Minnesota Statewide Hg Total Maximum Daily Load Meeting

National Atmospheric Deposition Program

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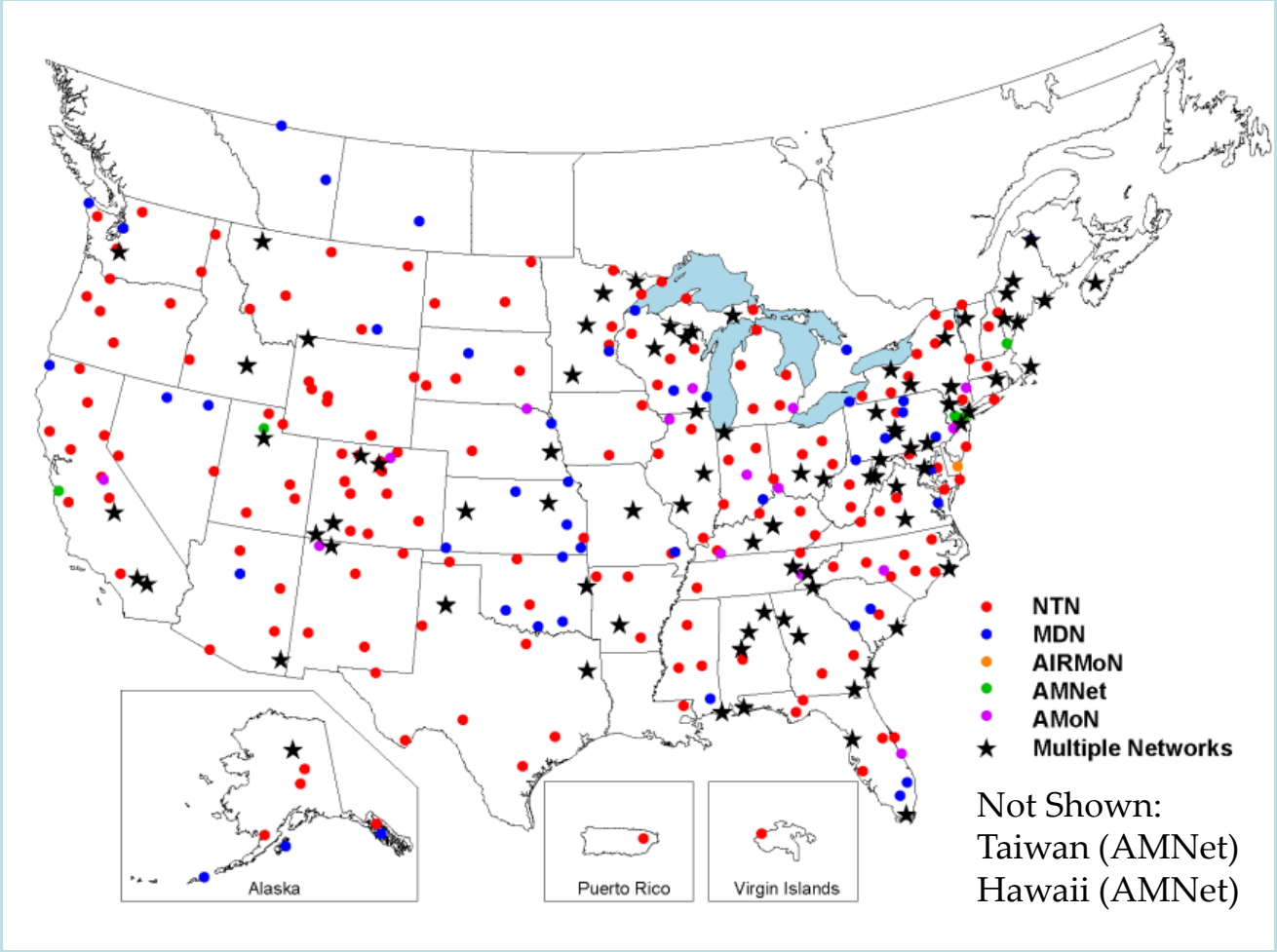
UNIVERSITY OF WISCONSIN-MADISON

Section 1. A Quick Update on All Things MDN/AMNet/MLN

- NADP is a Cooperative Research Support Project (USDA, @Un of Wisconsin)
  - Approximately $3.1 million dollars per year – direct support
  - We are a "National Research Support Project" (NRSP #3) of the US Department of Agriculture
  - measure wet deposition of pollutants ("precipitation")
    - Or pollution flux out of the atmosphere/into the biosphere
  - We also measure gaseous concentrations for dry deposition calculations
  - over North America at ~350 monitoring locations,
    - Hawaii, US Virgin Islands, Puerto Rico
    - and one site in Asia & Bermuda
  - ~ 600,000 historical precipitation samples for 10 analytes
    - Started in 1978, 45th year (NTN network)
    - Mercury measurements since 1996
    - Gaseous ammonia measurements since 2010

https://nadp.slh.wisc.edu/



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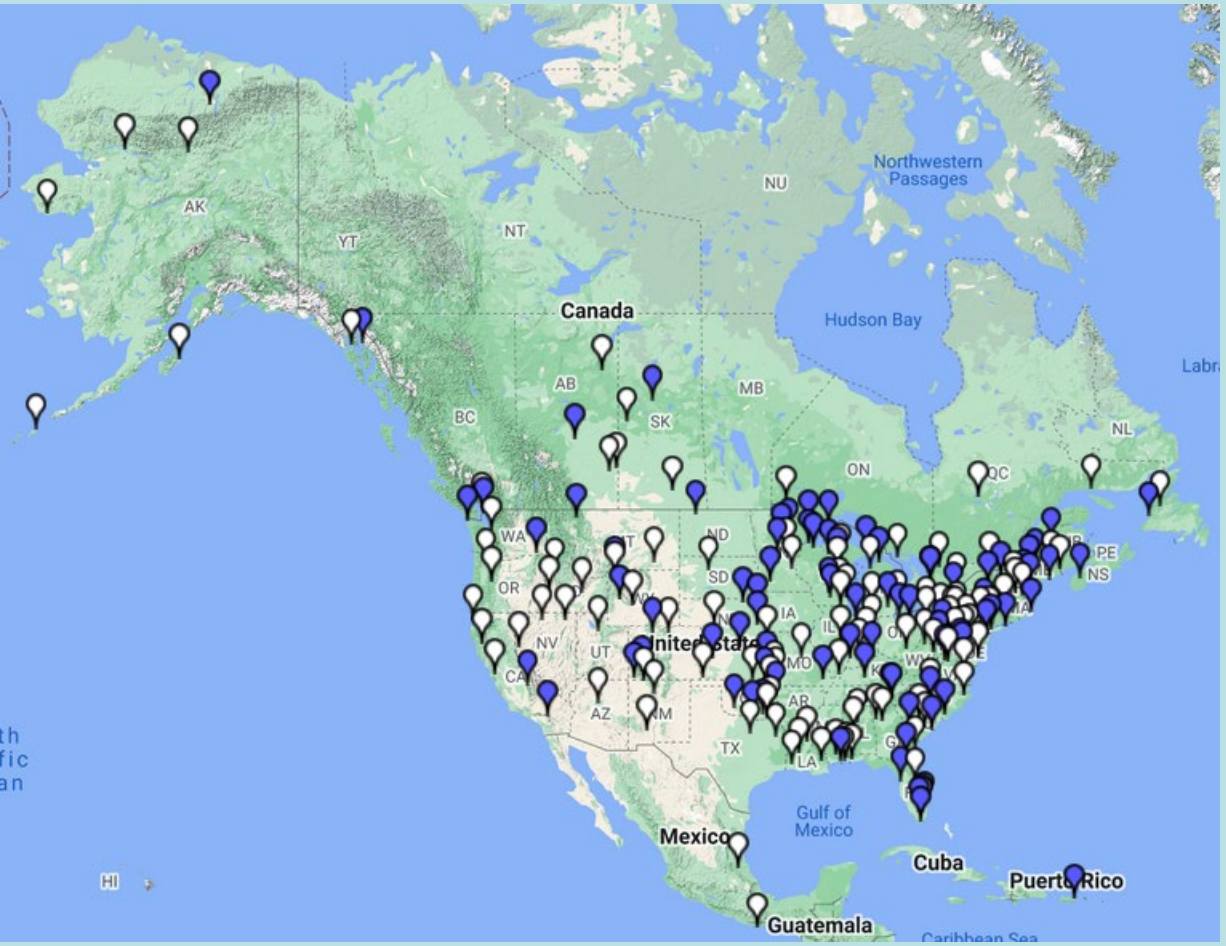
Mercury Deposition Network



- Currently: 85 active sites

- Brule River (WI08) was saved, now operating at WI92, operated by Nathan Kilger (Bad River Band of Lake Superior Chippewa, but will need long term funding (EPA R5 is involved, Michelle Becker). Also making PFAS measurements.

Possible Funding isuue

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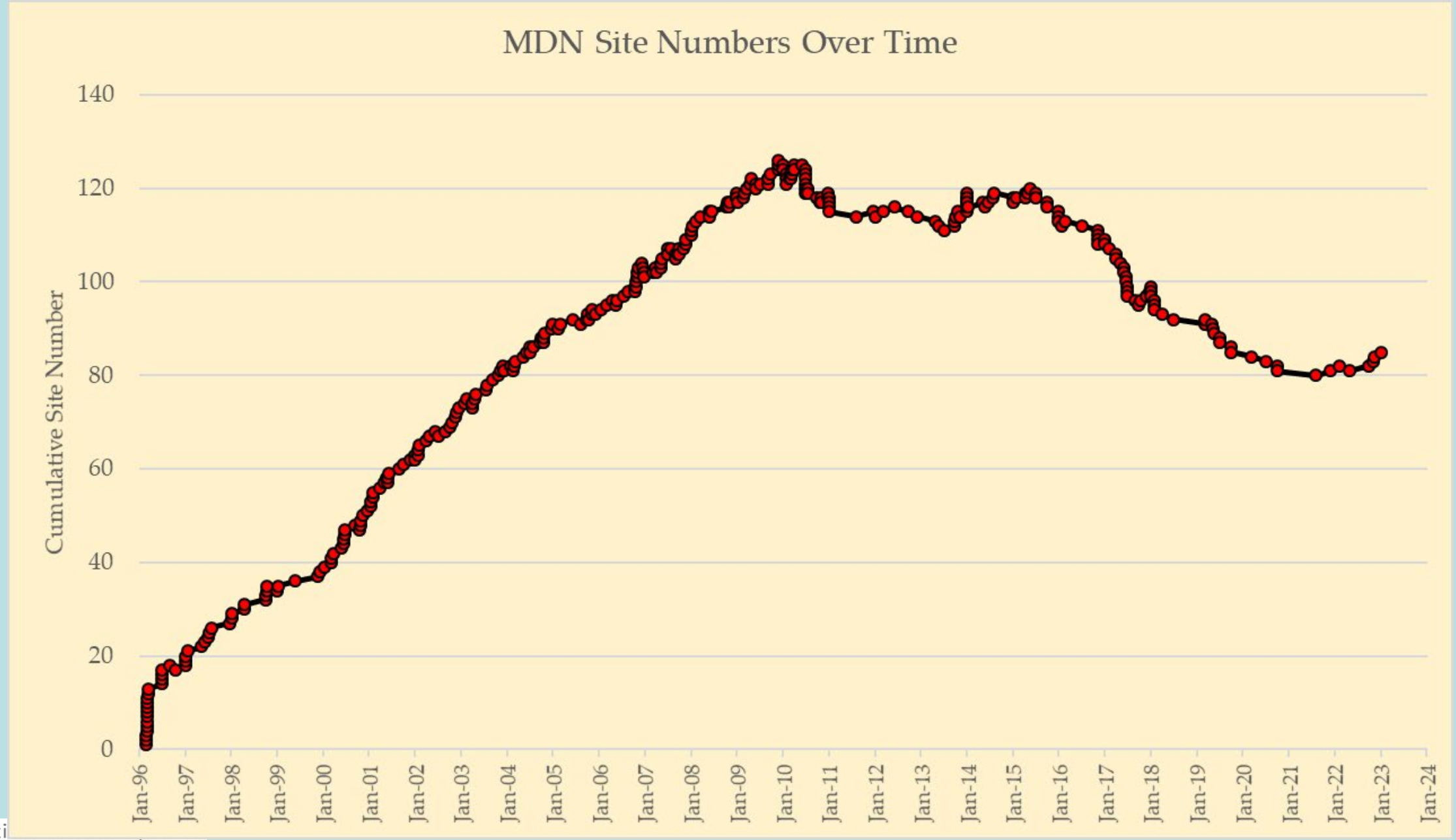

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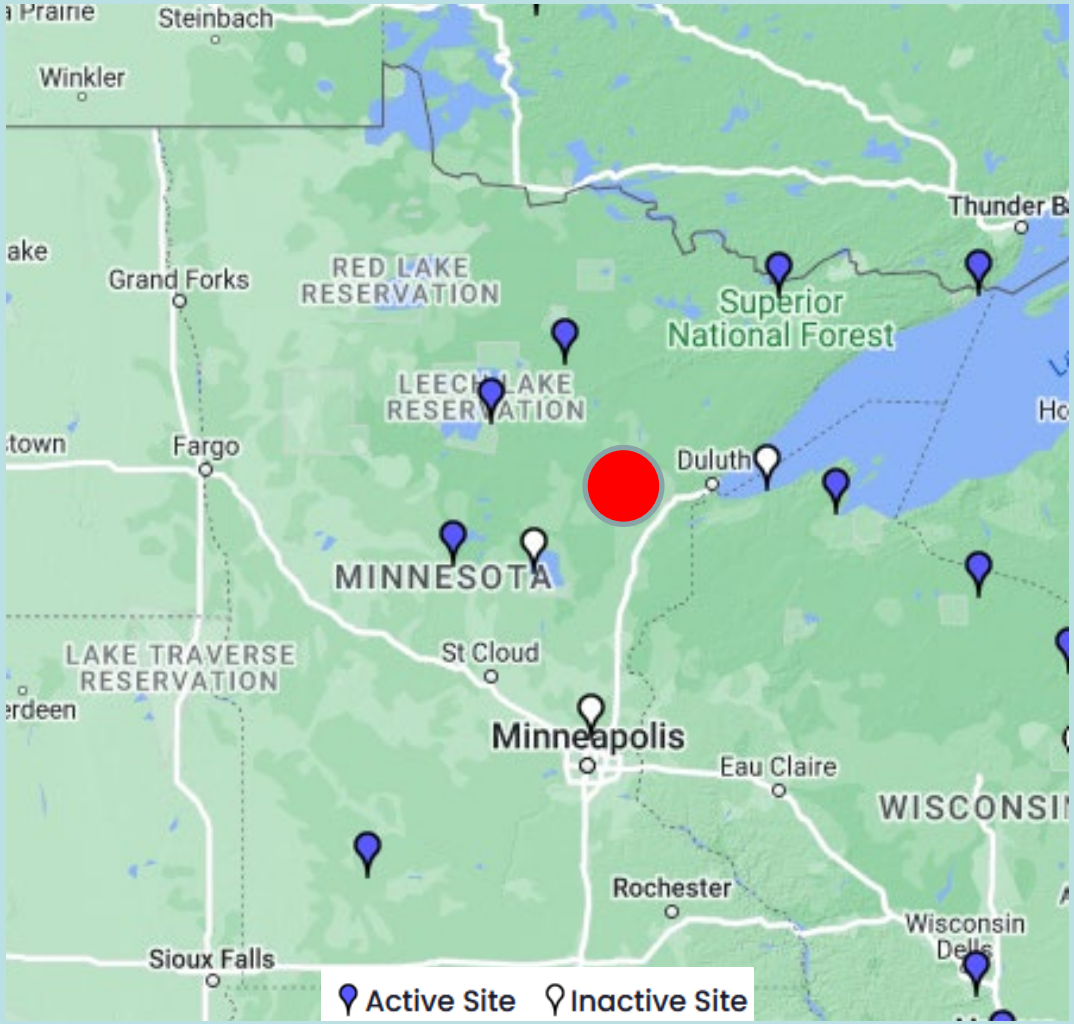
MN MDN Sites



Site	Site Name	County	Elev	Site Start	Site End	Acitve Inactive	Site Surround
MN06	Leech Lake	Cass	1311	6/23/2014		Active	Isolated
MN16	Marcell Experimental Forest	Itasca	431	2/27/1996		Active	Isolated
MN18	Fernberg	Lake	524	3/5/1996		Active	Isolated
MN23	Camp Ripley	Morrison	410	7/2/1996		Active	Isolated
MN27	Lamberton	Redwood	367	7/2/1996		Active	Isolated
MN97	Grand Portage Band of Chippewa	Cook	2	2/3/2022		Active	
MN22	Mille Lacs Band of Ojibwe	Mille Lacs	384	4/23/2002	4/3/2007	I	Isolated
MN98	Blaine	Anoka	275	2/5/2008	1/2/2018	I	Urban

MN05 Fond du Lac/EPA Region 5, should start soon

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Draft 2022 Map?

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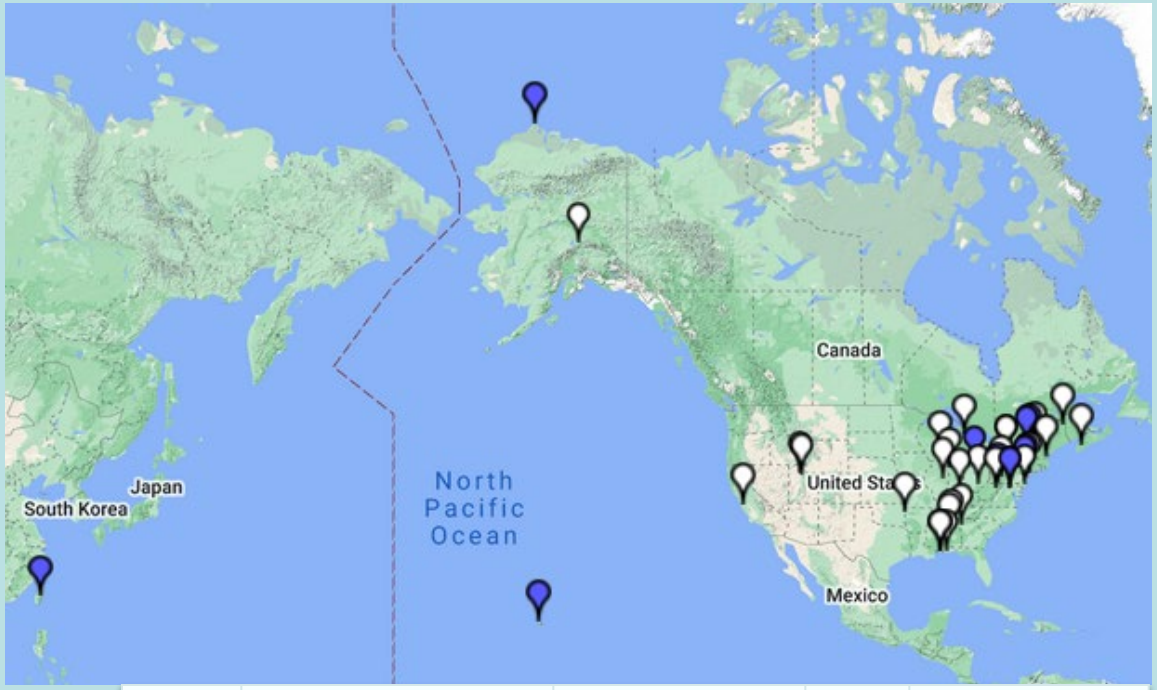
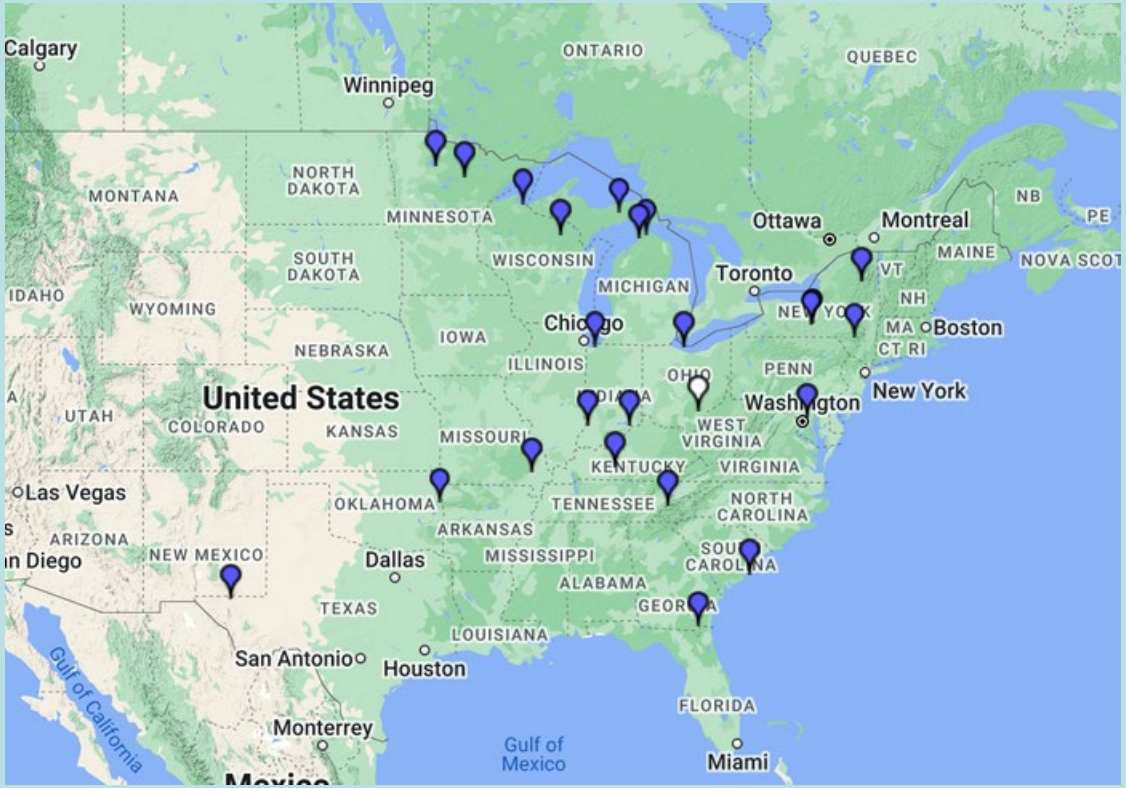
AMNet



AK95	Utqiagvik		AK	2021-10-08
HI00	Mauna Loa	Hawaii	HI	2010-12-30
MD08	Piney Reservoir	Garrett	MD	2008-01-01
MD98	Beltsville	Prince Georges	MD	2007-01-26
NJ30	New Brunswick	Middlesex	NJ	2015-10-01
NJ54	Elizabeth Lab	Union	NJ	2015-10-01
NY20	Huntington Wildlife	Essex	NY	2007-11-21
NY98	Whiteface Mountain	Essex	NY	2020-09-30
OH52	South Bass Island	Ottawa	OH	2011-12-31
TW01	Mt. Lulin		TW	2010-01-01

- Currently: 10 active sites
- Newest: a Tekran Elemental system was delivered to Dr. R. Sosa/UNAM, June
- Request for equipment, Vietnam (Nguyễn Lý Sỹ Phú, Guey-Rong Sheu's student)
- Ohio 02 (Athens) is purchasing all new equipment, new site and trailer

Mercury Litterfall Network (MLN)



- Currently: 24 active sites

- Newest:
  - KY10, Mammoth Cave National Park, 2021-09-08
  - TX22, Guadalupe Mountains NP, TX, 2021-09-01
  - TN97, Great Smokey NP (Jim Renfro) second site, for 1 year
  - MN02, Red Lake Nation
  - WI92, Bad River Nation

- Sampling for this year began in August

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Mercury Litterfall Network

- Measures mercury in litterfall (leaves, twigs, bark, etc.) and mercury flux to ground
- Nanograms mercury per square meter per year
- An estimate of dry deposition of mercury

– *Sampling for 11th season started in August*

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Section 2. A Few New Things You Might Find Interesting

Atmospheric Passive Hg Effort

- Things are moving along towards a MerPAS-based passive Hg capability
- 2 sets of NADP passive Hg sampler, MerPAS starting April 1 are now complete.
- There is a 1 month vs 2 month vs 3 month QC test ongoing at Eagle Heights
- Christa is working through the Canadian SOP for developing our "own" passives based on the MerPAS. First test of this is very soon.
- Overall Goal: determine how well we can make passive Hg samplers and how much it would cost for network operation

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New Bag Sampling for MDN?

- I have this new idea

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Section 3. Some Trends Results that Could Be Important?

A few years ago….

Science of the Total Environment 568 (2016) 546–556

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Trends in mercury wet deposition and mercury air concentrations across the U.S. and Canada

Peter S. Weiss-Penzias [a,*], David A. Gay [b], Mark E. Brigham [c], Matthew T. Parsons [d], Mae S. Gustin [e], Arnout ter Schure [f]

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What we wanted to do…

- Do a long term trends paper on Mercury deposition
- Then we got the idea to look at shorter term trends
  - these are less dependable due to less data
  - but they could get more directly to ecosystem response
- Hg Emissions were going down
- All the trends work was showing negative trends

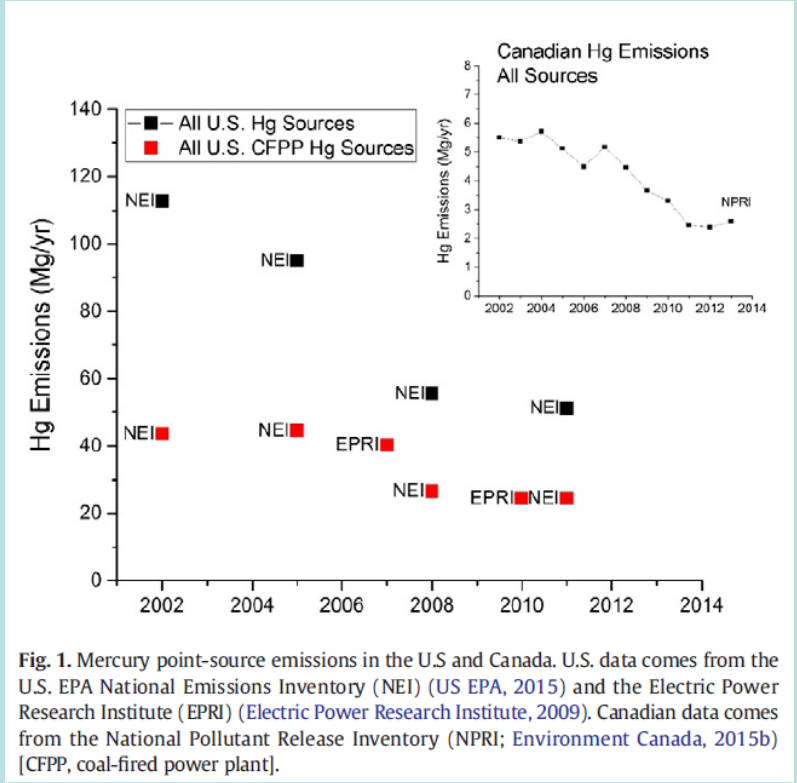

Fig. 1. Mercury point-source emissions in the U.S and Canada. U.S. data comes from the U.S. EPA National Emissions Inventory (NEI) (US EPA, 2015) and the Electric Power Research Institute (EPRI) (Electric Power Research Institute, 2009). Canadian data comes from the National Pollutant Release Inventory (NPRI; Environment Canada, 2015b) [CFPP, coal-fired power plant].

- We did trends at all MDN sites for availed years, but for different periods

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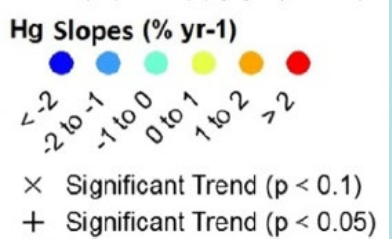
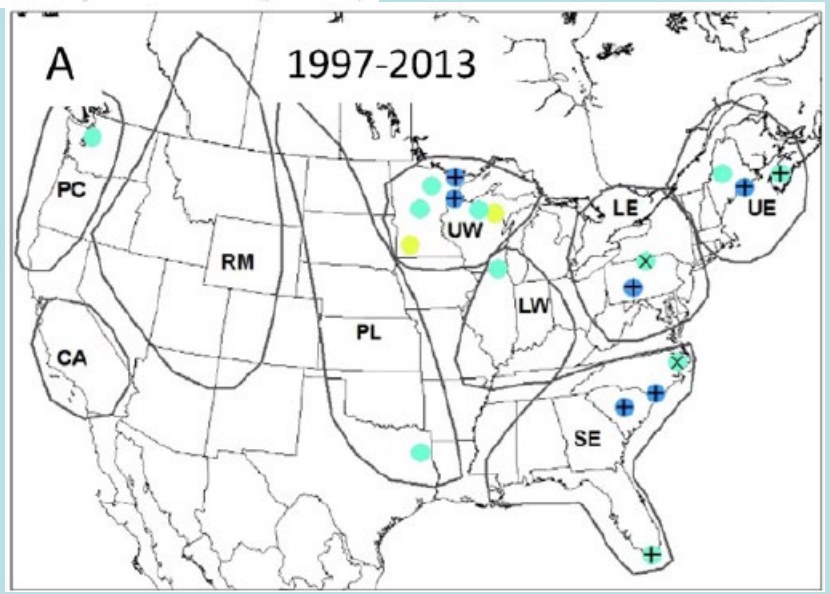
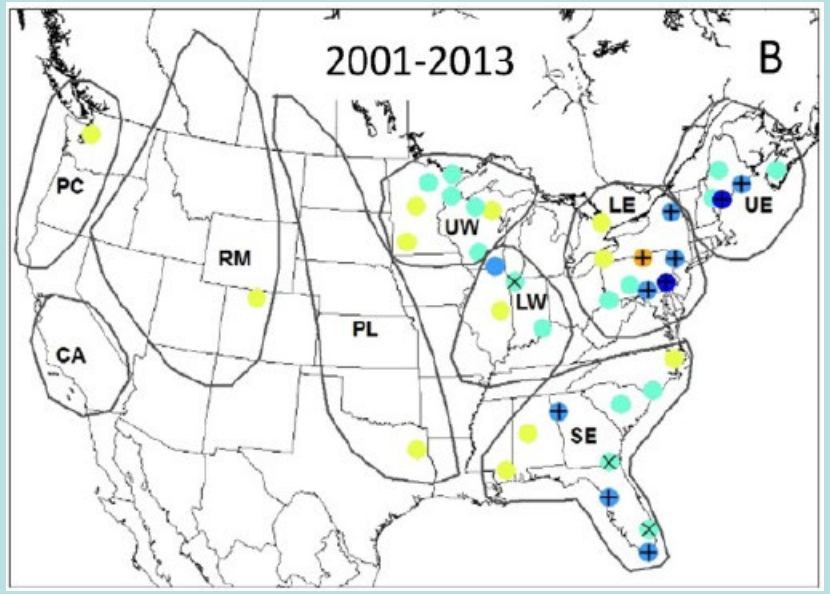
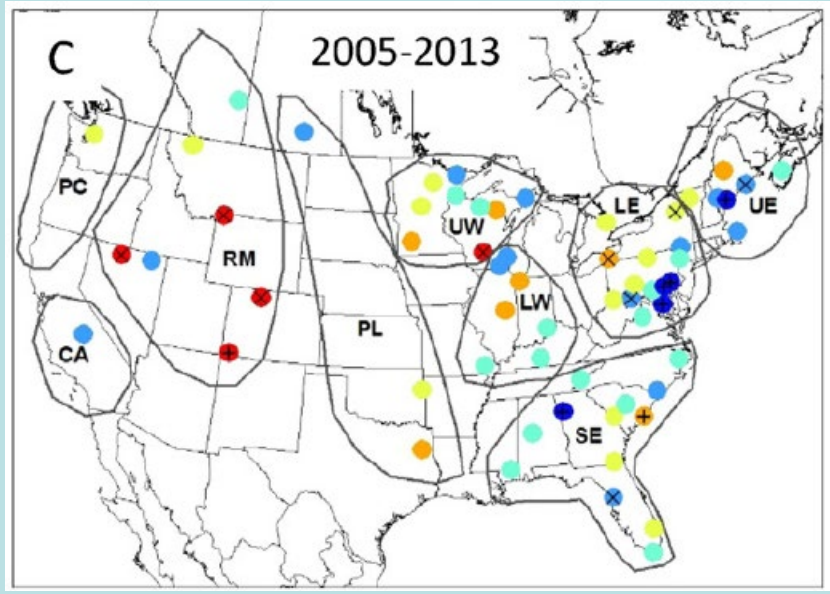
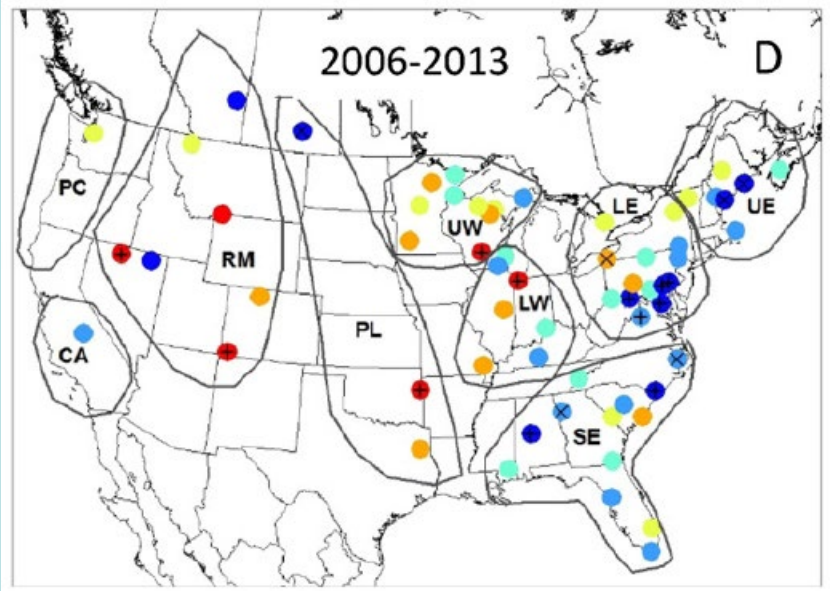
Trends we saw…

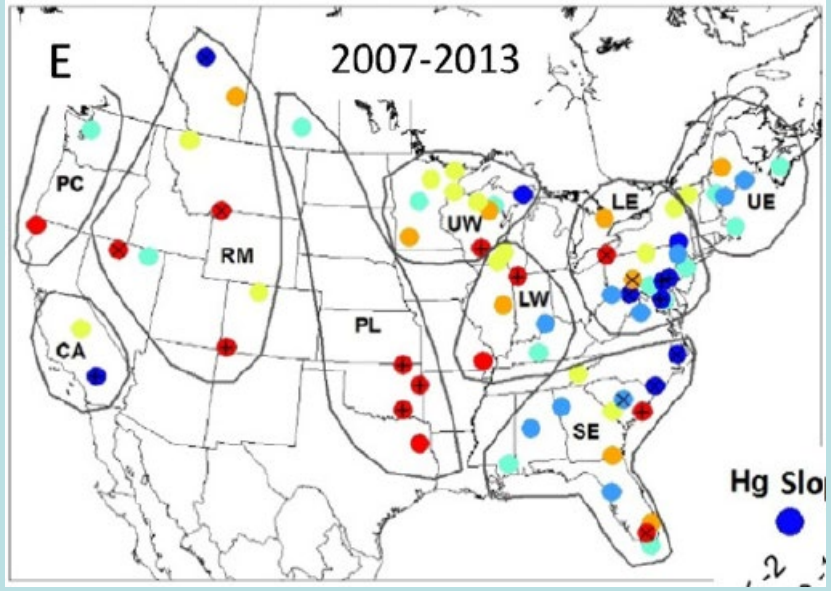


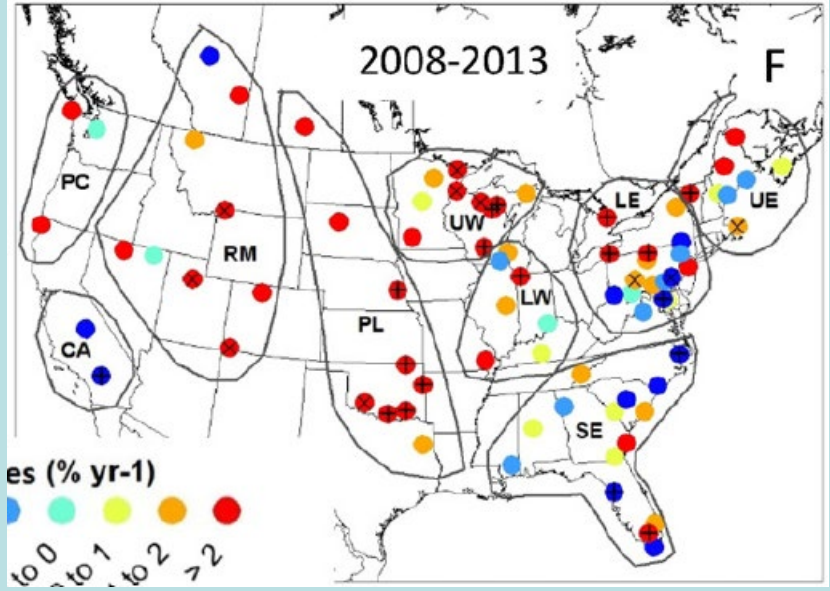












Regional Trends

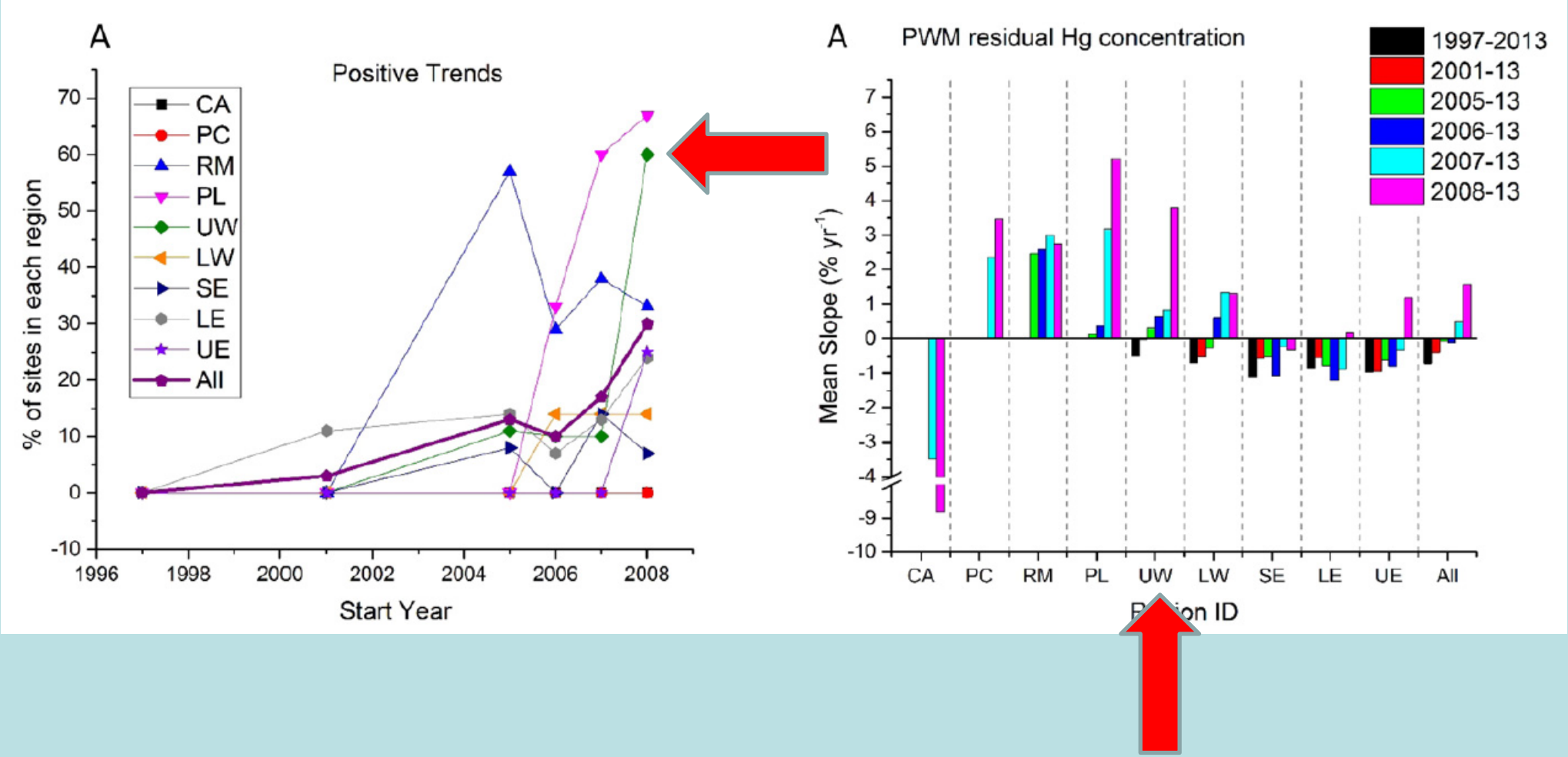


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Table 1
Trend analysis on PWM-residual Hg concentration, monthly sums of Hg deposition, and monthly sums of precipitation for the time periods shown by region and for all sites together using the regional Mann–Kendall (RMK) method. NT stands for "no trend" meaning statistical significance ($p < 0.05$) was not met. NA stands for "not appropriate," meaning that there were significant and dissimilar site and season trends so that a Mann–Kendall regional test was not valid. **Pos** and ***Neg*** indicate statistical significance and direction of the trend.

Region	2001–2013			2007–2013			2008–2013		
	Hg Conc	Precip	Hg Dep	Hg Conc	Precip	Hg Dep	Hg Conc	Precip	Hg Dep
California (CA)	–	–	–	NT	NT	NT	***Neg***	NT	NT
Pacific Coast (PC)	–	–	–	NT	NT	NT	NT	NT	NT
Rocky Mountain (RM)	–	–	–	**Pos**	NT	**Pos**	**Pos**	NT	**Pos**
Plains (PL)	–	–	–	**Pos**	NT	NT	**Pos**	NT	NT
Upper Midwest (UW)	NT	**Pos**	NT	NT	**Pos**	**Pos**	**Pos**	NT	**Pos**
Lower Midwest (LW)	NT	**Pos**	NT	**Pos**	NT	NT	NT	NT	NT
Southeast (SE)	***Neg***	NT	NT	NT	NT	NT	NT	NT	NT
Lower Northeast (LE)	NA	**Pos**	NT	NT	NT	NT	NT	NT	NT
Upper Northeast (UE)	***Neg***	**Pos**	NT	NT	NT	NT	NT	NT	NT
All	NA	**Pos**	**Pos**	NA	**Pos**	**Pos**	NA	NT	**Pos**

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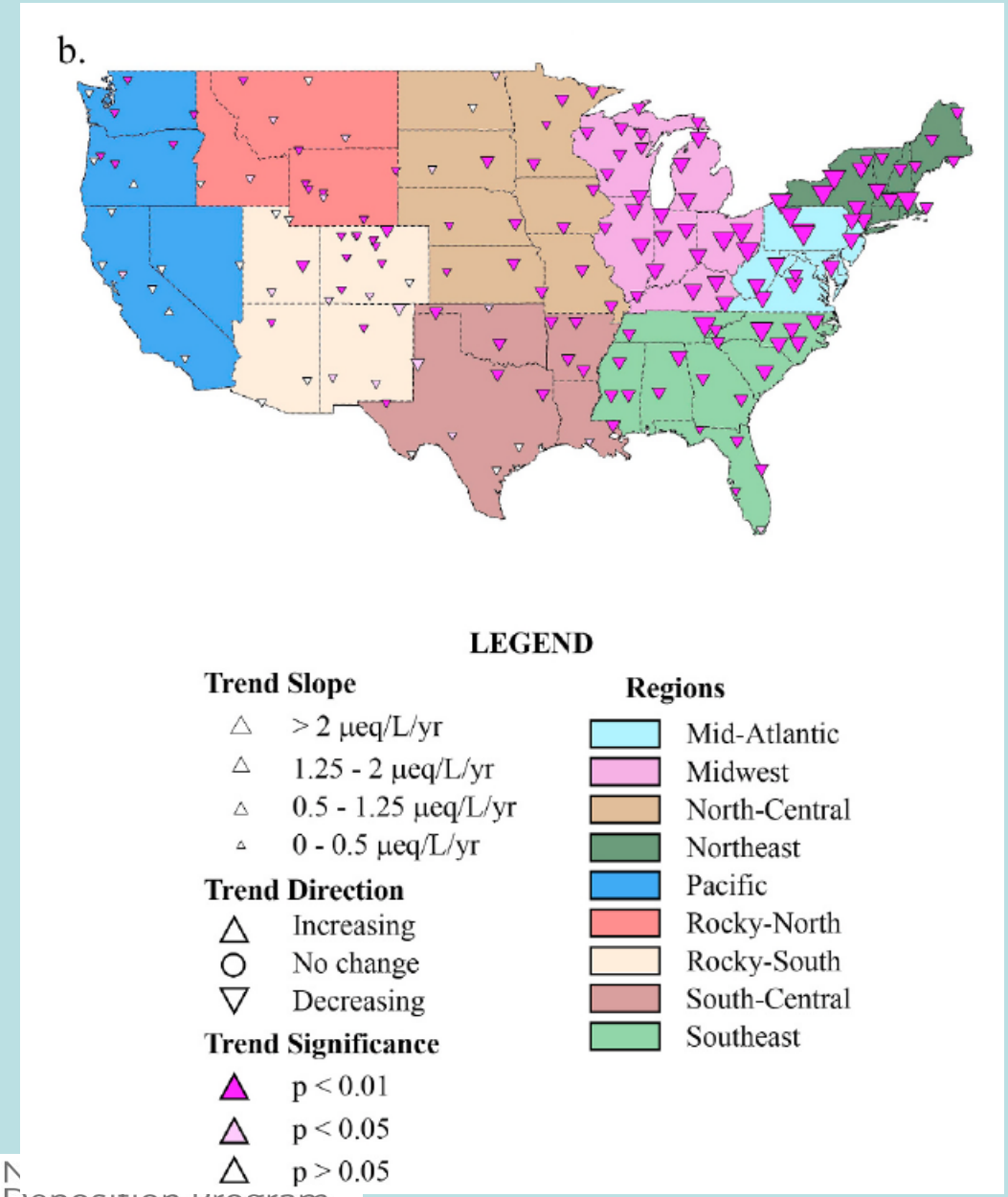
Message

- Just be careful working just with the long-term trends
- Short term might be more important for your TMDLs

Section 4. Sulfur and Nitrogen Trends

Sulfate Trends, 2000-2017



<u>Sulfate</u>

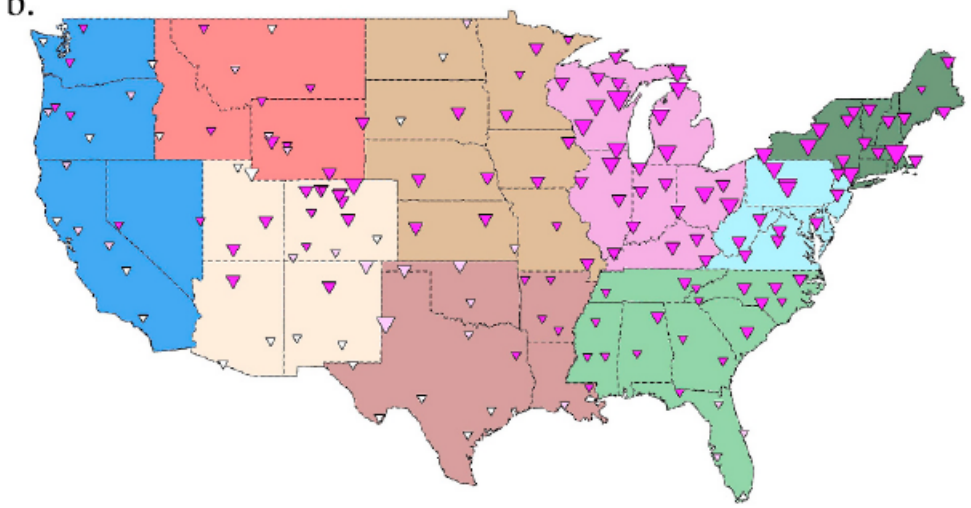
is going down,
Just about everywhere
Particularly in the East and Midwest

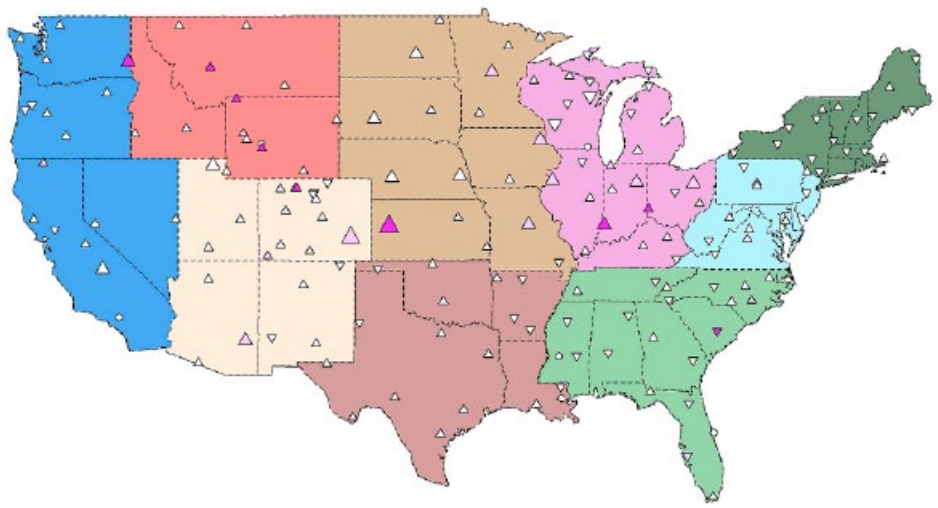
at 99% Confidence (1% error rate)

Nitrate Trends, 2000-2017

Ammonium Trends, 2000-2017

b.





LEGEND

Trend Strength

- △ > 1.125 µeq/L/yr
- △ 0.75 - 1.125 µeq/L/yr
- △ 0.375 - 0.75 µeq/L/yr
- △ 0 - 0.375 µeq/L/yr

Trend Direction

- △ Increasing
- ○ No change
- ▽ Decreasing

Trend Significance

- ▲ p < 0.01
- △ p <= 0.05
- △ p > 0.05

Regions

- Mid-Atlantic
- Midwest
- North-Central
- Northeast
- Pacific
- Rocky-North
- Rocky-South
- South-Central
- Southeast

<u>Nitrate</u>

is going down,

moderately, at 99% Confidence (1% error rate)

<u>Ammonium</u>

- Some increasing, some decreasing
- Not significant at 95%

Atmospheric Environment 247 (2021) 118219

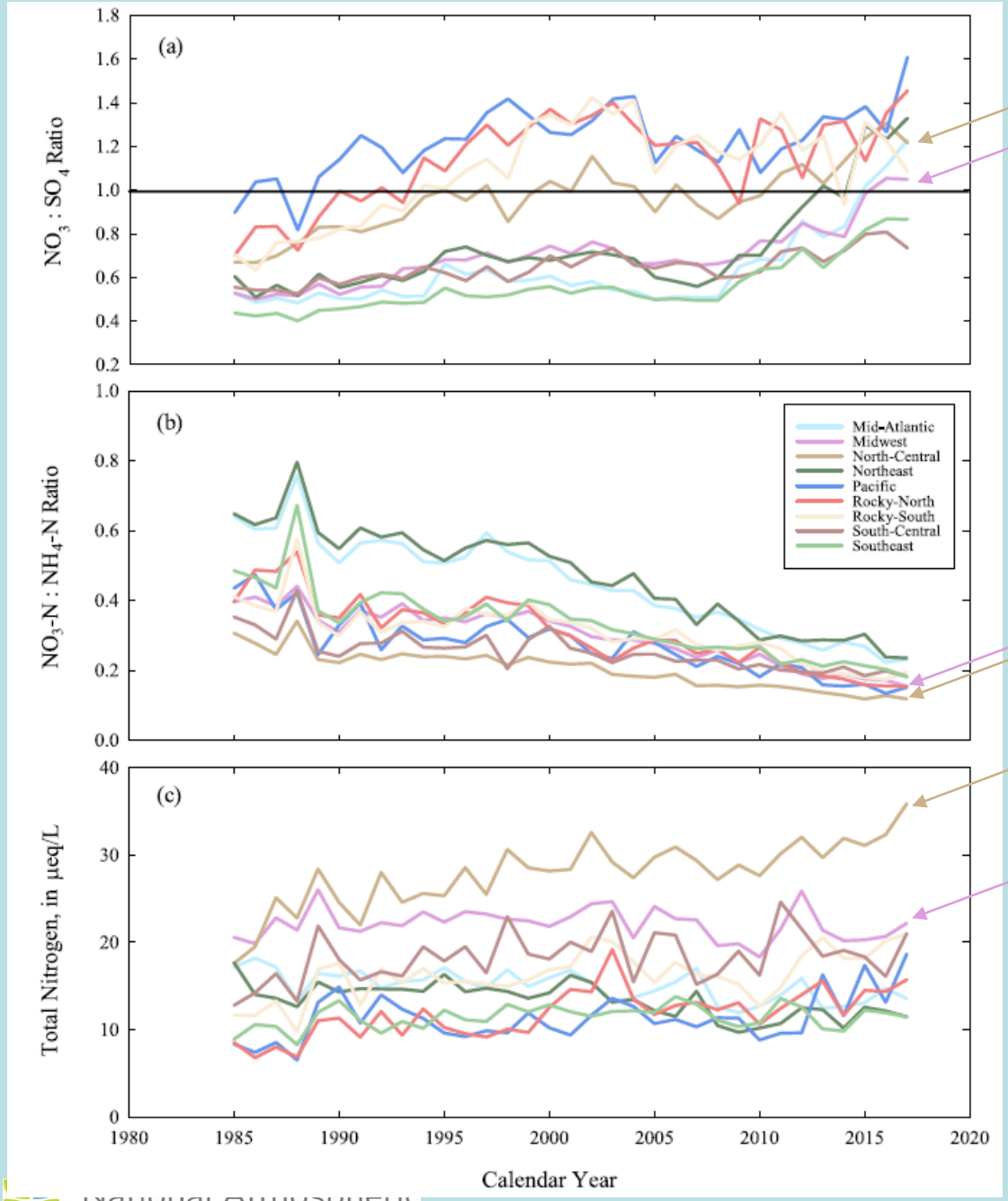
Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: http://www.elsevier.com/locate/atmosenv

Trends in precipitation chemistry across the U.S. 1985–2017: Quantifying the benefits from 30 years of Clean Air Act amendment regulation

Michael R. McHale [a,*], Amy S. Ludtke [b], Gregory A. Wetherbee [c], Douglas A. Burns [a], Mark A. Nilles [b], Jason S. Finkelstein [a]



NO3: SO4 Ratio

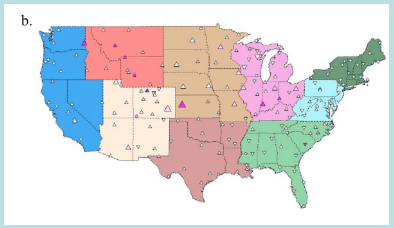
- Nitrate is now more important that sulfate
- Stronger in the west and southwest of MN

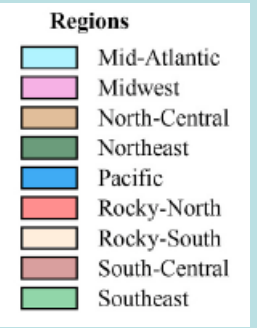
N (NO3): N (NH4)

- Ammonium N is more important than Nitrate N

Total N (NO3+NH4)

- Strongest nitrogen signal in the US, Midwest/North Central





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Percentage Ammonium of all Inorganic N (NH4 + NO3)

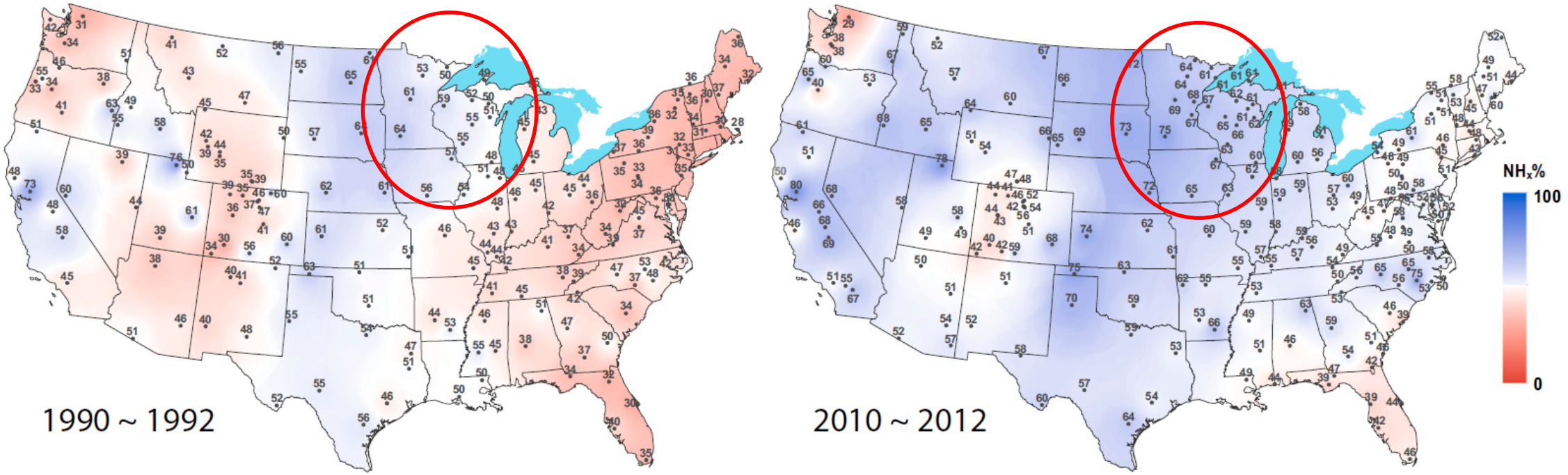

Fig. 1. Comparisons of the 3-y average NH_4^+ percentage of wet inorganic nitrogen deposition across the United States in 1990–1992 (*Left*) and 2010–2012 (*Right*). To help visualize spatial patterns, isopleths were produced by interpolating NH_4^+ mole percentages at individual monitoring sites using a cubic inverse-distance weighting of sites within 500 km of each observation station. The black dots on the map represent locations of sites with 3-y data available for each time period. The NH_4^+ percentage on a molar basis [$(NH_4^+\%) = (NH_4^+)/(NO_3^- + NH_4^+) \times 100\%$] is noted at each site.

Increasing importance of deposition of reduced nitrogen in the United States

Yi Li[a], Bret A. Schichtel[b], John T. Walker[c], Donna B. Schwede[d], Xi Chen[c], Christopher M. B. Lehmann[e], Melissa A. Puchalski[f], David A. Gay[e], and Jeffrey L. Collett Jr.[a,1]

5874–5879 | PNAS | May 24, 2016 | vol. 113 | no. 21

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Any Questions?

Minnesota Statewide Hg Total Maximum Daily Load Meeting

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Current Mercury Litterfall Sites

- Brand New "Official" Network
- 22 litterfall sites to run for the 11th year
- Sampling started in September

Site Name	
GA09	
IN21	
IN22	
IN34	
KY10	
MD99	
MI14	*Little Traverse* Bay *Bands* of Odawa Indians
MI48	
MN02	Red Lake
MN16	
MO46	
NY20	
NY67	
NY68	
NY88	
OH52	
OK99	Cherokee Nation
SC05	
TN11	
TN97	
TX22	
WI01	Bad River
WI10	Potawatomi

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New at NADP?

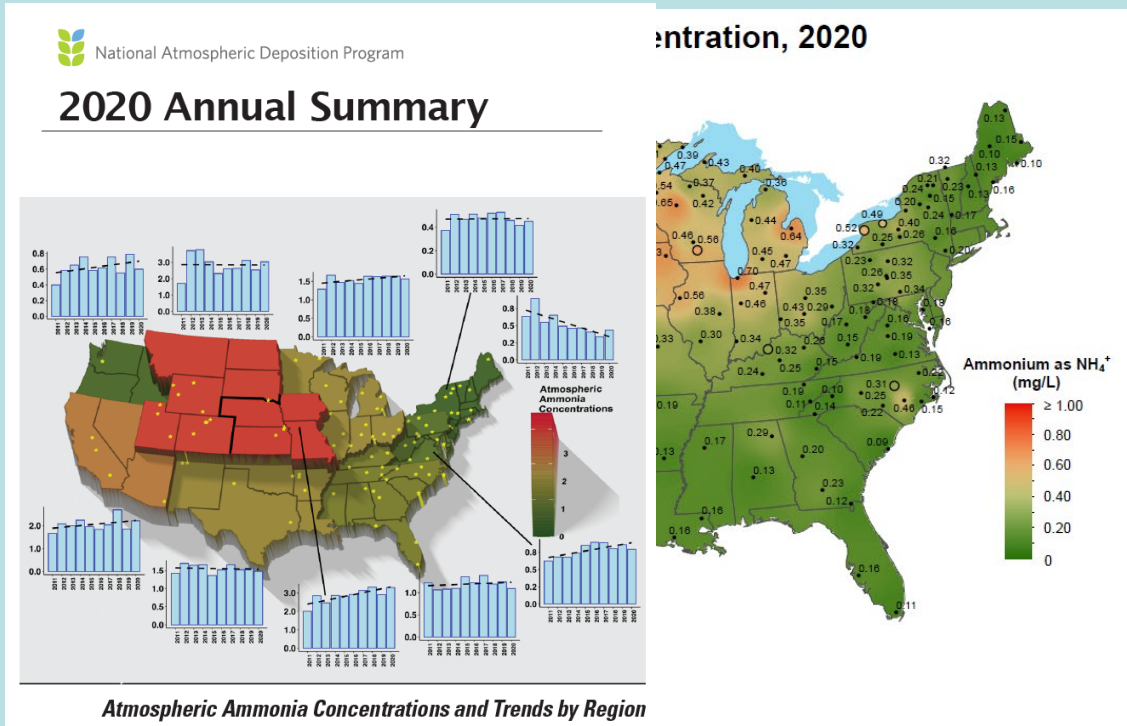
- Wrapping up our measurement quality assurance on the 2022 data

  for all networks

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U
1	siteId	labno	dateOn	dateOff	ph	Conduc	flagCa	Ca	flagMg	Mg	flagK	K	flagNa	na	flagNH4	NH4	flagNO3	NO3	flagCl	Cl	flagSO4
2	AB32	TQ1283SW	9/28/2016 16:00	10/5/2016 16:55	6.56	6.7		1.012		0.07		0.01		0.02		0.039		0.19		0.04	
3	AB32	TQ2000SW	10/18/2016 20:00	10/25/2016 18:00	4.73	14.5		0.33		0.037		0.064		0.056		0.343		1.812		0.091	
4	AB32	TQ2239SW	10/25/2016 18:00	10/31/2016 16:47	6.11	11.5		0.556		0.064		0.037		0.029		0.866		1.996		0.08	
5	AB32	TQ2482SW	10/31/2016 16:47	11/7/2016 17:00	6.48	7.1		0.846		0.082		0.026		0.039		0.125		0.283		0.042	
6	AB32	TQ2841SW	11/7/2016 17:00	11/15/2016 16:00	-9	-9		0.315		0.024		0.014		0.031		0.269		1.413		0.054	
7	AB32	TQ3103SW	11/15/2016 16:00	11/22/2016 18:30	7.35	51.2		8.271		0.699		0.347		0.353		0.164		2.52		0.188	
8	AB32	TQ3245SW	11/22/2016 18:30	11/28/2016 18:00	6.53	7.7		1.029		0.073		0.012		0.028		0.128		0.728		0.031	

- Drawing the maps for 2022

- Making the Annual Summary



Atmospheric Ammonia Concentrations and Trends by Region

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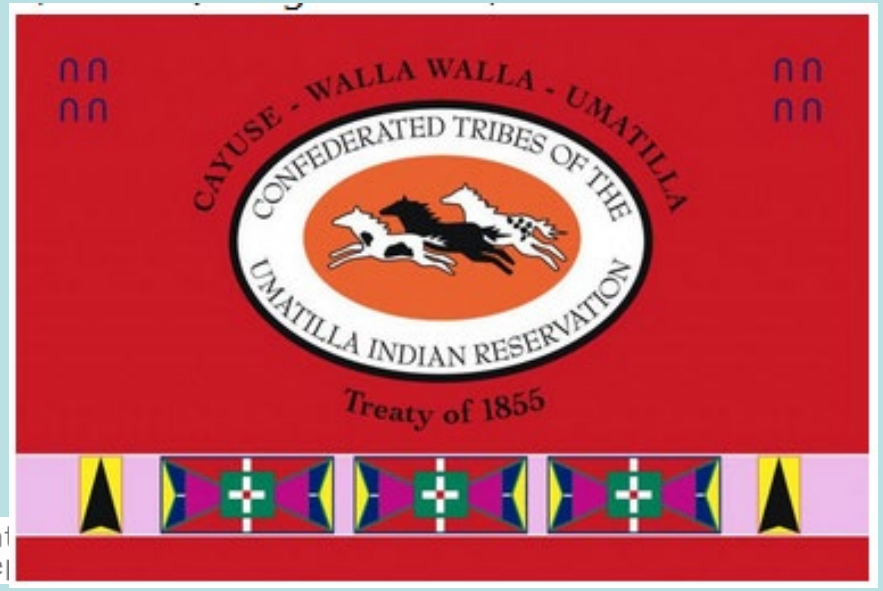
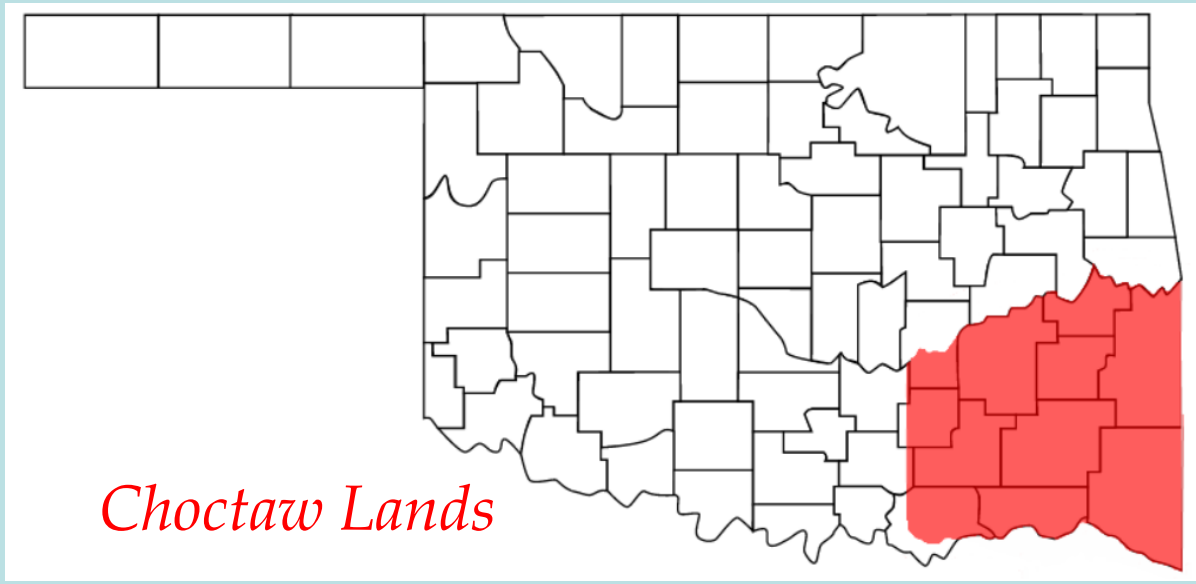
Working with Three Tribes Measuring PFAS

- Choctaw Nation (possible new site)
- Kansas Kickapoo Tribe (KS97
- Conf. Tribes of Umatilla Ind. Res. (WA04, soon)

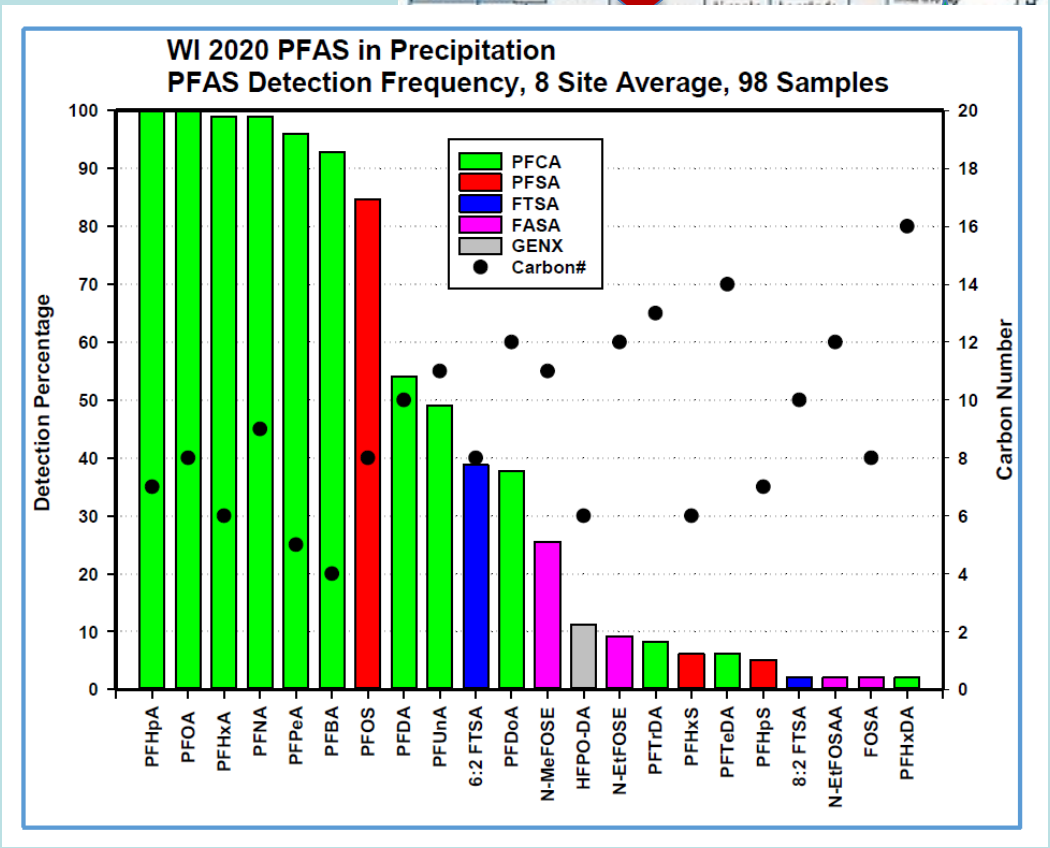




Per- and Polyfluoroalkyl Substances

Again, lots of interest PFAS. Is it in precipitation, too?

- Shafer et all doing quite a bit of analytical detection at UW Madison
- Looking at PFAS in precipitation at several sites
  - East Coast, NC, Kansas, Wisconsin
  - More sites being added
  - Longterm in NADP samples
- Intensive across the State of Wisconsin
  - Rural, urban, near source
- Starting a mass balance in/around Lake Superior
- Even measuring atmospheric concentrations in WI
  - With WI DNR
- His team determined concentrations in precipitation during 2019-20 in Wisconsin (right).



Detection levels are compound specific
Most 0.02 to 0.2 ng/L

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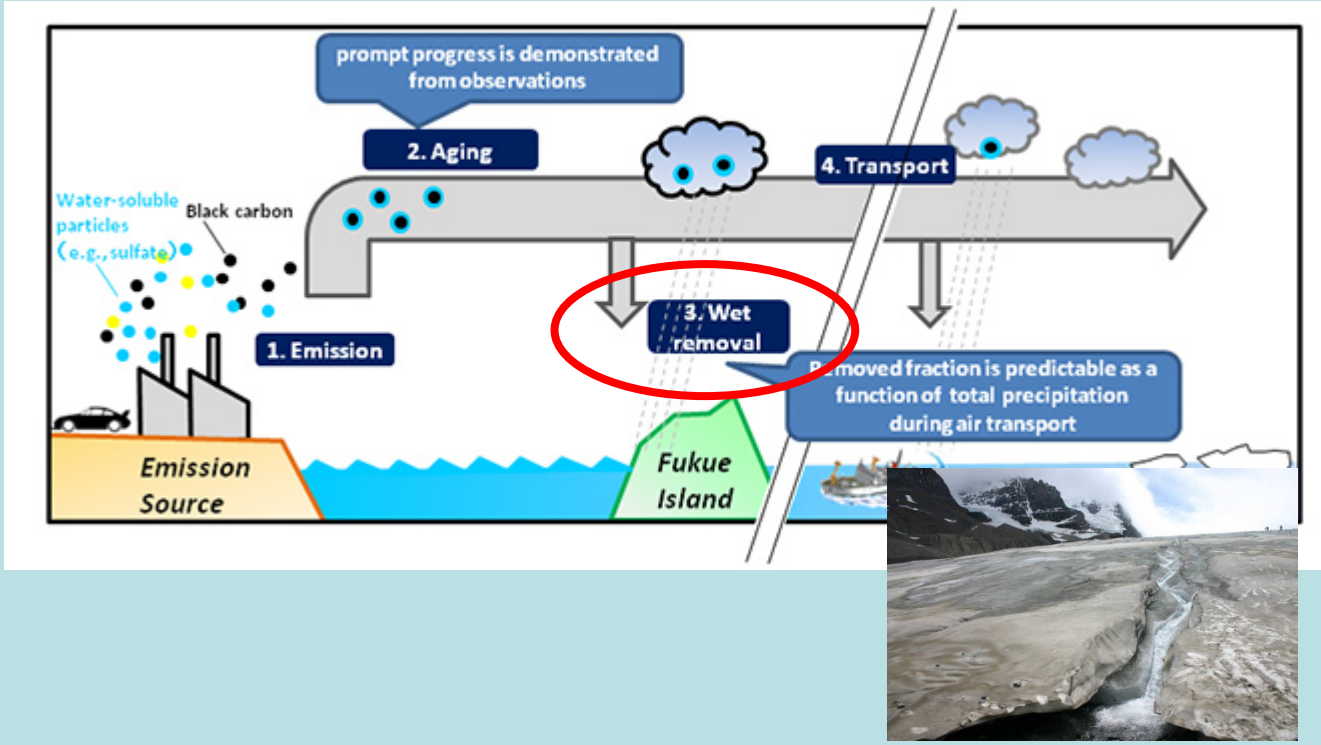
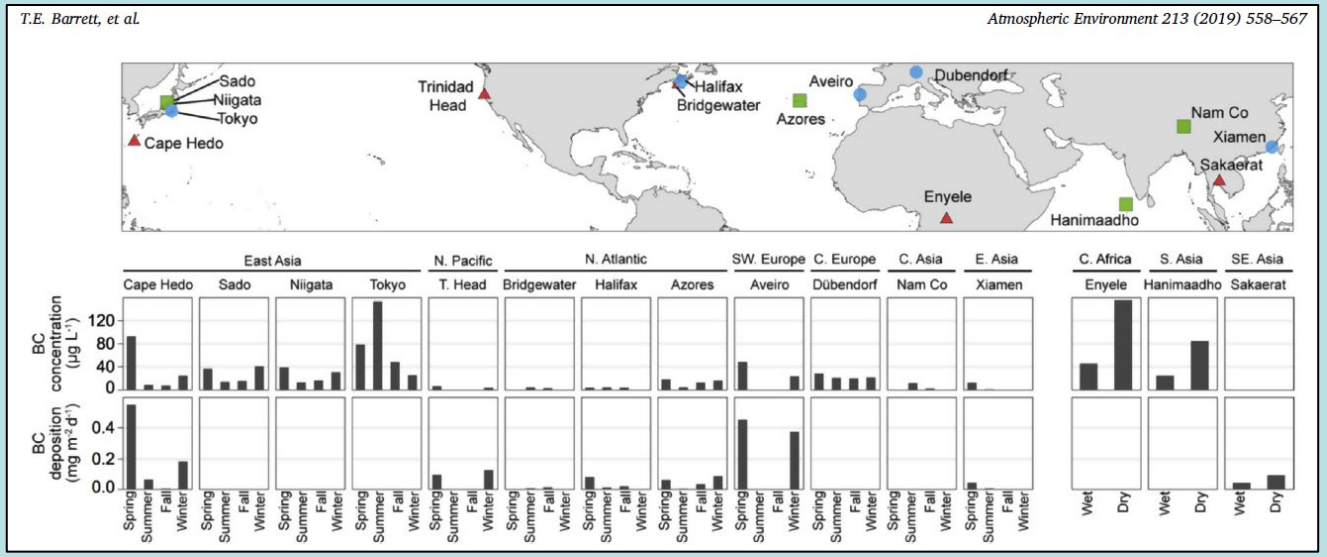
Black Carbon in Precipitation

- An important climate influence
- One of the dominant removal pathways
- Little is known about how much is wet depositing
- Wet deposition rates should be important to the modeling community



- We are testing measuring BC in wet deposition, <u>as a network</u> (repeatedly)



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A New Idea Coming

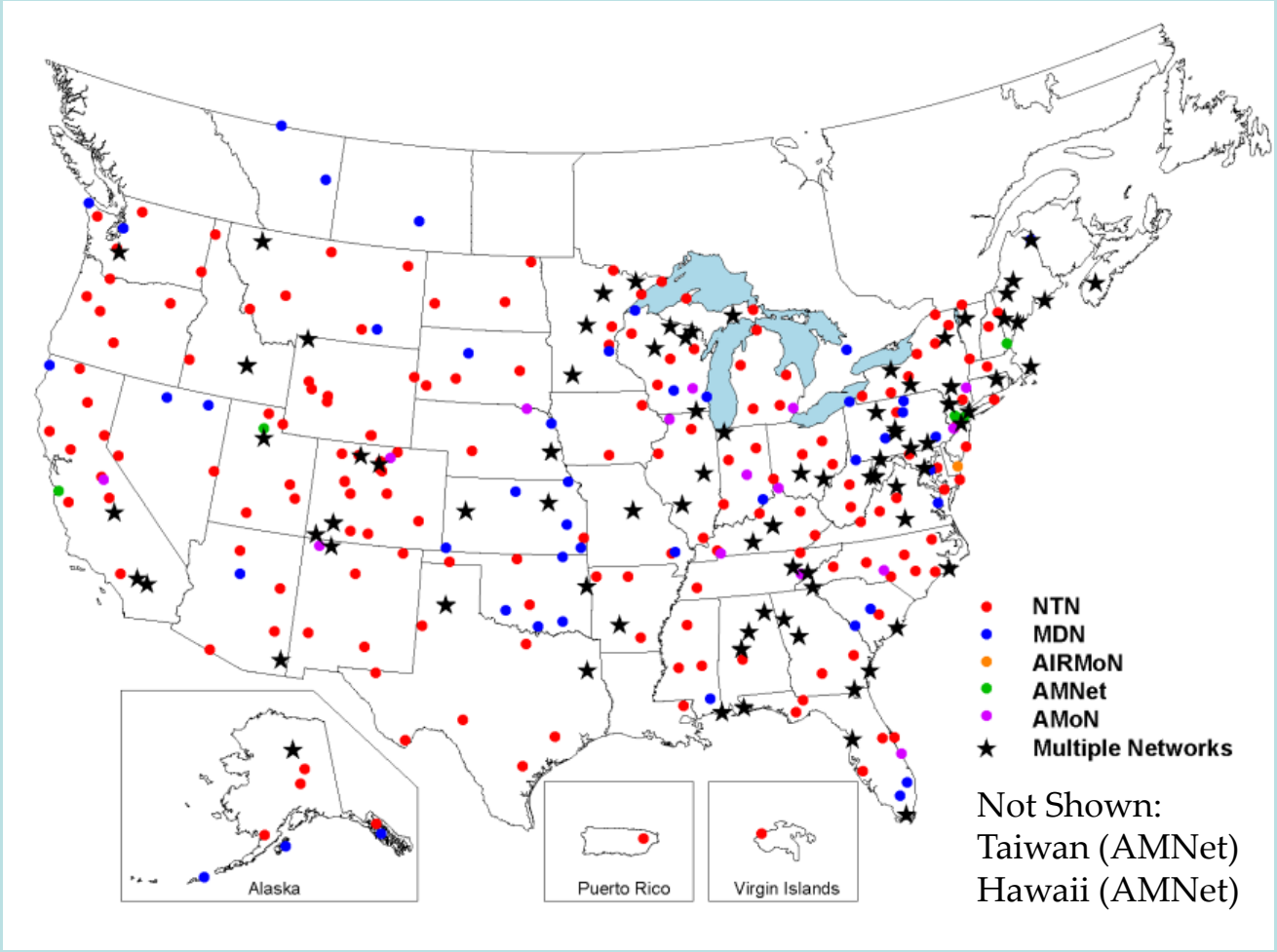
- Using Passive Hg measurement Devices
  (Tekran MerPAS technology)
- A low cost network to measure atmospheric concentrations of Hg, and determine if you have relatively high concentrations
- Possible dry deposition estimates from these
- Basic health research, impact to lands (dry deposition)
- Spatial patterns and trends
- Also support the United Nations effort for consistent global measurements of GEM

National Atmospheric Deposition Program

- NADP is a Cooperative Research Support Project (USDA, @Un of Wisconsin

  - Approximately $3.1 million dollars per year – direct support
  - We are a "National Research Support Project" (NRSP #3) of the US Department of Agriculture
  - measure wet deposition of pollutants ("precipitation")
    - Or pollution flux out of the atmosphere/into the biosphere
  - We also measure gaseous concentrations for dry deposition calculations
  - over North America at ~350 monitoring locations,
    - Hawaii, US Virgin Islands, Puerto Rico
    - and one site in Asia, starting a site in Bermuda
  - ~ 600,000 historical precipitation samples for 10 analytes
    - Started in 1978, 45th year (NTN network)
    - Mercury measurements since 1996
    - Gaseous ammonia measurements since 2010

https://nadp.slh.wisc.edu/



National Atmospheric Deposition Program

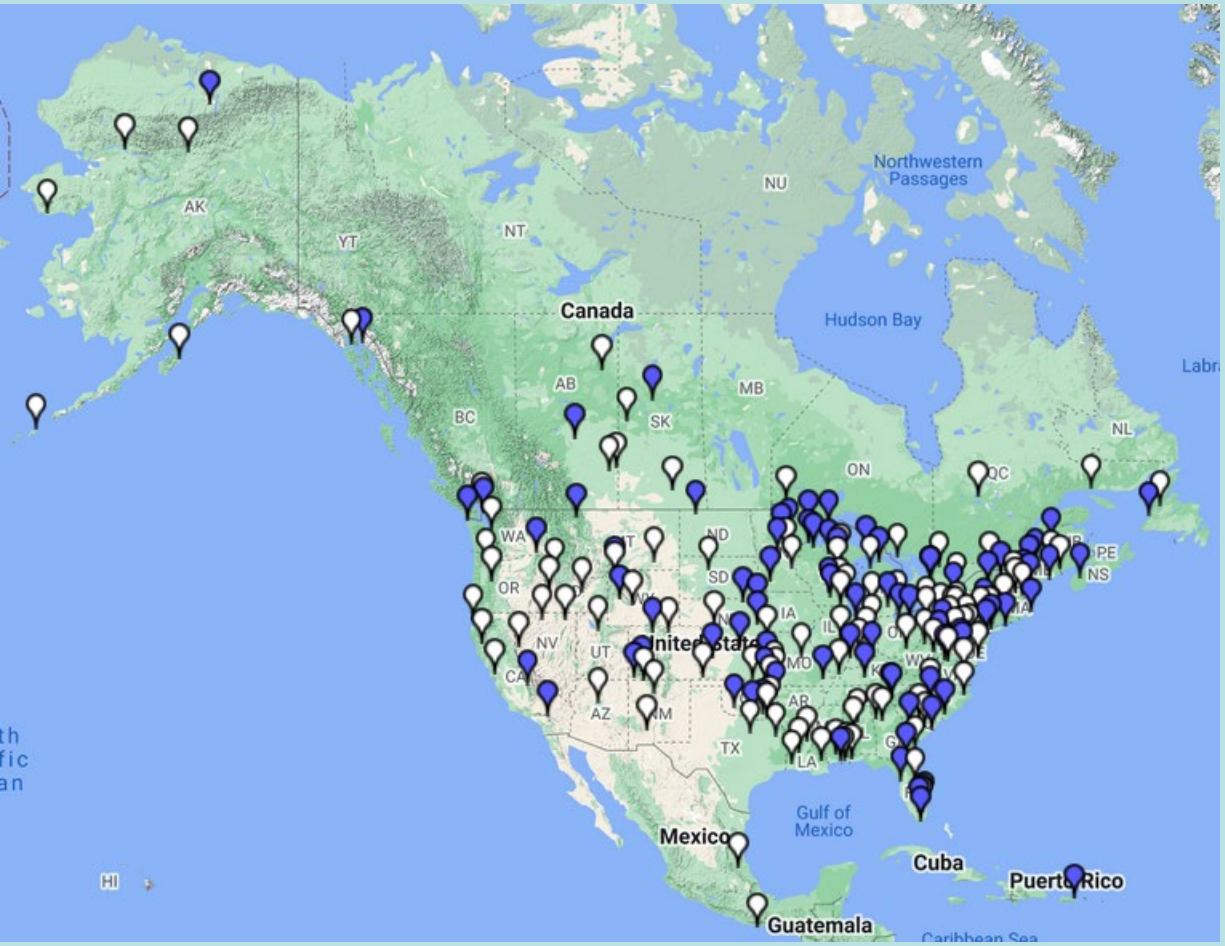
MELD

Program Office Report:
All Things Mercury…

DAG
5/2/2023

National Atmospheric Deposition Program

Mercury Deposition Network



- Currently: 85 active sites

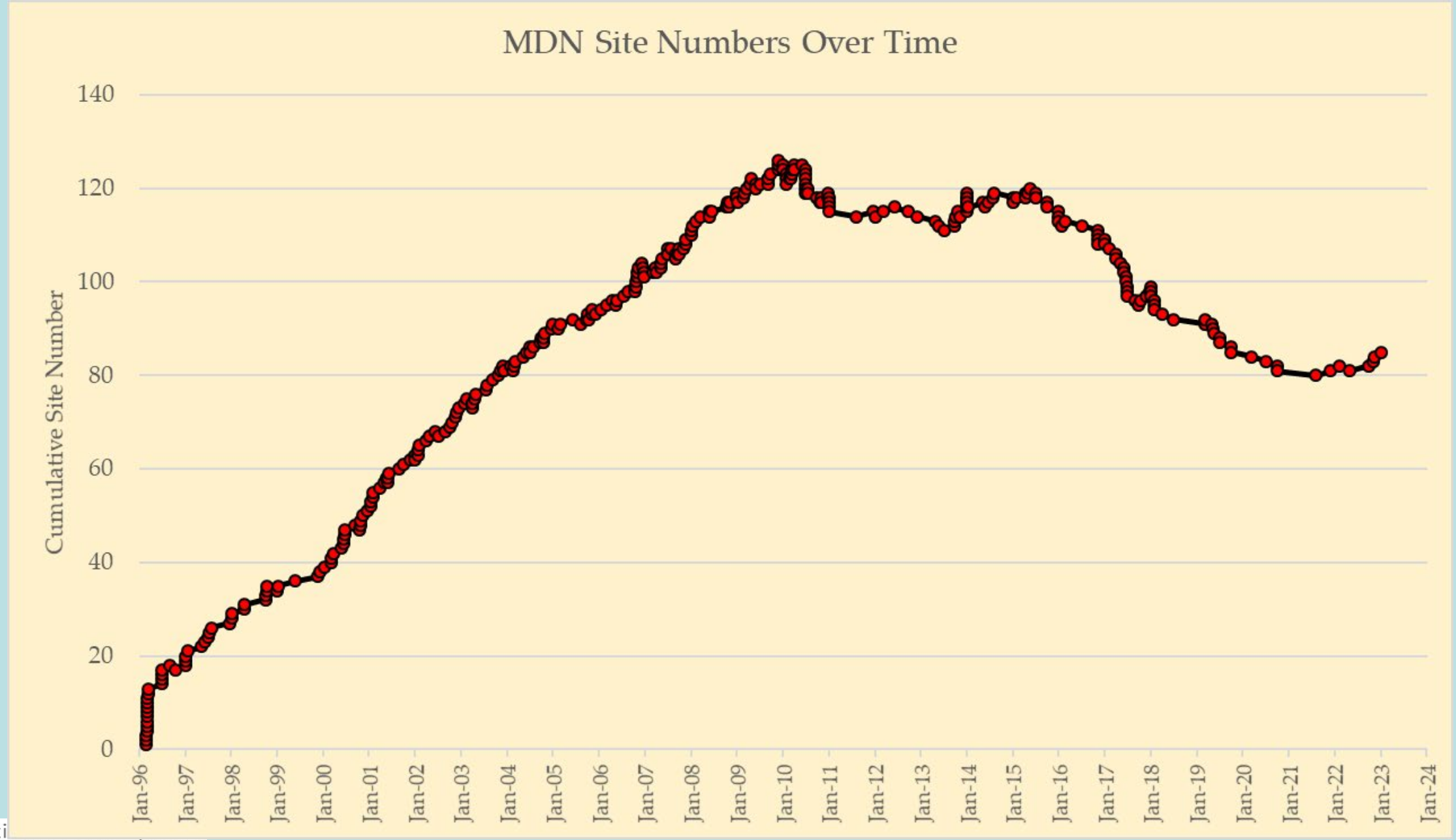
- Newest: WA04, Confederated Tribes of the Umatilla Indian Res. 1/3/2023

- Brule River (WI08) was saved, now operating at WI92, operated by Nathan Kilger (Bad River Band of Lake Superior Chippewa, but will need long term funding (EPA R5 is involved, Michelle Becker). Also making PFAS measurements.

- NE98 Santee Sioux, Oct 2022, Jerome Proctor

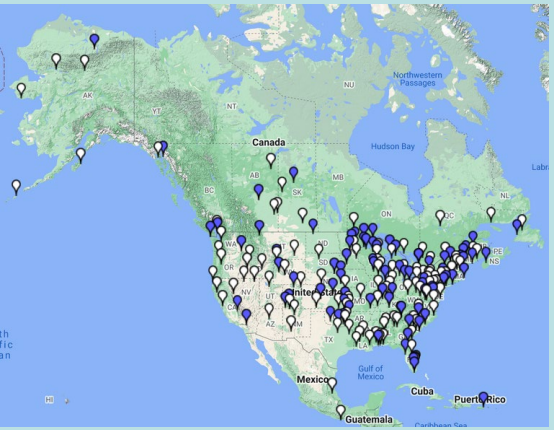
- AK02 Juneau, restart

National Atmospheric Deposition Program



Nati
Deposition Program

MDN: Recent Closings and Interest



- Last site to close: OH02 on Apr 26, 2022

Interested:

- SC03 Savannah River NL (D. Jackson's), should restart soon? Also NTN
- MN05 Fond du Lac/EPA Region 5, should start this summer
- WA03, Macah (C. Winke) would like a second site, might be in Olympic NP
- NVxx Pyramid Lake Paiute Tribe/EPA Region 9, interested in an MDN site, and funds should be available

Future

- KS05 Coffeeville, Kansas DHEP, will shut down 12/2023

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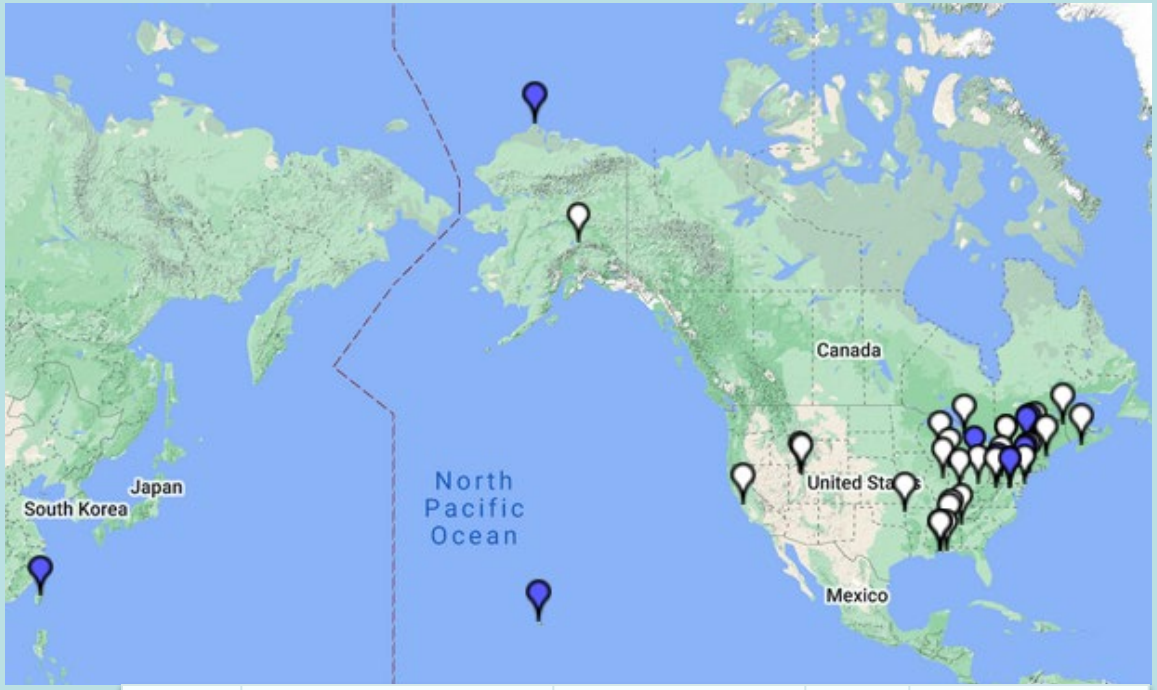
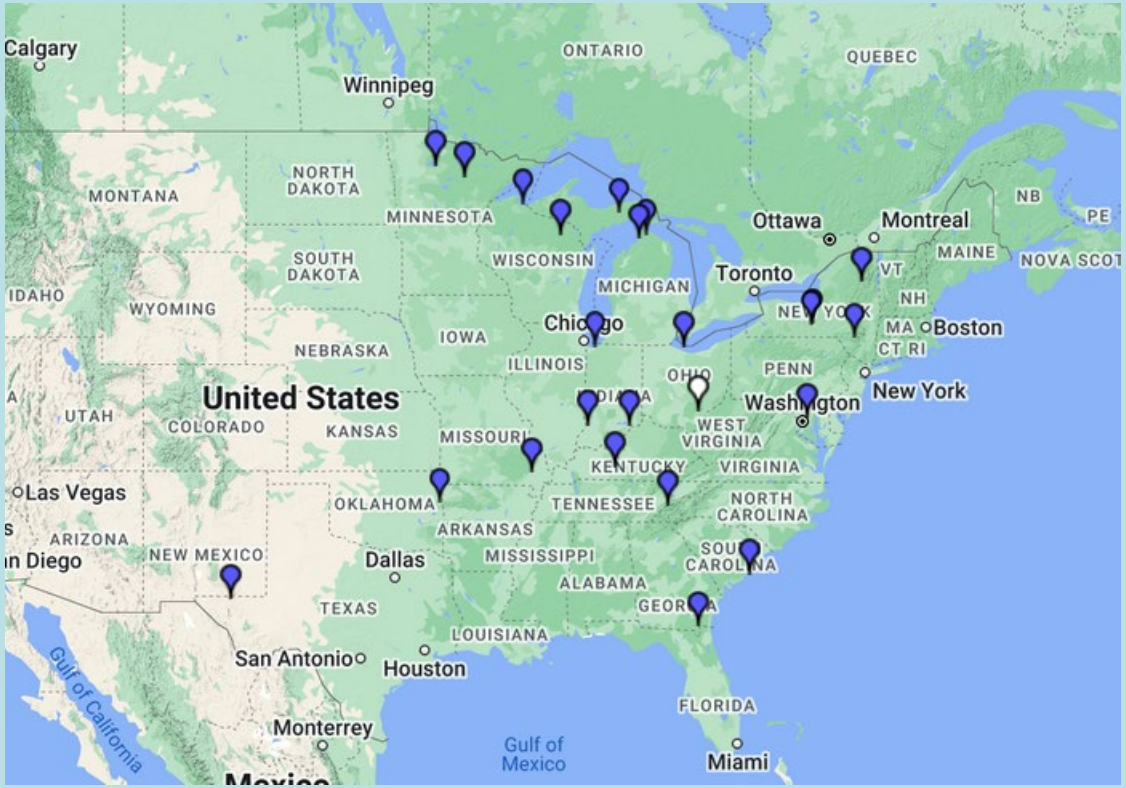
AMNet



AK95	Utqiagvik		AK	2021-10-08
HI00	Mauna Loa	Hawaii	HI	2010-12-30
MD08	Piney Reservoir	Garrett	MD	2008-01-01
MD98	Beltsville	Prince Georges	MD	2007-01-26
NJ30	New Brunswick	Middlesex	NJ	2015-10-01
NJ54	Elizabeth Lab	Union	NJ	2015-10-01
NY20	Huntington Wildlife	Essex	NY	2007-11-21
NY98	Whiteface Mountain	Essex	NY	2020-09-30
OH52	South Bass Island	Ottawa	OH	2011-12-31
TW01	Mt. Lulin		TW	2010-01-01

- Currently: 10 active sites
- Newest: a Tekran Elemental system was delivered to Dr. R. Sosa/UNAM last week
- Request for equipment, Vietnam (Nguyễn Lý Sỹ Phú, Guey-Rong Sheu's student)
  are we interested in this?

Mercury Litterfall Network (MLN)



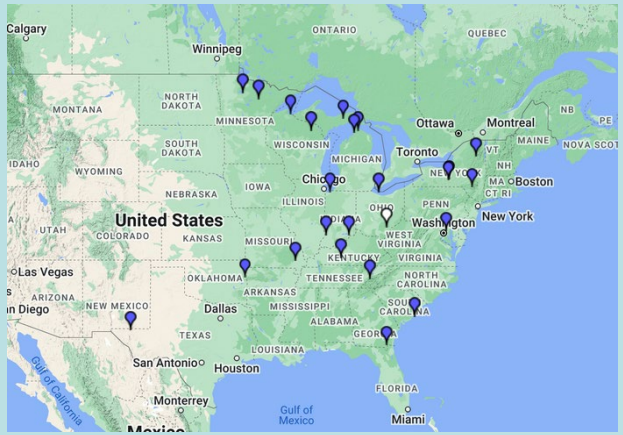
- Currently: 24 active sites

- Newest:
  - KY10, Mammoth Cave National Park, 2021-09-08
  - TX22, Guadalupe Mountains NP, TX, 2021-09-01
  - TN97, Great Smokey NP (Jim Renfro) second site, for 1 year

- Sampling for this year will begin in August

National Atmospheric Deposition Program

Litterfall: Recent Closings and Interest



- No closures

Interest

- Bay Mills Community, upper peninsula MI (J. Waesolek)
- WA03, C. Winke, has some interest here

National Atmospheric Deposition Program

Passive Hg Effort

- Things are moving along towards a MerPAS-based passive Hg capability
- Winston put out the first NADP passive Hg sampler, MerPAS on April 1
- There is a 1 month vs 2 month vs 3 month QC test ongoing at Eagle Heights
- Christa is working through the Canadian SOP for developing our "own" passives based on the MerPAS
- Overall Goal: determine how well we can make passive Hg samplers and how much we would need to charge for network operation

National Atmospheric Deposition Program

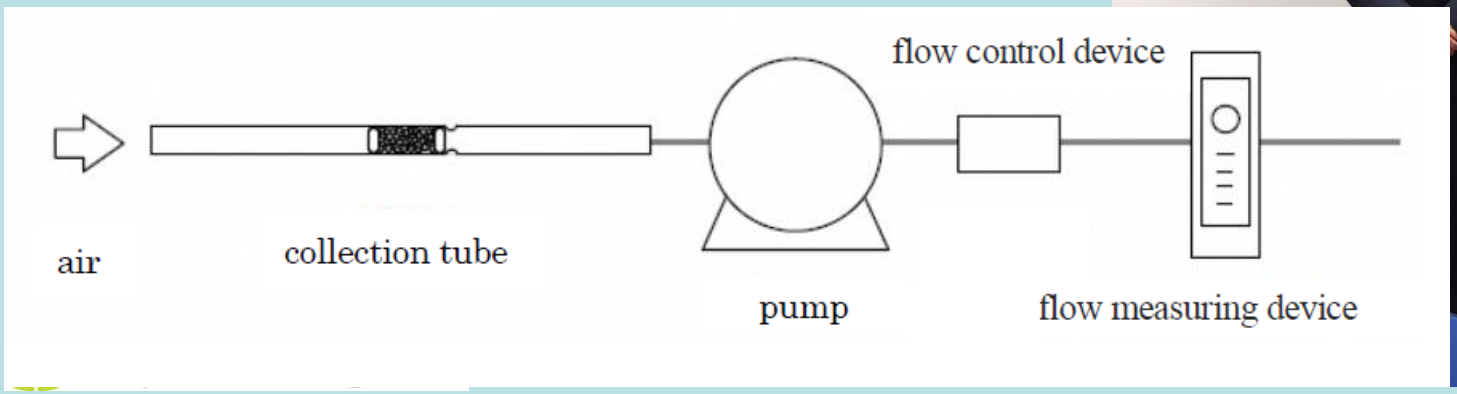
New Bag Sampling for MDN?

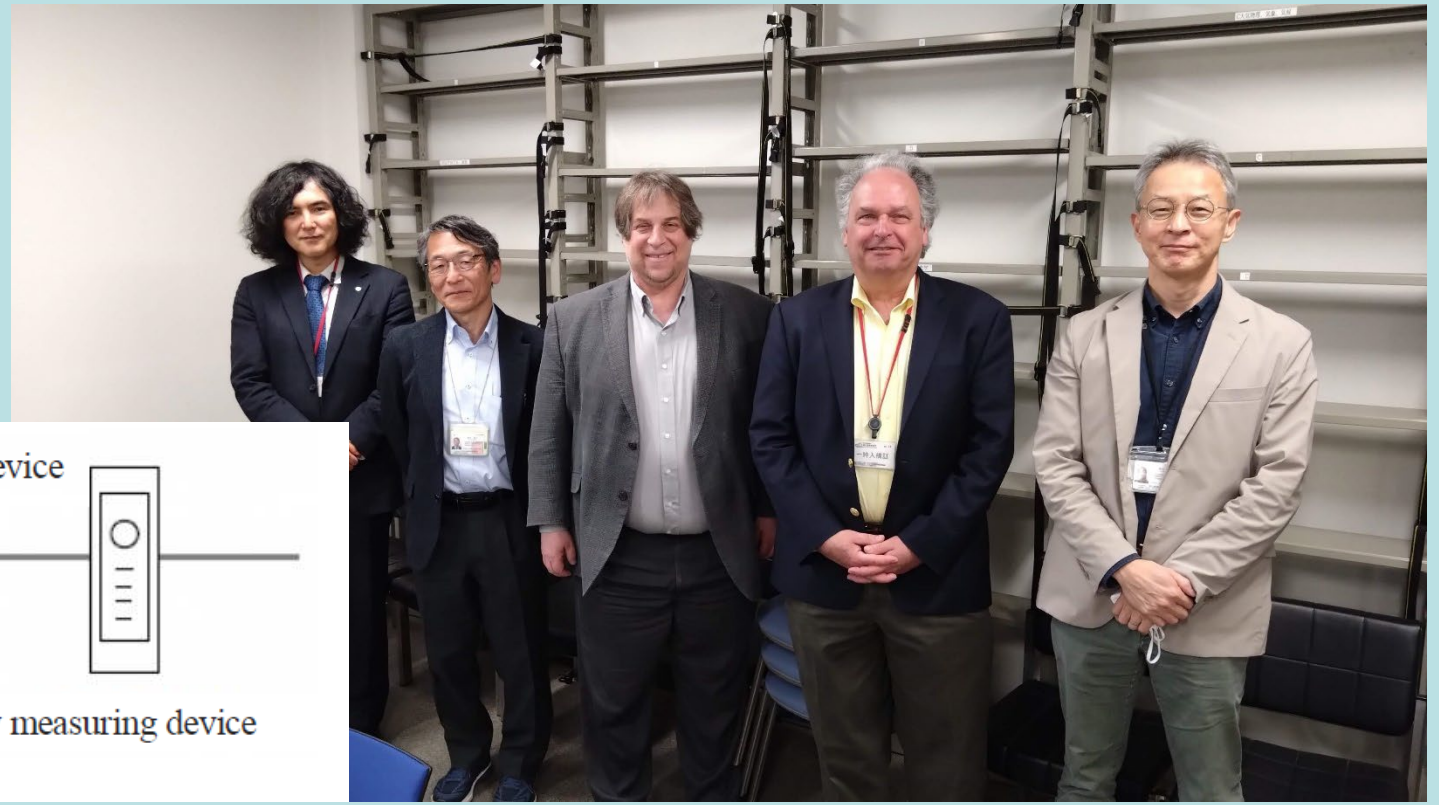
- I have this new idea

Bag sampling in the MDN
(presentation in Joint)

Hattori Tatsuya/Japan Method

- Says that the Japan manual method will run, now/as is, for a 7 day sample





National Atmospheric Deposition Program

10 Minute MELD Talk

Told Dave I would cover the basics of the networks

MDN, AMNet, Litterfall, and a couple of slides about Passives

Morning Dave, Good chatting with you and GRS yesterday. I like your idea of establishing passive sites on every Pacific Island. Will think more about that.

Just turning to NADP now and planning for Spring.

So as part of the MELD meeting, we (rick colleen and others) are planning a session on mercury monitoring to begin an effort to review the current state of mercury monitoring in the U.S. and develop some tools that help site sponsors identify and prioritize mercury data gaps for considering current and future Hg monitoring investments. Part of the effort is to think about how to better align the Hg atmospheric/wet dep monitoring with Hg biological and biogeochemical monitoring.

We plan on having a number of agency folks give an update on mercury monitoring activities in their agency. – What's really in place now? Wondering if you would be willing to give an update on NADP's mercury program. No more than 10 minutes. NPS (Kristi) and USGS (Collin and Sarah J), and others will offer similar updates. It's probably similar to the report you always give on the state of the network. We'd plan to do a deeper dive to look at Hg monitoring and tribal partners, long-term sites for trends, and how NADP's Hg data are used, and other aspects of the program.

Let me know what you think.
Dave

National Atmospheric Deposition Program