The National Atmospheric Deposition Program National Trends Network, a Premier Model of Multi-Sector Partnerships, Working to Provide New Information on PFAS Deposition in Precipitation

Martin Shafer, Mark Olson, James Schauer
University of Wisconsin-Madison, State Laboratory of Hygiene

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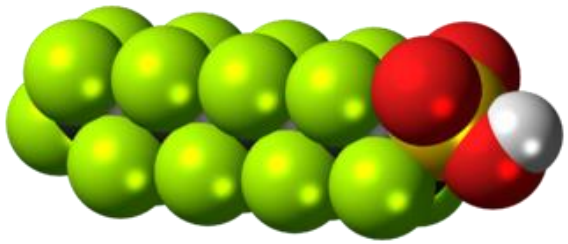


The National Atmospheric Deposition Program (NADP)

The NADP is one of our nation's premier long-term environmental monitoring programs, with data of the highest quality, and has been relied upon for four decades to help understand and mitigate some of the most pressing environmental problems of our times. Issues that directly impact people, ecosystems, and our built environment at local, regional and national scales.

The NADP monitors our nation's precipitation and atmosphere for a range of chemical constituents to determine SPATIAL and TEMPORAL trends in CONCENTRATION and DEPOSITION.

NADP Nationwide Importance

The NADP program is essential for facilitation of cleaner water, healthier air quality, more productive fisheries, smarter environmental planning, improved air quality and climate forecasting, healthier forests, and responsible environmental stewardship.

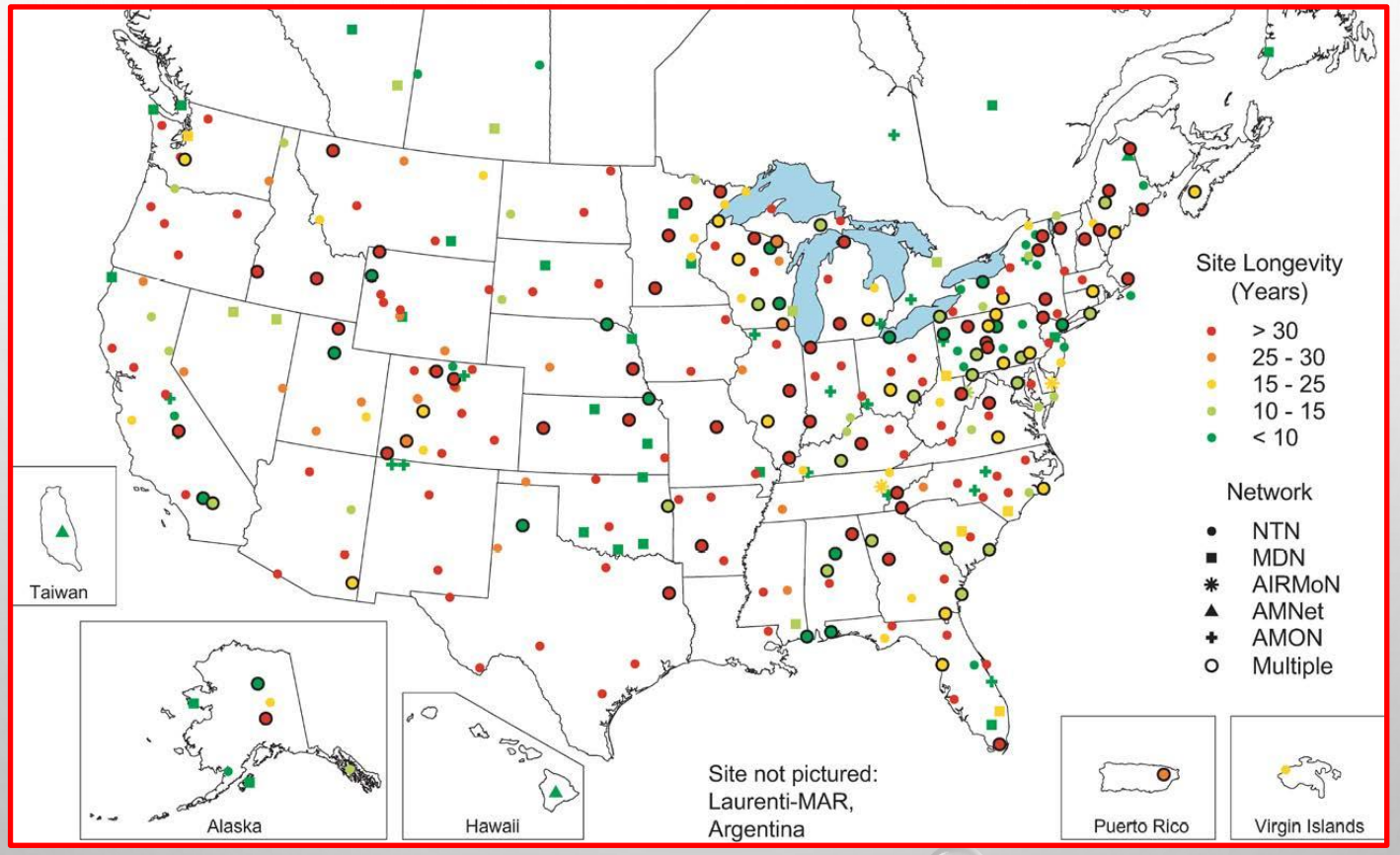
1. A critical tool to inform and evaluate the effects of environmental regulation on contaminant levels in key environmental compartments (including humans) [e.g. acid deposition, mercury deposition]
2. NADP data is key to understanding the ecosystem and human health impacts of anthropogenic emissions:
   a. direct and indirect effects of acid deposition on acid-sensitive watersheds – element leaching, food-web impacts, fisheries impacts
   b. impacts of acid deposition and nitrogen loading on our forests
   c. development of critical loading factors that protect the abundance and diversity of forest and aquatic ecosystems
   d. assessing Hg/MeHg cycling and human health implications, Hg advisories
   e. understanding the sourcing and impacts of ammonia in both rural and urban environments
3. An important resource for scientific research across multiple disciplines [e.g. in 2016 alone, 236 peer-reviewed publications used NADP data]

NADP SCOPE : Network Sampling Sites

Established in 1978, the NADP is the only network providing a long-term record of precipitation chemistry, and more recently air chemistry, across the US.

Over 350 sites with 500+ samplers are monitored.

Generating 20,000+ samples per year for chemical characterization.



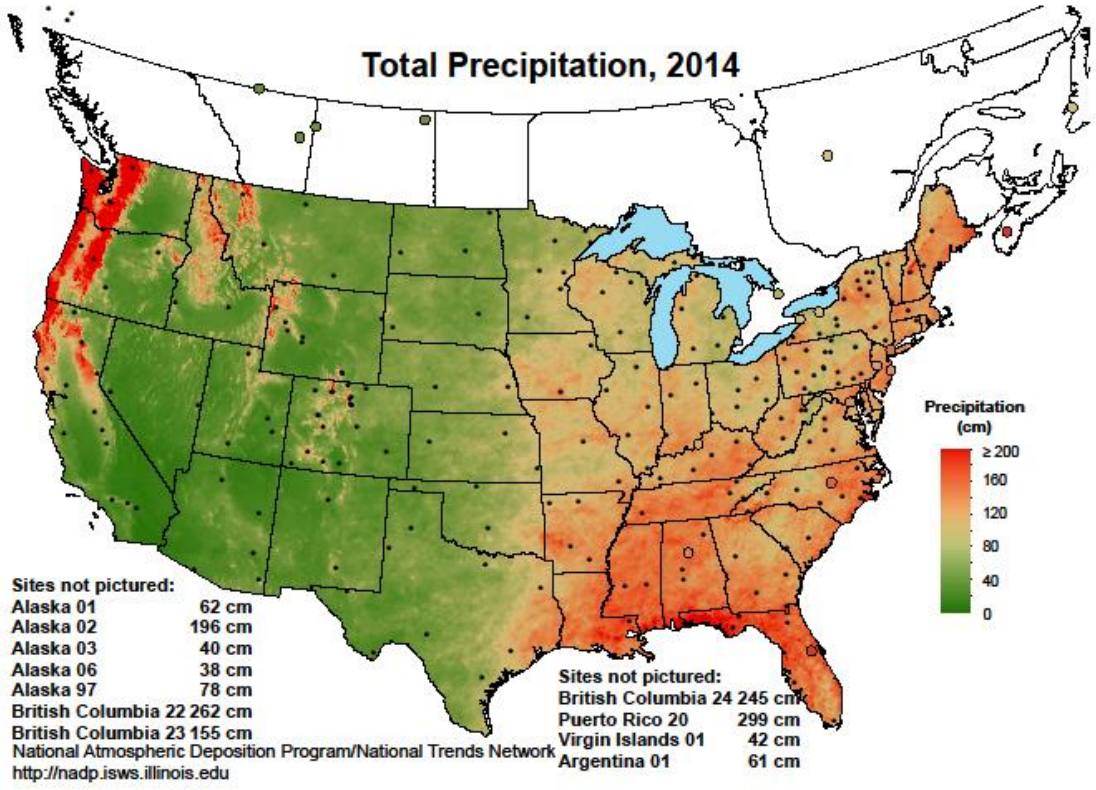
National Atmospheric Deposition Program

Operated by the Wisconsin State Laboratory of Hygiene

1. NTN: National Trends Network
2. MDN: Mercury Deposition Network
3. AMNet: Atmospheric Mercury Network
4. AMoN: Ammonia Monitoring Network

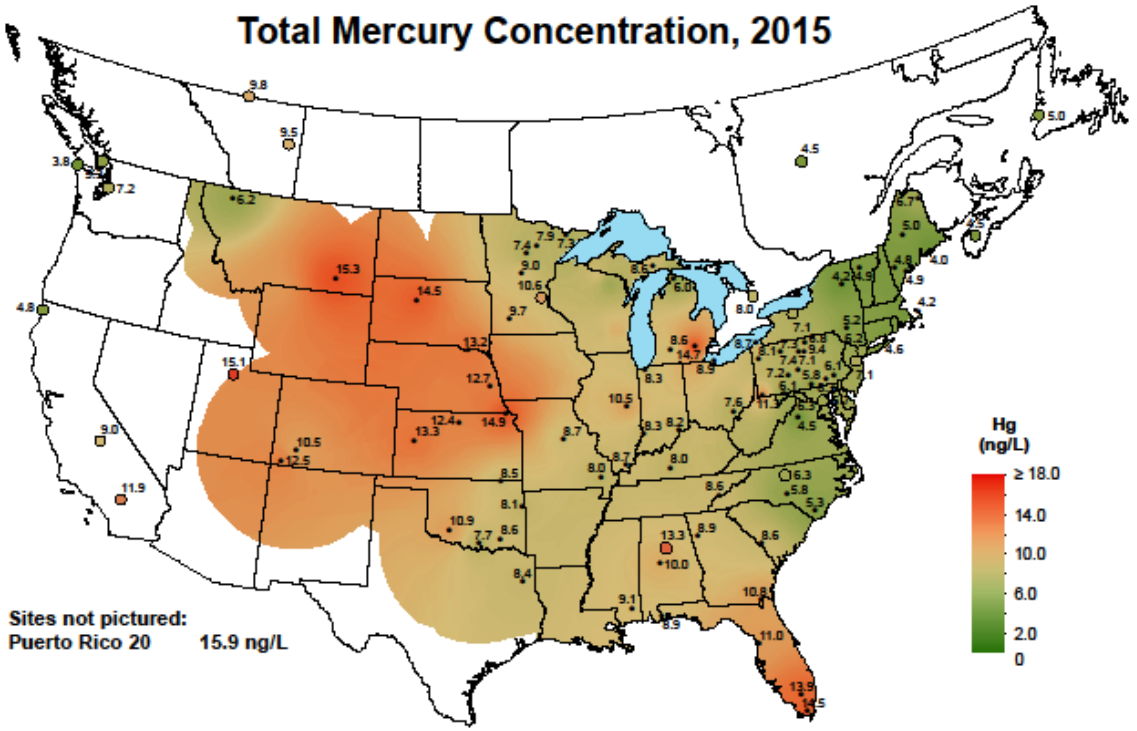
Network ID	Network Initiated	Sample Matrix	Collection Frequency	# of Sites (WI)	Core Analytes
NTN	1978	Precipitation	Weekly	259 (7)	Na, K, Mg, Ca, NH_4, pH Cl, NO_3, SO_4, PO_4, SpCond
MDN	1996	Precipitation	Weekly	88 (5)	HgT, MeHg
AMoN	2010	Air (Gas)	Biweekly	110 (5)	NH_3
AMNet	2009	Air (Gas & PM)	Semi-Cont.	18 (0)	GEM, GOM, PBM

NADP – NTN : Data Product : Precipitation



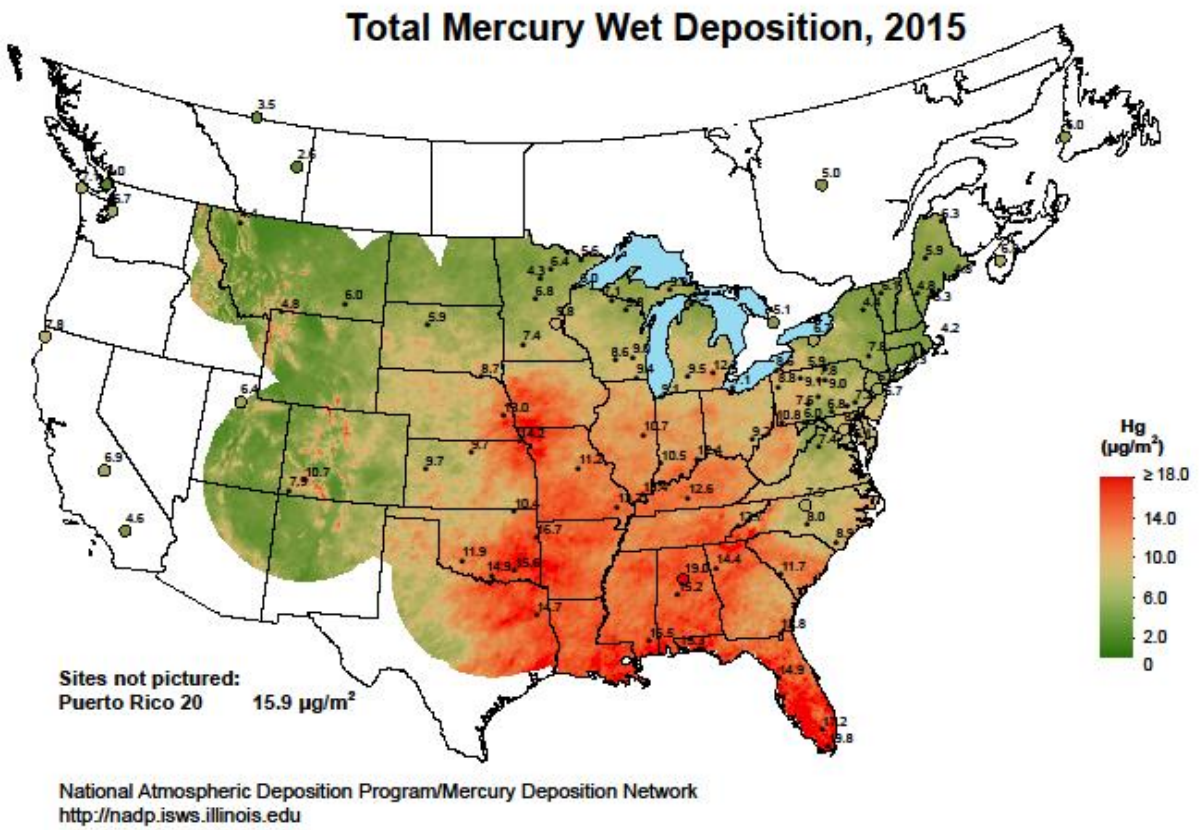
ETI NOAH IV
Rain Gauge

NADP – MDN: Data Product : Hg Concentration



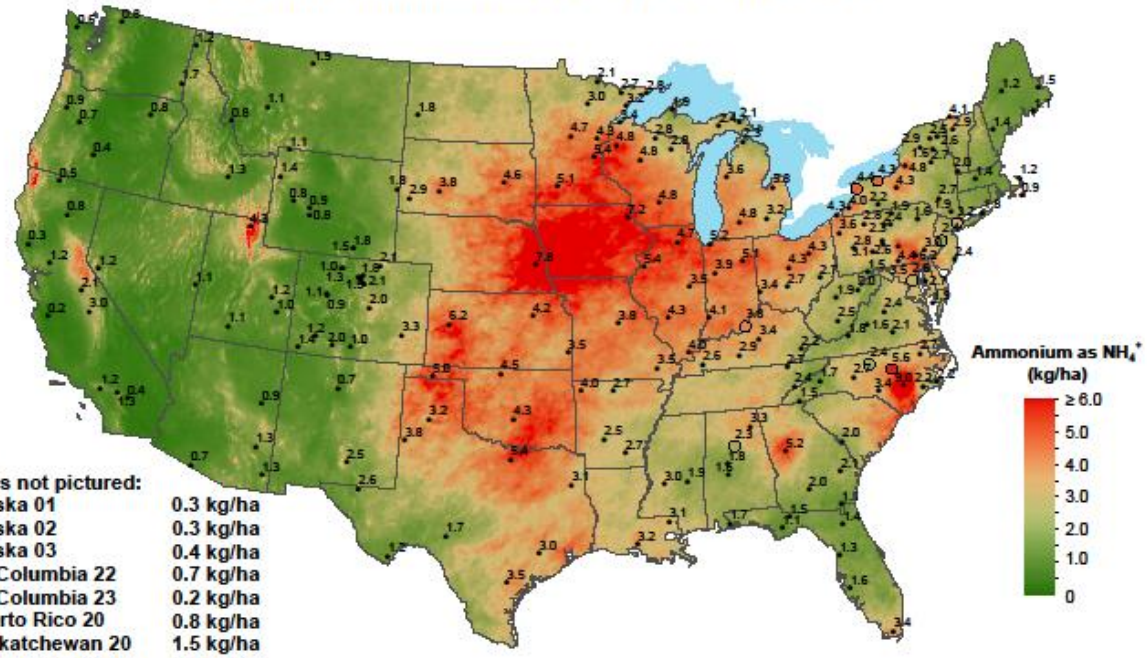
National Atmospheric Deposition Program/Mercury Deposition Network
http://nadp.isws.illinois.edu

NADP – MDN: Data Product : Hg Deposition



NADP – NTN: Data Product : Ammonium Deposition

Ammonium ion wet deposition, 2015



Sites not pictured:

Alaska 01	0.3 kg/ha
Alaska 02	0.3 kg/ha
Alaska 03	0.4 kg/ha
Br. Columbia 22	0.7 kg/ha
Br. Columbia 23	0.2 kg/ha
Puerto Rico 20	0.8 kg/ha
Saskatchewan 20	1.5 kg/ha
Saskatchewan 21	1.1 kg/ha
Virgin Islands 01	0.4 kg/ha

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

The NADP is a Cooperative Program among 5 major Federal Agencies and over 100 other State, Tribal, Local Governments, Universities, Private Companies & NGOs.

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

Menominee Nation

Sault Ste. Marie Tribe of Chippewa Indians

Grand Traverse Band of Ottawa and Chippewa Indians

Sisseton-Wahpeton Oyate

Seal of the Cherokee Nation Sept. 6, 1839

Universities

Universidad de Puerto Rico

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

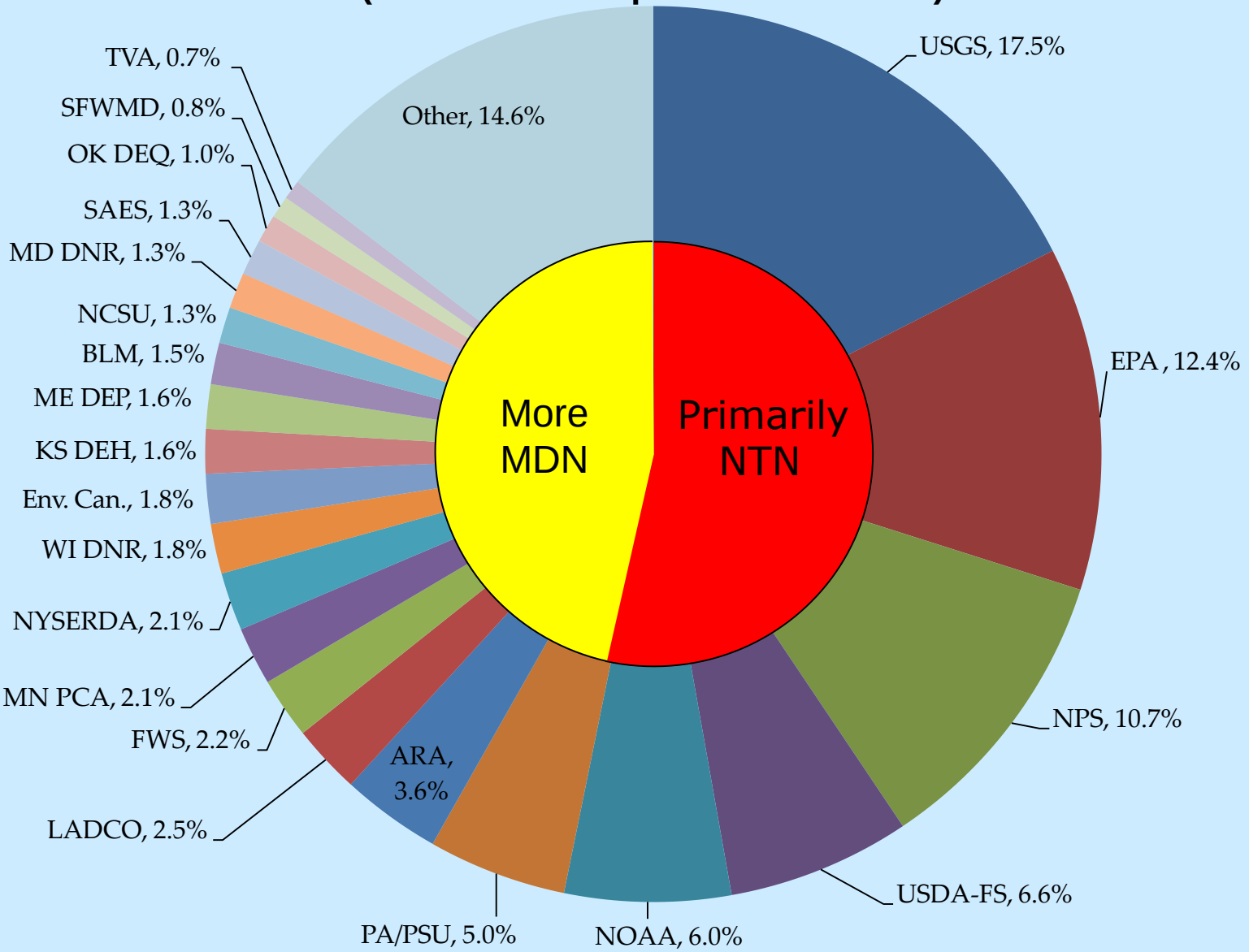
EPA Taiwan

Environment Canada | Environnement Canada

NEW YORK STATE OF OPPORTUNITY. NYSERDA Sponsored

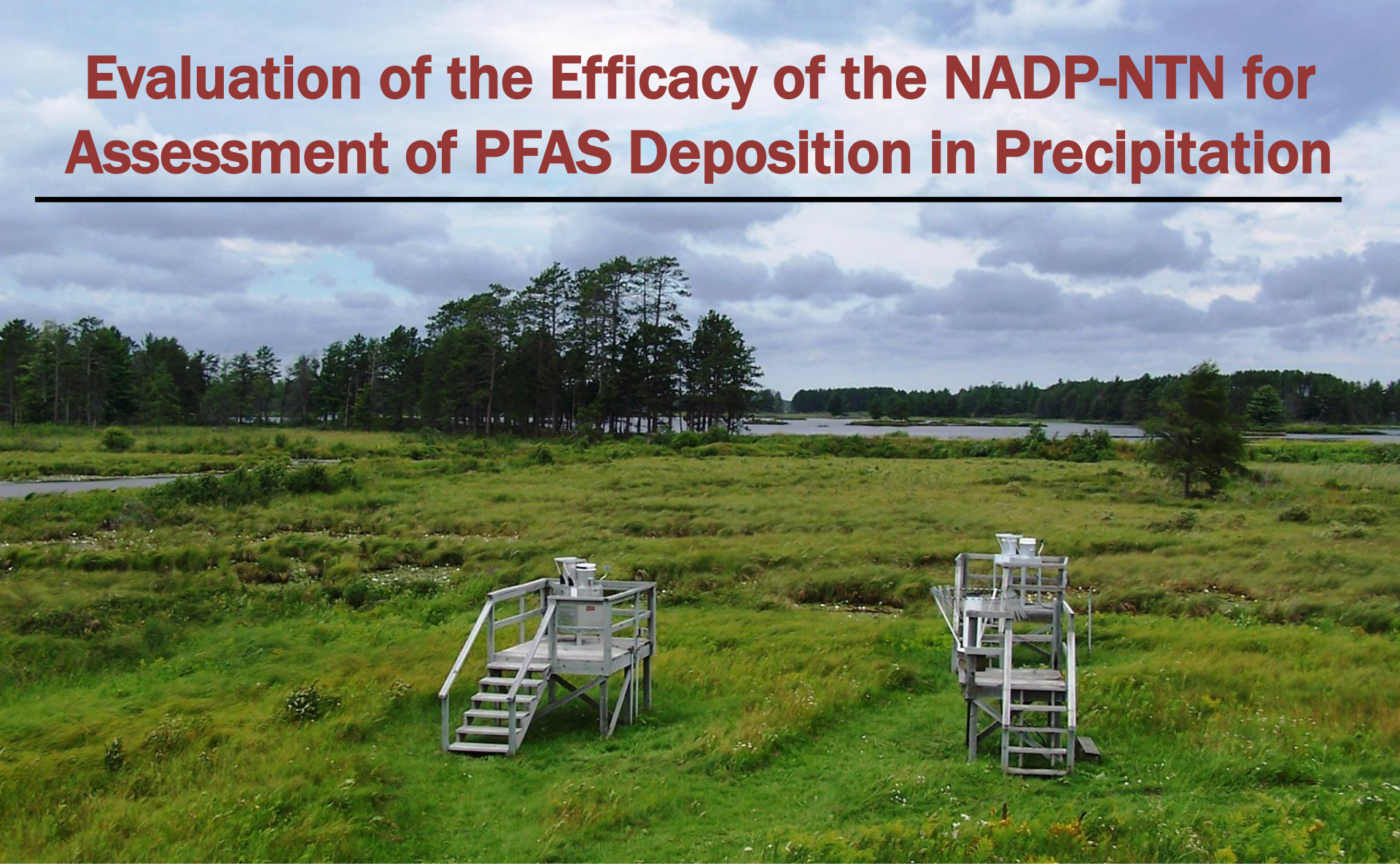
SOUTHERN COMPANY Energy to Serve Your World

Total Program Funding for the NADP (PO, CAL, HAL) was ~3.5M in 2016 with ~55% from 5 main Federal Partners and ~45% from all other Organizations (via Site Subscription Fees / MOAs)



Funding stable over past decade and NADP enjoys broad support in congress

Evaluation of the Efficacy of the NADP-NTN for Assessment of PFAS Deposition in Precipitation



PFAS Dispersal & Atmospheric Processing

Atmospheric Transport, Processing and Deposition is Underappreciated and Under-Studied

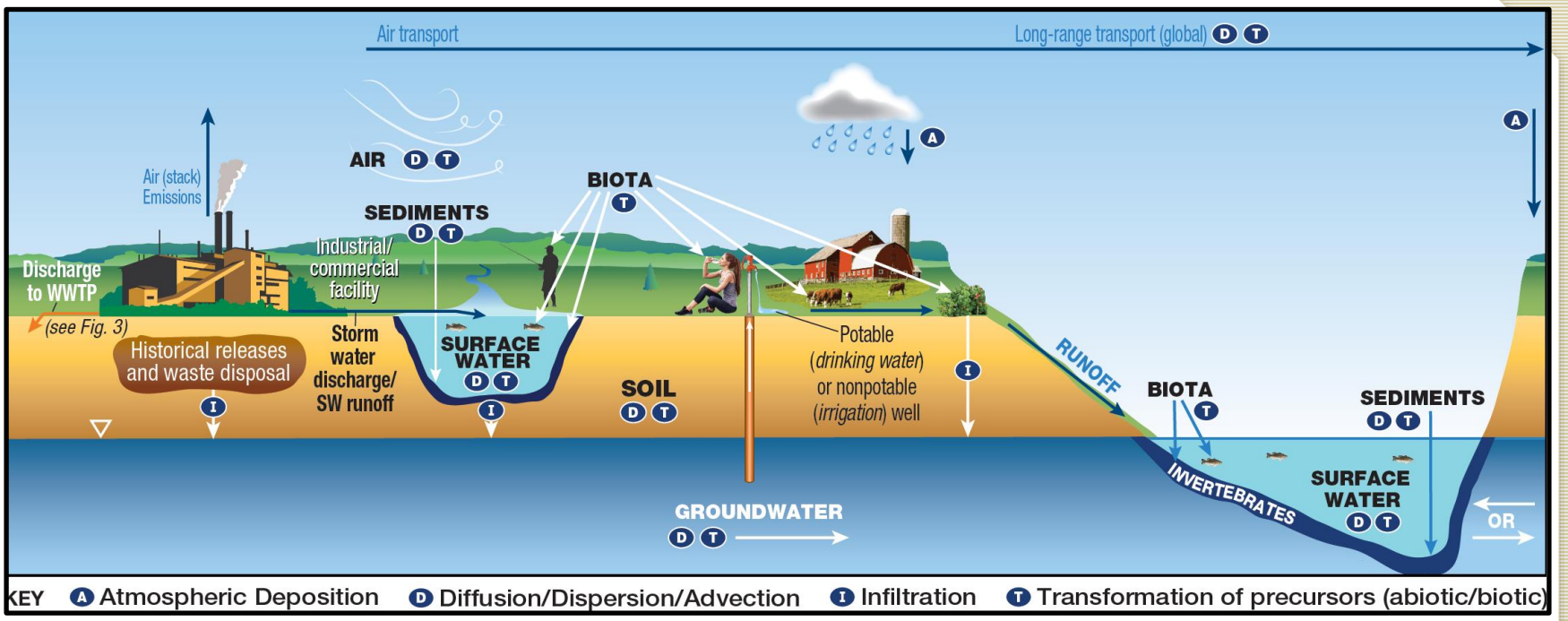


Figure from ITRC

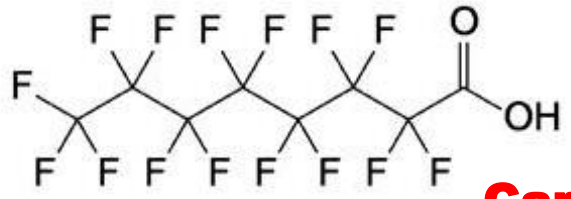
Industrial Sources

1. Paper mills
2. Metal finishers
3. Textile mills
4. Foam factories
5. PFAS factories
6. (manufacturing aids)

Major Entry Points

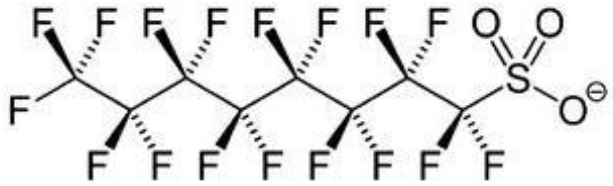
1. Industrial Sites
2. Fire Fighting Training
3. Commercial Fugitive Emissions
4. Landfills
5. WWTP

PFAS Compounds



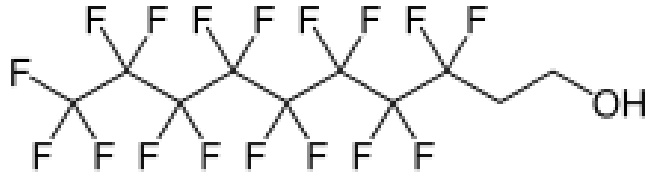
Perfluorooctanoic acid (PFOA)

Carboxylic Acids

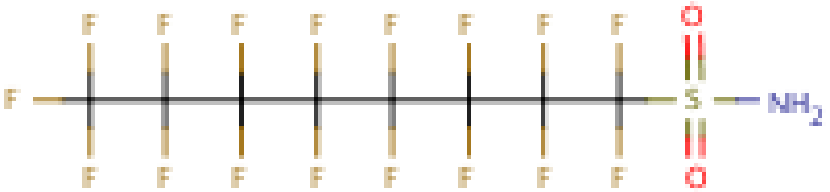


Perfluorooctanesulfonate (PFOS)

Sulfonates



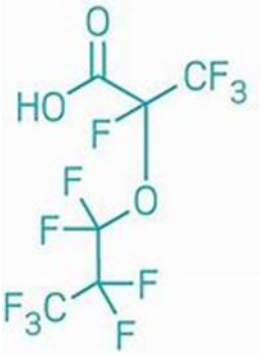
Fluorotelomers



Sulfonamides

>4500 compounds known/suspected
220 with authentic standards
50 with "routine" robust methods
18 in EPA 537.1 (drinking water)
3-5 with regulatory limits (States)

1. **-C_nF_{2n}-head →**
2. **Repel oil and water**
3. **Chemical and Thermal stability**
4. **Reduce friction**
5. **High surface activity**



HFPO-DA

GenX

Buck et al. 2011 **National Atmospheric Deposition Program**

Atmospheric Deposition of PFAS via Precipitation

Goals of the 2019/2020 NADP/WSLH Pilot Study

- Assess the efficacy of the NADP infrastructure and current sample collection methods, for PFAS studies
- Broaden the number of PFAS compounds evaluated
  - Few studies quantify more than 20 compounds
- Initiate a synoptic overview study of PFAS concentrations in precipitation across the US
  - Extant data is quite limited
- Improve the Quality Assurance documentation of PFAS precipitation studies
  - limited QA in many of few published studies

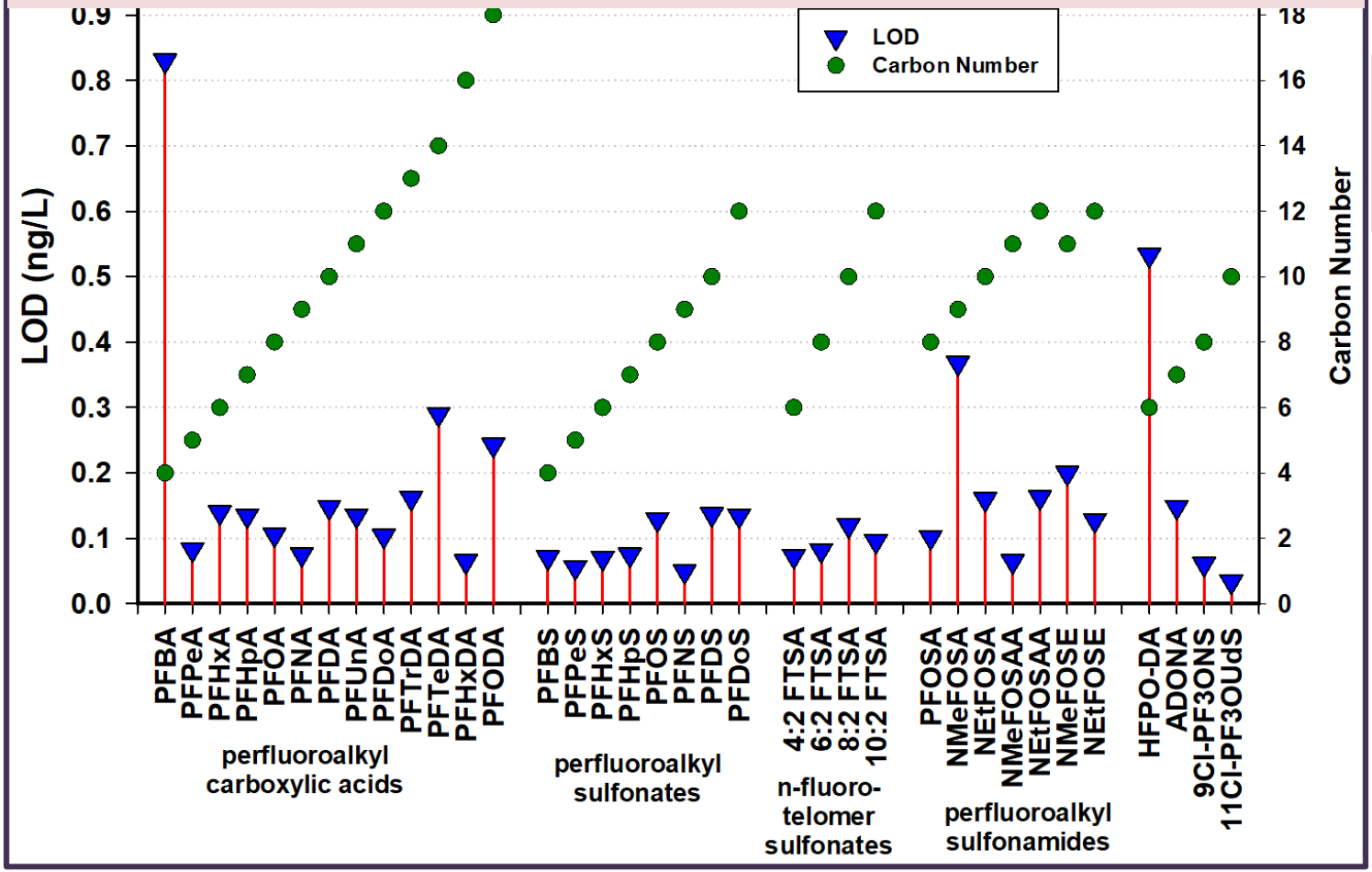
NTN Wet-Only Collector

PFAS Analytical Methods

- **Analytical methods**:
  - ✓ ISO Method 21675 (PFAS in Water by LC-MS/MS). 36 PFAS compounds. 26 isotopically-labeled internal-standards
  - ✓ 500 mL sample volume; entire sample extracted
  - ✓ Automated SPE (Oasis-WAX; 8-station Promochrom Tech.)
  - ✓ Sciex QTRAP 5500 LC/MS/MS, Waters Acquity UPLC
- **Contamination Control**:
  - ✓ QC'd polypropylene collection bottles
  - ✓ Gloves worn during sampling
  - ✓ NO Teflon or related materials

PFAS Method Performance Outcomes in Precipitation

Detection Level (LOD) & Carbon # of the 36 Quantified PFAS Compounds



LODs
Typically in Range of 0.15 to 0.2 ng/L

Spike Recoveries
Typically in Range of 90 to 110% (4 ng/L spike)

National Atmospheric Deposition Program
NADP

Outcomes of Efficacy Study: BLANKS

A. System Blanks:

1. Both Bucket & Bag Collectors
2. Both Lab & Field Deployments
3. 7-day Trials, Run in Triplicate

I. High Purity Water (7-day field conditions)

1. **Bags:** no detects for 36 species (except PFOA, 0.23 ng/L, one sample)
2. **Buckets:** no detects for 36 species (except PFOA, 0.44 ng/L, one sample)
3. **NTN Bottle:** no detects for 36 species

II. Methanol Rinses

I. **Buckets:** no detects for 36 species

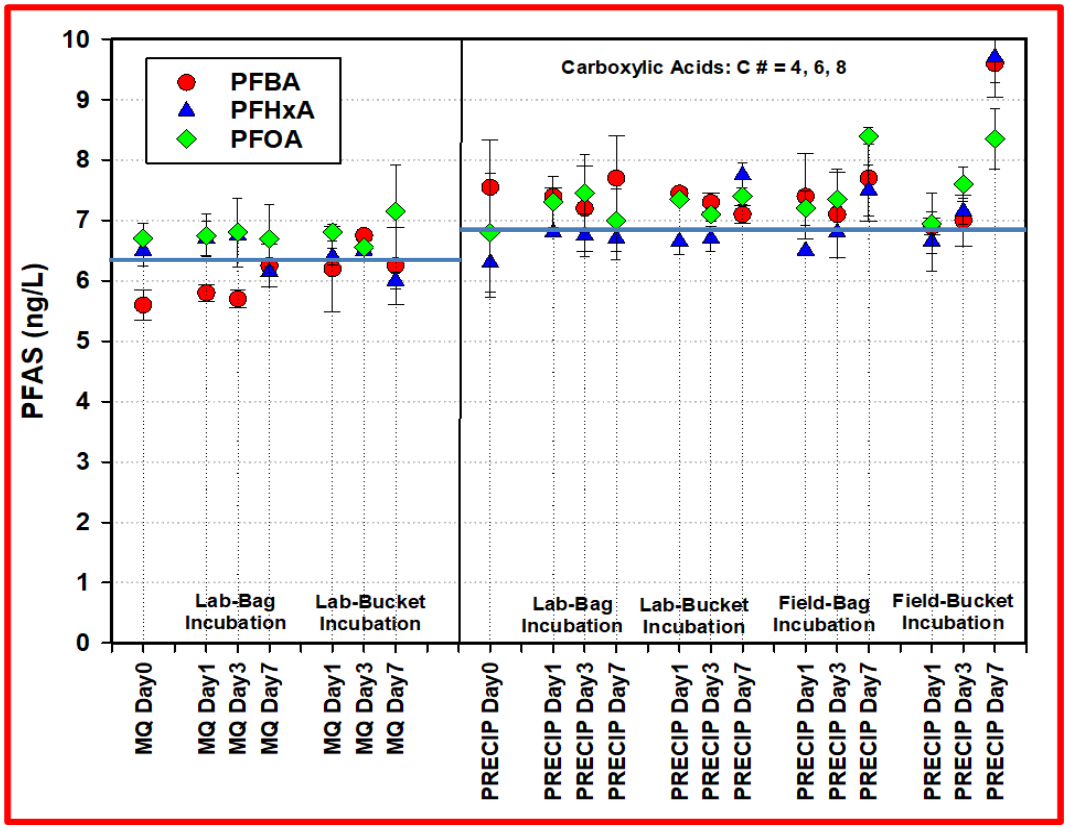
Bucket Washers

Outcomes of Efficacy Study: RETENTION STUDIES

B. PFAS Retention/Loss Studies

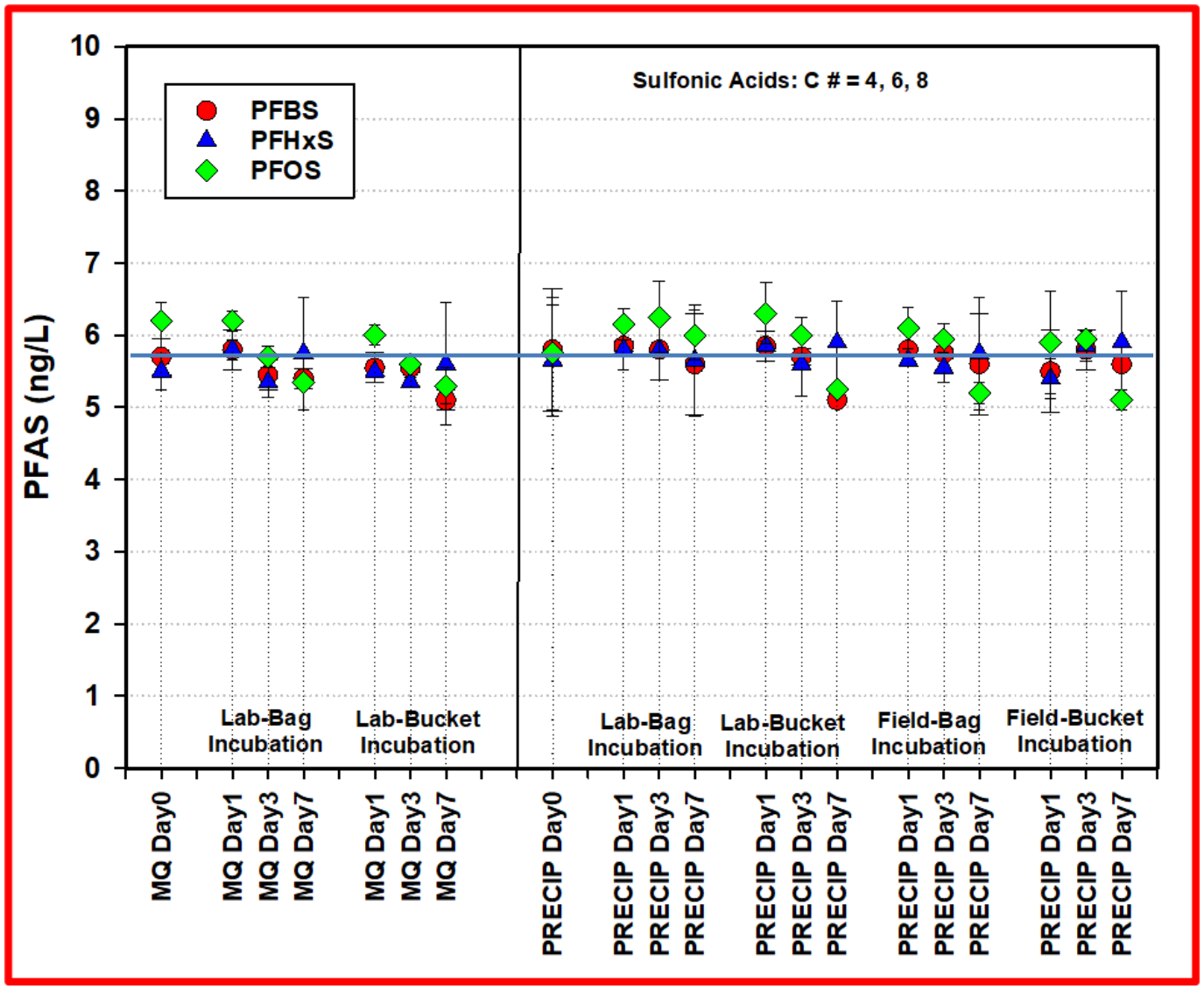
1. Both Bucket & Bag Collectors in Lab & Field Deployments
2. Both MQ & Precipitation Matrices
3. Kinetic Studies (0, 1, 3, 7-day samples)
4. Spiked with 36-PFAS Compound Mixture

Carboxylic Acids
C# = 4, 6, 8



PFAS Retention/Loss Study

Sulfonic Acids
C# = 4, 6, 8



National Atmospheric Deposition Program

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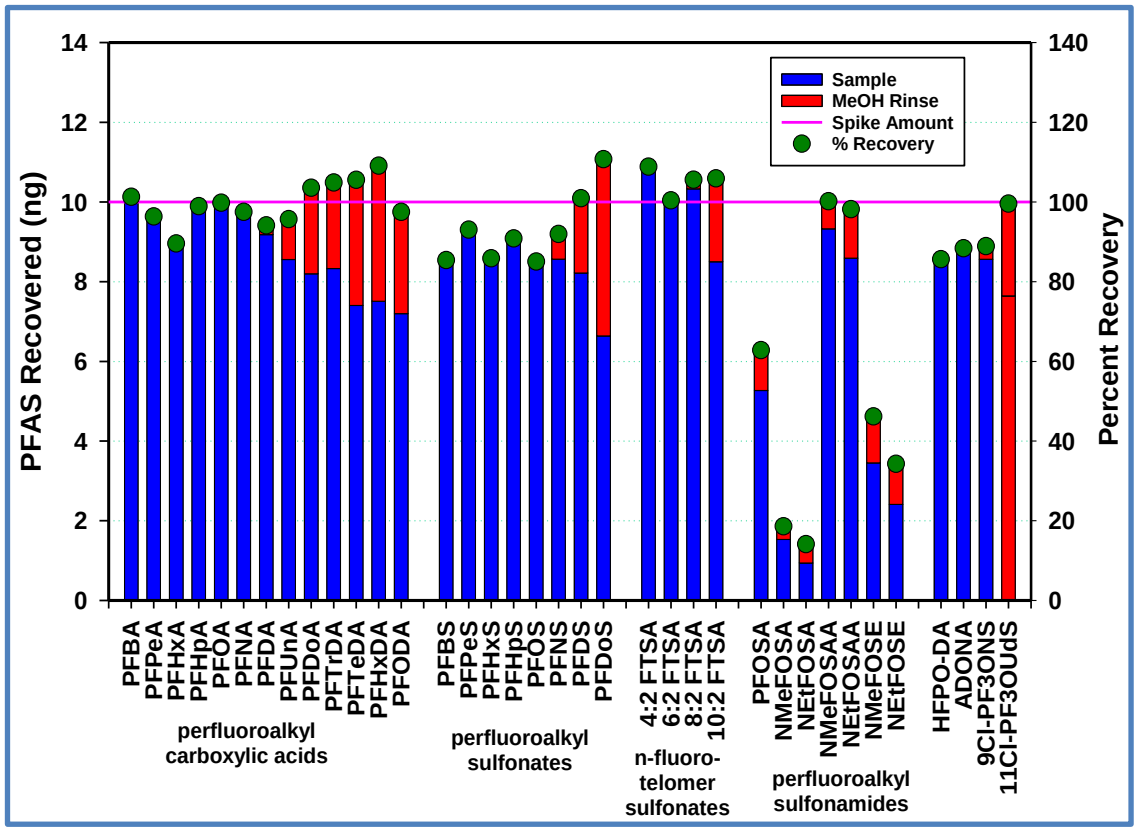
Outcomes of Efficacy Study: RETENTION STUDIES



10 ng Spike in 2L of MQ

7-Day Exposure

50 mL MeOH Bucket Rinse

Average of Triplicate Buckets

Outcomes of Efficacy Study: SUMMARY

Loss of PFAS is minimal for compounds of carbon number <10 under current (and planned) NTN protocols.

Losses are observed for longer-chain (>10 carbon) PFAS compounds.

- But recoverable with a methanol rinse of the bucket

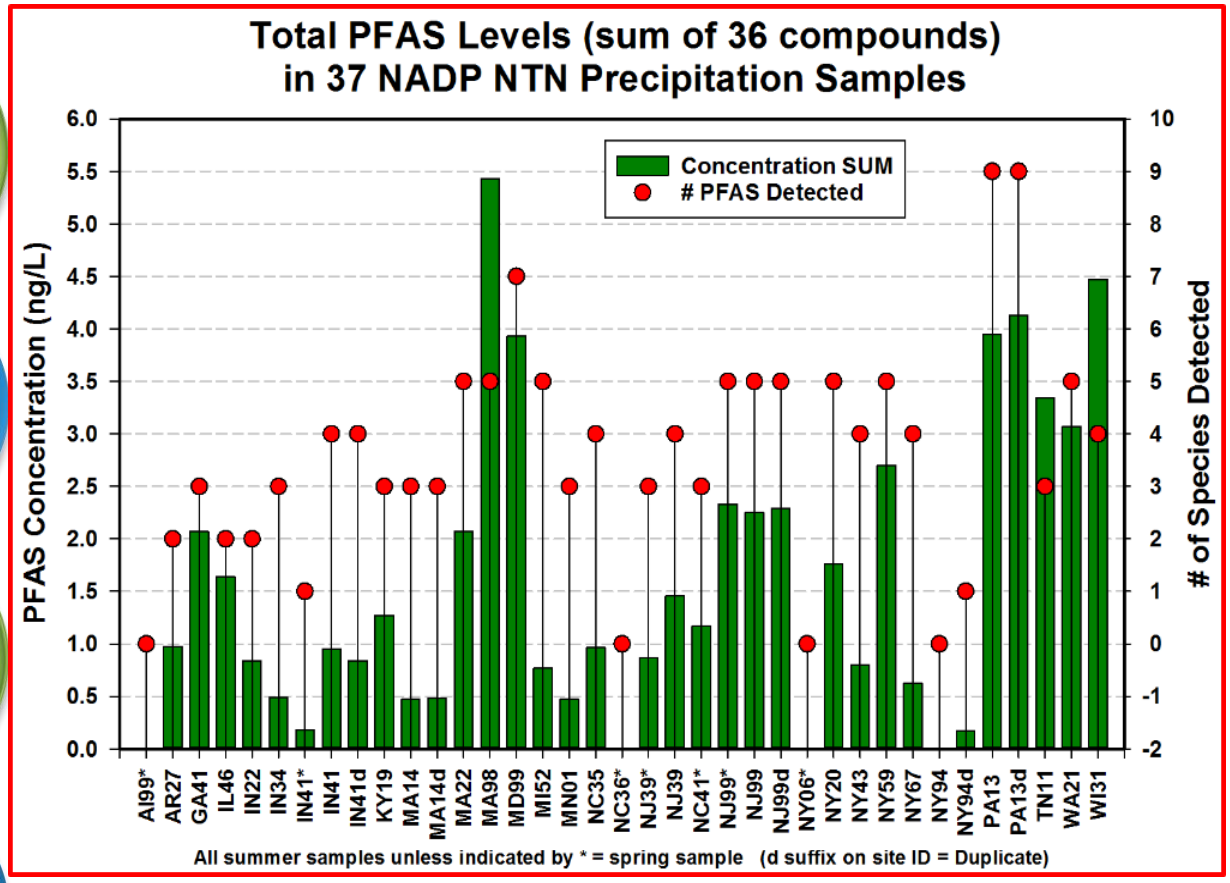
- **The current NTN protocols are "CLEAN" for a broad range of PFAS compounds.**
- **Alternate handling/collection protocols can be implemented to address losses of longer-chain compounds (MeOH rinsing).**
- **Precipitation (and Air) are effective monitoring matrices for detection of trends (likely better than other environmental receptors (e.g. fish))**

Atmospheric Deposition of PFAS via Precipitation

Pilot Synoptic Study: Key Findings

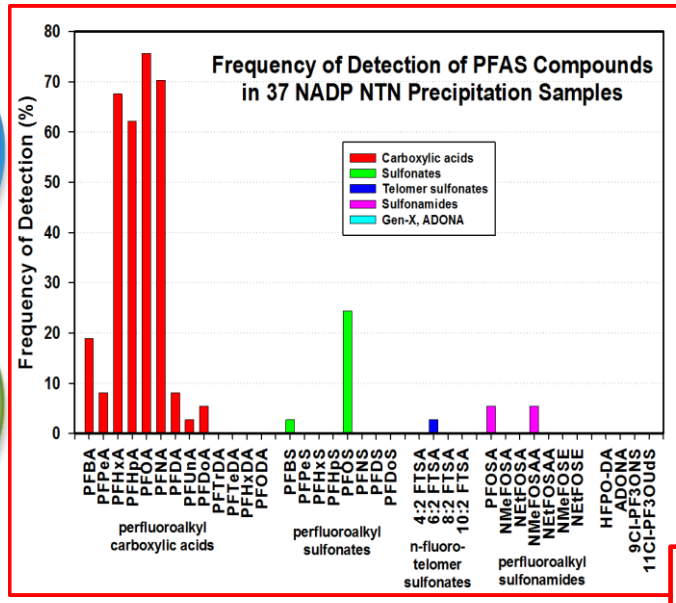
Levels of many PFAS compounds were low (1 ng/L), though the Σ exceeded 4 ng/L at several sites.

Sites in the mid-Atlantic states generally had the greatest # of detectable PFAS species and the highest concentrations.



30 Sites, 37 Samples, Summer & Spring 2019

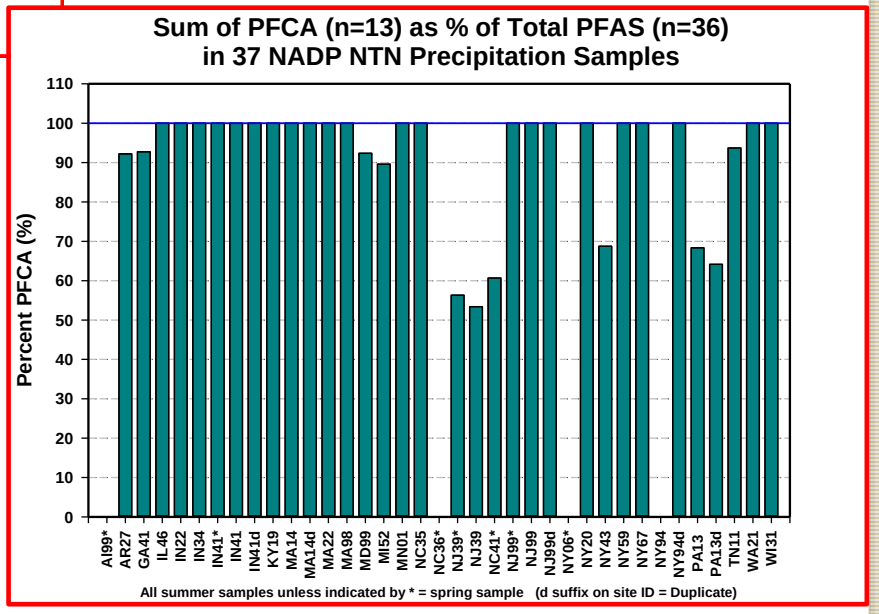
Atmospheric Deposition of PFAS via Precipitation



Pilot Synoptic Study: Key Findings

PFHxA, PFHpA, PFOA and PFNA were each present in nearly 70% of all samples.

The carboxylic acid compounds were by far the most frequently detected and largest class contribution to the total targeted PFAS.



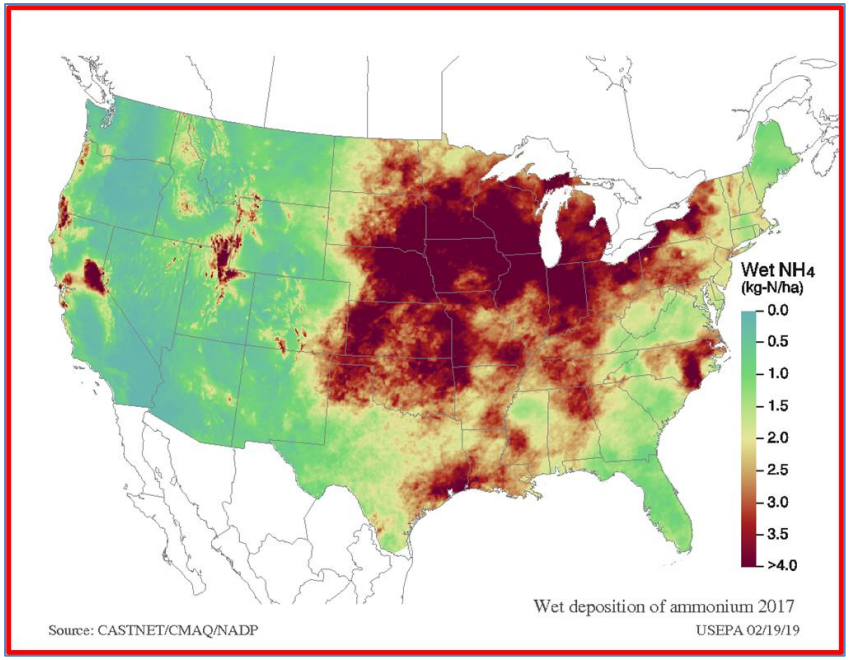
Atmospheric Deposition of PFAS via Precipitation

Pilot Synoptic Study: Key Findings

PFAS Deposition Fluxes

Concentrations of 0.2 to 6.0 ng/L equate to a wet deposition PFAS flux of 0.7 to 21 ng/m^2/day (at an annual precipitation volume of 125 cm/year).

This flux is significant for many environments (e.g. large lakes with long residence times – for Lake Michigan → annual flux of 4.4×10^{14} ng/year → 0.1 ng/L/year PFAS accumulation throughout the water column)



Field & Laboratory Effort Complete. Manuscript Draft Prepared

WSLH-NADP PFAS TOOL-BOX

- Developed a standardized robust protocol (SOP) for PFAS wet-deposition measurements using the NADP-NTN infrastructure
- Incorporates optimized analytical methods
- Could support site-specific, State, regional, and national PFAS wet-deposition efforts
- Model (process) for other emerging contaminants

Regulatory Limits and Reference Concentrations

- **EPA Reference Concentration: 70 ng/L (PFOA+PFOS)**
- **State Drinking Water Limits: 5 – 70 ng/L**
- **WI proposed 20 ng/L WQL, 2 ng/L action level**
- **Research suggests biological impacts at < 1 ng/L**

NADP

Atmospheric Deposition of PFAS

Major Unresolved Issues

- The role of point, regional, and global emission sources at a given location
- Primary emission source versus secondary (reactive transformation) pathway
- Is source reconciliation possible from compound “fingerprint” profiles?
- Emission factors from major classes of emission sources
- The magnitude of dry deposition
- Composition of PFAS pool. Unaccounted for fraction, oxidizable fraction, C2, C3, >C12?

Partnerships and Follow-up Studies to Address Major Unresolved Issues

NADP & EPA & States & WSLH

- Several States, as well as USEPA, have expressed interest in establishing precipitation monitoring as well as PFAS deposition modeling programs

NADP & EPA & WSLH & WDNR

- Sharing of precipitation extracts for non-targeted PFAS analysis at EPA ORD

WSLH & NADP & Researchers

- Method Exchange

Atmospheric Deposition of PFAS via Precipitation

Wisconsin Precipitation PFAS Intensive

1. All 7 NADP-NTN Sites in Wisconsin
2. 14 Weeks (April – July 2020)
3. WDNR Funded: NADP, WSLH Partners
4. Optimized PFAS Sampling Protocols with MeOH rinsing
5. Comprehensive Analytical Protocols
   a. 36 Targeted PFAS (LC/MS) - WSLH
   b. Total Organic Fluorine (CIC) - WSLH
   c. Non-Targeted Analysis (LC/MS) - EPA

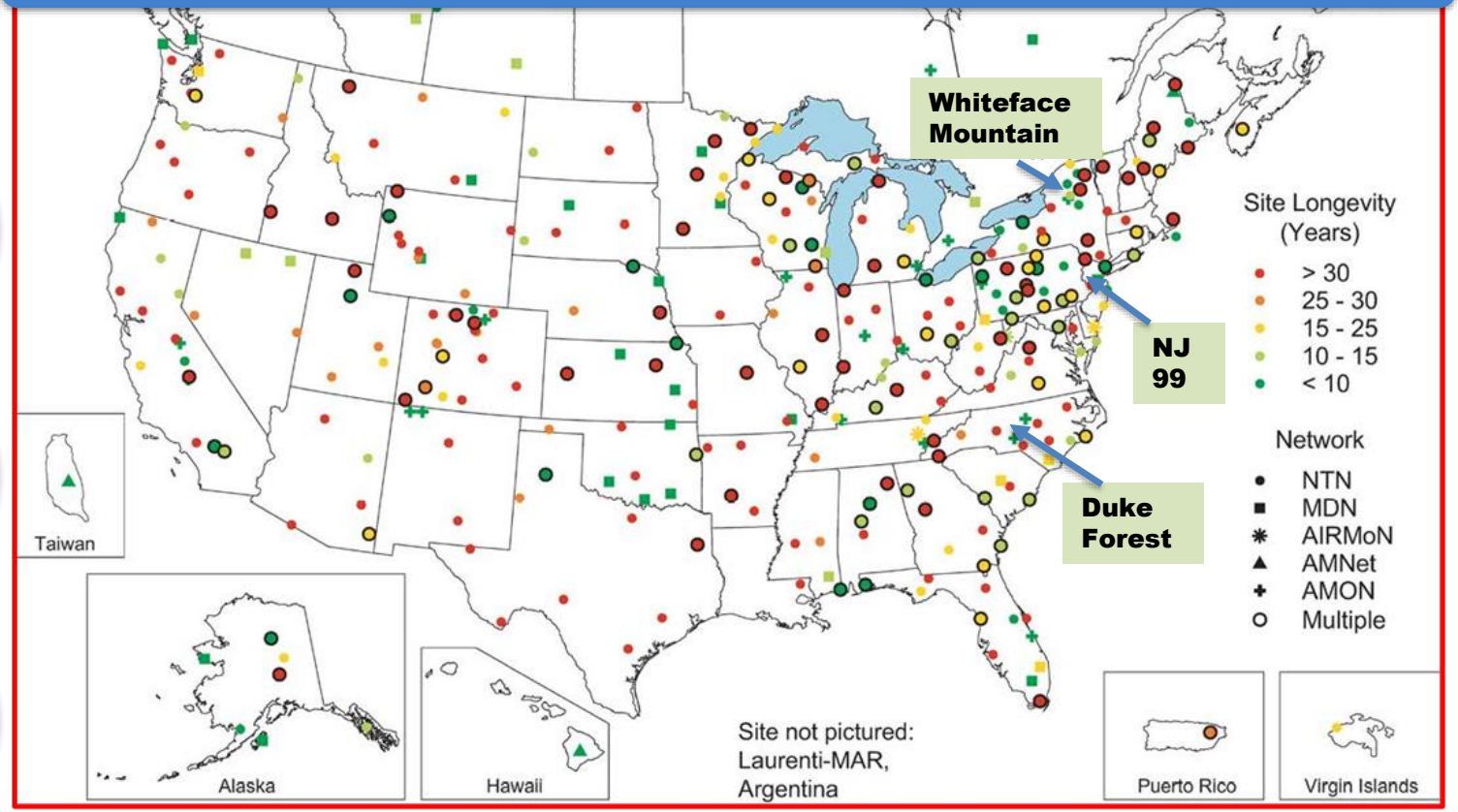
This initiative incorporates further method enhancements for neutral PFAS species that are very important to atmospheric transport and transformations

NADP

National Atmospheric Deposition Program

Operated by the Wisconsin State Laboratory of Hygiene

Expand "synoptic" sampling using NADP infrastructure



Deposition Modeling (CMAQ, etc.)

QUESTIONS Thank You

Acknowledge: NADP: Mark Olson, Amy Mager & her team, Camille. WSLH: Erin Mani & PFAS analytical team. WDNR: Mark Allen, Katie Praedel. EPA: Melissa Puchalski, Donna Schwede, John Offenberg

PFAS Measurement Approaches

- **Total**
  - PIGE
  - XRF
  - TOF/CIC
  - EOF/CIC
- **Non-targeted**
  - Discovery
  - Semi-Quant
  - Pathway analysis
- **Total Oxidizable Precursor (TOP)**
  - Oxidative conversion of targeted & unknown precursors
- **Targeted**
  - 12-50 species
  - Quantitative
  - Tox relevant
  - Small fraction of total