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

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National Atmospheric Deposition Program
PFAS Dispersal & Atmospheric Processing

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

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

PFAS found in remote environments (aquatic, atmosphere and terrestrial) far from any known sources.
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 $\rightarrow$ carboxylic acids
2. Perfluorotelomeralcohols $\rightarrow$ 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
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**.
NADP Monitoring Sites

Synoptic Overview of PFAS Deposition and/or More Targeted Collections
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
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
PFAS Compounds

>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. \(-C_n\text{F}_{2n}\)-head ➔
2. Repel oil and water
3. Chemical and Thermal stability
4. Reduce friction
5. High surface activity

Buck et al. 2011
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)
NTN Network Efficacy for PFAS Measurement

A. System **Blanks**: Bucket & Bag Collectors
   - High-purity water $\rightarrow$ collectors

B. PFAS Retention/Loss Studies
   - Water, spiked with 36 PFAS compounds at low ng/L levels $\rightarrow$ collectors

Retirement/Loss Study Experimental Matrix

<table>
<thead>
<tr>
<th>Sample Matrix</th>
<th>Incubation Location</th>
<th>Collector Type</th>
<th>Day 0</th>
<th>Day 1</th>
<th>Day 3</th>
<th>Day 7</th>
</tr>
</thead>
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<tr>
<td>MQ</td>
<td>Lab</td>
<td>Bag</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>MQ</td>
<td>Lab</td>
<td>Bucket</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Precip</td>
<td>Lab</td>
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<td>Bucket</td>
<td>1</td>
<td>2</td>
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<td>2</td>
</tr>
</tbody>
</table>

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
PFAS Retention/Loss Study

Carboxylic Acids
C# = 4, 6, 8

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PFAS Retention/Loss Study

Carboxylic Acids
C# = 9, 10, 11
PFAS Retention/Loss Study

Sulfonic Acids
C# = 4, 6, 8
PFAS Retention/Loss Study

Gen-X & Related

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![Graph showing PFAS retention and loss study results.](image-url)
PFAS Retention/Loss Study

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FTSA
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 Recovered (ng)

Percent Recovery

Sample
MeOH Rinse
Spike Amount
% Recovery

perfluoroalkyl carboxylic acids
perfluoroalkyl sulfonates
n-fluorotelomer sulfonates
perfluoroalkyl sulfonamides
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

- Carboxylic acids
- Sulfonates
- Telomer sulfonates
- Sulfonamides
- Gen-X, ADONA

![Graph showing frequency of detection of various PFAS compounds](image-url)
PFAS Levels (ng/L) in Precipitation

Median and Maximum @ 30 NTN Sites

PFAS Concentration (ng/L)

perfluoroalkyl carboxylic acids
perfluoroalkyl sulfonates
n-fluorotelomer sulfonates
perfluoroalkyl sulfonamides

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PFAS Method Performance Outcomes in Precipitation

PFAS Method Precision
Two Precipitation Sample Duplicates

Duplicate Comparison - Two Sites

[PFAS] ng/L

- PFBA
- PFHxA
- PFHpA
- PFOA
- PFNA
- PFDA
- PFDoA
- PFOS
- PFOSA
- NMFeOSAA

- PA13
- PA13d
- NJ99
- NJ99d

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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.
- PFHxS, 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
• Concentrations of **0.2 to 6.0 ng/L** equate to a wet deposition PFAS flux of **0.7 to 21 ng/m²/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 $4.4 \times 10^{14}$ 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

Ammonium Wet Deposition

Source: CASTNET/CMAQ/NADP

Wet deposition of ammonium 2017
USEPA 02/19/19

- 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)
QUESTIONS

Thank You

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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)

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

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

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

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