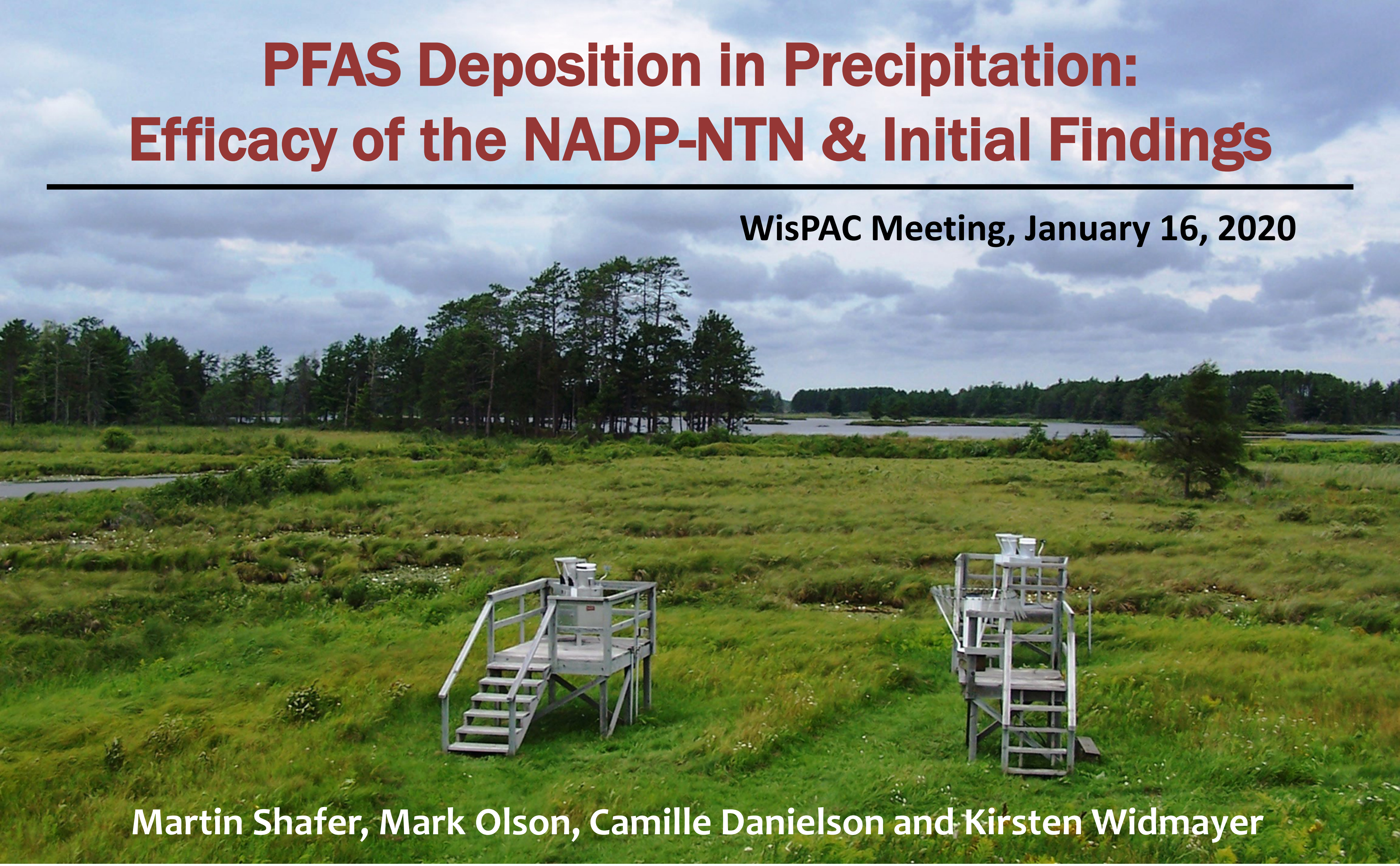
PFAS Deposition in Precipitation: Efficacy of the NADP-NTN & Initial Findings

WisPAC Meeting, January 16, 2020



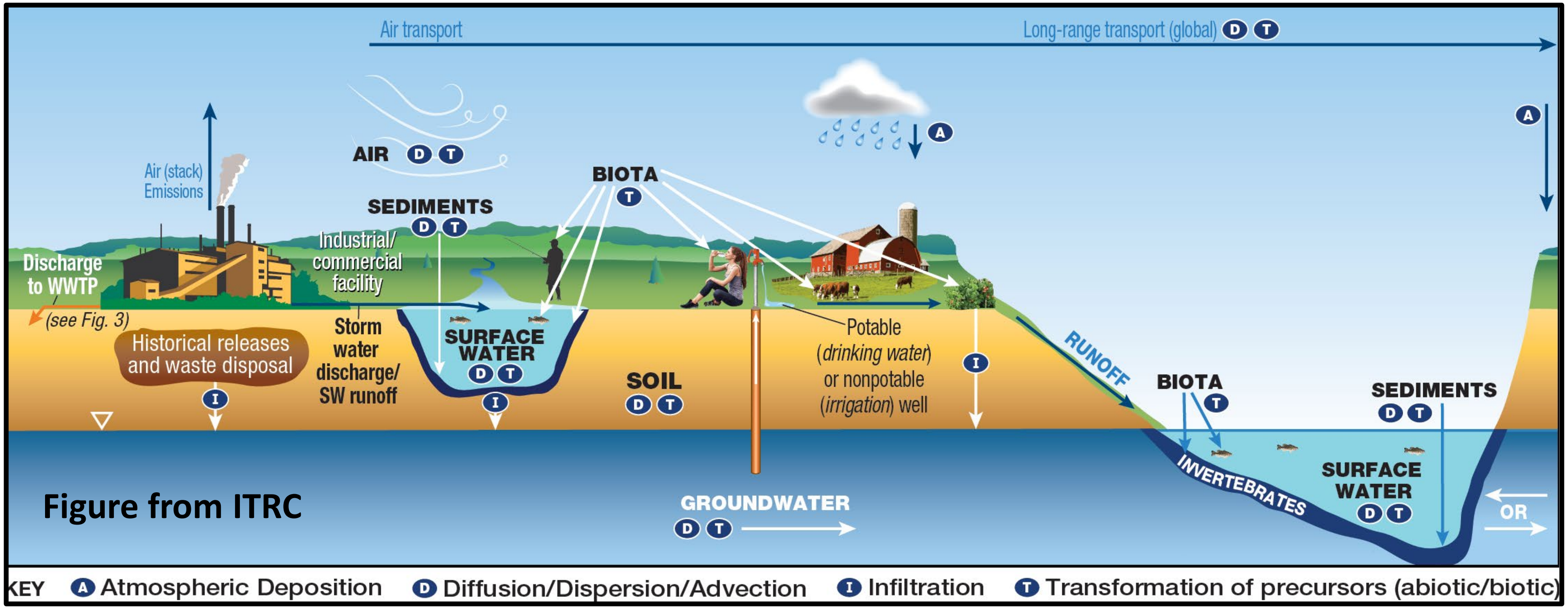
Martin Shafer, Mark Olson, Camille Danielson and Kirsten Widmayer

State Laboratory of Hygiene, School of Medicine & Public Health, University of Wisconsin-Madison

NADP

PFAS Dispersal & Atmospheric Processing

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



PFAS found in remote environments (aquatic, atmosphere and terrestrial) far from any known sources)

NADP

1. Direct Industrial Emissions (1° & 2°)
2. Precursor Emissions
3. Particle Injection
4. POTW/Land-Spreading
5. Foam Use

PFAS Dispersal & Atmospheric Processing

Short & Long-Range Transport in the Atmosphere

1. Vapor phase (e.g. neutral (more) volatile precursors)
2. Aerosol phase (e.g. ionic compounds & long-chain)

Transformations in the Atmosphere

1. Perfluoroalkanesulfonamides → carboxylic acids
2. Perfluorotelomeralcohols → carboxylic acids

Removal (Deposition) from the Atmosphere

1. Wet Deposition (precipitation/rain)
2. Dry Deposition

Atmospheric fate and transport of PFAS strongly dependent upon the specific PFAS compound

Hg analogy

NADP

Atmospheric Cycling Important in Dispersal of PFAS

Goals & Approach: Wet Deposition

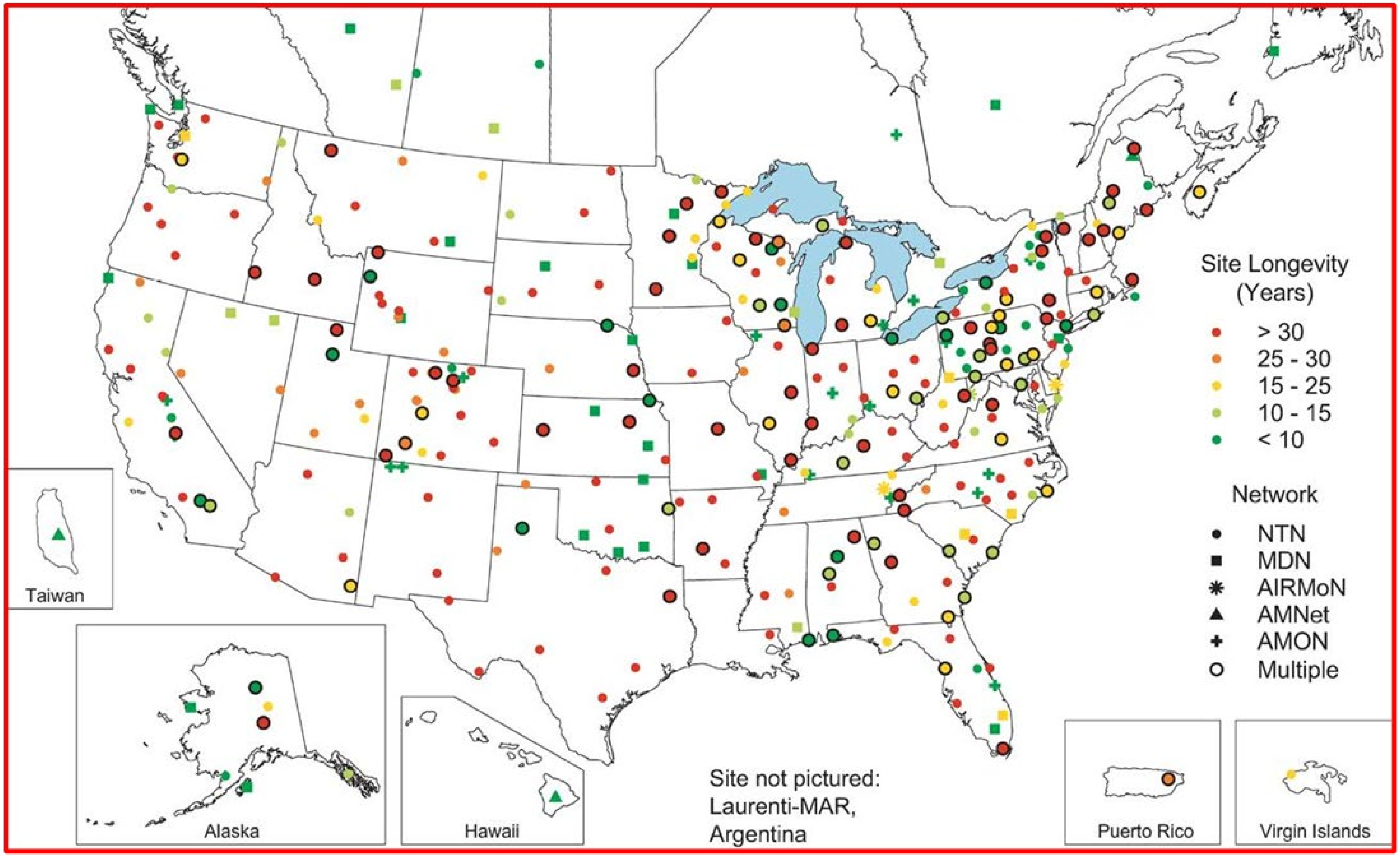
The NADP-NTN currently comprises 263 sites across the US and Canada, collecting 7-day wet-only precipitation samples. The Wisconsin State Laboratory of Hygiene at the UW-Madison operates all of the NADP networks and is home to the analytical laboratories that support these networks.

- Design and implement **field and laboratory experiments** to determine whether the NADP/NTN sampling network as currently configured (or with certain modifications) **would support robust PFAS concentration and deposition monitoring**
- Apply **ISO method 21675** (36 PFAS compound) to the NTN network evaluation studies and precipitation monitoring
- Perform **PFAS measurements** on geographically diverse **precipitation samples** from the NADP National Trends Network (NTN) to assess PFAS levels and **deposition fluxes**.

National Atmospheric Deposition Program

NADP

NADP Monitoring Sites



Synoptic Overview of PFAS Deposition and/or More Targeted Collections

NADP

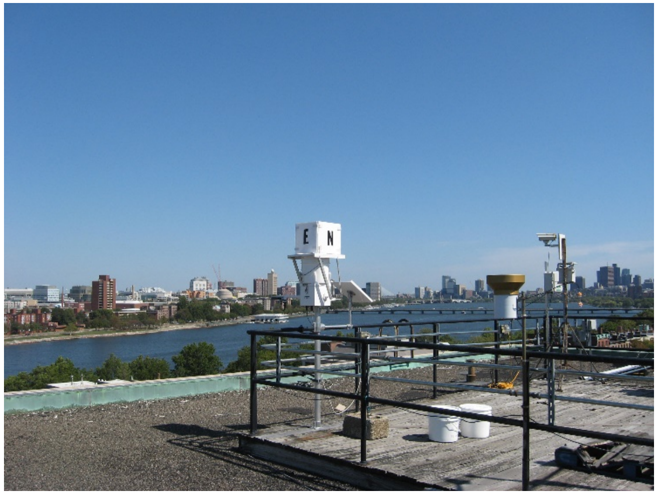
National Atmospheric Deposition Program

Wisconsin NTN and MDN NADP Sites

- WI06, UW Arboretum, Dane County
- WI08, Brule River, Douglas County
- WI10, Potawatomi, Forest County
- WI31, Devil's Lake, Sauk County
- WI35, Perkinstown, Taylor County
- WI36, Trout Lake, Vilas County
- WI37, Spooner, Washburn County

Red = NTN & MDN
7 NTN & 5 MDN Sites

1. Super-site in development at Eagle Heights (UW-Madison)
2. Ability to deploy "temporary" and/or mobile NTN collectors



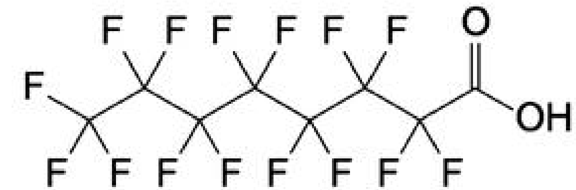
PFAS Analytical Methods

- **Analytical methods**:
  - ✓ ISO Method 21675 (PFAS in Water by LC-MS/MS). 36 PFAS compounds. 26 isotopically-labeled internal-standards
  - ✓ 500 or 250 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

National Atmospheric Deposition Program

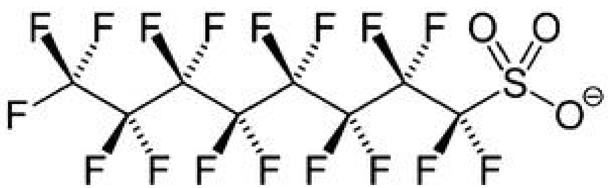
NADP

PFAS Compounds



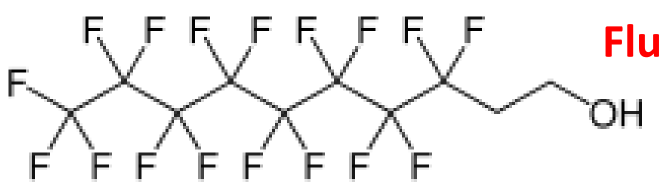
Perfluorooctanoic acid (PFOA)

Carboxylic Acids

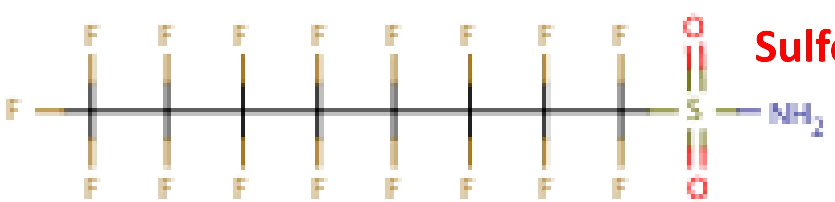


Perfluorooctanesulfonate (PFOS)

Sulfonates



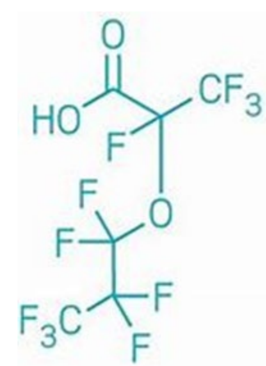
Fluorotelomers



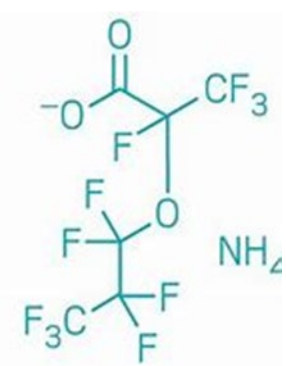
Sulfonamides

>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



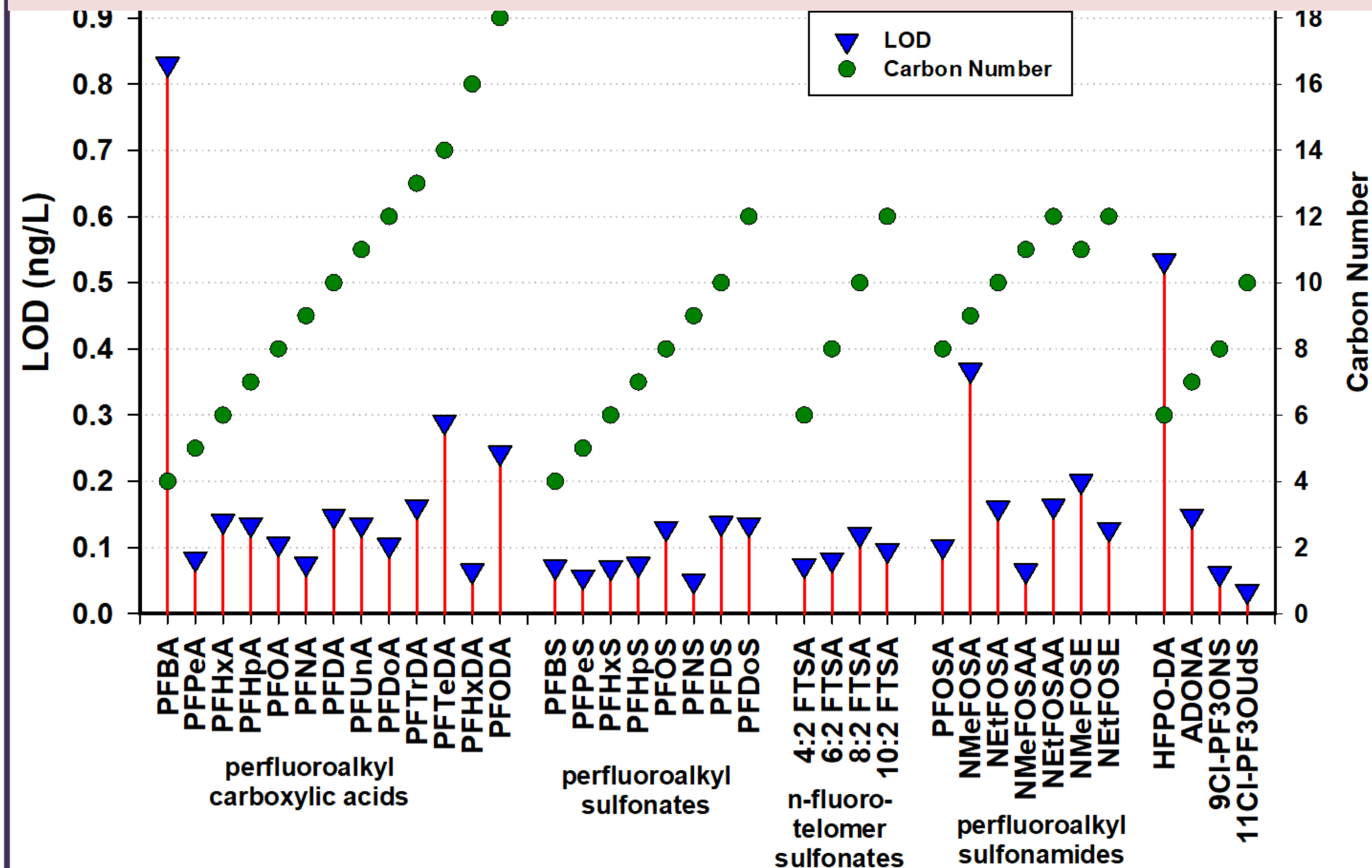
GenX

Buck et al. 2011

NADP National Atmospheric Deposition Program

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

NTN Network Efficacy for PFAS Measurement

A. System Blanks: Bucket & Bag Collectors

- ✓ High-purity water → collectors

B. PFAS Retention/Loss Studies

- ✓ Water, spiked with 36 PFAS compounds at low ng/L levels → collectors

Retention/Loss Study Experimental Matrix

Sample Matrix	Incubation Location	Collector Type	Day 0	Day 1	Day 3	Day 7
MQ	Lab	Bag	1	2	2	2
MQ	Lab	Bucket	1	2	2	2
Precip	Lab	Bag	1	2	2	2
Precip	Lab	Bucket		2	2	2
Precip	Field	Bag		2	2	2
Precip	Field	Bucket	1	2	2	2

System blank trials run in triplicate.
Values in table are number of replicates for retention/loss studies.

Network Efficacy: Field Method Blank Outcomes

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

   I. **Bags:** no detects for 36 species (except PFOA at 0.23 ng/L in 1 sample)
   II. **Buckets:** no detects for 36 species (except PFOA at 0.44 ng/L in 1 sample)
   III. **NTN Bottle:** no detects for 36 species

II. **Methanol Rinses**

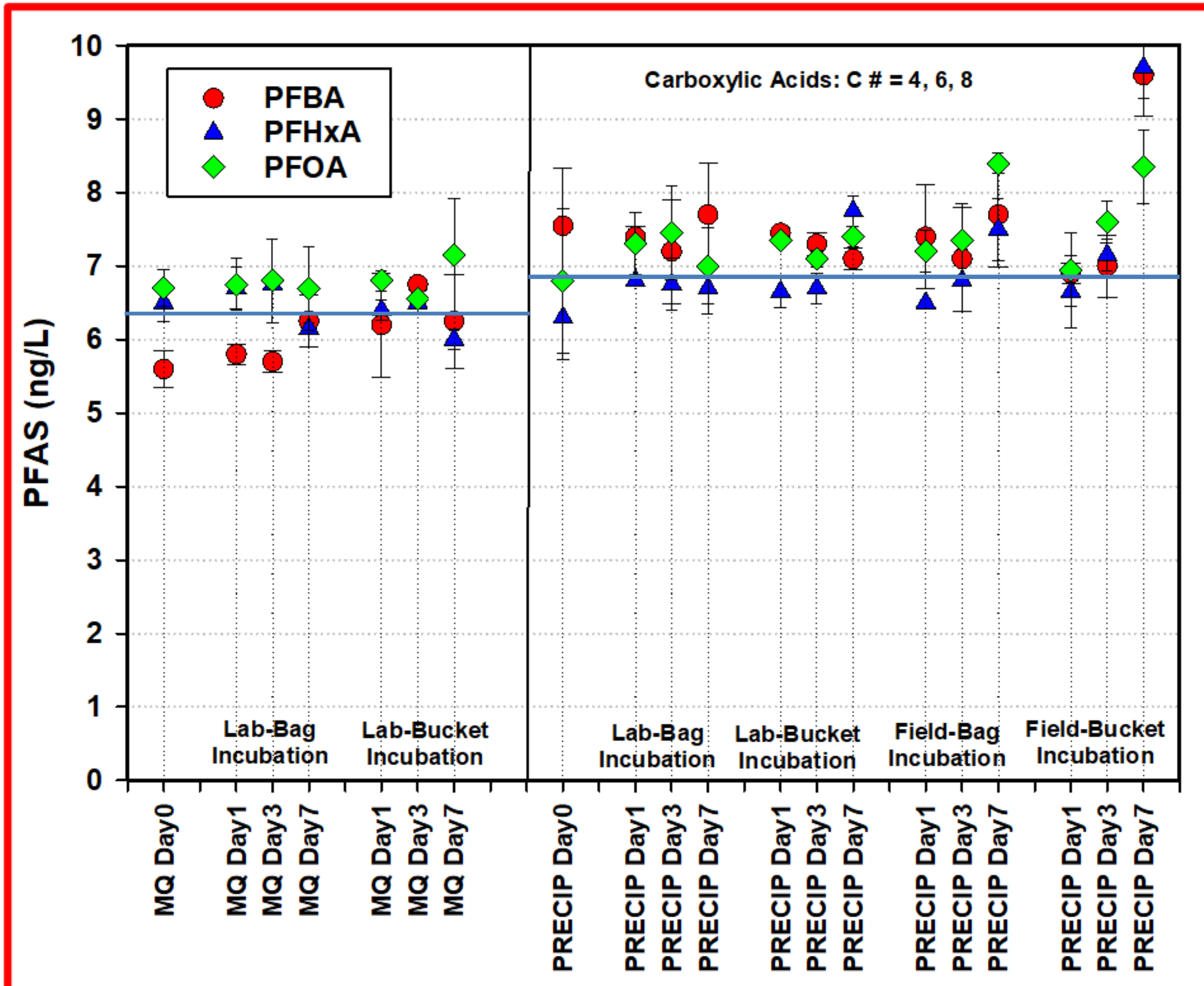
   I. **Buckets:** no detects for 36 species

Bucket Washers

Buckets

NADP National Atmospheric Deposition Program

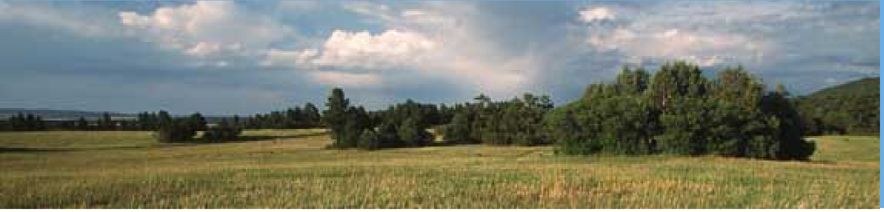
PFAS Retention/Loss Study



Carboxylic Acids
C# = 4, 6, 8

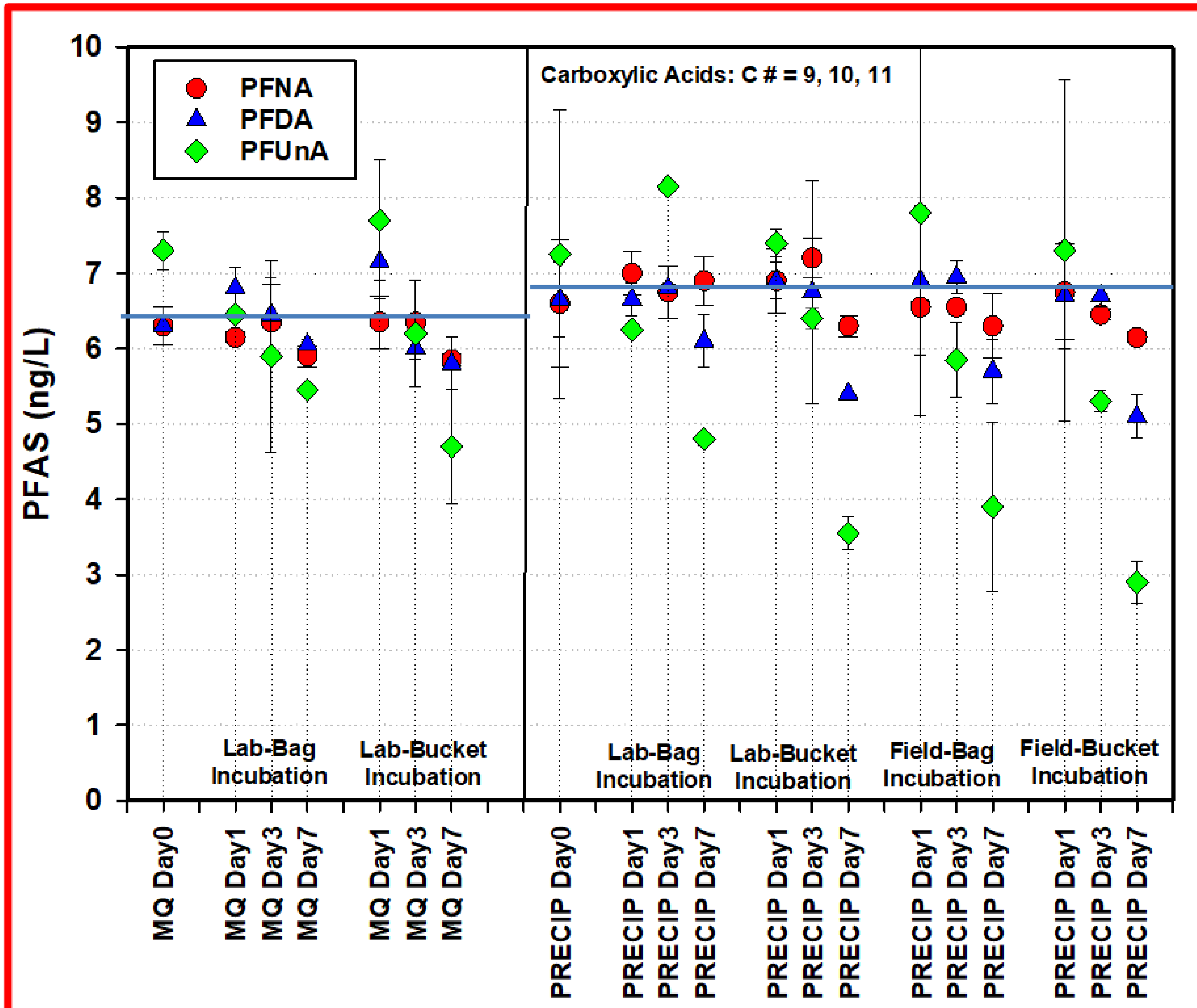
National Atmospheric Deposition Program

NADP



PFAS Retention/Loss Study

Carboxylic Acids
C# = 9, 10, 11

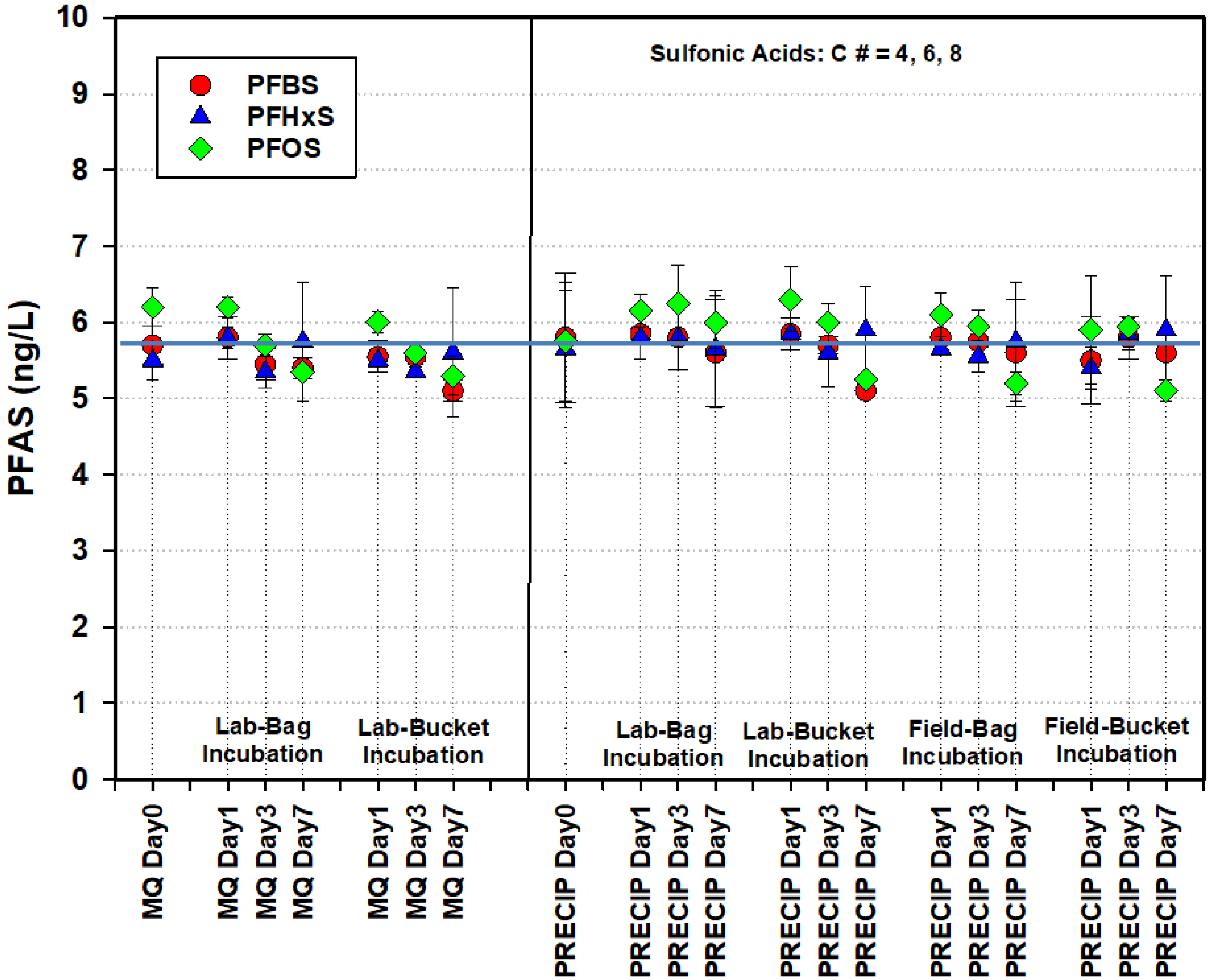


National Atmospheric Deposition Program

NADP

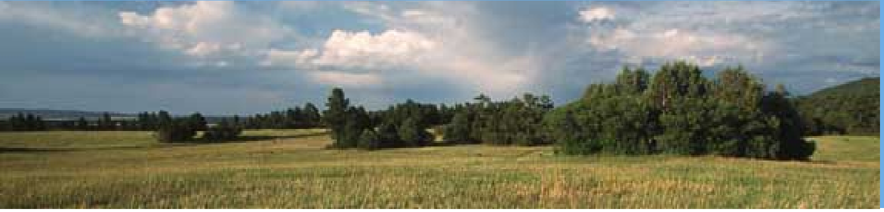
PFAS Retention/Loss Study

Sulfonic Acids
C# = 4, 6, 8



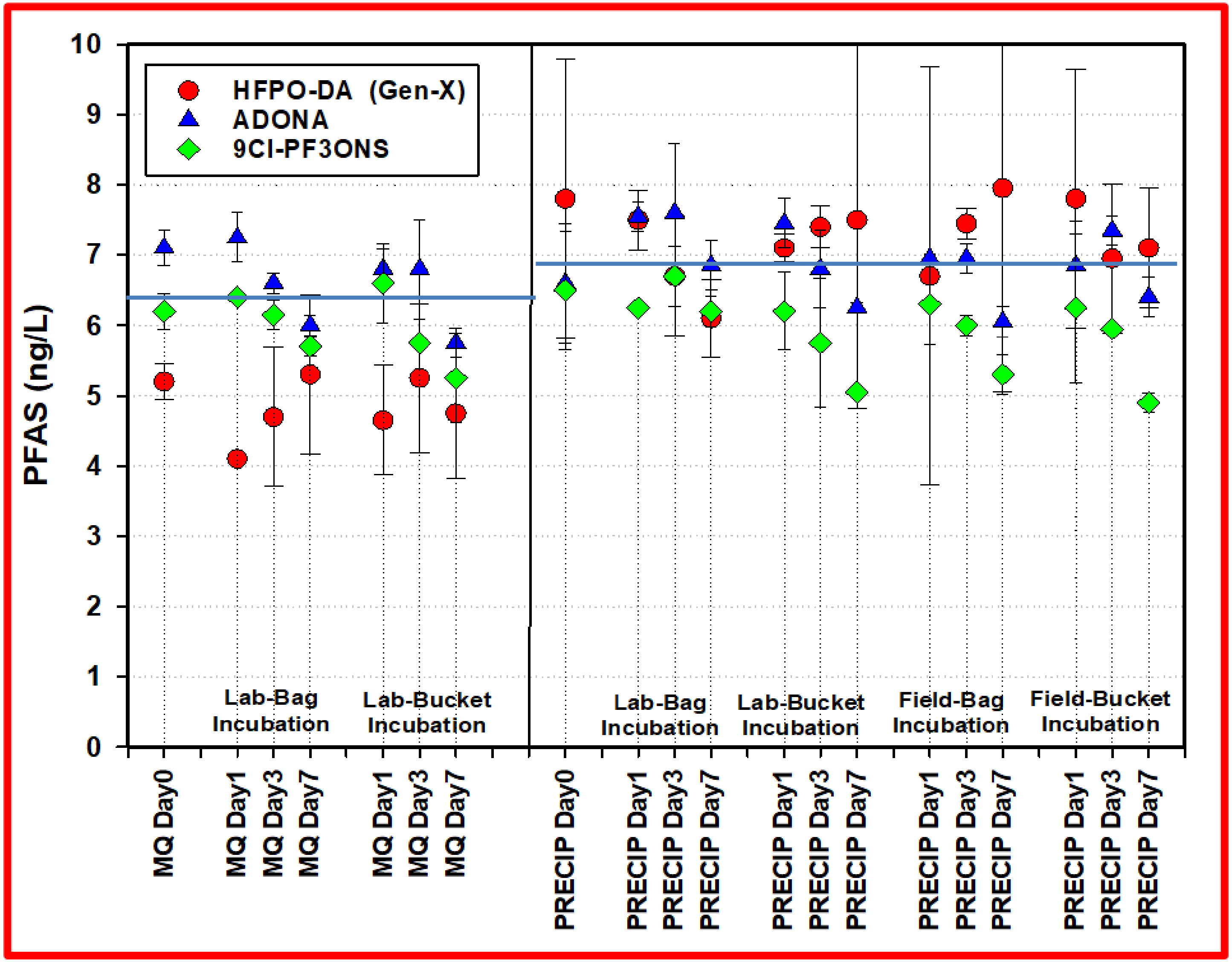
National Atmospheric Deposition Program

NADP



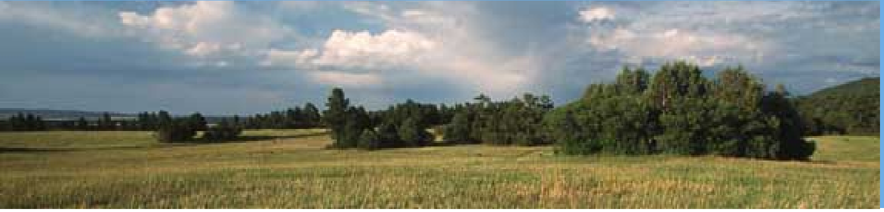
PFAS Retention/Loss Study

Gen-X & Related



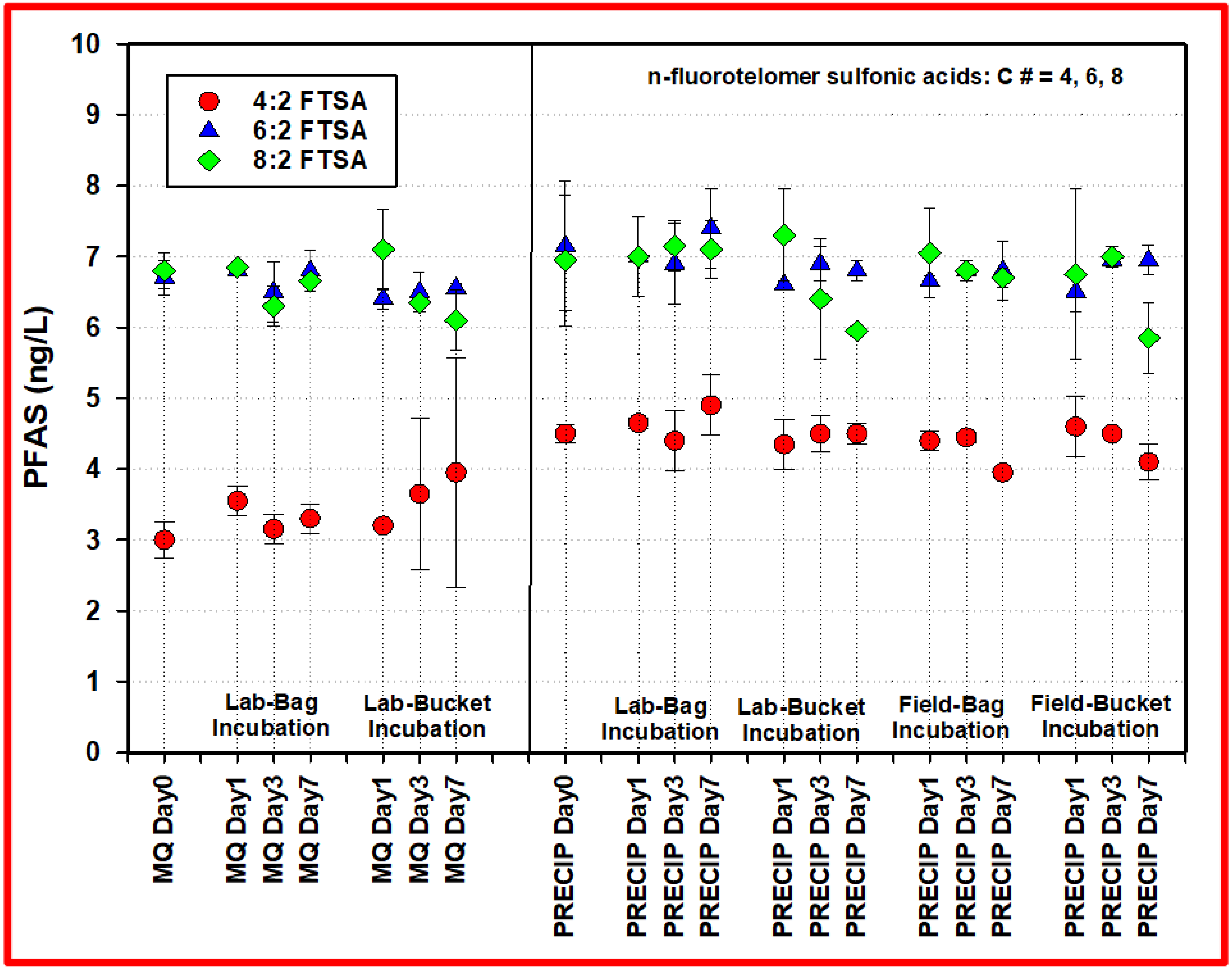
National Atmospheric Deposition Program

NADP



PFAS Retention/Loss Study

FTSA



National Atmospheric Deposition Program

NADP

PFAS Retention/Loss Study

- Loss of PFAS in the NTN collector is minimal for compounds of carbon number <10 under current (and planned) NTN protocols.
- Losses are observed for longer-chain (>10 carbon) PFAS compounds.
  - ✓ Where did the PFAS go?
  - ✓ Are they recoverable?

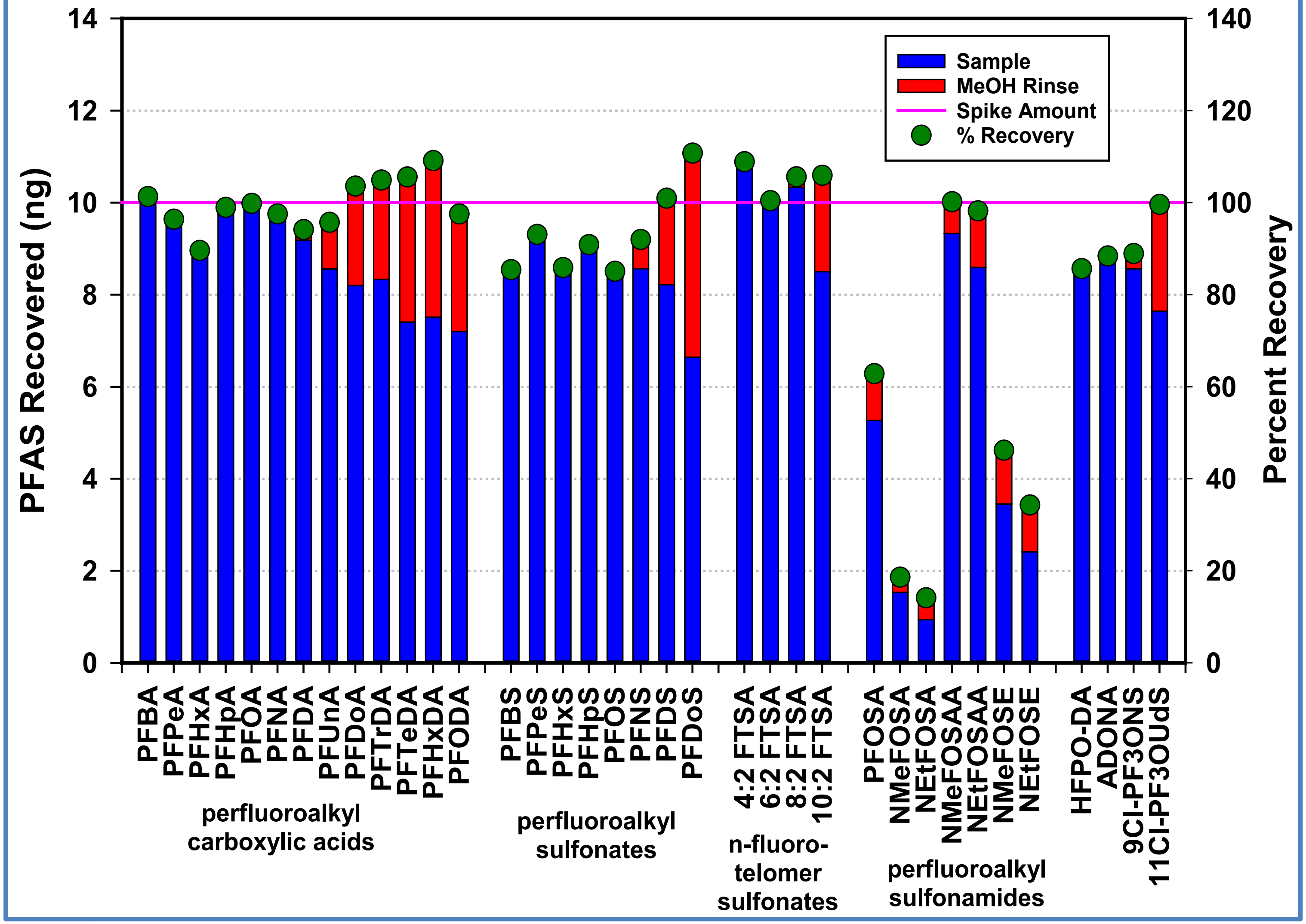
PFAS Retention/Loss: Methanol Bucket Rinse

10 ng Spike in 2L of MQ

7-Day Exposure

50 mL MeOH Bucket Rinse

Average of Triplicate Buckets



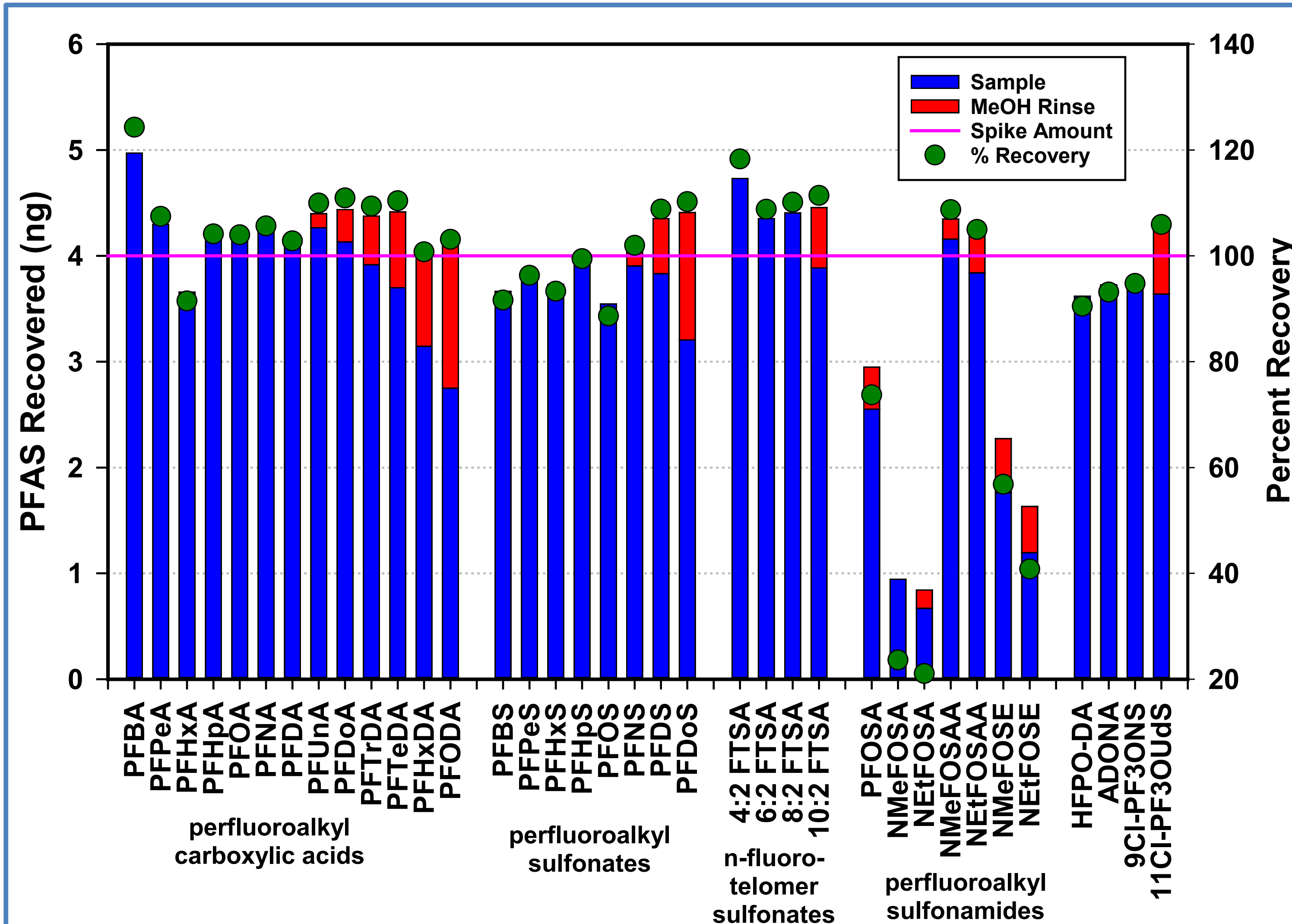
PFAS Retention/Loss: Methanol Bucket Rinse

4 ng Spike in 2L of MQ

7-Day Exposure

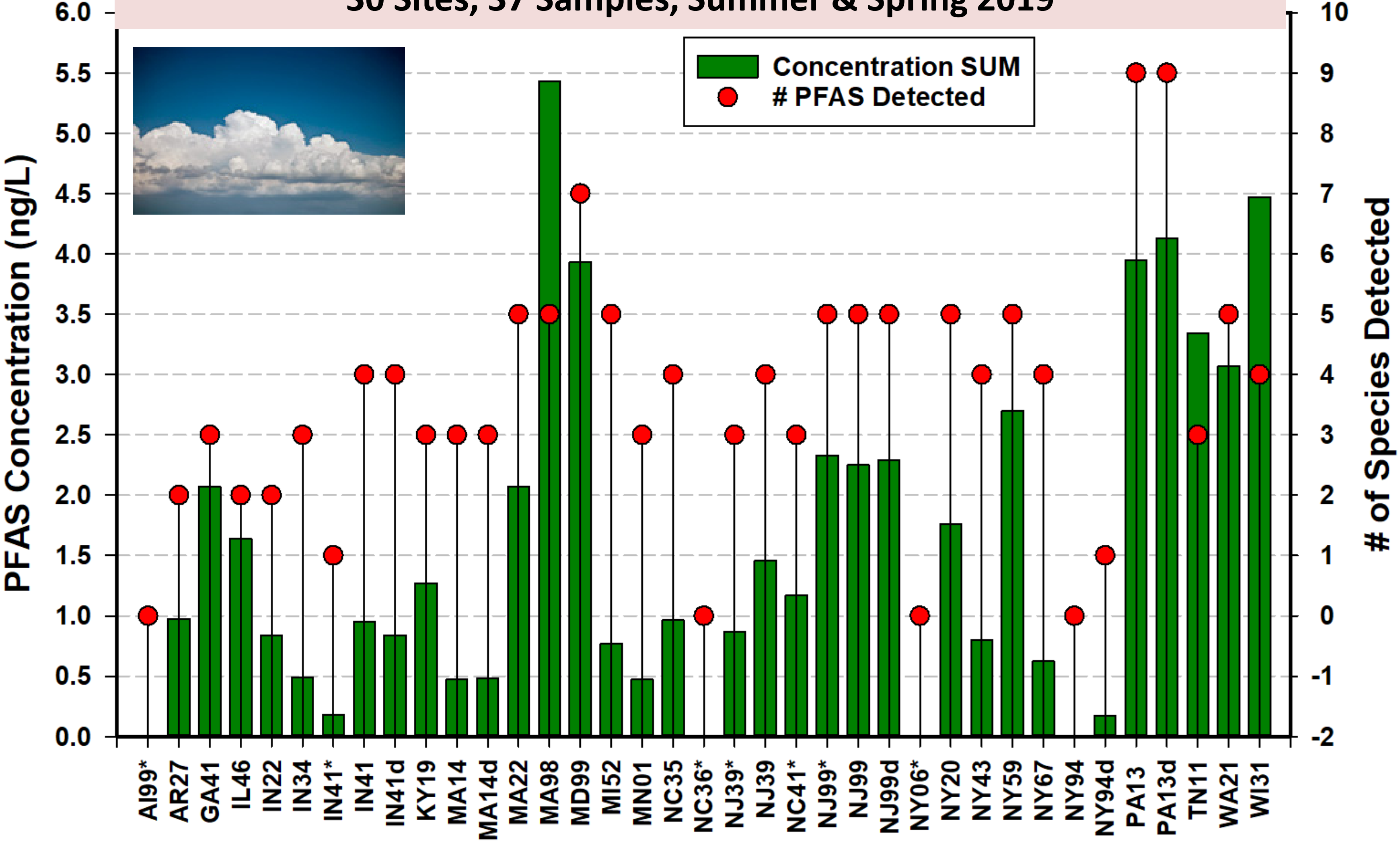
50 mL MeOH Bucket Rinse

Average of Triplicate Buckets



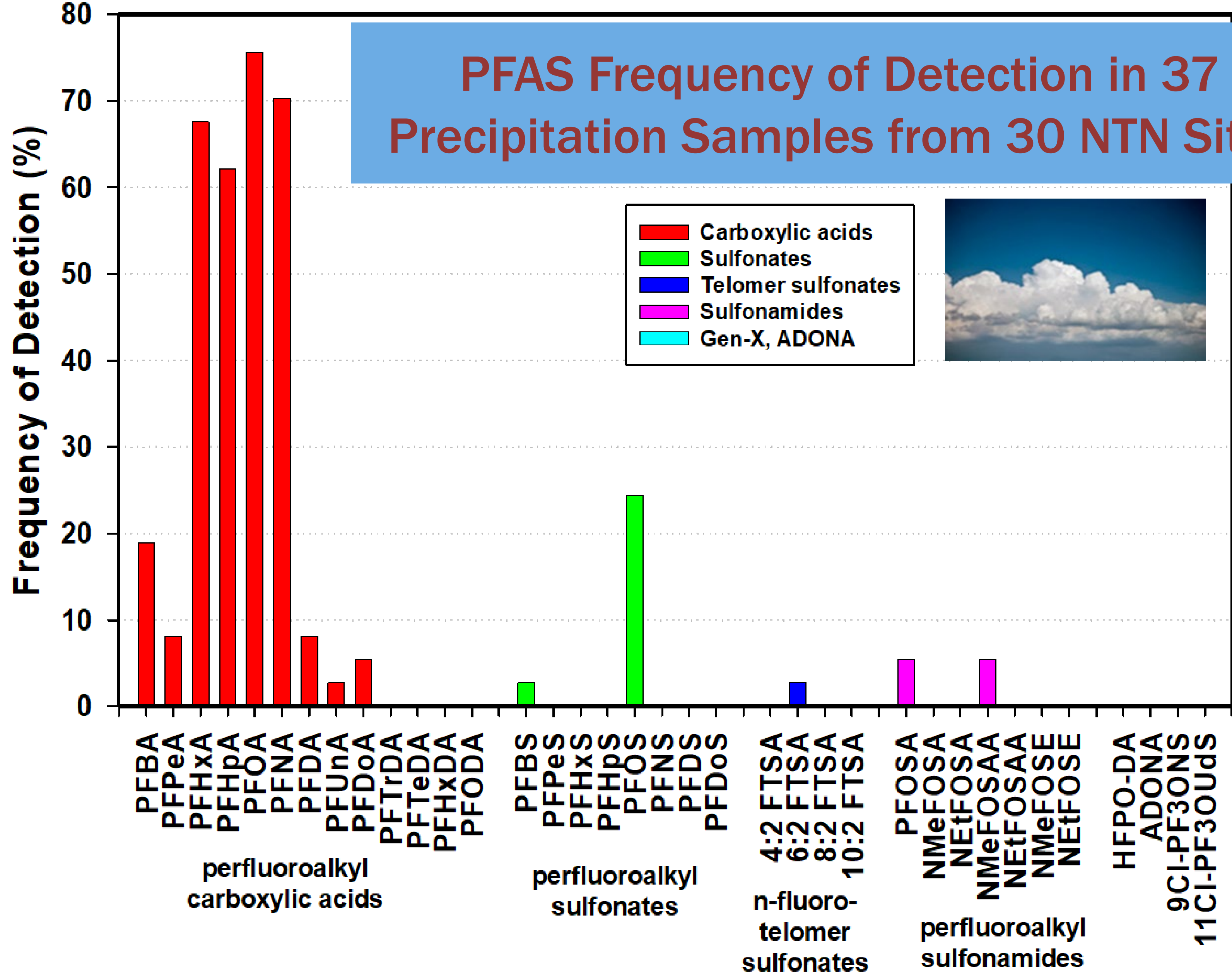
PFAS Levels (ng/L) in Precipitation

30 Sites, 37 Samples, Summer & Spring 2019

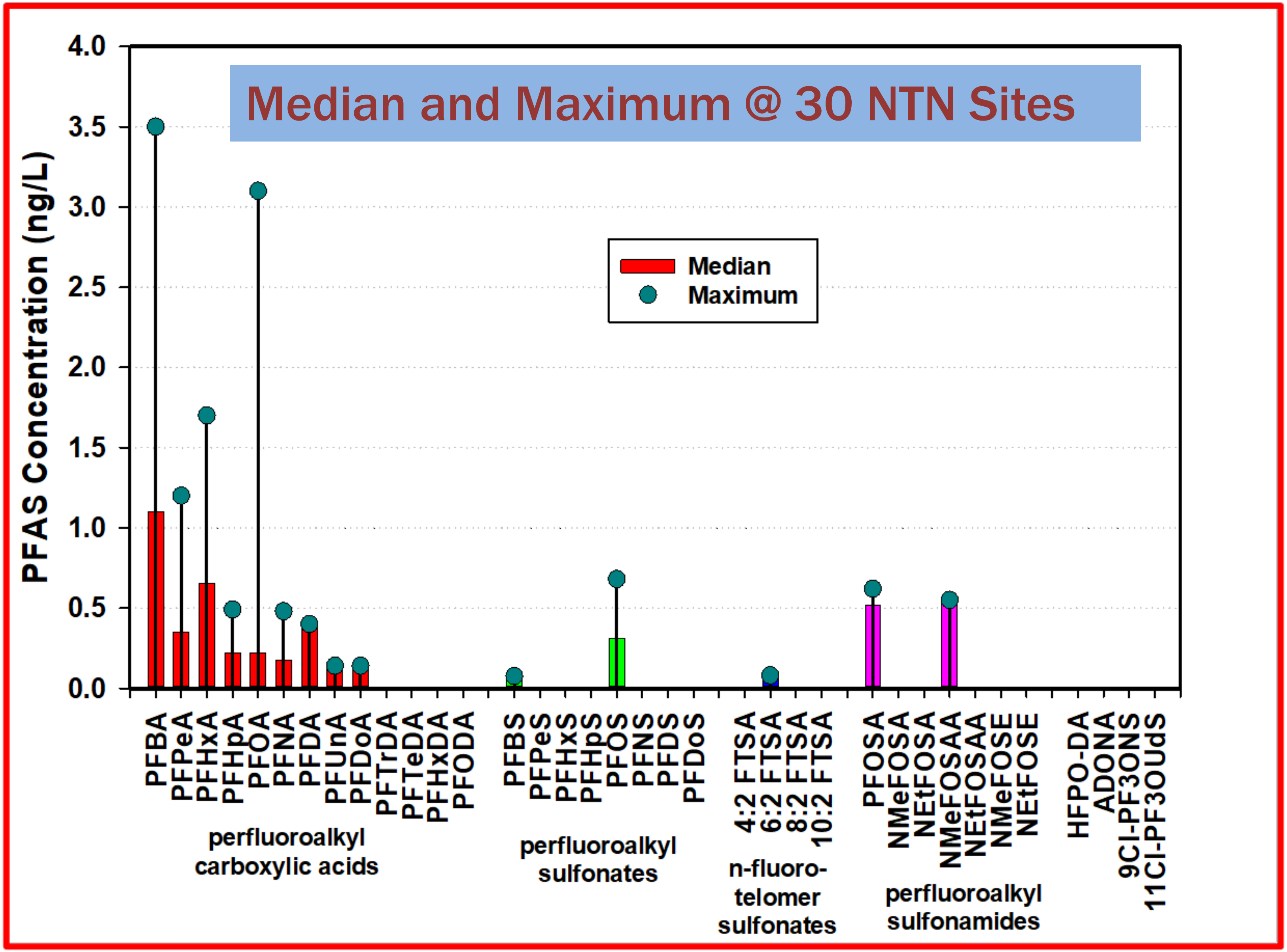


All summer samples unless indicated by * = spring sample (d suffix on site ID = Duplicate)

PFAS Frequency of Detection in 37 Precipitation Samples from 30 NTN Sites



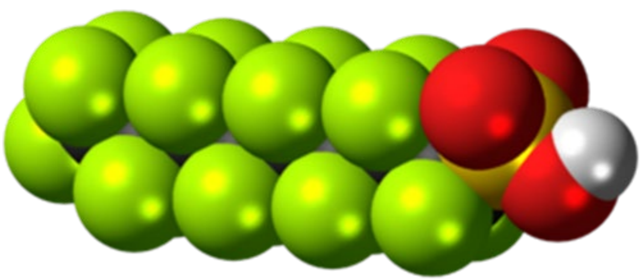
PFAS Levels (ng/L) in Precipitation

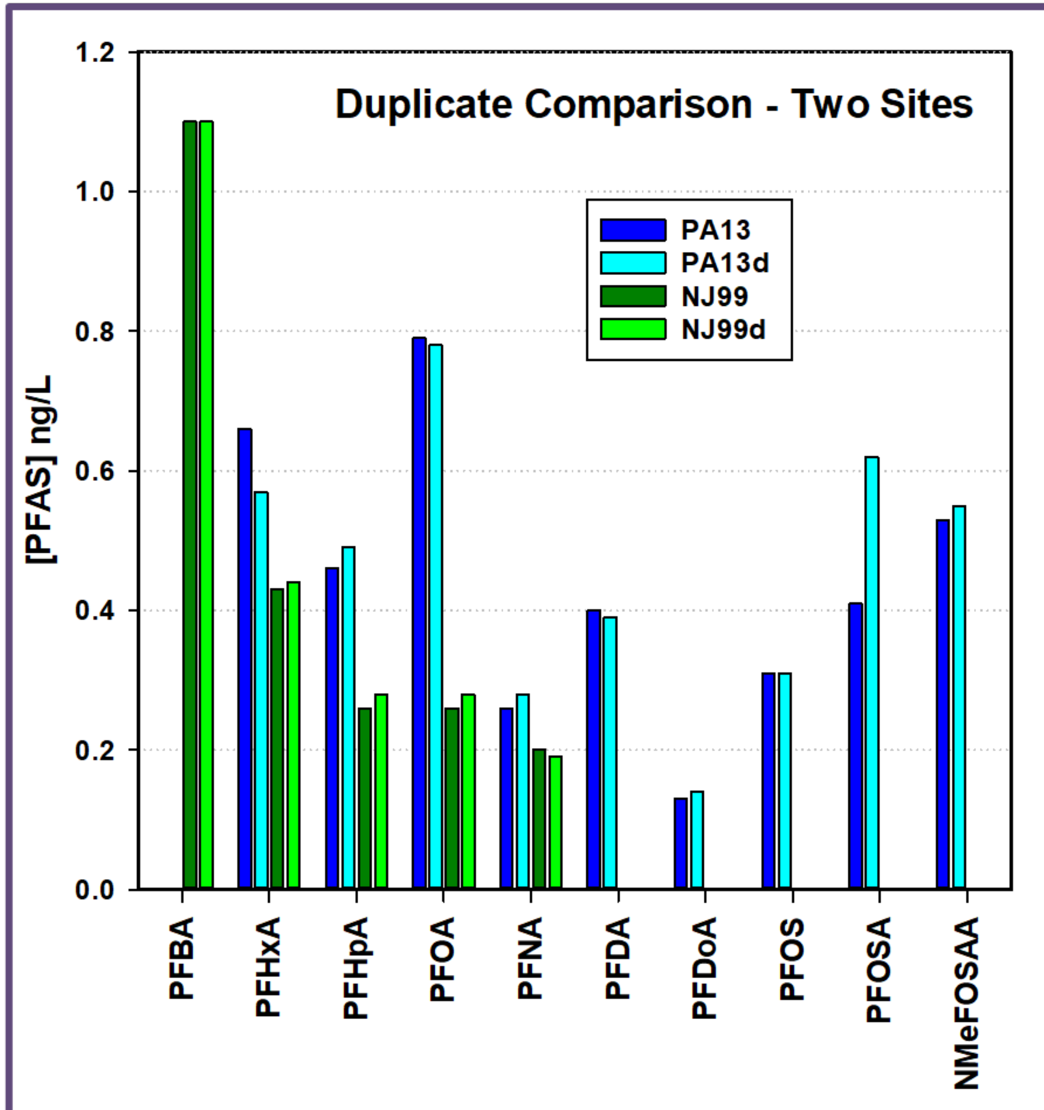


PFAS Method Performance Outcomes in Precipitation

PFAS Method Precision

Two Precipitation Sample Duplicates





PFAS Occurrence Summary

- **Concentrations of most PFAS compounds were low, generally < 1 ng/L, though the sum of the quantified species exceeded 4 ng/L at several sites.**
  - **The carboxylic acid compounds were by far the most frequently detected.**
  - **PFHxA, PFHpA, PFOA and PFNA were each present in nearly 70% of all samples.**
  - **Shorter-chain PFAS compounds dominated.**
- **Precipitation from sites in the mid-Atlantic states generally had the greatest number of detectable PFAS species and the highest concentrations.**

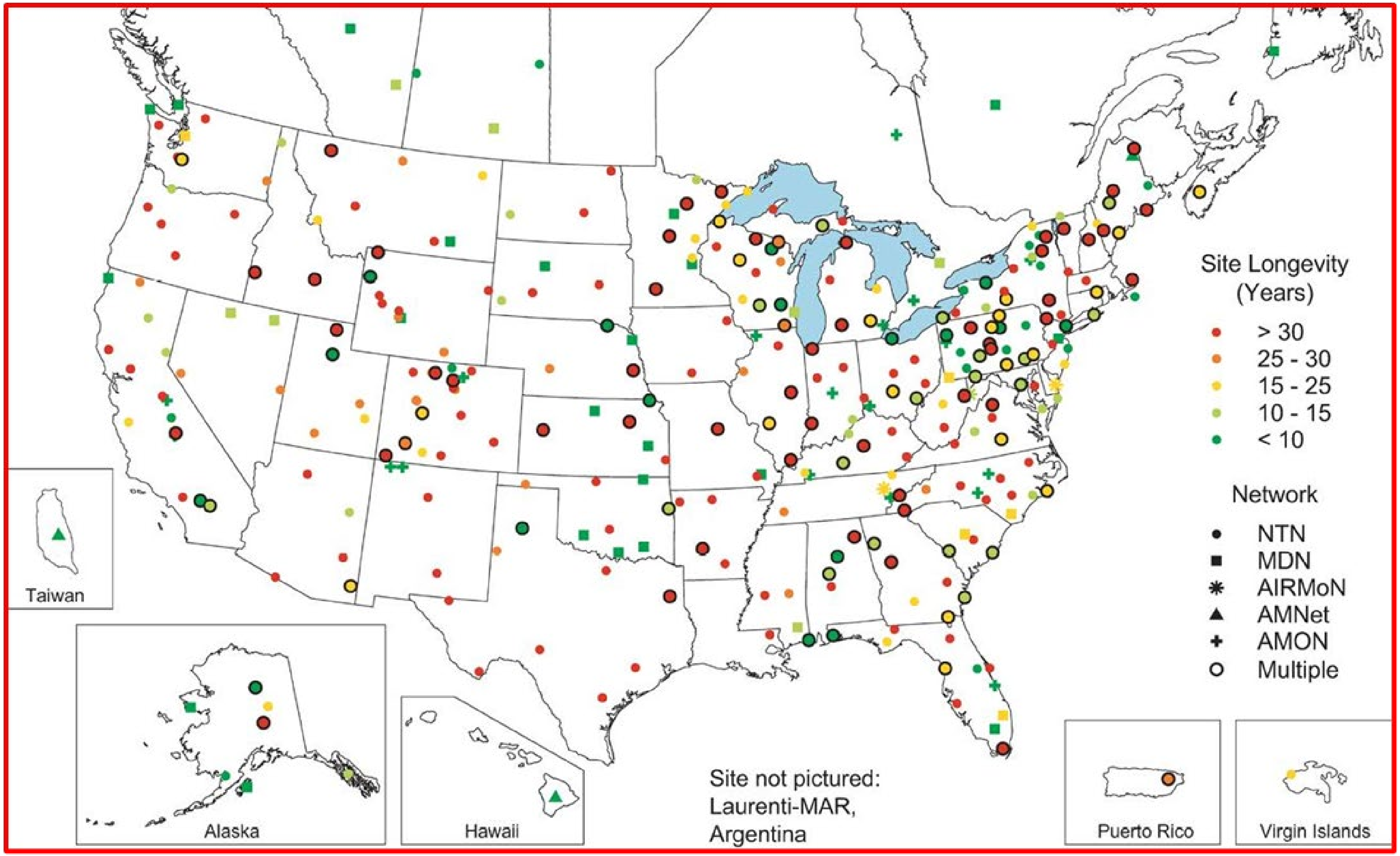
Regulatory Limits and Reference Concentrations

- **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**

PFAS Deposition Fluxes

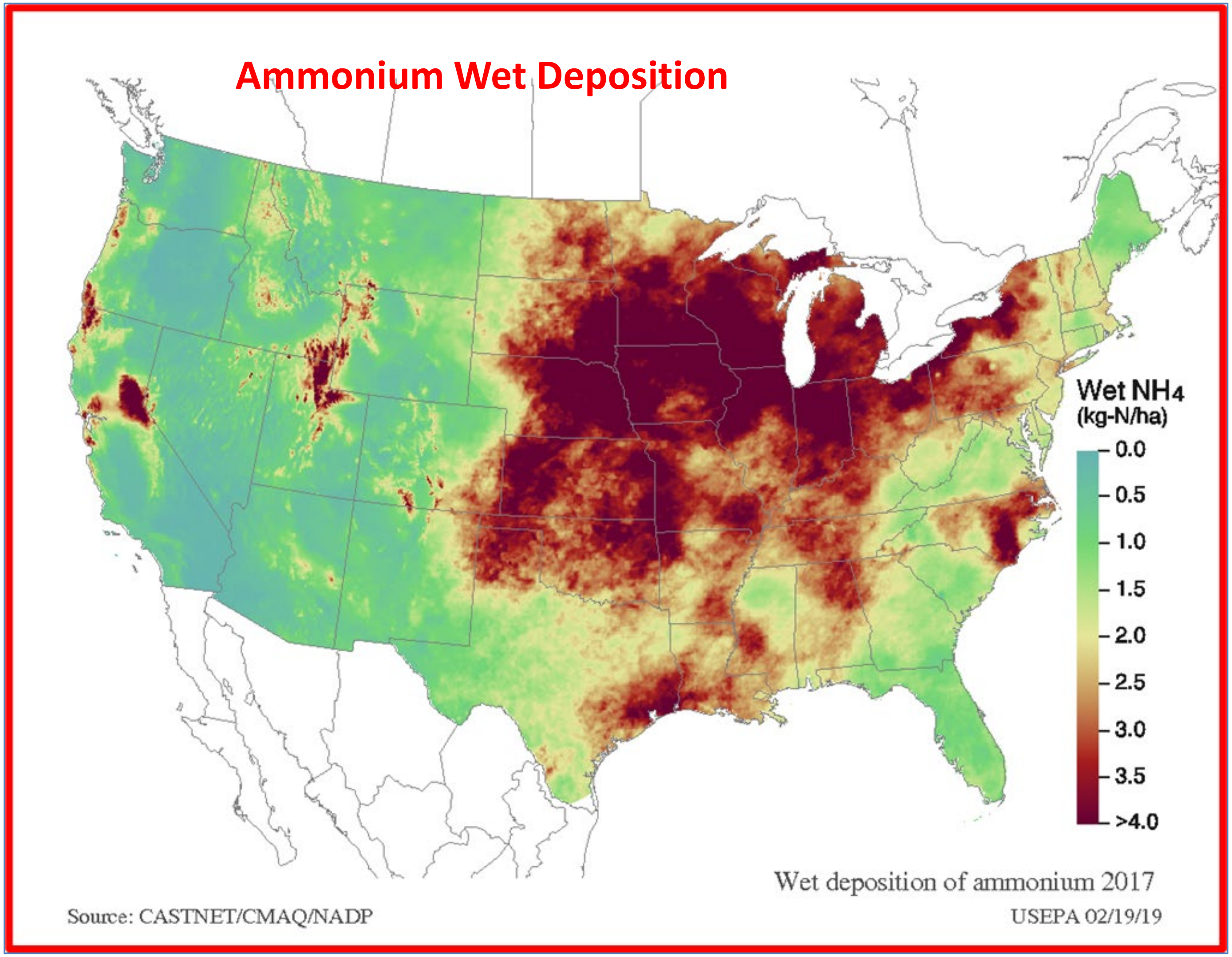
- Concentrations of **0.2 to 6.0 ng/L** equate to a wet deposition PFAS flux of **0.7 to 21 ng/m^2/day** (at an annual precipitation volume of 125 cm/year).
- This flux is significant for many environments (e.g. large lakes with long residence times – for Lake Michigan → annual flux of $4.4x10^{14}$ ng/year → 0.1 ng/L/year PFAS accumulation throughout the water column)

NADP Monitoring Sites



Synoptic Overview of PFAS Deposition and/or More Targeted Collections

Potential for PFAS Deposition Maps



a. Synoptic Overview
b. Seasonality
c. Regional Trends
d. “Hot-Spots”
e. Species Trends
f. Transformations

Summary and Where Next?

- The current NTN protocols are "CLEAN" for a broad range of PFAS compounds.
- Loss of PFAS during collection is minimal for compounds of carbon # <10 under current protocols.
- Advance alternate handling/collection protocols to address losses of longer-chain compounds (rinsing, resin collection).
- Determine the phase distribution (particle-partitioning) of PFAS in precipitation and in air samples (dry-deposition).
- Robust Network sampling program (spatial/temporal)

National Atmospheric Deposition Program
NADP

Wisconsin State Laboratory of Hygiene
UNIVERSITY OF WISCONSIN–MADISON

School of Medicine and Public Health
UNIVERSITY OF WISCONSIN–MADISON

QUESTIONS

Thank You

National Atmospheric Deposition Program

NADP

Sources & Exposure

Product Sources

1. Coated textiles
2. Treated paper
3. Non-stick coatings
4. Food Packaging
5. Foams (AFFF)
6. Personal care products
7. Paints, varnishes

Industrial Sources

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

We are all burdened with PFAS
NHANES (serum)
1-8 micrograms/L
Median =
4 micrograms/L

Major Exposure Routes

1. Food
2. Drinking Water
3. Consumer Products
4. Hand-Mouth

Major Entry Points

1. Fire fighting training
2. Industrial sites
3. Landfills
4. WWTP

Atmospheric Cycling Important in Dispersal

PFAS Measurement Approaches

- **Total**
  - PIGE
  - XRF
  - TOF/CIC
  - EOF/CIC
- **Non-targeted**

- **Total Oxidizable Precursor (TOP)**

- **Targeted**
  - 12-50 species
  - Quantitative
  - Tox relevant
  - Small fraction of total