Continuous Monitoring of Mercury Deposition in North America: the National Atmospheric Deposition Program

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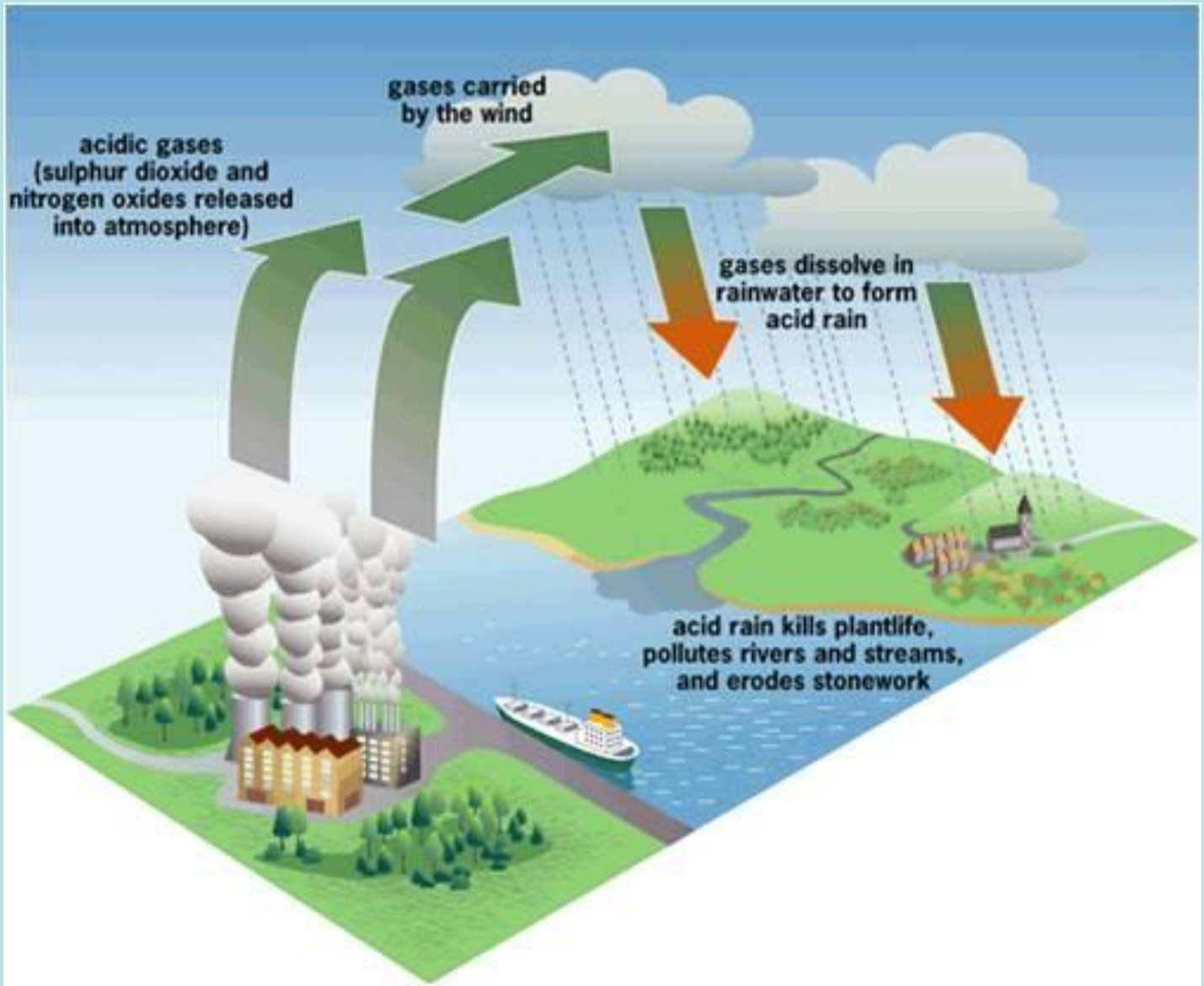
National Atmospheric Deposition Program

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

What is Wet Deposition?



Atmospheric Deposition is the key input of Mercury in water bodies

Environ. Sci. Technol. **2006**, *40*, 6261–6268

Mercury in Soils, Lakes, and Fish in Voyageurs National Park (Minnesota): Importance of Atmospheric Deposition and Ecosystem Factors

J. G. WIENER,*,† B. C. KNIGHTS,‡
M. B. SANDHEINRICH,†
J. D. JEREMIASON,§ M. E. BRIGHAM,∥
D. R. ENGSTROM,⊥ L. G. WOODRUFF,∥
W. F. CANNON,# AND S. J. BALOGH△

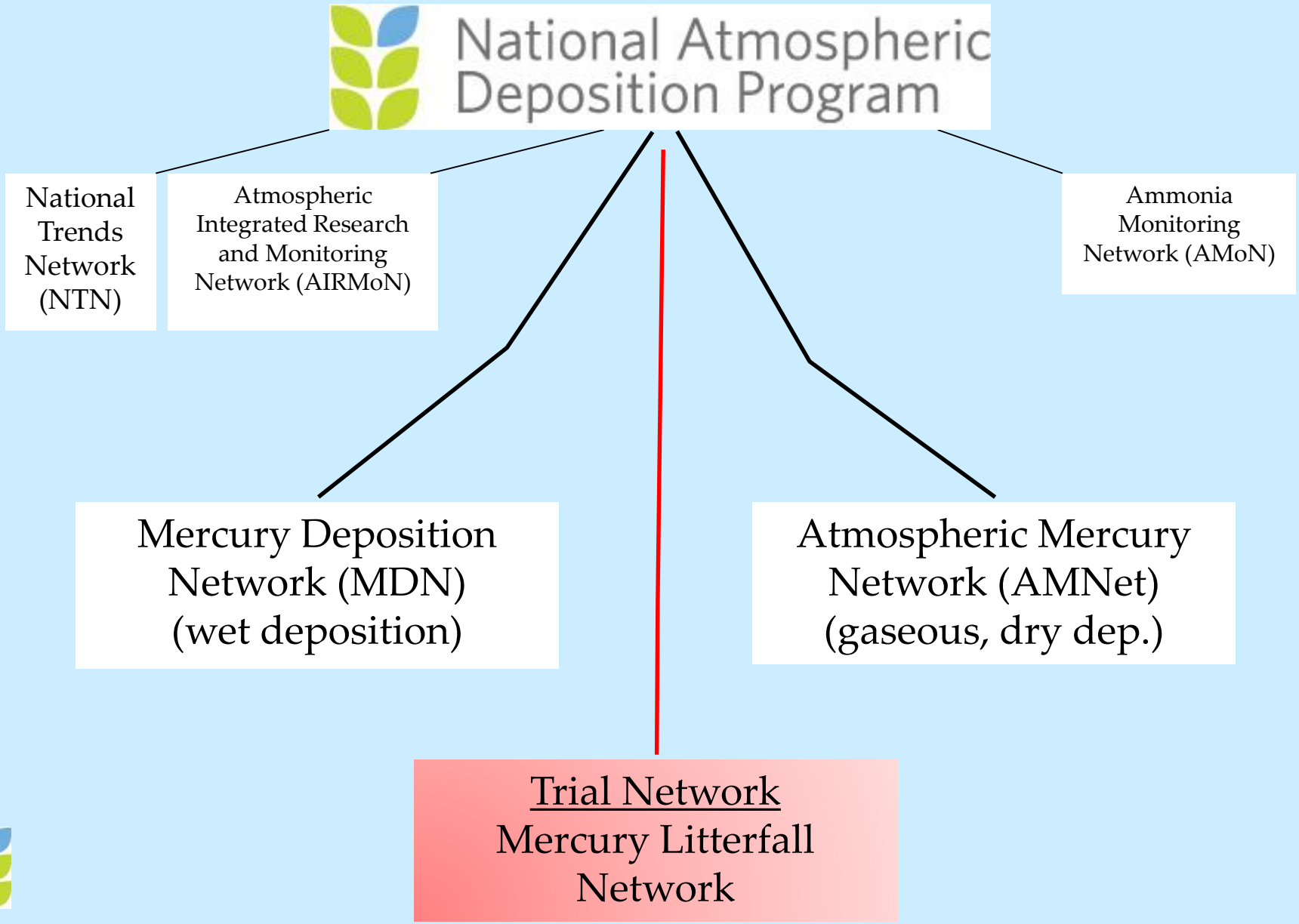
- Hg source to water bodies is *overwhelmingly atmospheric deposition and anthropogenic*

"We conclude that nearly all of the mercury in fish in this seemingly pristine landscape was derived from atmospheric deposition, that most of this bioaccumulated mercury was from anthropogenic sources, and that both watershed and lacustrine factors exert important controls on the bioaccumulation of methylmercury."

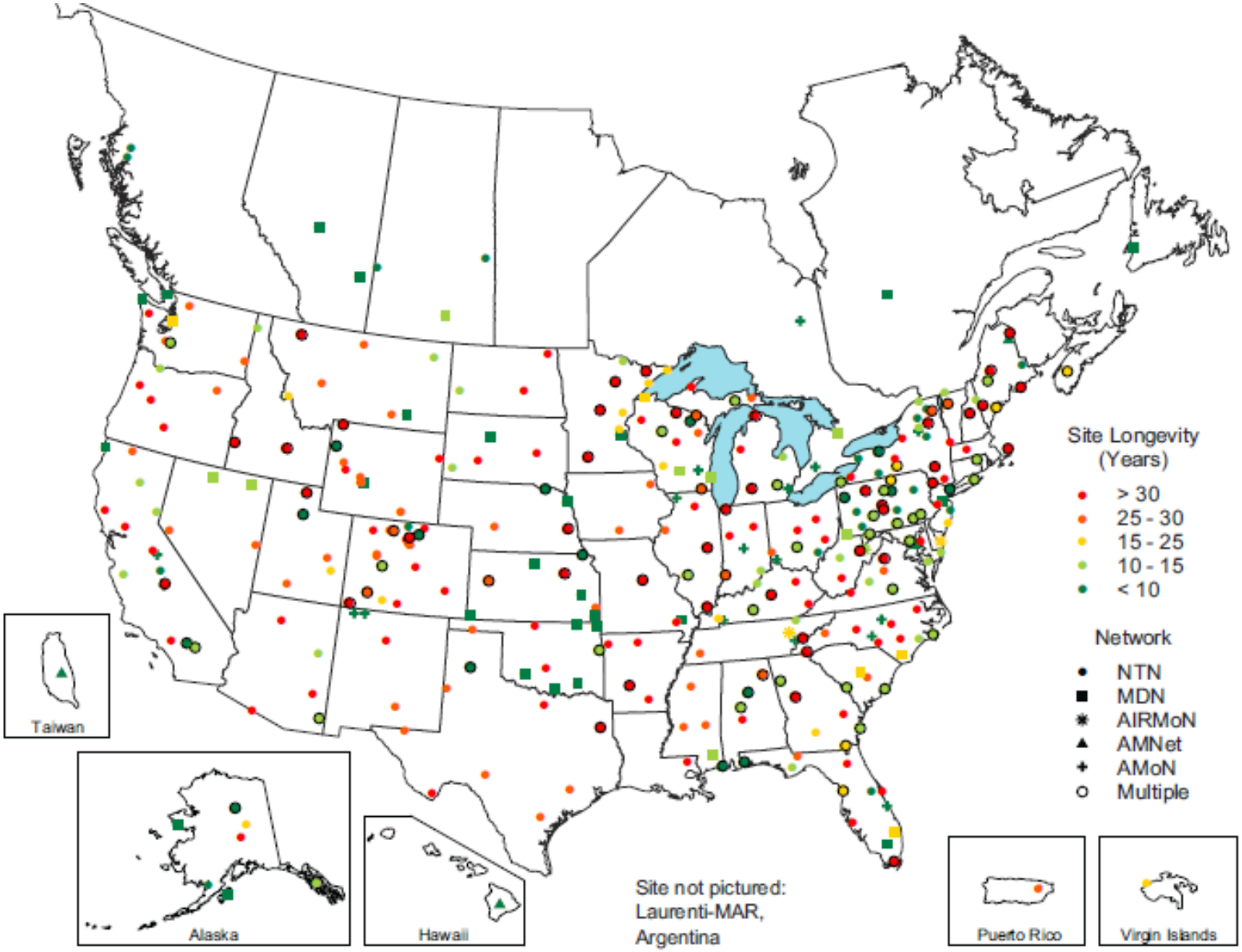
The NADP is a Cooperative Research Program *(Un. Of Illinois)*

- Measure wet deposition of pollutants
  - Three networks (NTN, AIRMoN, Mercury Deposition Network)
- Monitor the rate of pollution movement to the surface
  - Two networks (dry deposition est., AMoN, Atmospheric Mercury Network)
- North America
  - US, Canada, and some in Mexico
  - Also Taiwan, South America, Hawaii
- Owned and operated by our members
  - Decisions made by our members
  - Started in 1978, 37th year
- Over 500,000 precipitation chemistry samples

NADP is Five Separate Networks



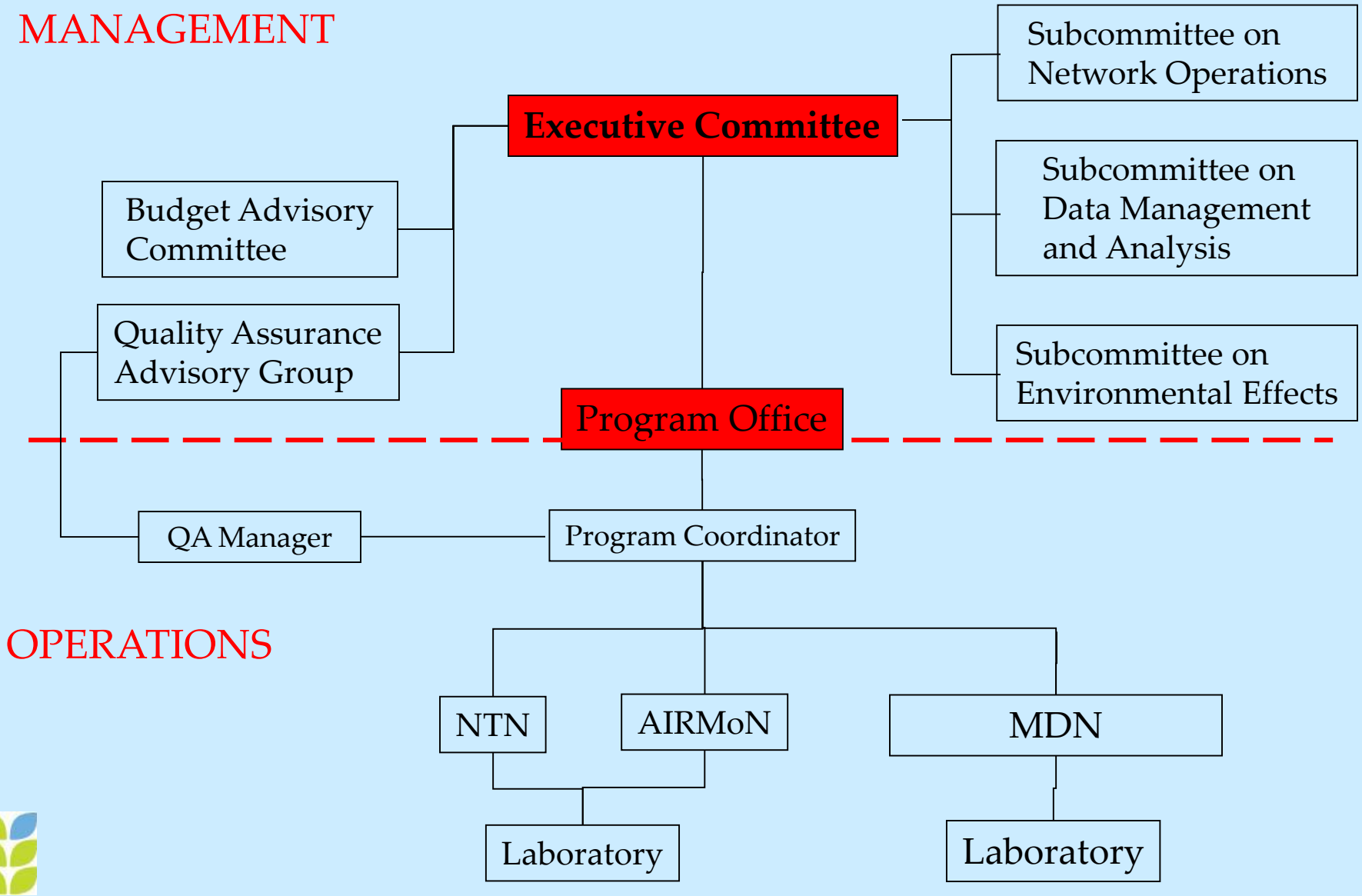
NADP - All Network Sites



NADP's Goal

To monitor the chemistry of precipitation (rain and snow) and the atmosphere as consistently and as accurately as we can, for long periods to determine changes over time (trends).

Organization



Who is NADP?

National Atmospheric Deposition Program

The NADP Cooperators

(100+ total agencies)

Federal Agency Members

USGS science for a changing world

U.S. Department of the Interior Bureau of Land Management

NOAA

USDA Forest Service

Caring for the Land and Serving People

USDA

EPA United States Environmental Protection Agency

The National Park Service

NRSP-#3

USDA United States Department of Agriculture National Institute of Food and Agriculture

SAAESD

Tribal Organizations

Great Seal of the Menominee Nation

Sault Ste. Marie Tribe of Chippewa Indians

Turtle Mountain Band of Chippewa Indians

Seal of the Cherokee Nation Sept. 6, 1839

Universities

Universidad de Puerto Rico 1903

PennState

UNC Universidad Nacional de Córdoba

CORNELL UNIVERSITY

PURDUE UNIVERSITY

Washington State University

US States

WISCONSIN 1848

OKLAHOMA

Other Organizations

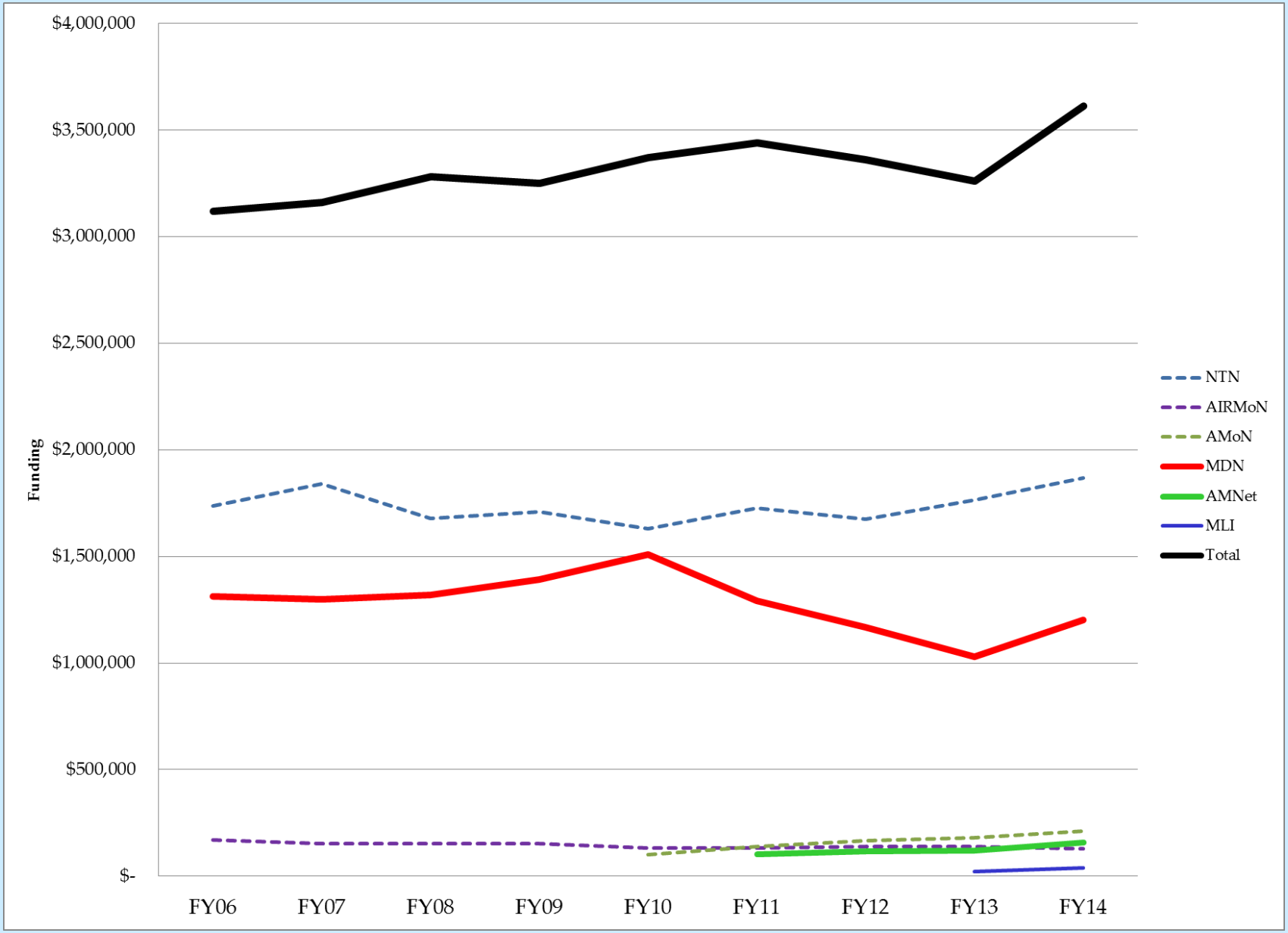
EPRI Providing Science and Technology Solutions to Our Global Energy Customers

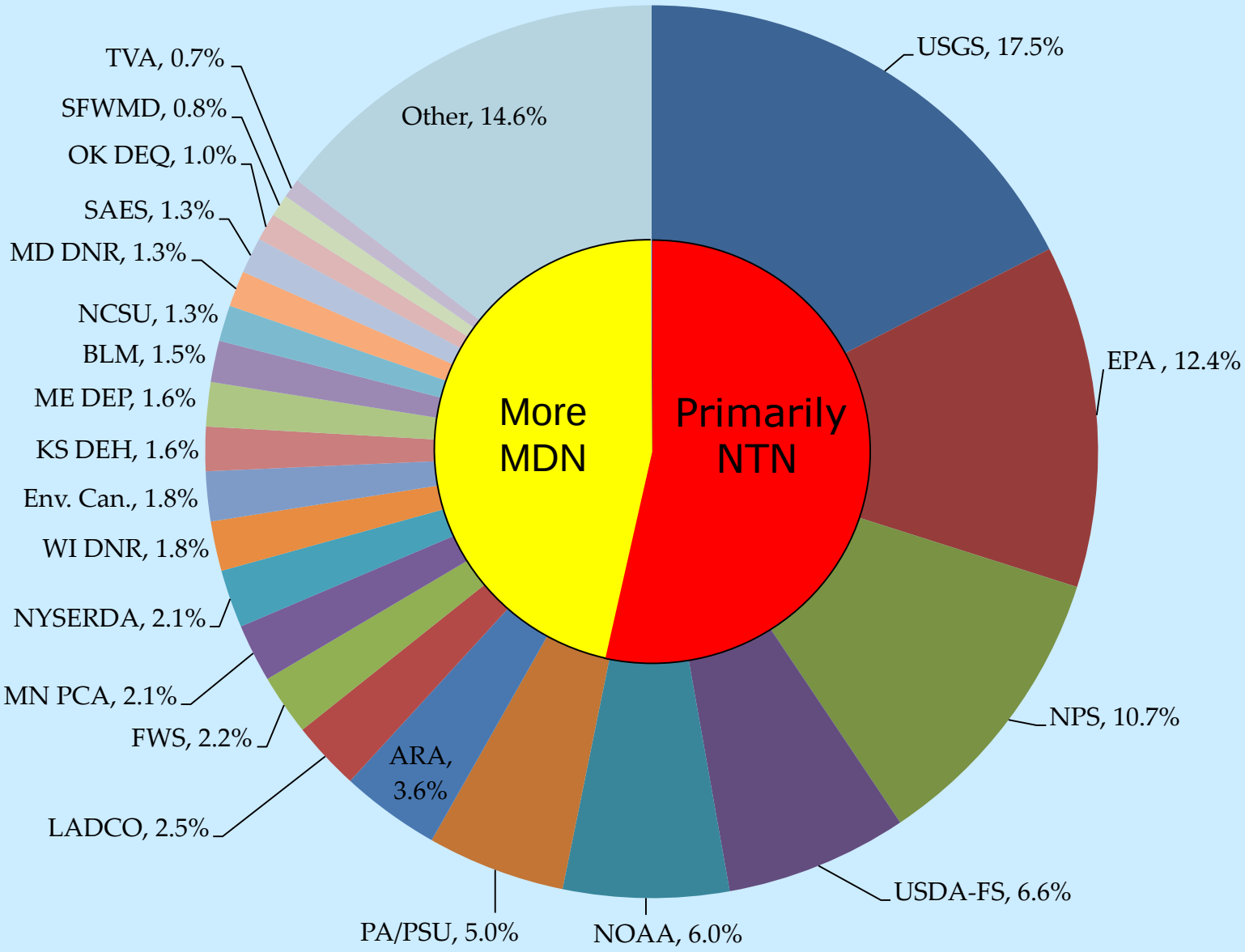
EPA Taiwan

Environment Canada | Environnement Canada

NEW YORK STATE OF OPPORTUNITY. NYSERDA Sponsored

SOUTHERN COMPANY Energy to Serve Your World


$4,000,000
$3,500,000
$3,000,000
$2,500,000
$2,000,000
$1,500,000
$1,000,000
$500,000
$-
Funding
FY06
FY07
FY08
FY09
FY10
FY11
FY12
FY13
FY14
NTN
AIRMoN
AMoN
MDN
AMNet
MLI
Total


USGS, 17.5%
EPA , 12.4%
NPS, 10.7%
USDA-FS, 6.6%
NOAA, 6.0%
PA/PSU, 5.0%
ARA, 3.6%
LADCO, 2.5%
FWS, 2.2%
MN PCA, 2.1%
NYSERDA, 2.1%
WI DNR, 1.8%
Env. Can., 1.8%
KS DEH, 1.6%
ME DEP, 1.6%
BLM, 1.5%
NCSU, 1.3%
MD DNR, 1.3%
SAES, 1.3%
OK DEQ, 1.0%
SFWMD, 0.8%
TVA, 0.7%
Other, 14.6%
More MDN
Primarily NTN

Cost	MDN	MDN - daily	Methyl Mercury	AMNet
Program Office (Management)	$2,700	$2,700	$0	$6,000
Analytical Chemistry	$6,994	$20,982	$1,950	$0
NED (equipment insurance)	$182	$182	$0	$0
TOTAL	$9,876	$24,539	$1,950	$6,000
Estimated shipping	$1,040	$3,120		
Total w/shipping	$10,916	$27,659	none	none

All data, all maps, all information

free of charge

http://nadp.isws.illinois.edu

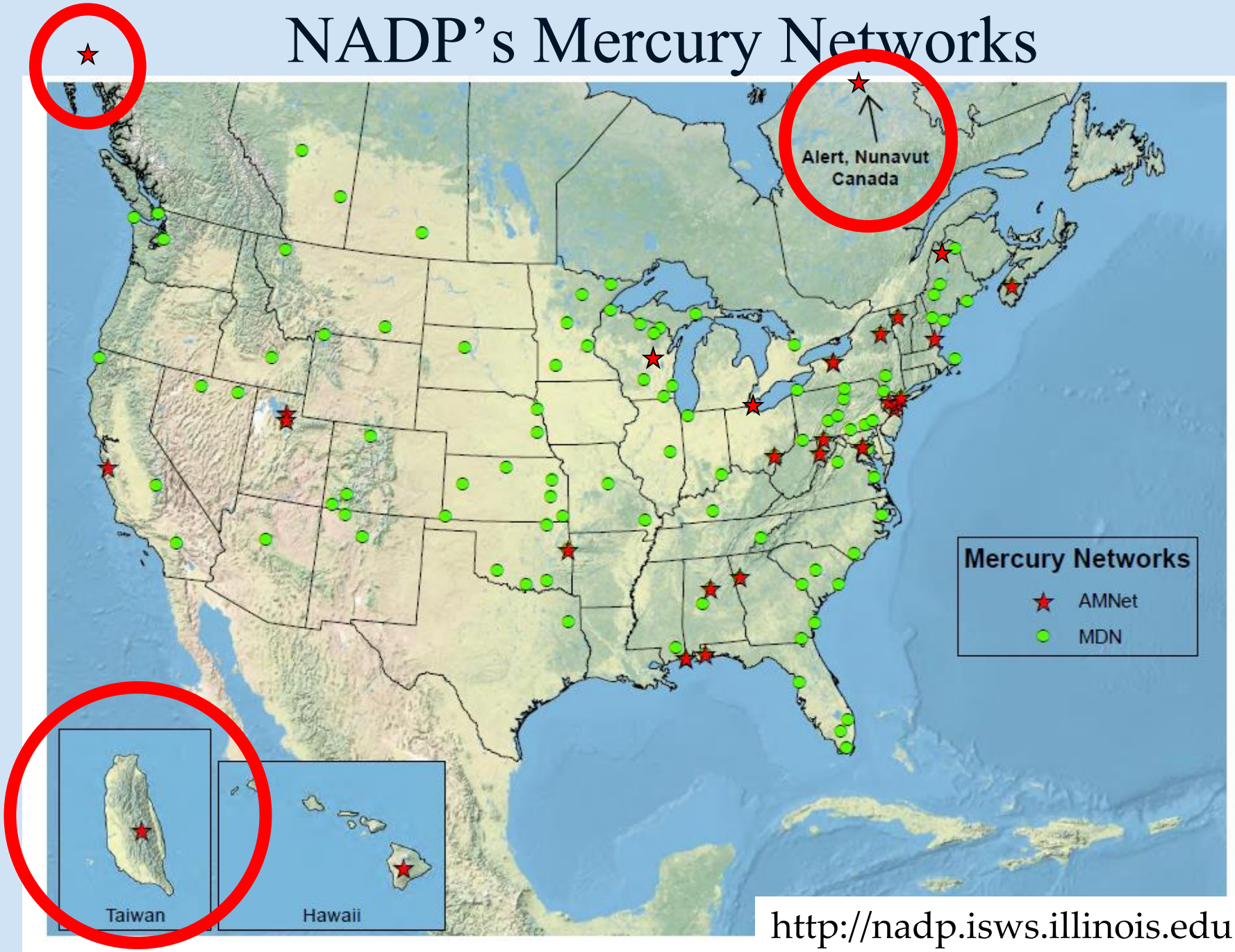
National Atmospheric Deposition Program/MDN

Weekly Mercury Concentrations and Depositions

SiteID	Date On	Date Off	RGPPT	SVOL	SUBPPT	HgConc	HgDep	Sample Type	QR	Notes	YrMonth	DateMod
			mm	ml	mm	ng/L	ng/m²					
MT05	10/28/2003 16:24	11/04/2003 16:16	20.32	190.30	20.32	3.66	74.53	W	B	mz	200310	11/22/2004
MT05	11/04/2003 16:17	11/11/2003 19:00	13.34	200.40	13.34	--	--	W	C	mzu	200311	11/22/2004
MT05	11/11/2003 19:01	11/18/2003 21:05	18.80	245.80	18.80	--	--	W	C	zhu	200311	11/22/2004
MT05	11/18/2003 21:10	11/25/2003 15:57	30.73	228.00	30.73	--	--	W	C	dmzu	200311	11/22/2004
MT05	11/25/2003 16:10	12/02/2003 20:50	47.50	623.70	47.50	--	--	W	C	zhu	200311	11/22/2004
MT05	12/02/2003 21:10	12/09/2003 20:13	12.95	185.30	12.95	--	--	W	C	dmzu	200312	11/22/2004
MT05	12/09/2003 21:00	12/16/2003 18:50	24.89	163.40	24.89	1.14	28.57	W	B	mz	200312	11/22/2004
MT05	12/16/2003 19:06	12/23/2003 18:05	3.56	31.70	3.56	8.34	29.67	W	B	mz	200312	11/22/2004
MT05	12/23/2003 18:10	12/30/2003 17:35	12.95	89.10	12.95	1.48	19.22	W	B	m	200312	11/22/2004
MT05	12/30/2003 17:39	01/13/2004 20:29	11.18	120.10	11.18	3.64	40.71	W	B	ez	200401	11/22/2004
MT05	01/13/2004 21:15	01/20/2004 16:52	5.08	51.20	5.08	2.09	10.65	W	B	mz	200401	11/22/2004

What Does NADP Measure?

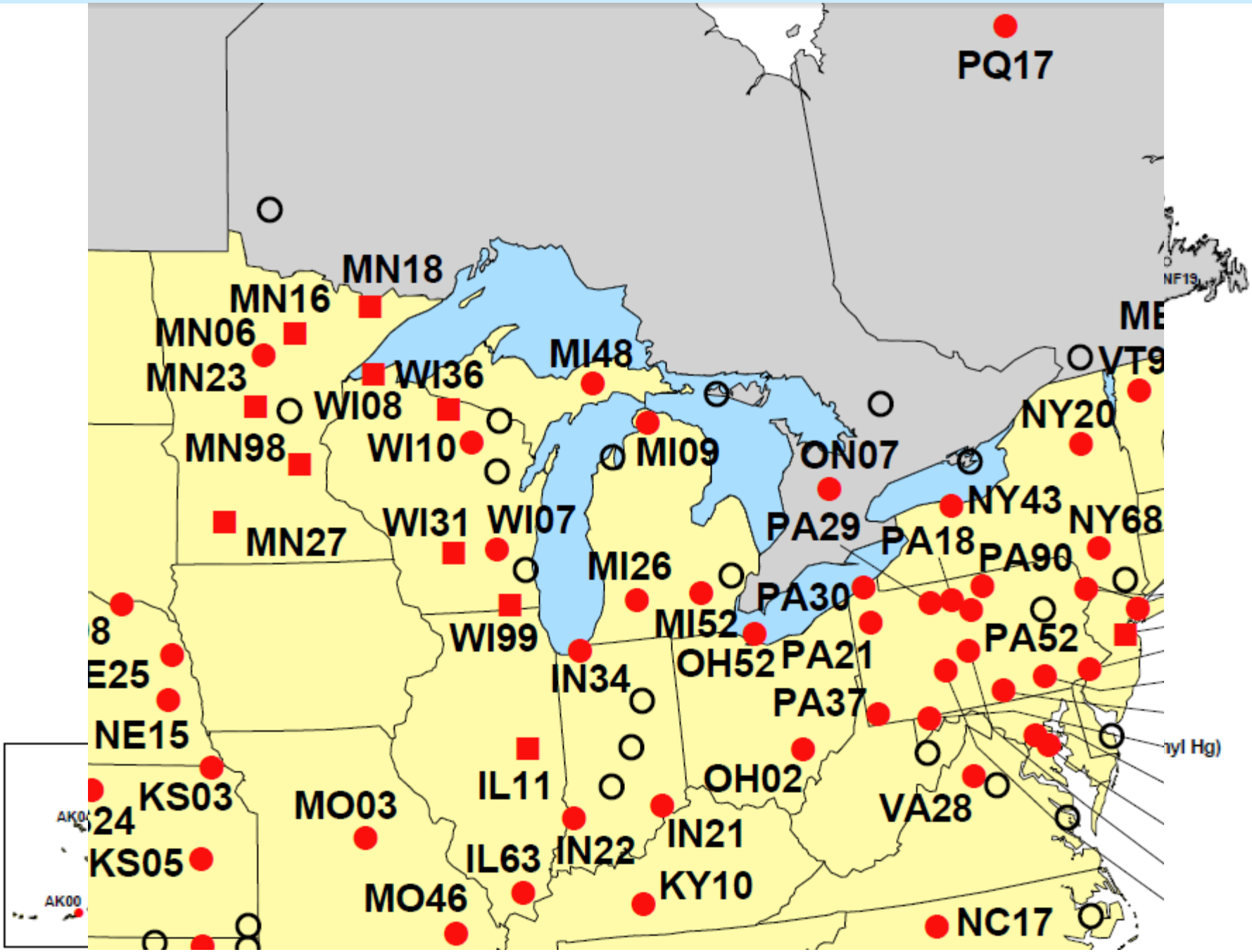
NADP's Mercury Networks



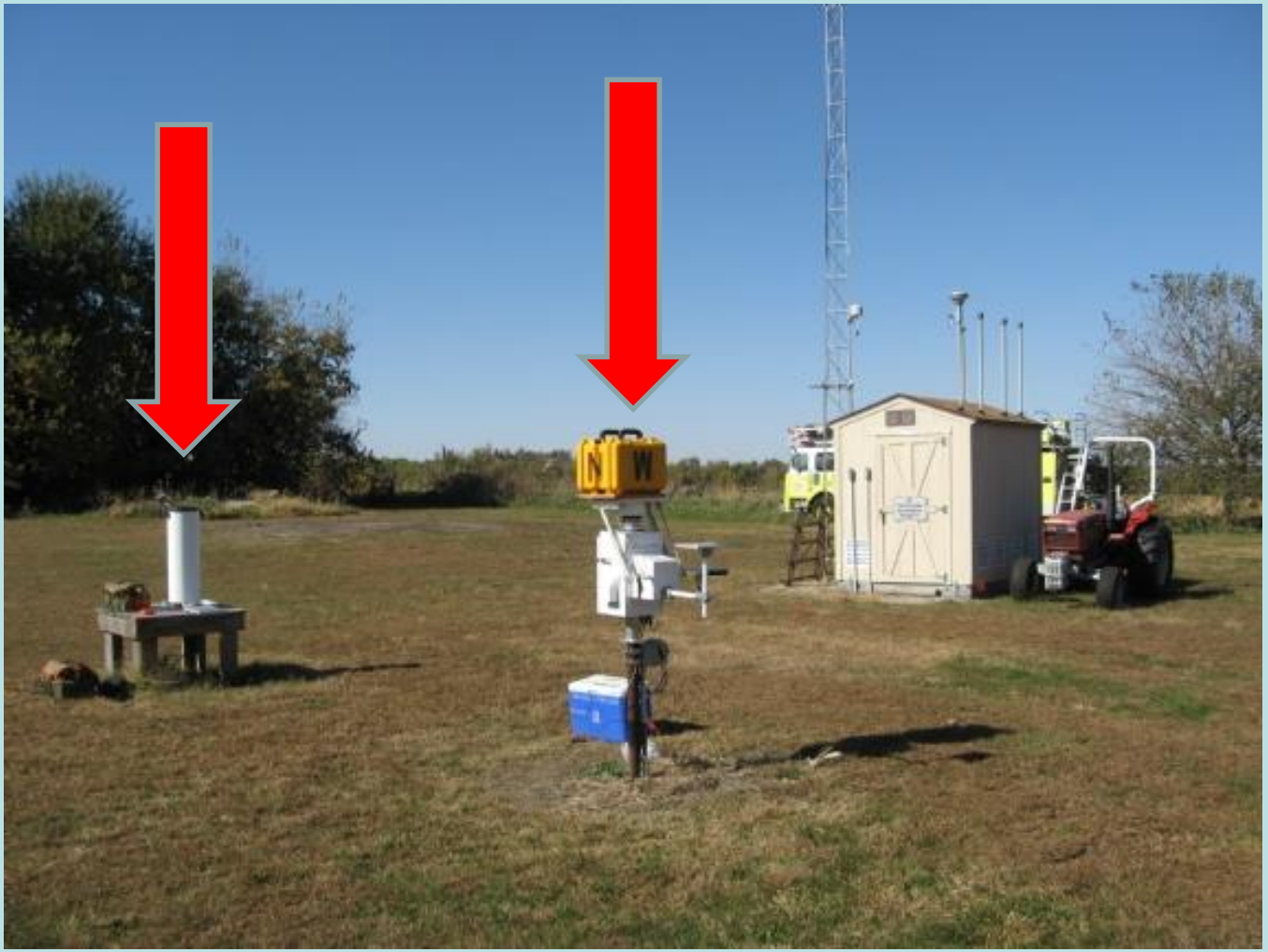
http://nadp.isws.illinois.edu

Mercury Deposition Network (MDN)

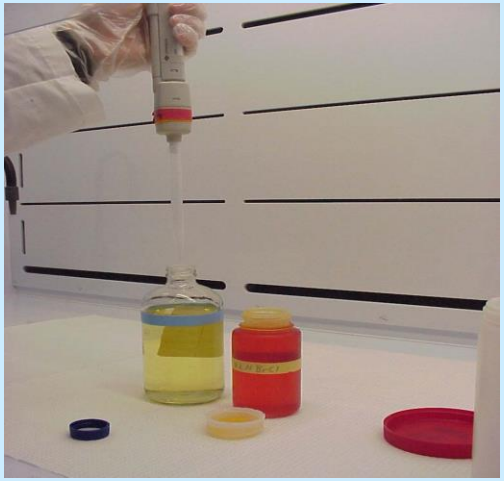
- **Collects one-week precipitation-only samples with MDN wet-dry collector**
- **Measures precipitation with gage (2 options)**
- **<u>Analyses</u>**
  Total Mercury
  Methyl Mercury
- **Optional "daily" mode**
- **118 Sites**


PQ17
MN18
MN16
MN06
MN23
WI36
MI48
WI08
MN98
WI10
MI09
ON07
NY20
VT9
NY43
NY68
MN27
WI31
WI07
PA29
PA18
PA90
MI26
PA30
MI52
WI99
OH52
PA21
PA52
IN34
PA37
NE15
KS03
IL11
OH02
MO03
VA28
IN21
IL63
IN22
KS05
KY10
MO46
NC17

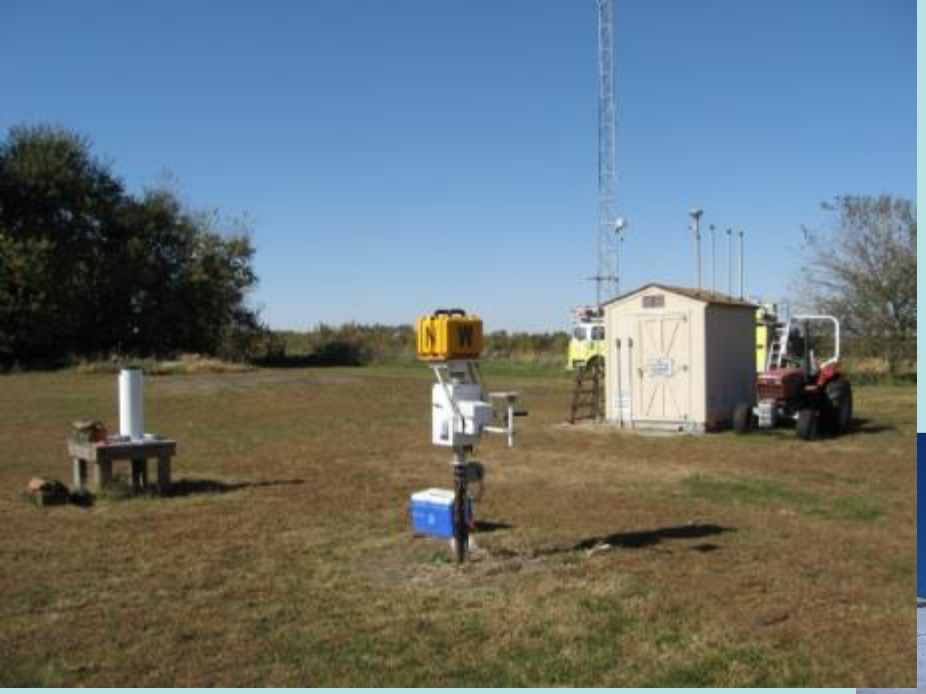
Typical MDN Wet Deposition Site



Total Hg Analysis via CVAFS
Modified US EPA Method 1631



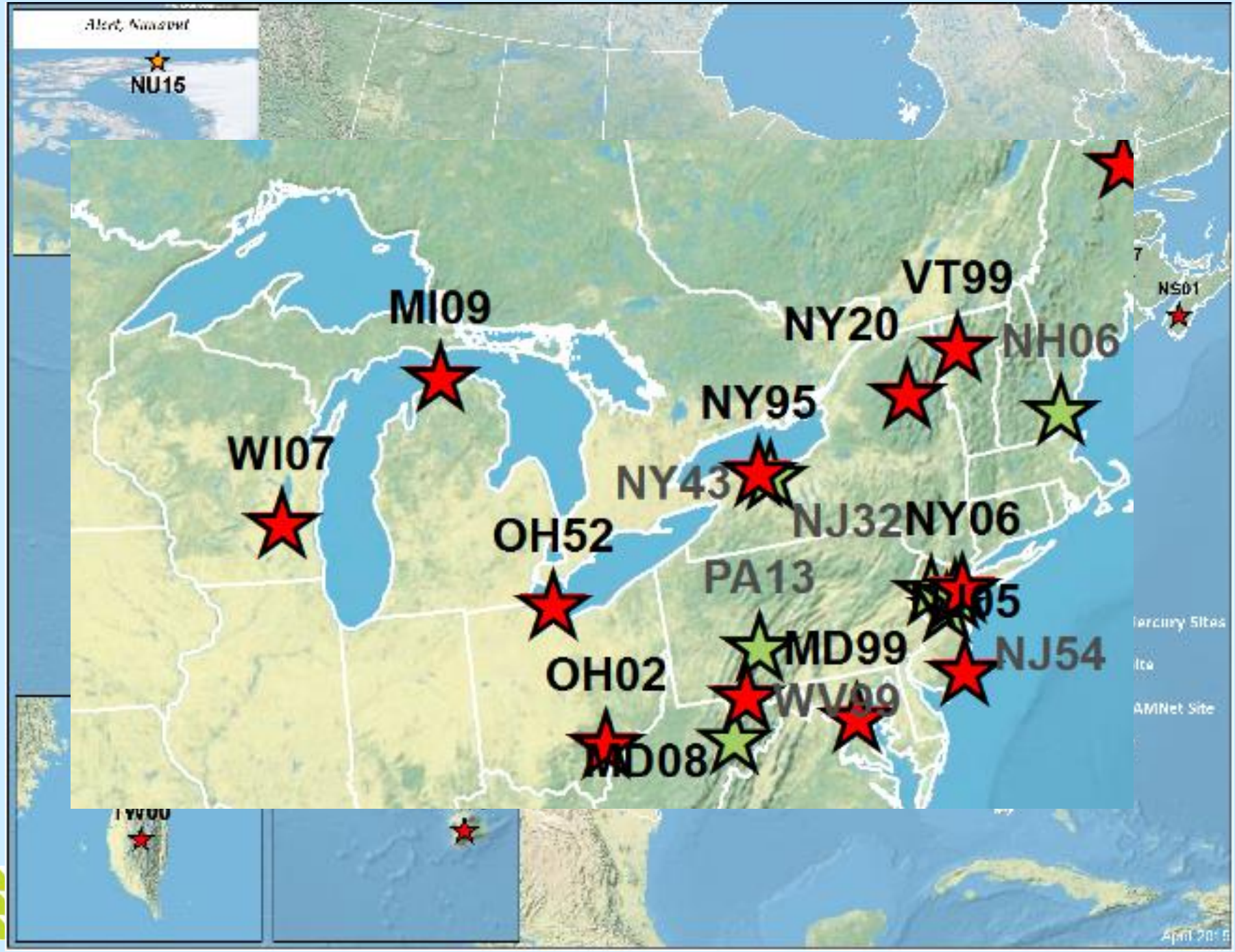
- *Cleanly collect sample in Borosilicate Glass*
- *Oxidize by BrCl converts Hg-org and Hg^o to Hg (II)*
- *Pre-reduction with NH_2OH to destroy free BrCl*
- *Reduction with $SnCl_2$ to convert Hg (II) to Hg^o*




WS

Atmospheric Mercury Net Network

- Mercury fractions
  - GEM (hourly)
  - GOM (2 hourly)
  - $PBM_{2.5}$ (2 hourly)
- Tekran Continuous Mercury Speciating System
  - 2537, 1130, 1135
- With wet deposition flux
  - Mercury Deposition Network
- Will estimate dry deposition flux
- 24 Sites currently; 600,000 observations


Alert, Nunavut
NU15
MI09
VT99
NY20
NH06
NS01
NY95
WI07
NY43
NJ32
NY06
OH52
PA13
MD99
NJ54
OH02
MD08

Estimate Dry Deposition

- Weekly GOM, PBM, and GEM (downward/net)
- flux (*F*) = *air concentration x dry deposition velocity* (V_d)

$$F = V_{deposition} * Concentration_{air}$$

where:

$$V_d = \frac{1}{R_a + R_b + R_c}$$

- R_a *as aerodynamic resistance,* R_b *as quasi-laminar resistance, and* R_c *as canopy resistance*

New Trial Network, Litterfall Mercury

- Started in 2012
- In cooperation with USGS
  and USGS Mercury Research Lab
- 14 stations (w/MDN)
- Monthly observations
  (May to Nov)

National Atmos
Deposition Pro

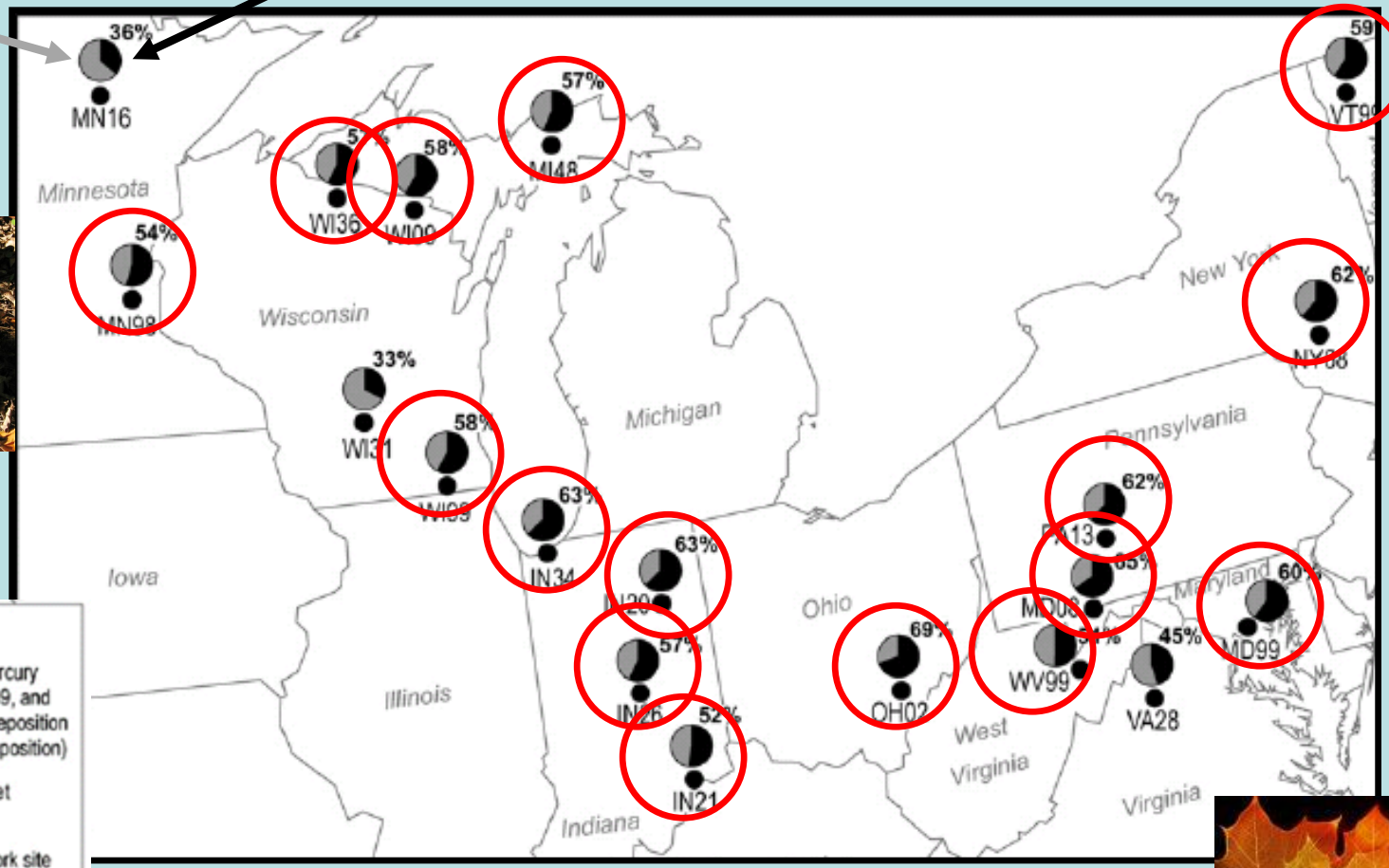
Litterfall Estimates Around the Great Lakes

Risch et al, 2012

Litterfall dry dep.

Wet Dep.

USGS
science for a changing world



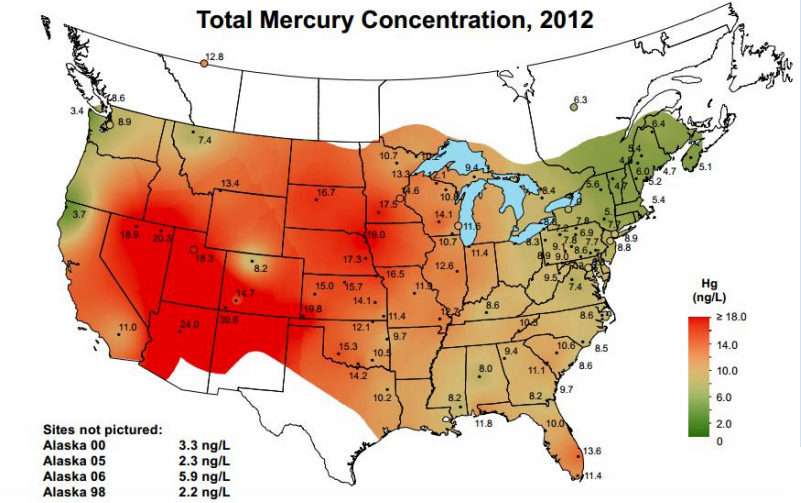
EXPLANATION

63% Mean annual litterfall mercury dry deposition, 2007-2009, and dry percentage of total deposition (dry plus wet mercury deposition)

Mean annual mercury wet deposition, 2007-2009

IN34 Mercury Deposition Network site and identification number

2013 MDN Wet Concentration Map



National Atmospheric Deposition Program/Mercury Deposition Network
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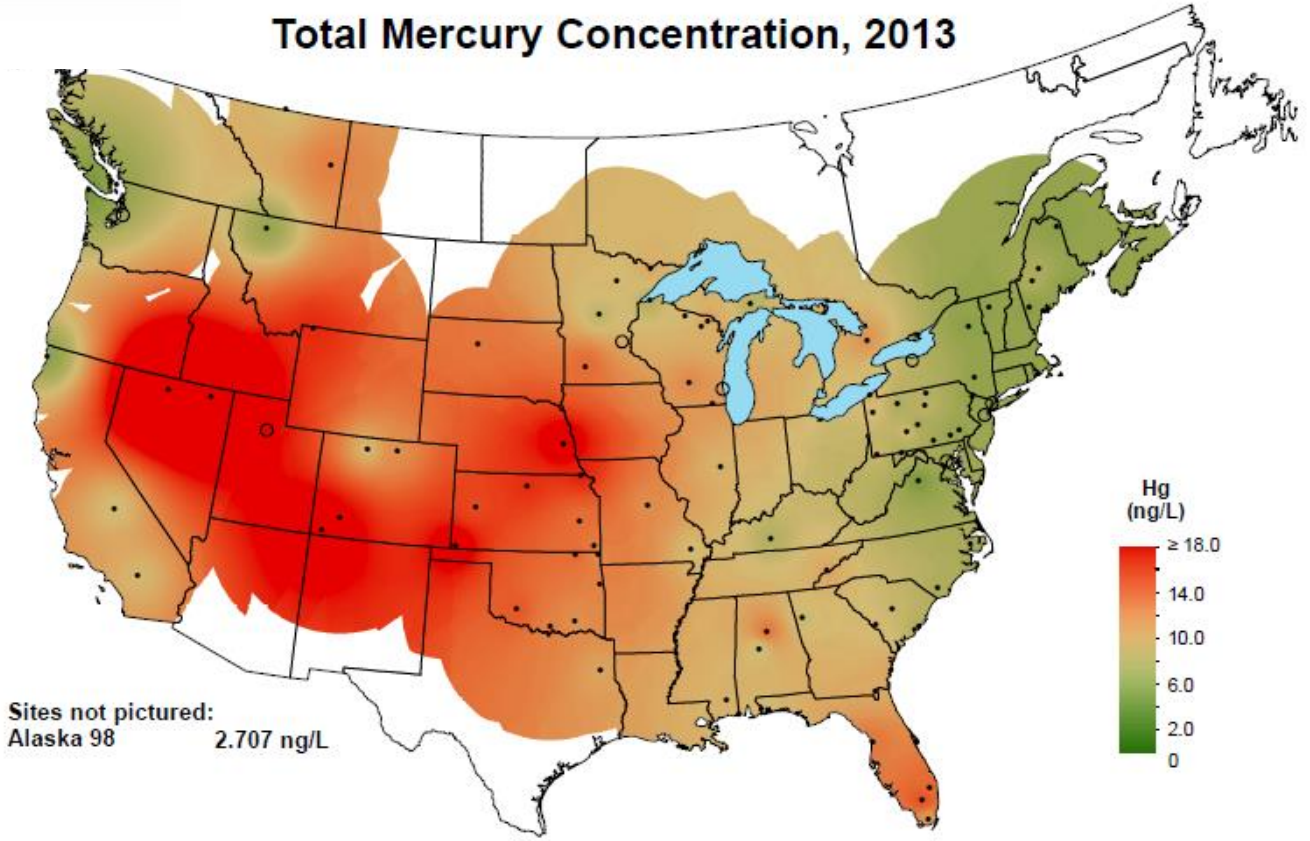

National Atmospheric Deposition Program/Mercury Deposition Network
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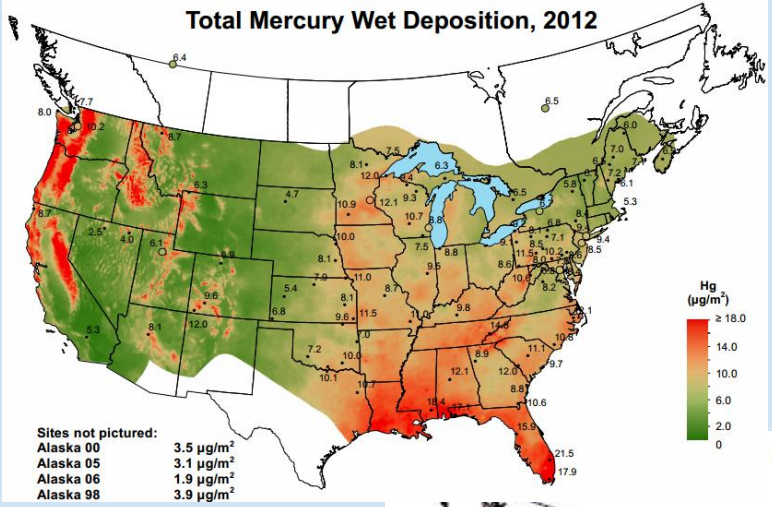
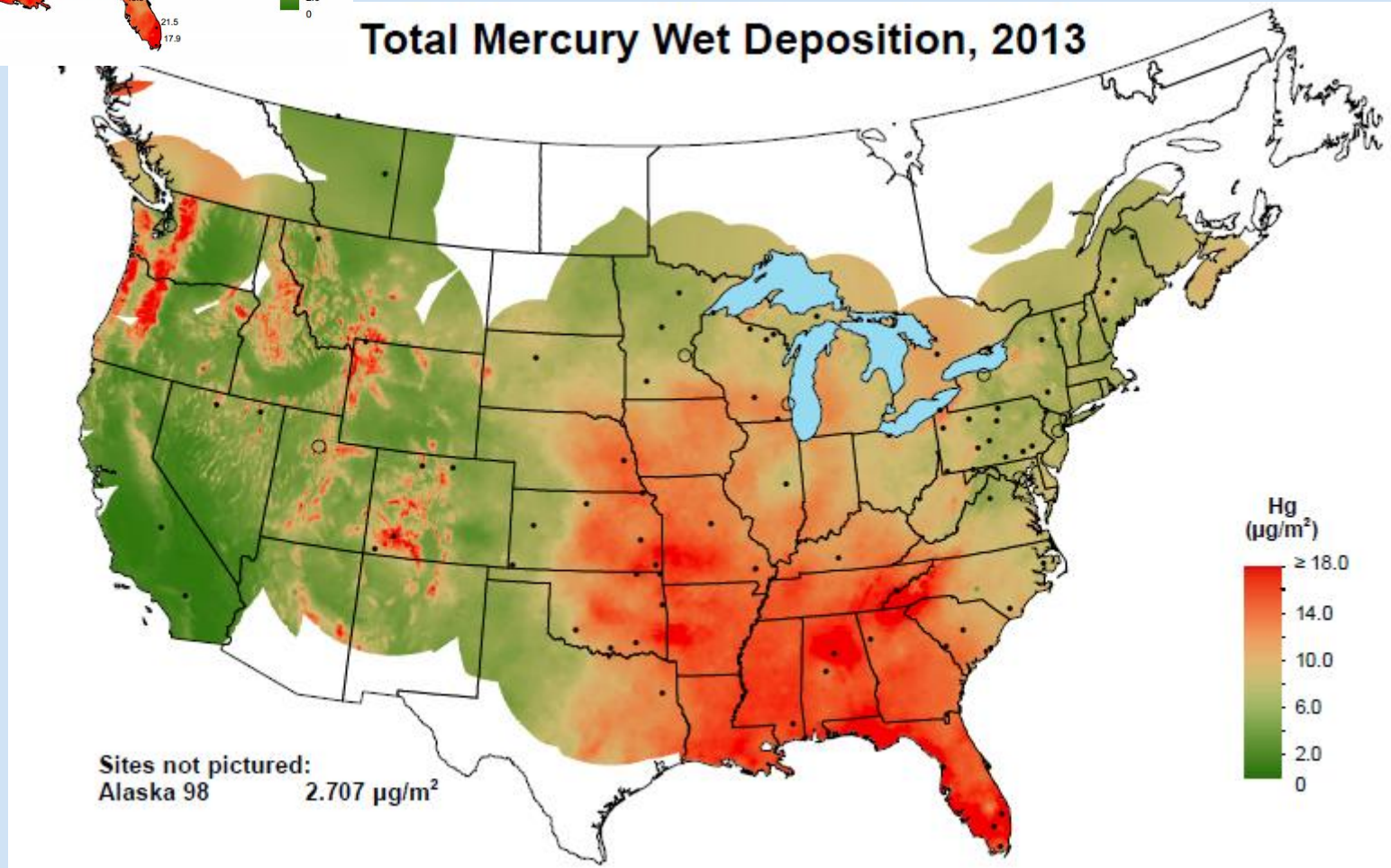
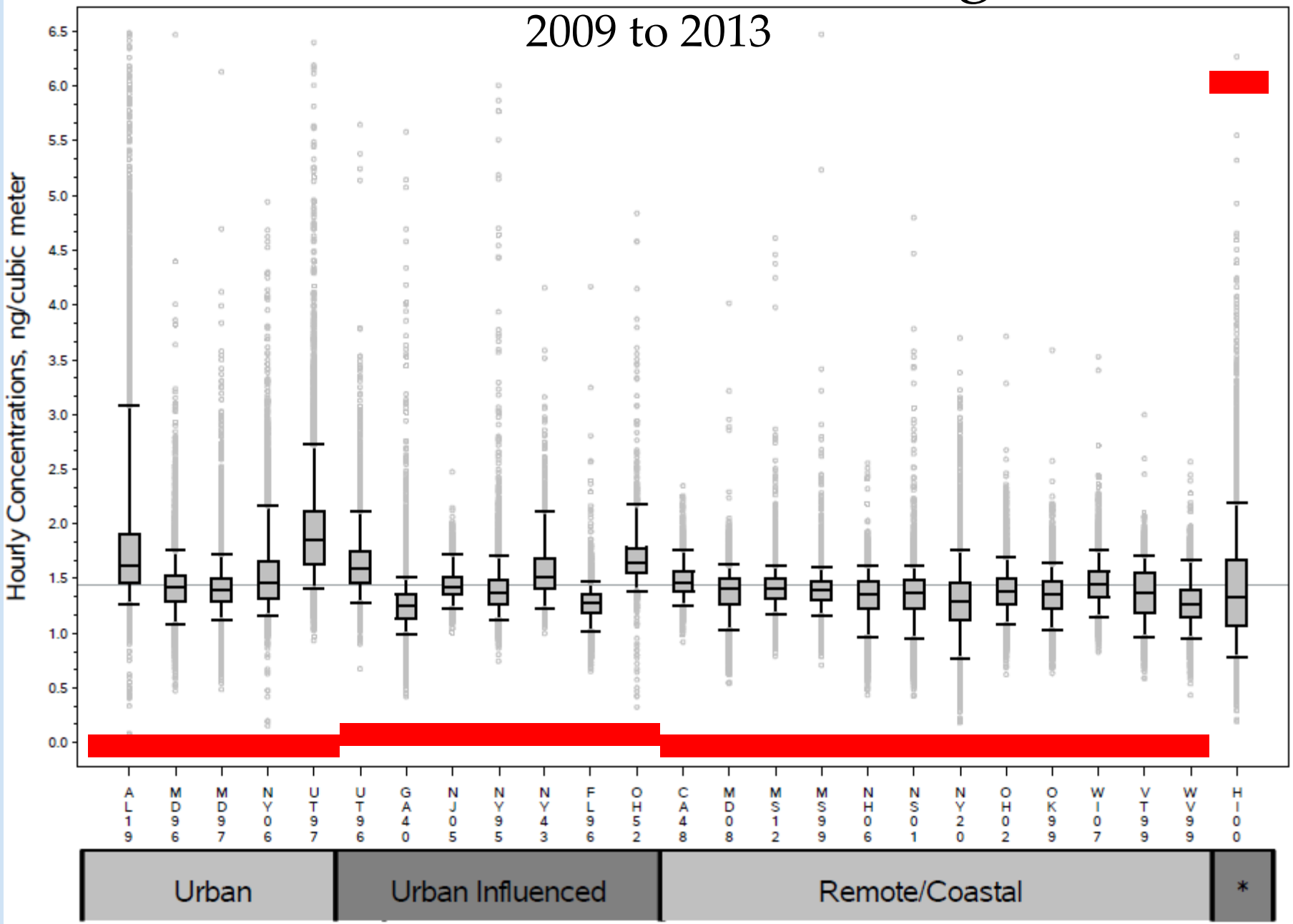
2013 MDN Wet Deposition Map



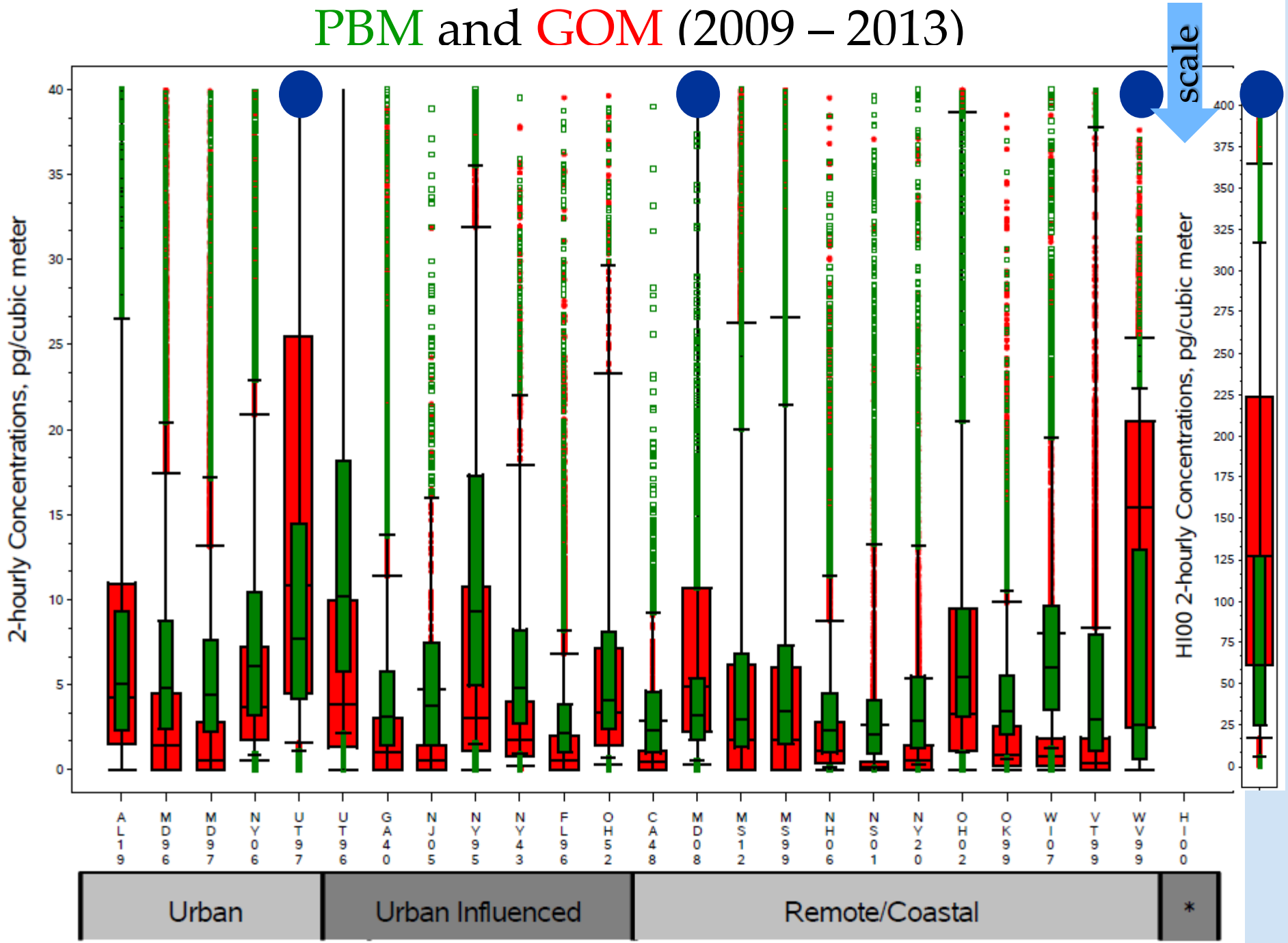


Gaseous Elemental Hg

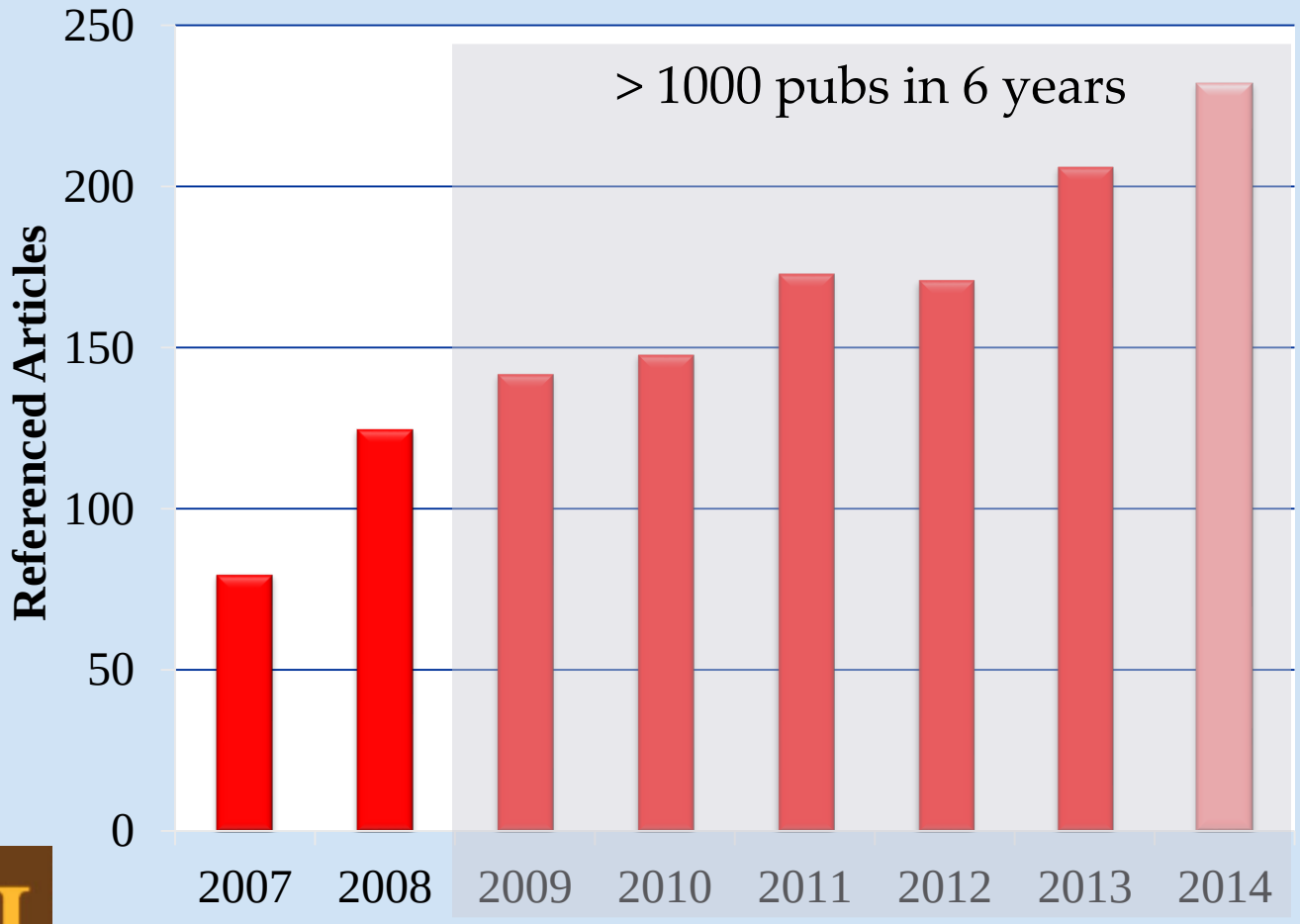
2009 to 2013



PBM and GOM (2009 – 2013)



The Real Value of NADP Data: Scientific Research



Thank you.

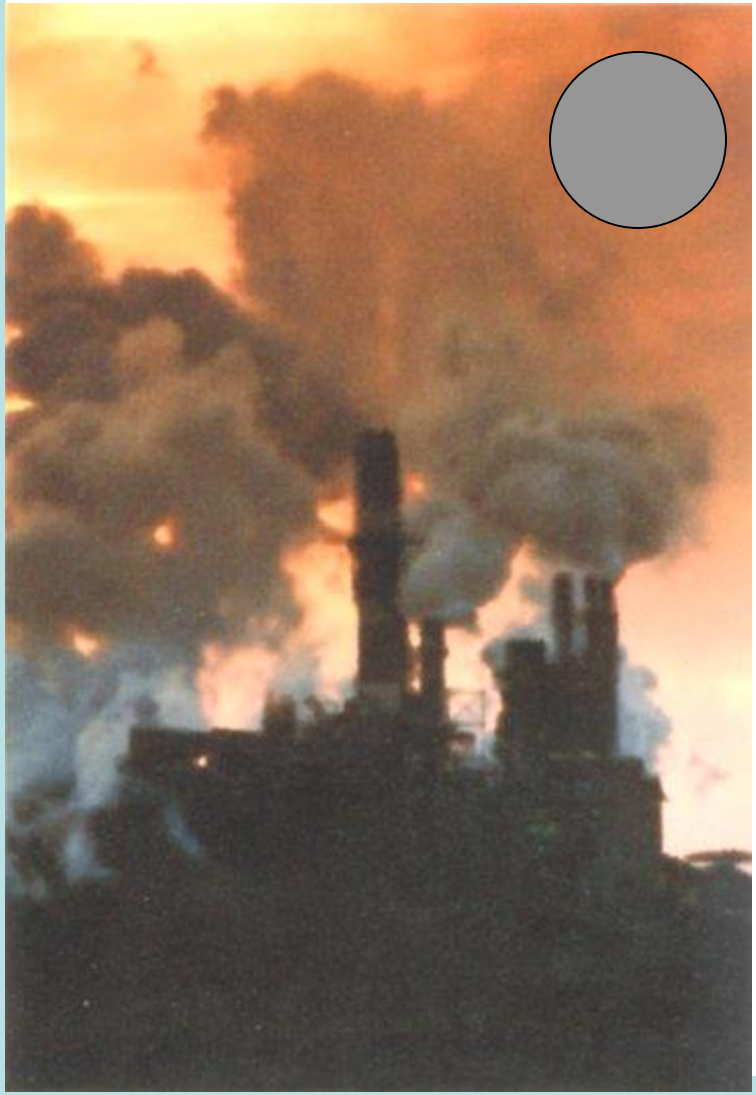
NADP QA Overview

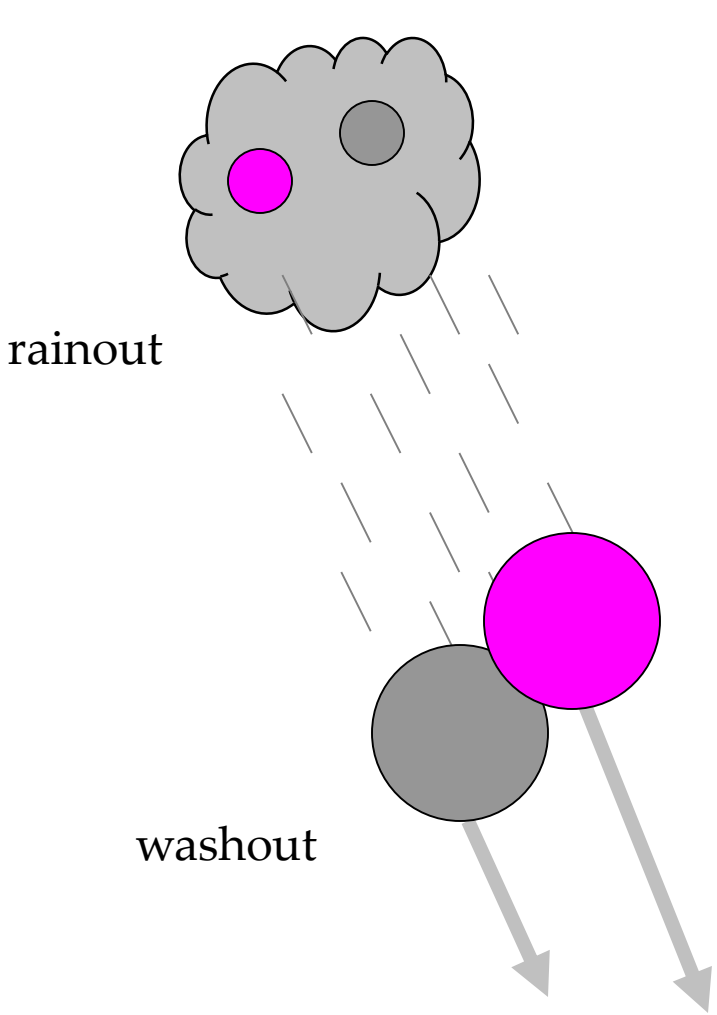
- Standard Operating Procedures
  - Field Operations, Data Management
    Site Survey, Siting Criteria
    Site pictures, information
- Scheduled blanks and spikes
  - Laboratory blanks
  - Field blanks
- 3rd Party QA Program (USGS & EPA)
  - Blind spike samples, Inter-lab compar
  - Site Audits
- Independent QA director
- Site setup and Support
- AMNet: Automated QA of data records

Strengths of the NADP Method

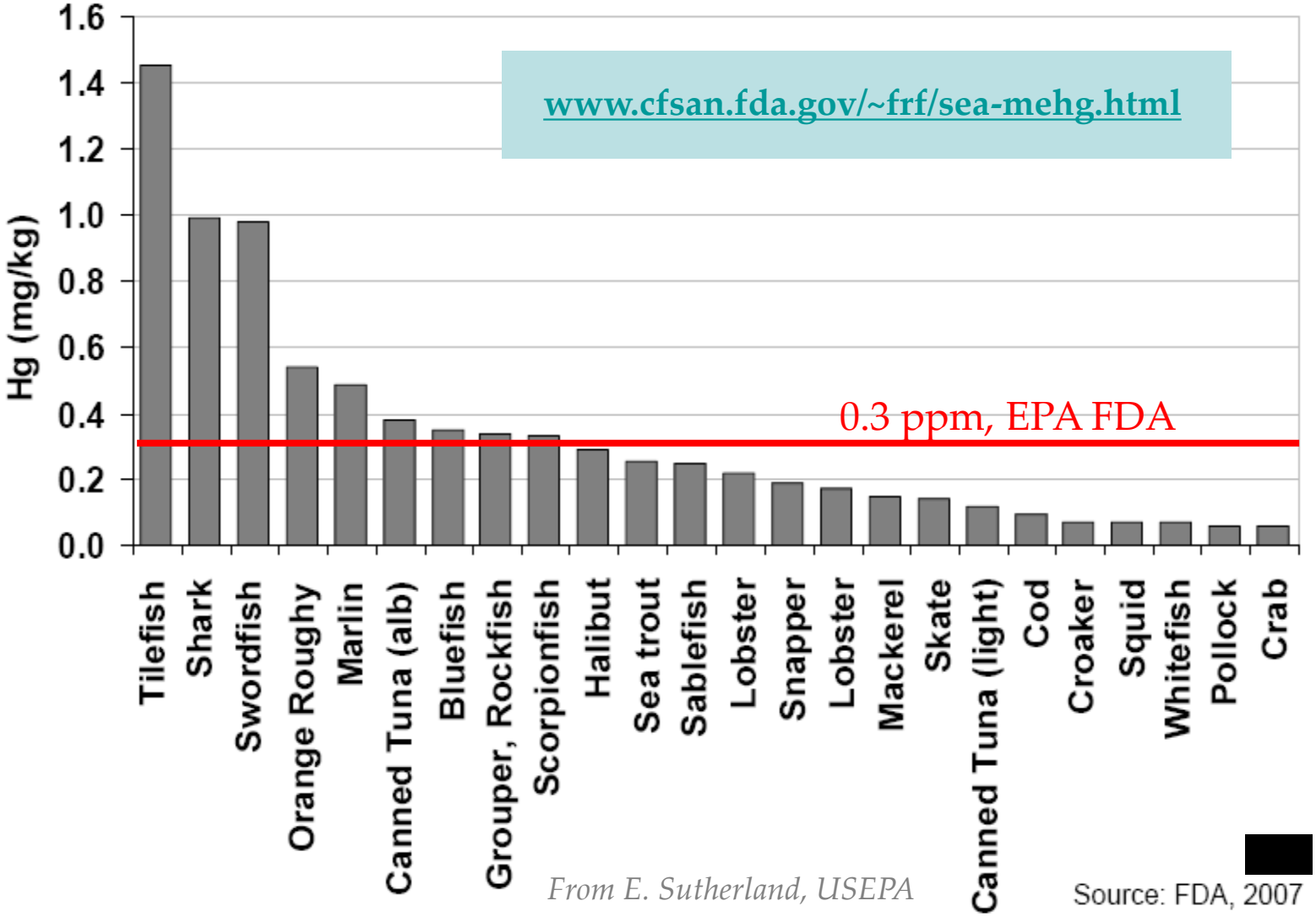
- Open & Collaborative Approach
- Common protocols
- Cost effective design to maximize monitoring dollars
- One laboratory for all samples (consistency)
- Dedicated operators
- Sharing of data (open access, reliability, its use keeps us relevant)
- Commitment to long term monitoring
  - federal agencies
  - state agencies
  - other

Wet Deposition of Pollutants





FDA Reported National Hg Values



From E. Sutherland, USEPA

Many Sources of Atmospheric Mercury

- Coal combustion
- Incineration
  - Medical
  - Trash
  - Cremation
- Industrial emissions (chlor-alkali)
- Cement production (Hg in lime)
- Mining
  - Hg use in gold and silver mining (amalgam formation)
  - Mining for Hg
  - taconite
- Automobile Recycling
- Mercury in Landfills
  - Fluorescent lamps
  - dental amalgams (also in sewers)
  - Thermometers
  - Batteries
  - Discarded electrical switches
- Others will surface
  - Other carbon fossil fuels (gas/oil/diesel)?

- Volcanoes (St. Helens)
- Naturally enriched ores/soils
  - Plate tectonic boundaries
  - Cinnabar (HgS), taconite, others
- Soils and rocks (0.08 to 0.5 ppm in crust)
- Evaporation
  - Soils
  - Fresh water and Oceans
- Natural forest fires
  - Tree bark (wood fire places)
  - soils

- Volatilization from rocks?

- Wind Blown reintroduction
  - Mine tailings
  - Industrial contaminated soils

- Evolving Gases
  - Mines, industrial areas
  - Waste facilities (municipal in particular)
  - Out of soil

AMNet Quality Assurance Overview

- Field Operations SOP
  - operation, reporting, etc.
  - weekly/monthly/quarterly maintenance
- Data Management SOP
- Site Survey SOP
  - siting criteria
- Quality Assurance Plan
- Site pictures, information

Available on the NADP Webpage

Automated Quality Assurance

- Upon import of raw data, flags are assigned to each observation
- AMNet currently utilizes 51 Quality Assurance flags, most are automated
  - 23 are warning flags which leave the data valid
  - 26 are control flags which invalidate the data
- Then manual review, with final flag assignment
- QA system available for GMOS

Examples of QA Flags

Data Flag*	Description	Mercury Species
null	Data meets criteria used in the automated scripts	All
A1	$\lvert(\text{Air cartridge bias}_i - \text{Air cartridge bais}_{i+1})/\text{Air cartridge bias}_i\rvert > 0.10$ for 24 consecutive hours	GEM
A2	$\lvert(\text{Air cartridge bias}_i - \text{Air cartridge bais}_{i+1})/\text{Air cartridge bias}_i\rvert > 0.15$ for 24 consecutive hours	
B0	Baseline voltage < 0.01V	All
B1	Baseline voltage < 0.05V, or Baseline voltage > 0.25V	
B2	$\lvert\text{Baseline voltage}_i - \text{Baseline voltage}_{i+1}\rvert > 0.01$V	
B3	Baseline deviation > 0.10V for 5 consecutive readings	
B5	Baseline deviation > 0.20V	
C0	$\lvert(\text{Calibration}_i - \text{Calibration}_{i+1})/\text{Calibration}_i\rvert > 0.10$	
C1	$\lvert(\text{Calibration cartridge bias}_i - \text{Calibration cartridge bais}_{i+1})/\text{Calibration cartridge bias}_i\rvert > 0.10$	
C2	$\lvert(\text{Calibration cartridge bias}_i - \text{Calibration cartridge bais}_{i+1})\rvert/\text{Calibration cartridge bias}_i > 0.20$	
C5	$\lvert(\text{Calibration}_i - \text{Calibration}_{i+1})/\text{Calibration}_i\rvert > 0.05$	
E0	First GEM from each cartridge	GEM
E1	GEM < 1.00 ng/m^3 for same cartridge	
E5	$\lvert(\text{GEM}_i - \text{GEM}_{i+1})/\text{GEM}_i\rvert > 0.50$ for same cartridge	
F1	72 hours < Time between calibrations < 144 hours	All
F2	Time between calibrations > 144 hours	
G0	GOM = 0 pg/m^3 for more than 24 hours	GOM
G1	Cycle(H) < 0.70 x GOM, or Cycle(I) > 0.20 x GOM, or Cycle(J) > 0.10 x GOM	
G2	GOM < 0 pg/m^3	
L1	GEM cycles < 24 before desorption	GOM $PBM_{2.5}$
L2	GEM cycles <> $\text{GEM cycles}_{\text{historical}}$	
M2	Status = M2 (multiple peaks)	All
M3	Status > M2 (multiple peaks)	
NP	Status = NP (no peak)	GEM
OL	Status = OL (overload)	All

But it isn't just humans….












How Mercury is Wet Deposited?