Hemispheric Transport of Air Pollution (TF HTAP)

Terry Keating, EPA

Open-ended Science Group (OSG)

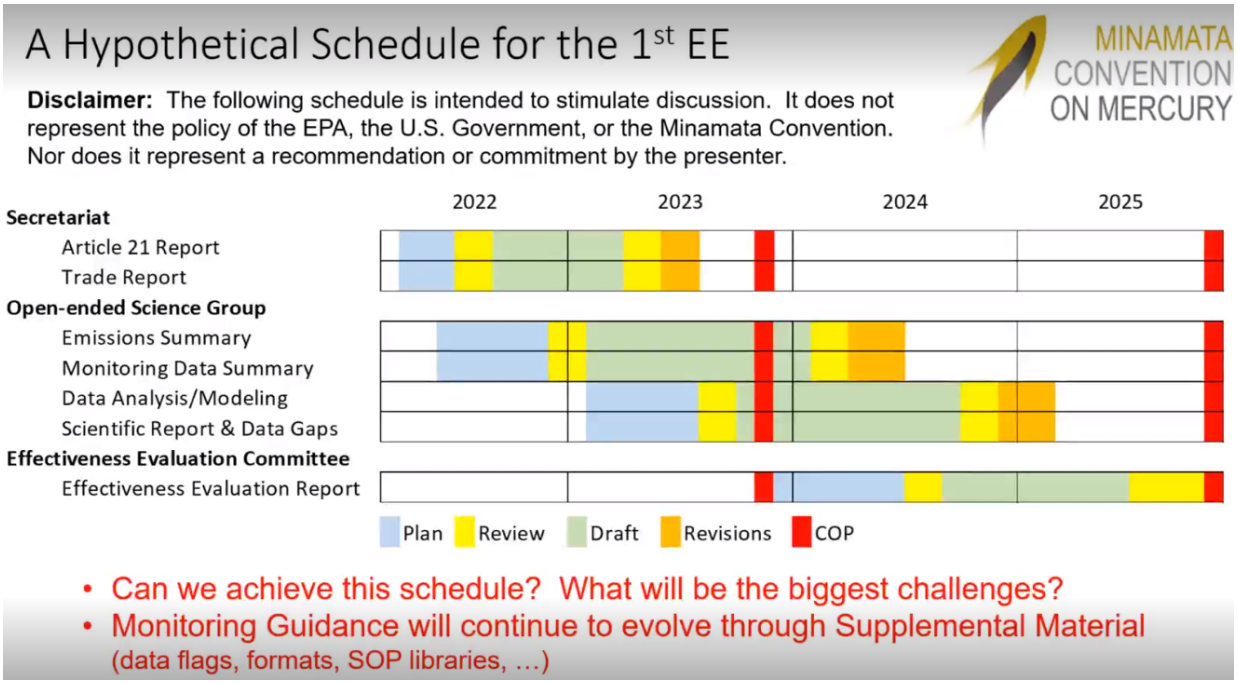
- Members – one expert nominated by each party
- Roster of additional experts

- Max of two in-person meetings
- Emissions, monitoring, analysis/modeling
- Plan, draft, "final"
- Maximum of two meetings – TBD when those will be held

Guiding Questions for Monitoring Objectives:

- Estimation of mercury concentration for areas without (i.e., background sites) or with (i.e., affected sites) local anthropogenic sources
- Identification of temporal trends
- Characterization of spatial patterns
- Estimation of source attribution of anthropogenic mercury
- Estimation of exposure and adverse impacts
- Quantification of key environmental processes to improve understanding of cause-effect relationships

Hypothetical schedule for the first EE

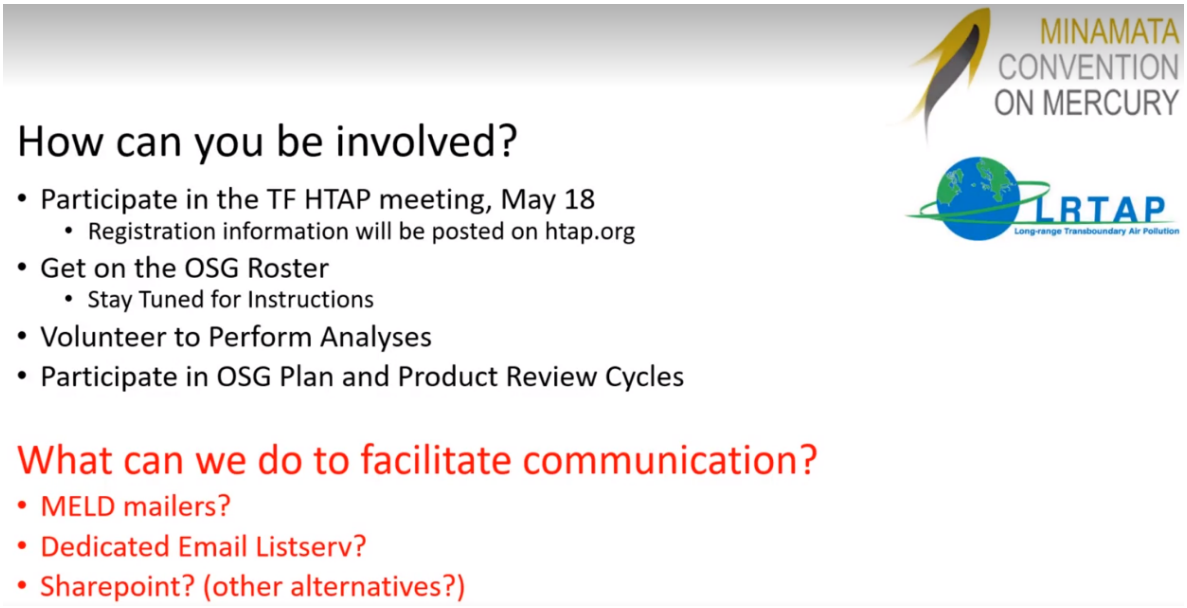


- Goal is to finish by Cop-6 in 2025

Can we apply HTAP to OSG?

- Side by side comparison of existing emissions estimates
  - Global and regional datasets
  - Sectoral and non-anthropogenic datasets
- Global and regional modeling intercomparison & evaluation
  - Present year surface flux comparison
  - Trend attribution?
- What work can be completed by 2023? By 2024?

How to Get Involved



Updates: Intercomparison of Active and Passive Techniques for GEM and Reactive Mercury Measurements

Winston Luke, NOAA

- **Motivation**: We need alternate/simpler/lower-cost methods to measure GEM, COM, and PBM, Reactive Mercury (RM) to reduce measurement bias, reverse decline of AMNet sites, and expand Hg monitoring networks worldwide for effective evaluation

Tiered Approach to Hg Monitoring for Minamata EE

- Tier 1 – default, aka price of entry. Documents mercury trends and spatial distribution in air and in wet dep over broad geographic areas.
- Tier 2 – optional. Explains temporal trends and attributes mercury sources to mercury concentrations in biota.
- Tier 3 – optional. Improves representativeness of the measurements and understanding of key processes using advanced measurement techniques and sophisticated research.

Locations of Intercomparisons

- Eagle Heights, Madison, WI
- Beltsville AMNet, MD (MD99)
- National Central University AMNET (TW00), Taipei

Two Phases to Intercomparisons

- Phase I – Spring/Summer 2022?
    - Deploy Tekran MerPAS and NADP's Passive samplers ("N-PAS"?) at Eagle Heights and Beltsville, MD.

Measurement Summary – Phase I: Spring/Summer 2022 (?)

Instrument	GEM	GOM	PBM	Beltsville, MD	NCU Taipei, Taiwan	Eagle Hts, Madison, WI	Temporal Resolution	Goal	Who Does Analysis?
Tekran MerPAS (duplicate)	Y			Y		Y	4 weeks	Compare to N-PAS and Tekran; sampler precision	Tekran
NADP-PAS (duplicate)	Y			Y		Y	4 weeks	Compare to MerPAS and Tekran , sampler precision, blanks	NADP

- Phase II – Fall 2022?
    - Assuming acceptable results in Phase I, deploy N-PAS samplers at Beltsville and at NCU, Taiwan.

Measurement Summary – Phase II: Fall 2022 (?)

Instrument	GEM	GOM	PBM	Beltsville, MD	NCU Taipei, Taiwan	Eagle Hts, Madison, WI	Temporal Resolution	Goal	Who Does Analysis?
Tekran Speciation	Y	Y	Y	Y	Y		continuous, hourly	Average & compare to MerPAS, Japan manual, USGS	NOAA
Tekran Difference	Y	Y (RM)		Y			continuous, hourly	Compare GOM/PBM averages to GOM+PBM average from Tekran Speciation, RMAS	NOAA
NADP MerPAS (duplicate)	Y			Y		Y?	4 weeks	Compare to USGS, Tekrans, Japan; sampler precision	NADP
ECCC MerPAS (duplicate)	Y			Y?	Y?	Y?	Quarterly	Compare monthly MerPAS to ECCC (quarterly), Japan, USGS, Tekran Speciation and Difference; sampler precition	ECCC
NCU Passive Hg (duplicate)	Y				Y		4 weeks	Compare to MerPAS, Tekran Speciation, Japan Method; sampler precision	NADP
Japan Manual Method (duplicate)	Y			Y	Y	Y?	1 week	compare to MerPAS GEM, USGS, Tekrans; sampler precision	MOEJ
U Nevada RMAS		Y (RM)		Y?			2 weeks	Compare to Tekran Speciation and Difference (w/filter)	UN Reno
USGS GEM Isotope Sampler	Y			Y?			2 weeks	Compare to Tekrans, MerPAS, Japan	USGS

Questions to Answer

Questions to Answer

Phase I

How do the N-PAS samplers compare to Tekran's MerPAS samplers (precision, accuracy, blanks) at two locations?

Phase II

How do the N-PAS samplers (monthly) compare to quarterly ECCC passives?

How do the N-PAS GEM concentrations compare to a monthly average Tekran (speciation and difference systems), manual gold trap method, USGS Isotope method?

How do these comparisons vary at different sites (Beltsville, NCU)?

How does the NOAA Difference system (RM) compare to Tekran speciation, RMAS? Effect of different substrates to remove RM (GEM side)?

Percent Difference, GEM/PBM & GOM, versus Tekran (accuracy)

Percent Difference, Duplicate N-PAS & Japan Manual (accuracy and precision)

Average blank associated with a monthly N-PAS sample

Issues to Address

- Can Japanese method be adapted to run for seven days at reduced flow rate?
- Need to check with ECCC, UNR, USGS on participation
    - S. Steffen (ECCC) is in!
- Best start time and duration for all groups
- Manpower considerations

Isotopic Examination of Atmospheric Sources within the Great Lakes: Intercomparison of Active and Passive TGM Collectors

Sarah Janssen, USGS

- Sources of Hg to Lake Superior – **Objective**: to assess Hg fingerprints in atmospheric endmembers and measure tributary water to differentiate sources
- Expected bigger precipitation input, but the data match litterfall and soil (sources are watershed derived).
- Next Steps:
    - **Intercomparison**: working with ECCC and UToronto to compare active and passive Hg isotope samplers (USGS TGM sampler vs. MerPAS units)
    - **Sites**

Site	Site Type	Partner	Active TGM	MerPAS	Precip
Evansville, Manitoulin District, Ontario, Canada	Remote	ECCC	X	X	
Huron Mainstee National Forest, Oscoda, MI	Remote	USDA	X	X	
University Center, MI	Urban	Saginaw Valley State University	X	X	X
Outside Bay City, MI (TBD)	Rural	Saginaw Valley State University	X	X	
Bad River, WI **	Rural	Bad River Band	X	X	X
Eagle Heights, WI	Urban	NADP	X	X	X

** Bad River, WI is the most well characterized TGM isotope site, original data was collected for the pilot work in 2016-2018, collection started again in 2021

- **Lab Method**: switched to activated carbon traps (more comparable to passive samplers)

Tribal Connections: Opening Remarks

David Schmeltz, EPA

- EPA currently has 7 tribally operated CASTNET sites, with an 8th site coming soon in Southern California.
- Tribal lands overlap with gaps in active NADP/MDN sites (particularly out west), and they are interested in mercury data and research.

- Encourage folks to continue giving presentations to form tribal partnerships – e.g., National Tribal Forum on Air Quality (NTFAQ) in Tulsa, OK (May 2022). The following talks are sneak previews of what folks will be presenting there.

An analysis of mercury data from the Bad River Band of Lake Superior Chippewa, northern Wisconsin

Doug Burns, USGS

Objectives

- Compile existing disparate Hg data, collected in variety of environmental compartments over several years by several different agencies.
- Evaluate risk to human and ecosystem health.
- Identify data gaps and make recommendation.

Background

- Bad River tribal landscape has high DOC ("brown water"), high suspended sediment, and a history of disturbance (mining in headwaters)
- Data files spanned about 12 years, on surface waters, bed sediment, biota, and wild rice.

Findings

- **Surface waters:**
    - FTHg concentration moderately high – exceeds State of Wisconsin Human and Wildlife Criteria by more than 2-fold
    - Methylation efficiency is high (10.9%)
- **Bed sediment**: relatively low THg concentrations
- **Fish**: State of Wisconsin fish consumption guidelines (0.05 mg/kg for children and 0.16 mg/kg for general population)
    - Walleye consumption is a concern for general population
        - Blood Hg levels of Chippewas correlated with how recently Walleye was consumed (Peterson et al. 1994)
        - Strong linear relationship between fish length and Hg concentration. 23.7 in and 19.8 in. GLIFWIC recommend not to consume Walleye more than 20 in.
- Levels in bald eagle feathers and river otter fur are the highest of any biota in this study, consistent with regional vales. May be sublethal neurological effects on bald eagles and river otters.
- **Wild rice**: Hg concentrations were higher than surface water but lower than fish.
- Ratio of MeHg/THg is high
- **Data**: Burns, D.A., 2020, Mercury data from the Bad River Watershed, Wisconsin, 2004–2018: U.S. Geological Survey data release, https://doi.org/ 10.5066/ P9HRS2C3.
- **Report**: Burns, D.A., 2020, Compilation of mercury data and associated risk to human and ecosystem health, Bad River Band of Lake Superior Chippewa, Wisconsin: U.S. Geological Survey Open-File Report 2020–1095, 19 p., https://doi.org/10.3133/ ofr20201095

Dragonfly Mercury Project: Tribal and EJ-related Updates

Collin Eagles-Smith, USGS; Sarah Nelson, AMC; Colleen Flanagan Pritz, NPS

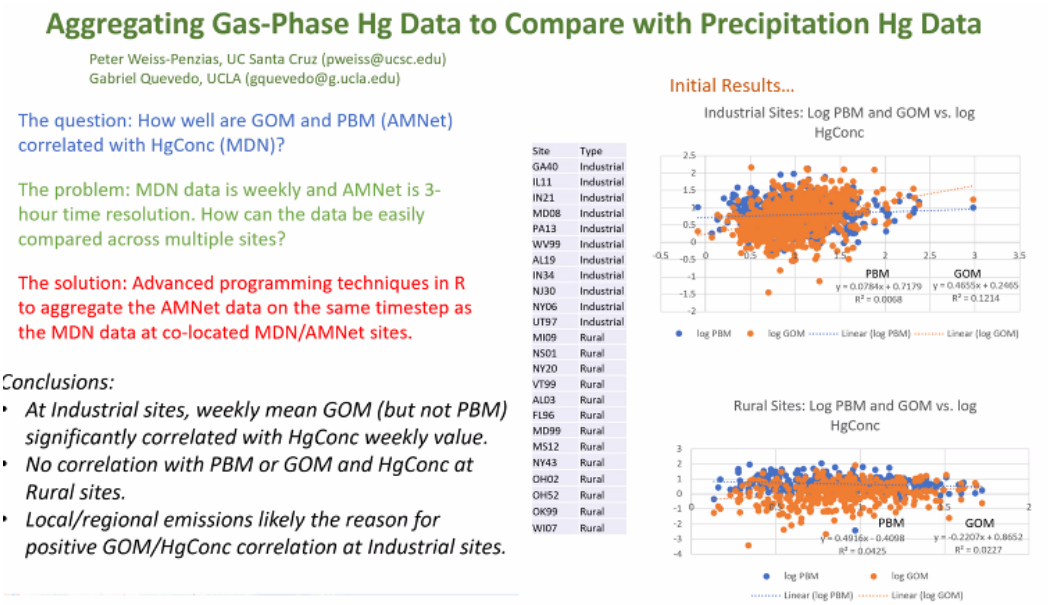
- **Tribal Engagement:** pilot partnership with Penobscot Nation and Houlton Band of the Maliseet Indians, in partnership with Katahdin Woods & Waters NM in northeastern U.S. Also, Grand Canyon river trip with tribal youth, in partnership with Grand Canyon Youth and Ancestral Lands Program.
- **Dragonfly Mercury Project Data Visualization Dashboard:** Dragonfly Mercury Project Data Visualization Tool (U.S. National Park Service)
- **Merrimack River Watershed:** connecting people to place in remote and urban settings while informing mercury risk at local to national scales.
    - Branch of DMP sampling in partnership with Appalachian Mountain Club and Dartmouth College in the EJ communities of Lowell and Lawrence, MA. Also partnering with local teachers to engage students
    - Use EPA's Environmental Justice Screening and Mapping Tool to see local proximity to Superfund sites
- Dragonfly sampling at the UW Arboretum (recently designated a NPS National Natural Landmark) – inaugural sampling, in partnership with a professor of Ecotoxicology from Beloit College. Potential future meeting field trip?

Round Robin

Aggregating Gas-Phase Hg Data to Compare with Precipitation Hg Data

Peter Wiess-Penzias, UC Santa Cruz and Gabriel Quevedo, UCLA

- **The Question**: How well are the GOM and PBM (AMNet) correlated with HgConc (MDN)?
- **The Problem**: MDN data is weekly and AMNet is 3-hour time resolution. How can the data be easily compared across multiple sites?
- **The Solution**: advanced programming techniques in R to aggregate AMNet data on same timestep as MDN data at co-located sites
- **Findings:**
    - **Industrial sites**: GOM (but not PBM) is significantly correlated with HgConc. Local/regional emissions likely the reason.
    - **Rural sites**: No correlation with GOM or PBM and HgConc.



- G. Wetherbee: cool start! Encourage you to look at precip data on NADP website too.
- S. Steffen: let's connect offline, and we may be able to get you two more datasets.

Other notes from Joint:

- There is interest from Jamie Schauer in a "Mercury Portfolio - Panel Discussion" to strategize on all NADP Hg networks at the next MELD meeting.

Next Steps

Hope to see you in Knoxville in the fall!