Water Soluble Organic Nitrogen Characterization Study

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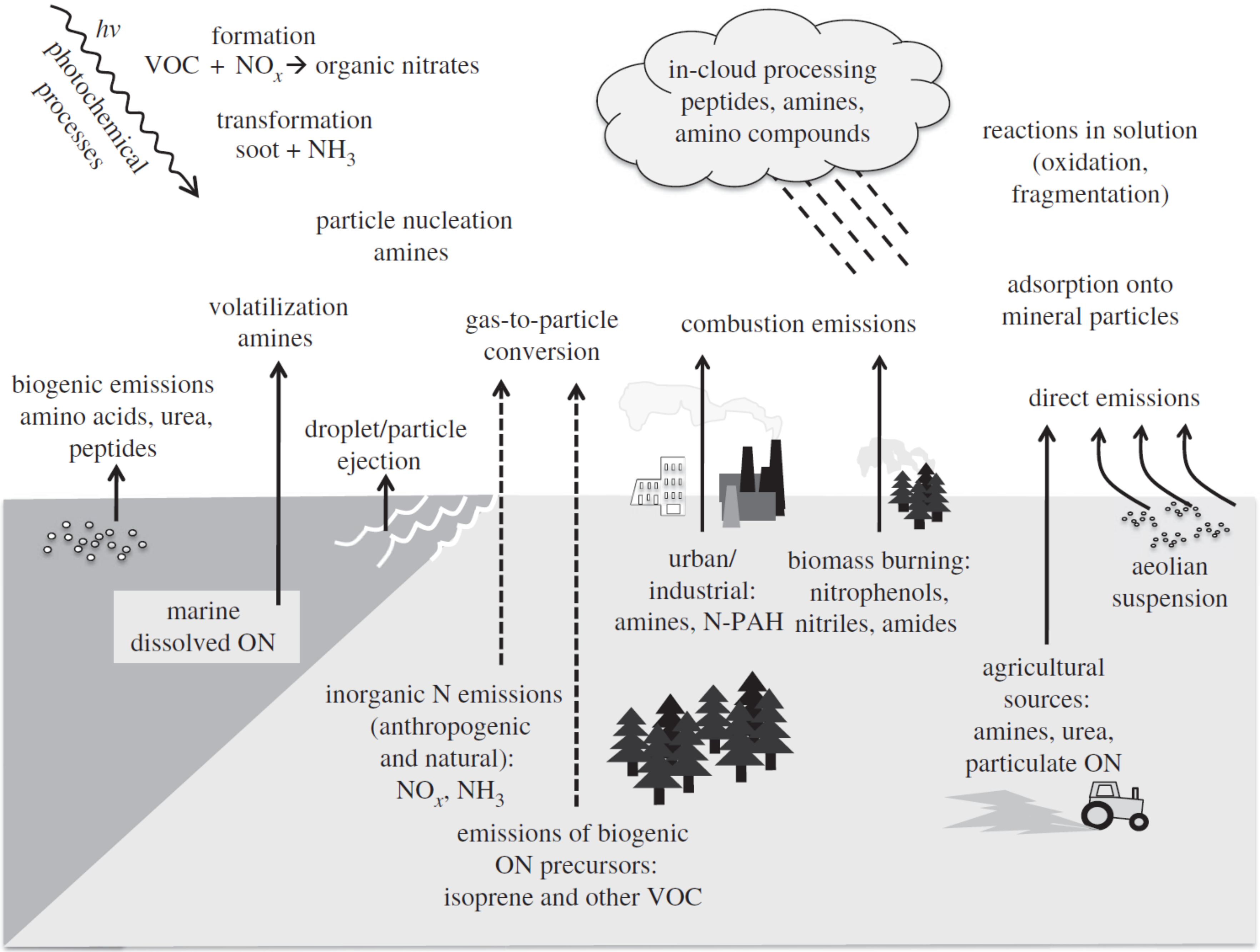


Organic forms of nitrogen (N) are an important, routinely unmeasured, component of atmospheric deposition to terrestrial and aquatic ecosystems.

Global datasets of precipitation chemistry indicate that water soluble organic nitrogen (WSON) contributes ~ 25% of the total N in wet deposition, on average.

In the U.S, annual averages of WSON range from 2.6% to 33%

Source: Jickells, et al 2013

Example: Nitrogen Budgets

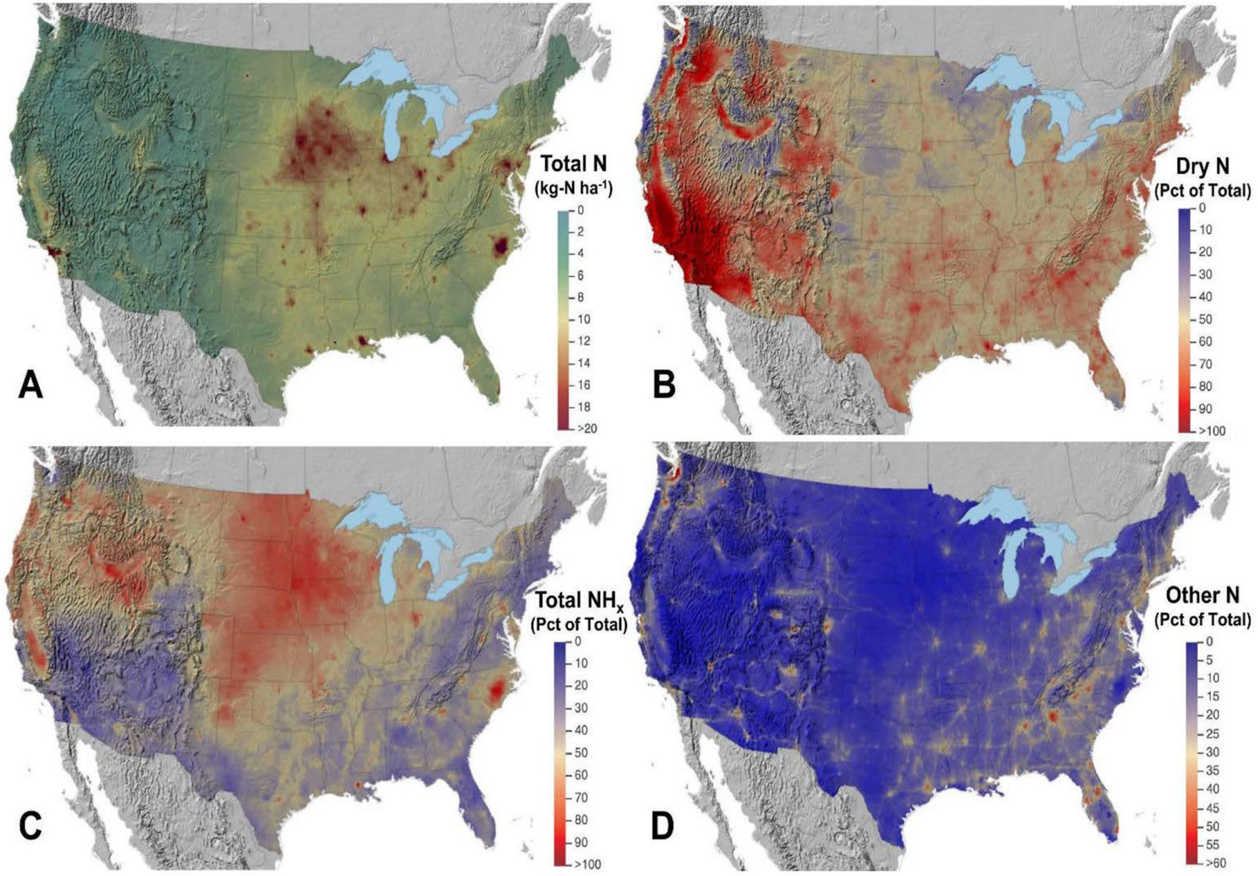
Summary of total deposition maps derived from the TDep MMF procedure (Schwede and Lear, 2014; NADP, 2018) (NADP, 2018) for the continental U.S., averaged over the period 2014–2016, of:

(A) total N deposition,

(B) percentage of total N deposition attributed to dry deposition,

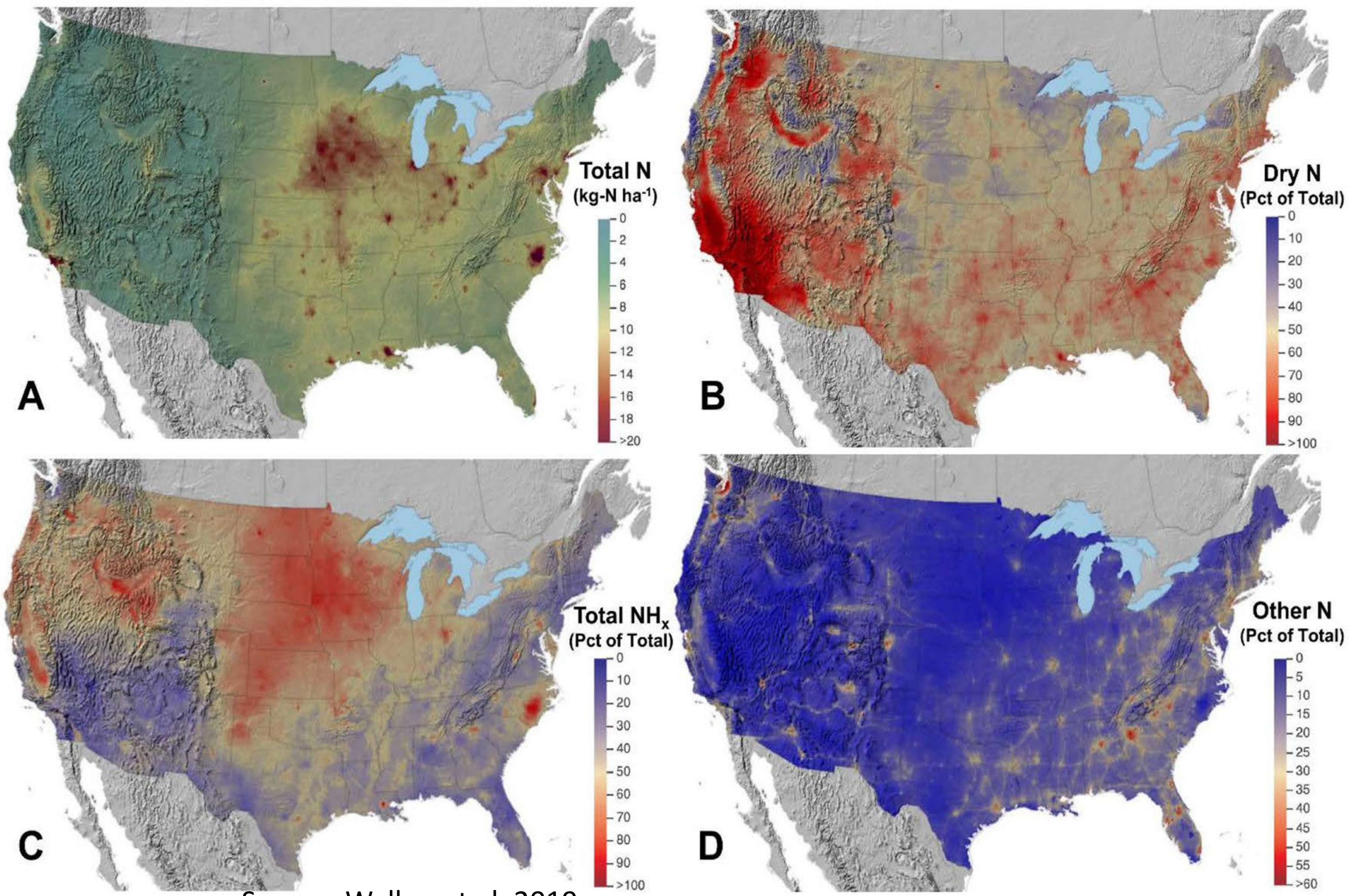
(C) percentage of total deposition attributed to reduced N ($NH_x = NH_3 + NH_4^+$), and

(D) percentage of total deposition attributed to dry deposition of N species not measured at CASTNET sites (i.e. "Other N"). "Other N" comprises NO, NO_2, HONO, N_2O_5, and organic N.



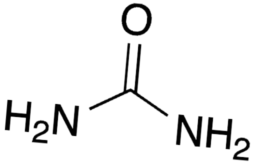
Source: Walker et al, 2019

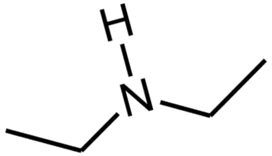
"Other N" fraction contributes ~ 13% of total deposition over the CONUS on average, with much larger contributions in urban areas and along major roadways.

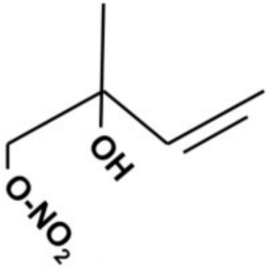


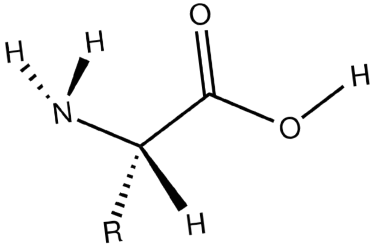
Source: Walker et al, 2019

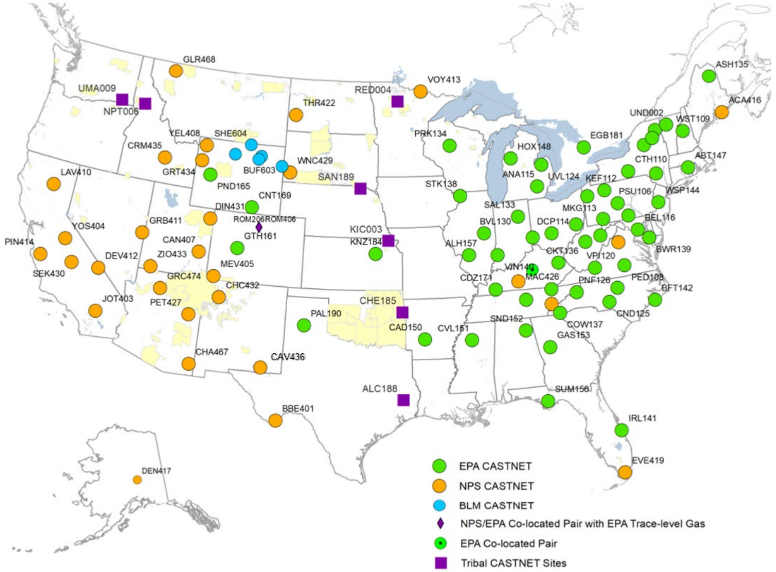
Quantifying WSON sampled by CASTNET filter packs





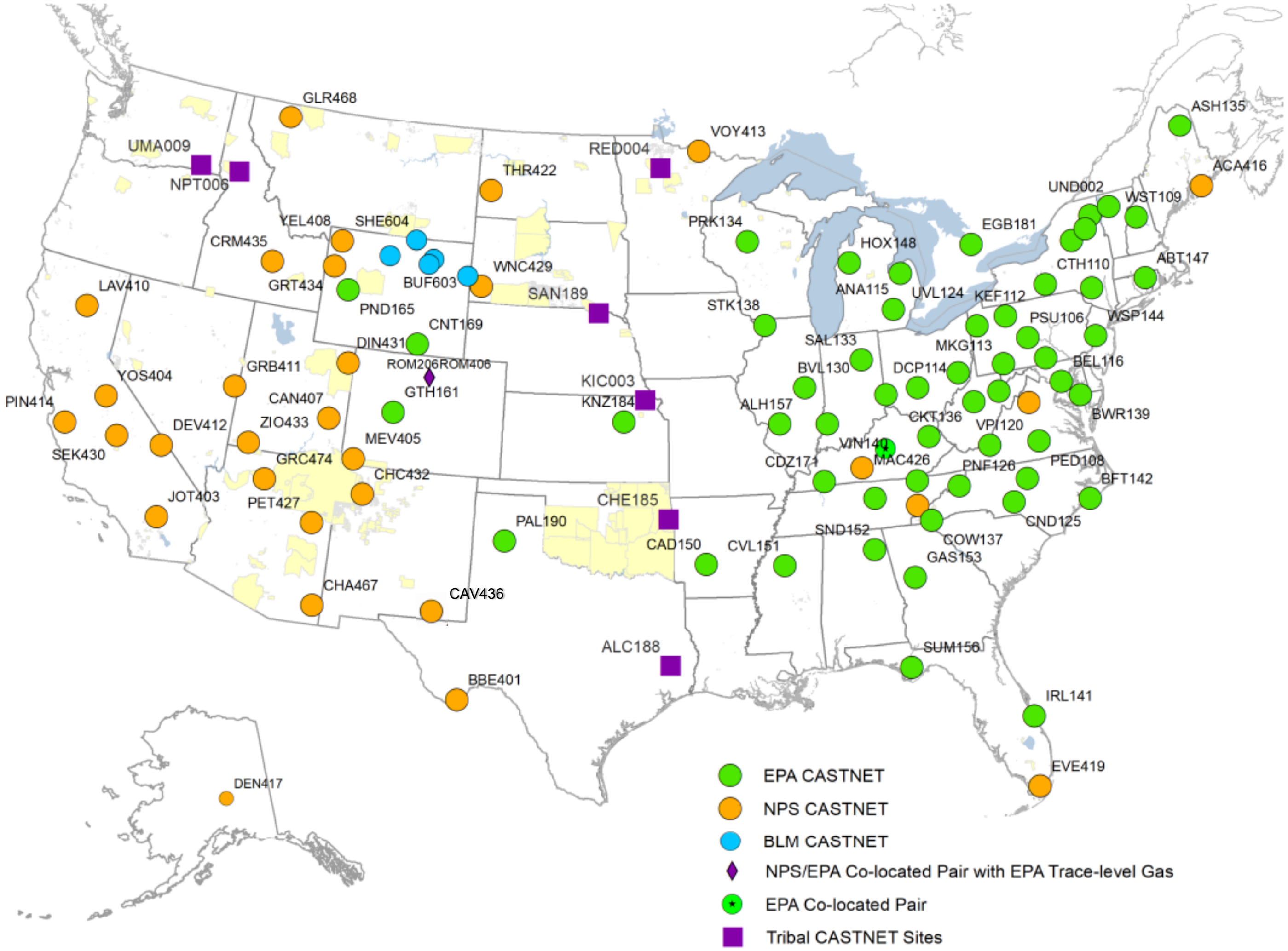






- Although organic nitrogen constitutes approximately one quarter of atmospheric nitrogen globally, its sources, deposition mechanisms, and ecological impacts are poorly understood.
- <u>Near-term goal</u>: To constrain spatial and temporal variability, this project sought to develop robust methods to quantify bulk WSON sampled on filter packs from the CASTNET monitoring network.
- <u>Long-term goal</u>: Incorporate routine measurements of bulk organic nitrogen into CASTNET sampling and analytical protocols.
- Goals are consistent with recommendations in Walker et al, 2019.

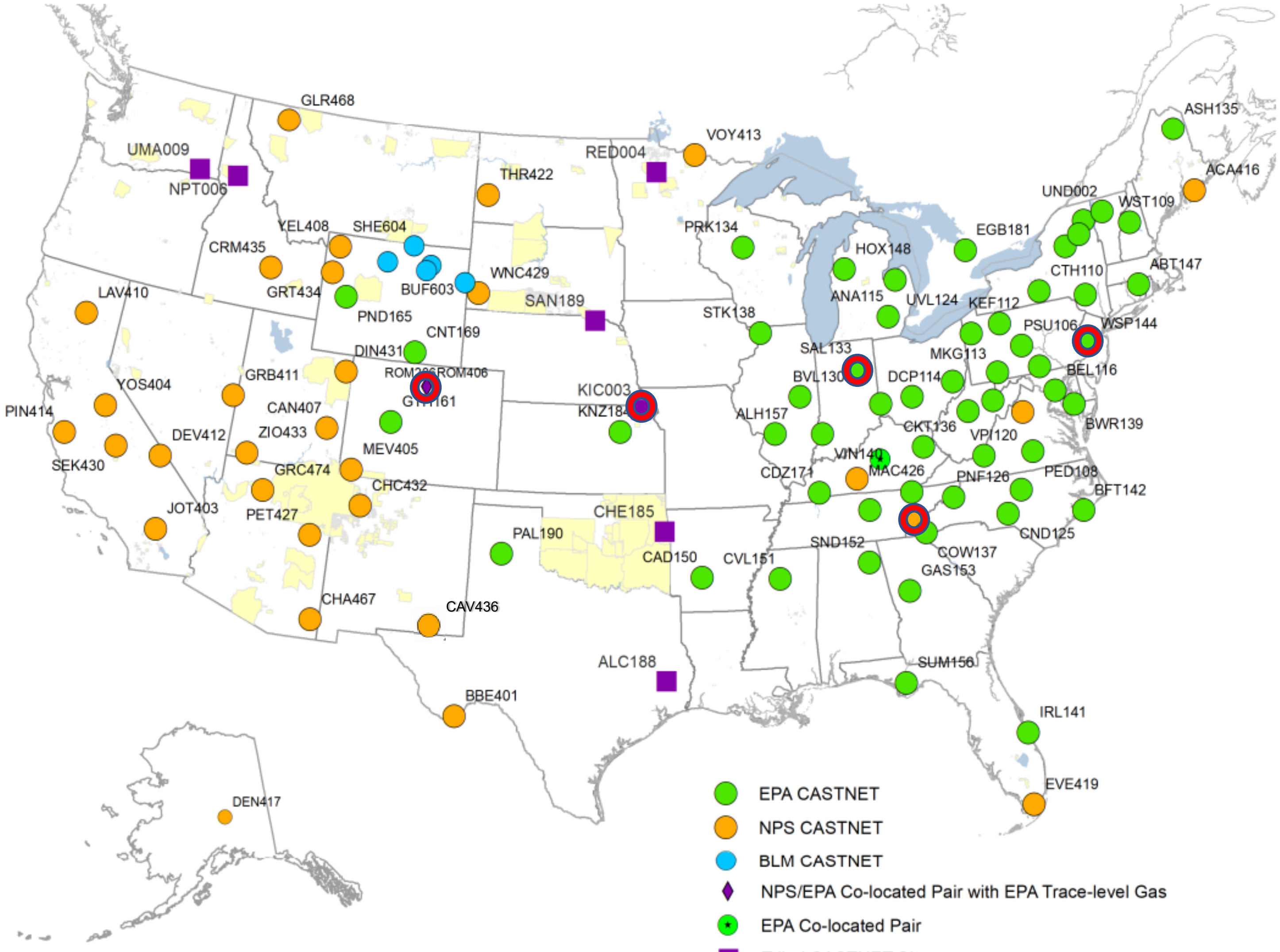
Clean Air Status and Trends Network (CASTNET)



CASTNET monitoring sites (colored by coordinator)

- Long term monitoring program
- ~100 sites
- SO_4^{2-}, NH_4^+, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_2, and HNO_3 measured.
- Established to assess effectiveness of emission reduction programs in 1990 Clean Air Act Amendments
- Managed & operated by U.S. EPA with support from BLM, NPS, and tribes

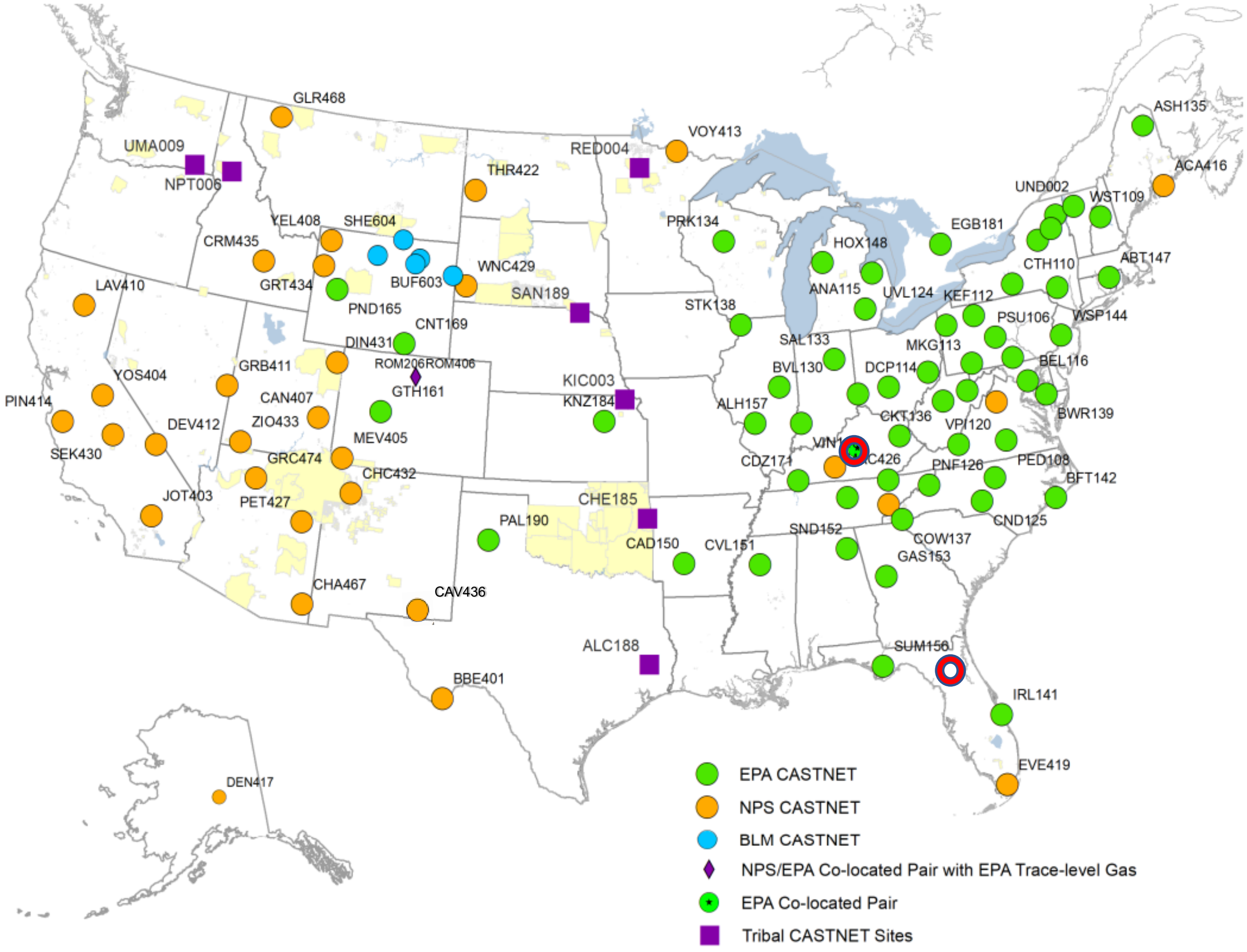
WSON Pilot Study



WSON Study Sites ( )

- Measurement of WSTN and WSON at 5 CASTNET sites
- Study period January – March 2021
- Initial assessment showed that WSTN and WSON could be determined using the CASTNET Teflon filter

WSON Storage Study



WSON Storage Study Sites ( )

- An assessment of the stability of nitrogen containing compounds during storage and handling of CASTNET filter samples
- Study period March – June 2021
- Co-located sampling at the Gainesville, FL laboratory test site and MCK131/231, KY

$$WSON = TN - (NO_3^- + NH_4^+)$$

Teflon

Nitrate (NO_3^-)

IC Dionex ICS-1600

Total Nitrogen (TN)

Shimadzu TOC-V_{CSH}+TNM-1

Ammonium (NH_4^+)

Bran+Luebbe AutoAnalyzer 3

Proposed WSON storage tests

Preliminary tests

- Initial storage tests examined differences in TN between samples stored at room temperate versus refrigerated for a range of storage times.
- Results showed that refrigerated samples were more stable than samples stored at room temperature but no relationship with length of storage time in either refrigerated or room temp samples.

Additional proposed tests

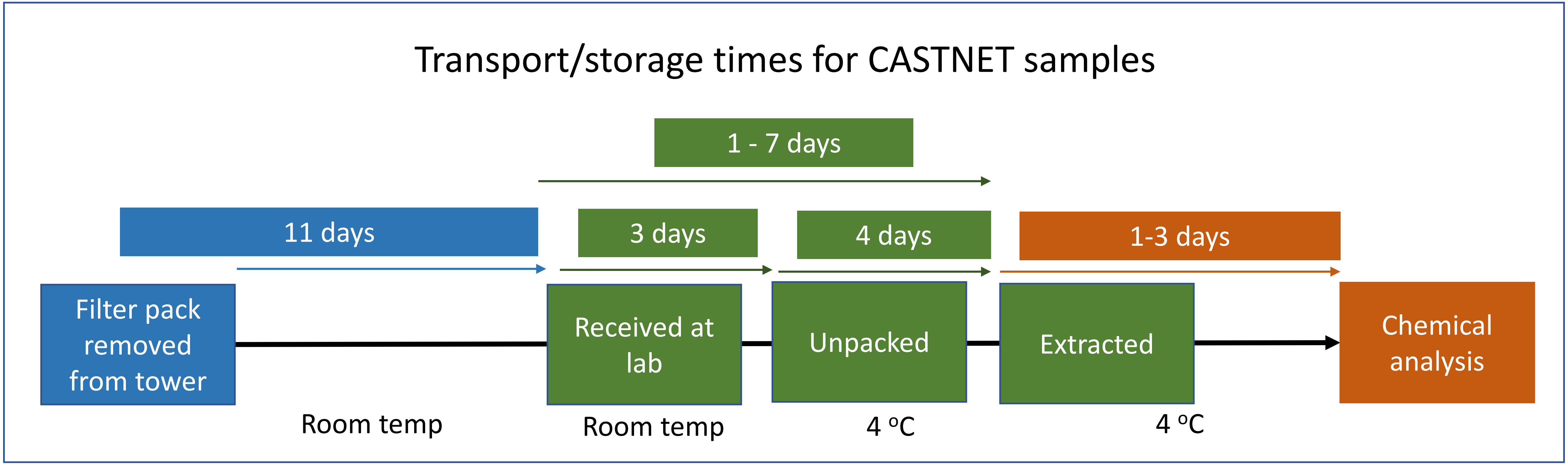
Build on preliminary tests in a few ways:

- New tests encompass typical network shipment and storage times.
- Analyses will include TN, NH4, and NO3, rather than TN only, so that effects on WSON can be quantified.
- Includes comparison of refrigerated versus frozen extracts.

Questions to be addressed

- Is there a change in WSON between when the filter pack is removed from the tower and when it enters cold storage at the lab?
- Is there a change in WSON between when the filter pack enters cold storage and when the extract is analyzed?
- Is there a difference in analyte concentrations in extracts that are refrigerated versus frozen?

Transport/holding times for CASTNET samples

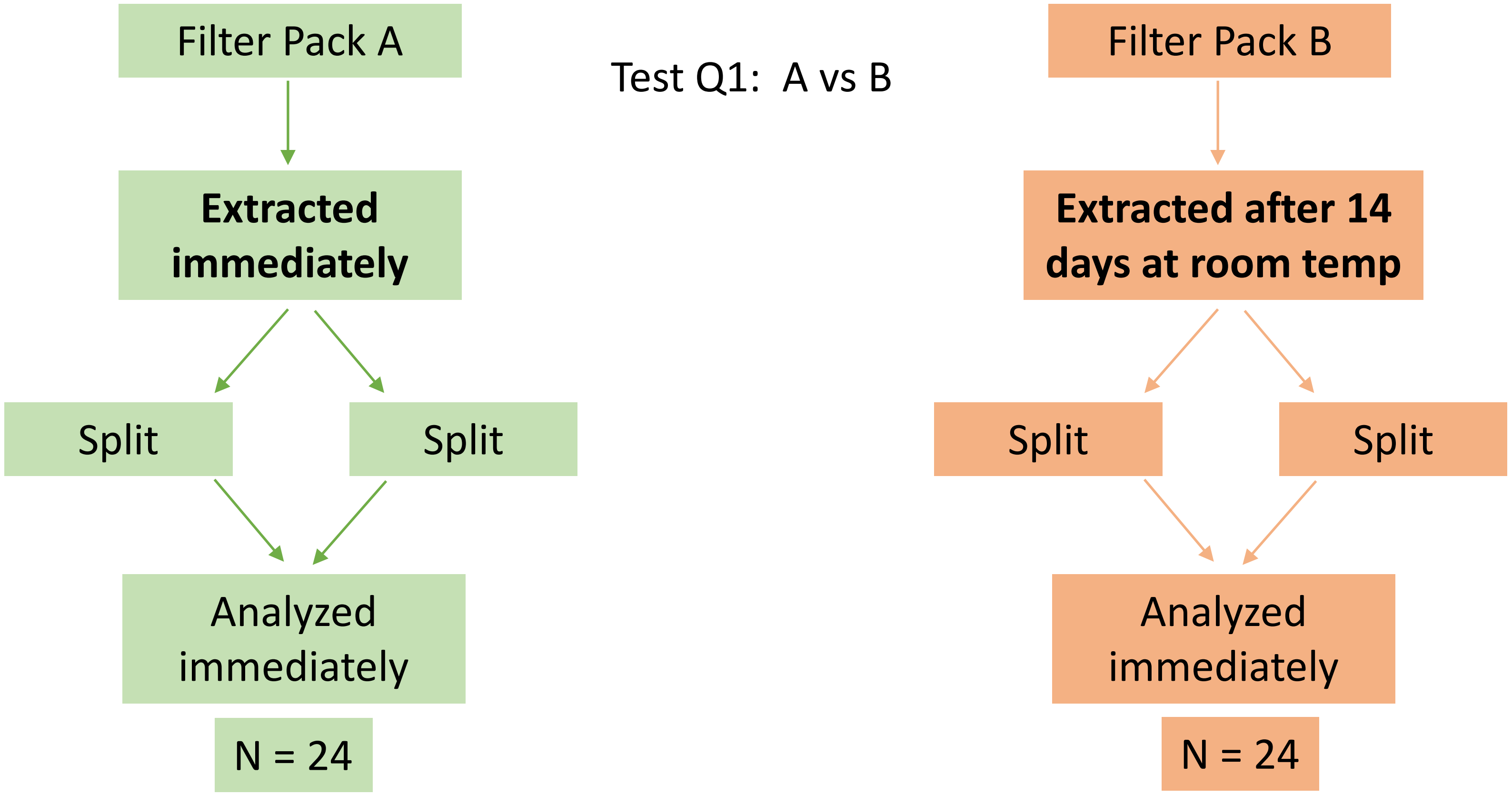


- Based on analysis of 2019 network wide statistical distribution of difference between "Date Off" and date of receipt of filter pack at lab.
  - 90^{th} and 95^{th} percentiles of 9 days and 12.4 days. Chose 11 for test scenarios.
- Maximum possible lab storage times were used for test scenarios.
- Wood has since switched to USPS Priority Mail for return shipments. Most returns now take 2 – 4 days.

Test 1 – Gainesville duplicate filter packs

Question: 1. Is there a change in WSON between when the filter pack is removed from the tower and when it enters cold storage at the lab?

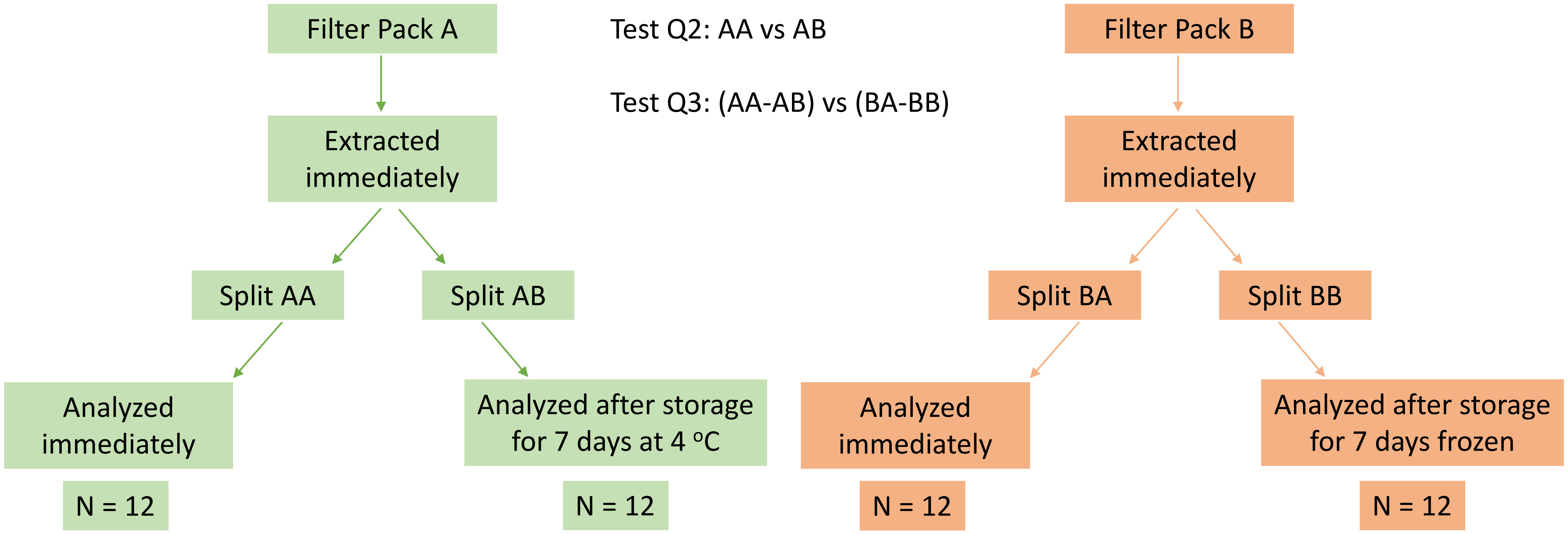
Approach: Duplicate filter packs collected at Gainesville for 12 weeks (Spring 2021).



Test 2 – Mackville duplicate filter packs

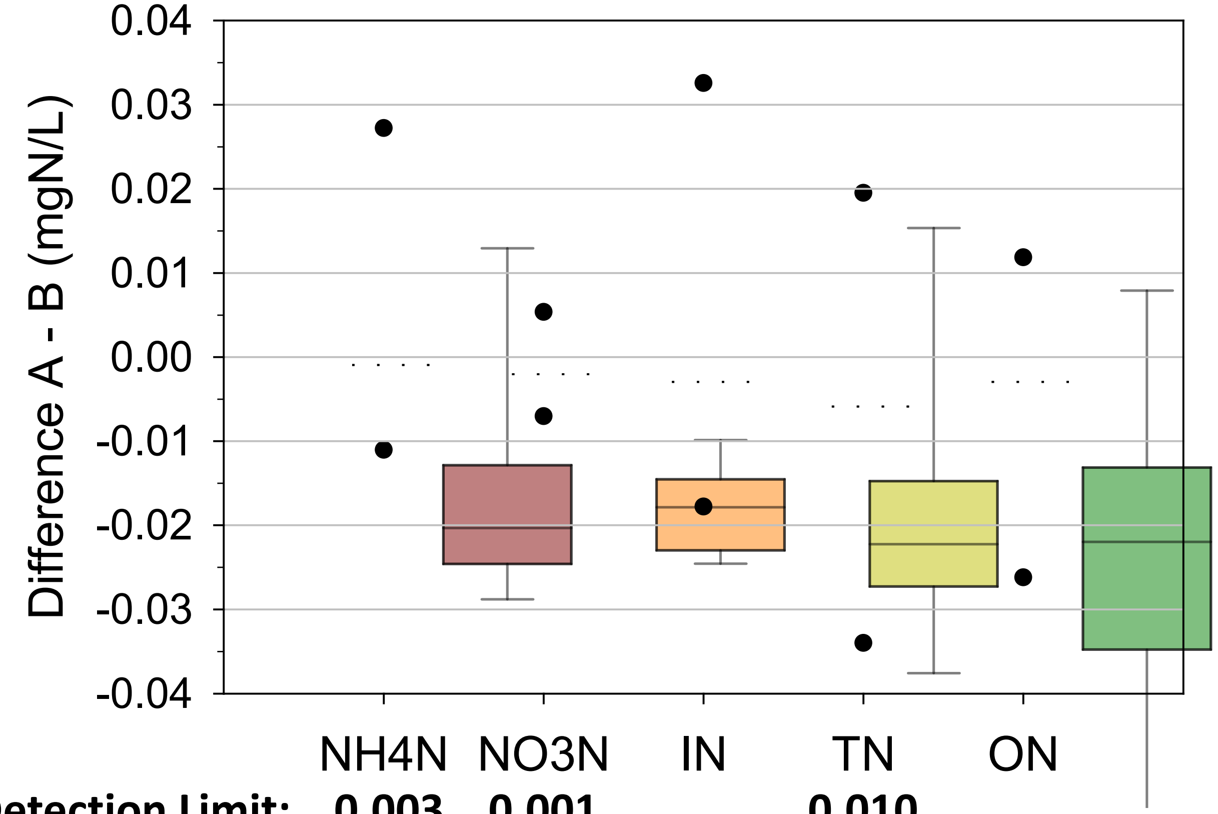
Questions: 2. Is there a change in WSON between when the filter pack enters cold storage and when the extract is analyzed? 3. Is there a difference in analyte concentrations in extracts that are refrigerated versus frozen?

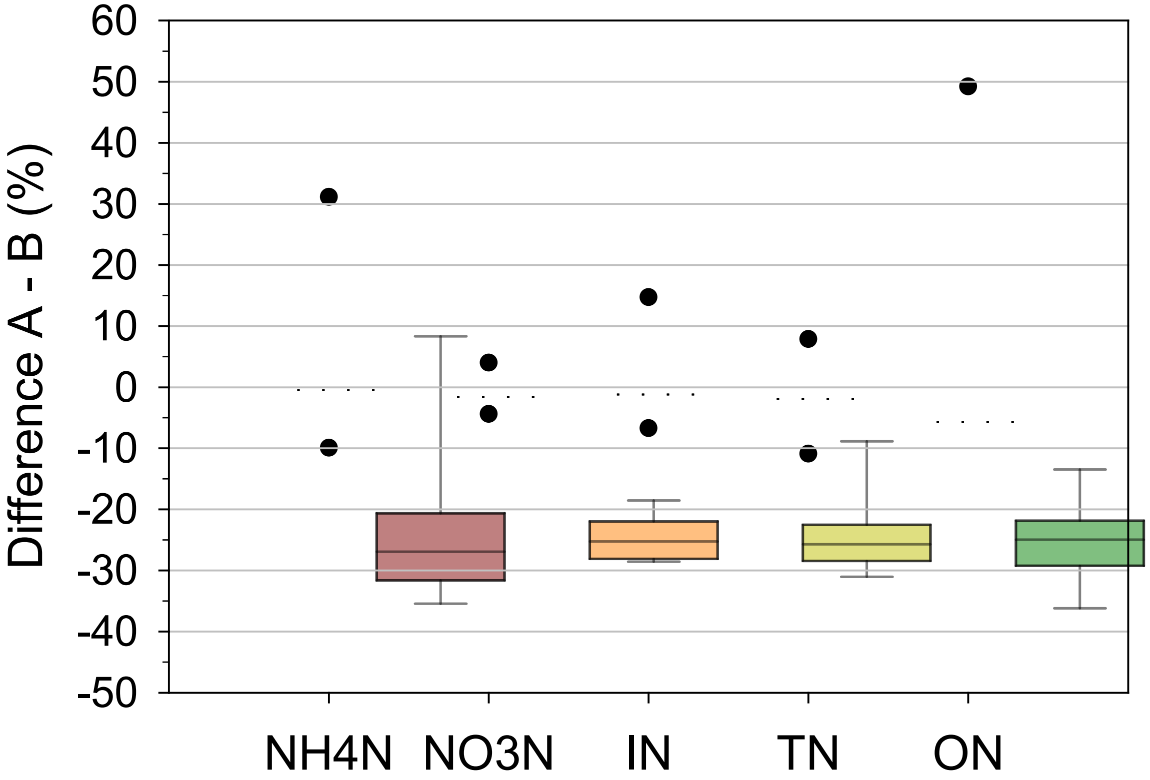
Approach: Duplicate filter packs form Mackville analyzed for 12 weeks (Spring 2021).



GNV – Storage results

Differences between extracted /analyzed immediately (A) versus stored for 14 days at room temperature (B)





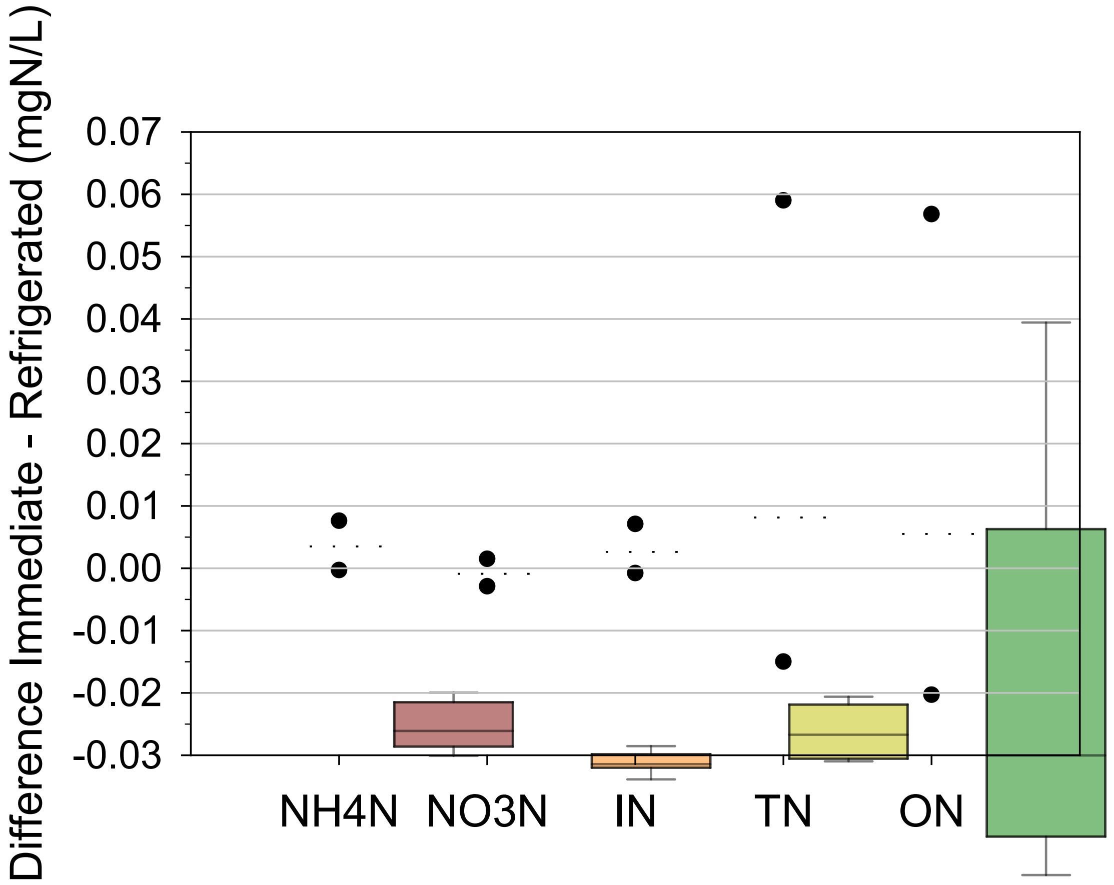
Detection Limit: 0.003 0.001 0.010

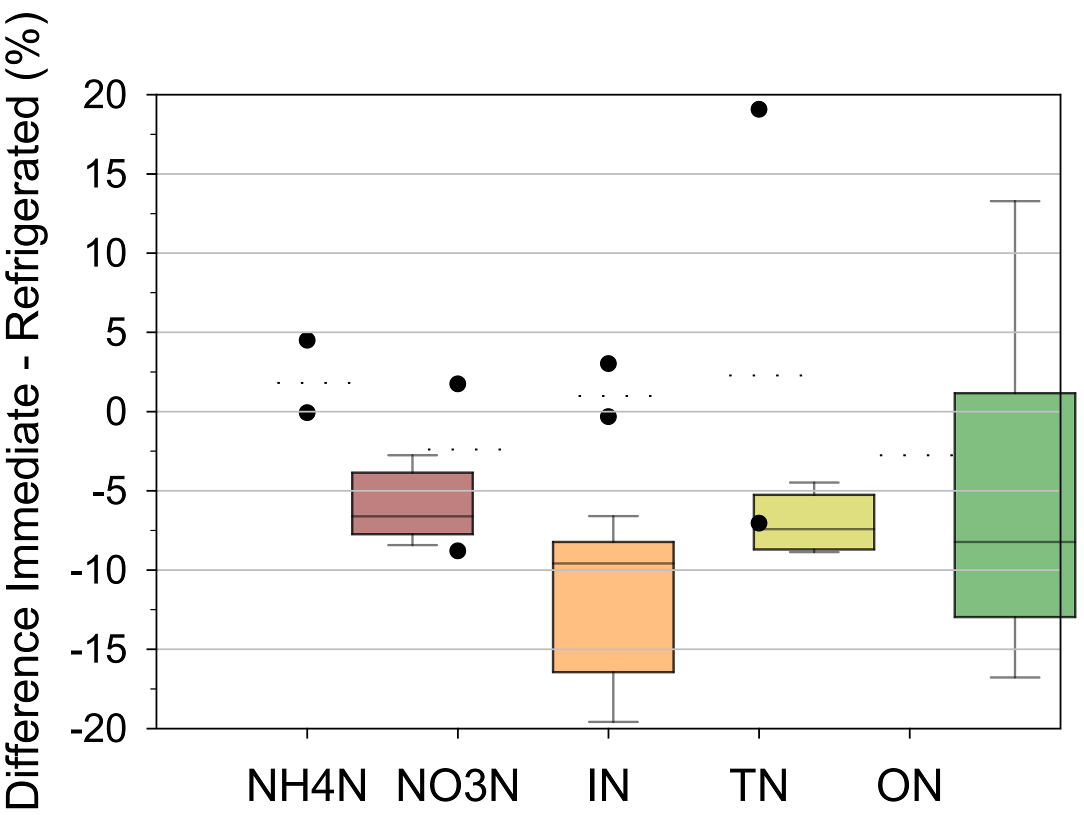
- Concentrations generally increased during storage, but changes were small.
- Movement from particle to solution over time?
- Variability (%) large for ON due to its lower concentrations.
  Averaging additional TN replicate injections should help decrease variability.

Median % difference	
NH4N	-3.2
NO3N	-1.9
TN	-1.7
ON	2.2

MCK – Refrigeration

Differences between extracted /analyzed immediately versus refrigerated for 7 days

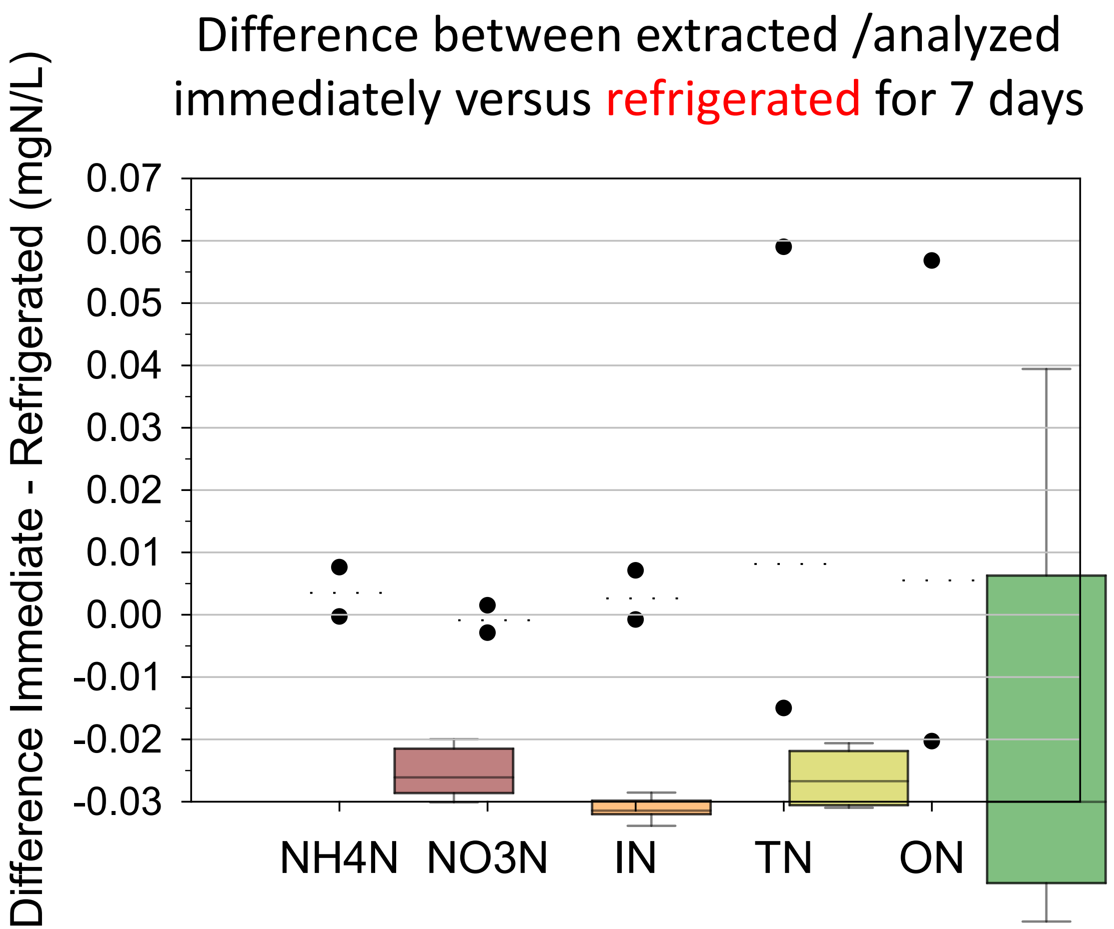


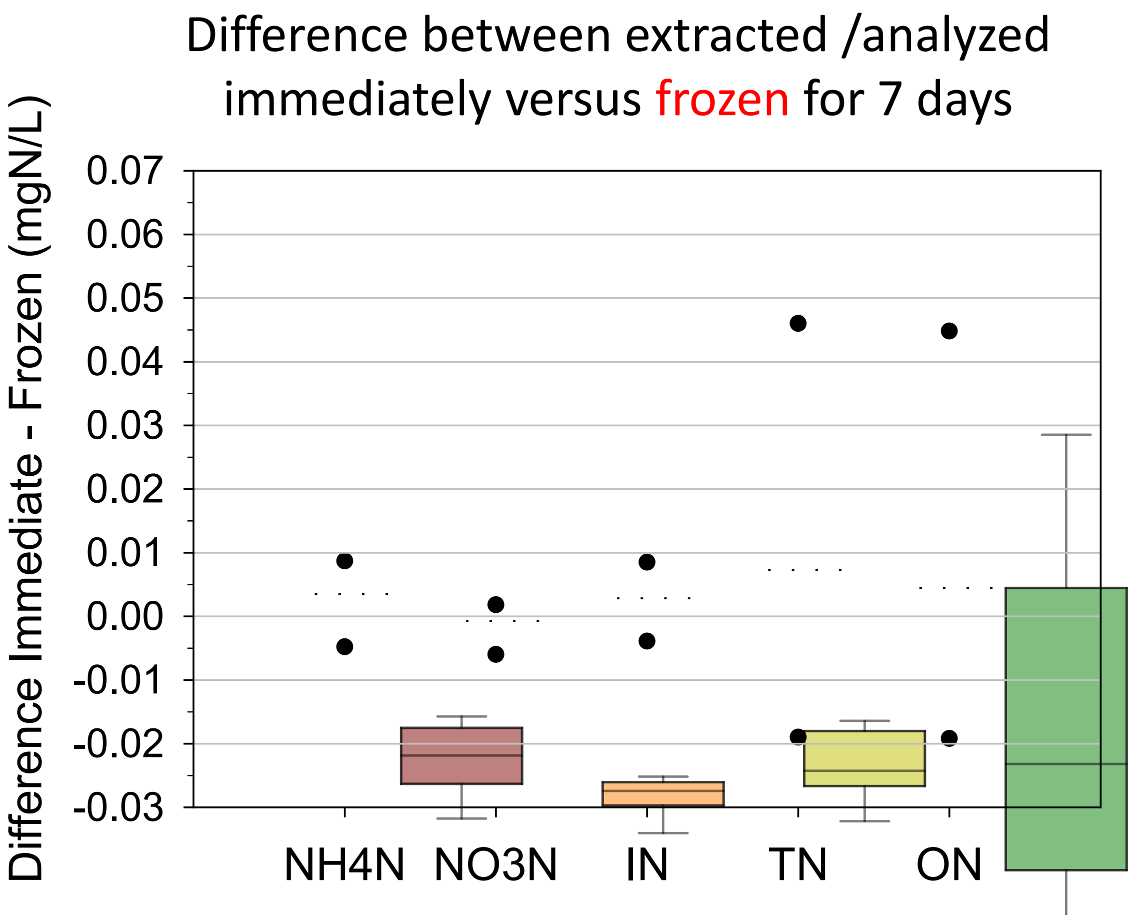


- Results indicate a small loss of NH4N during refrigeration offset by a small increase in NO3N, possibly indicative of nitrification.
- Changes are small overall
- Variability (%) large for ON

Median % difference	
NH4N	1.4
NO3N	-0.8
TN	0.2
ON	-9.2

MCK – Refrigeration versus freezing

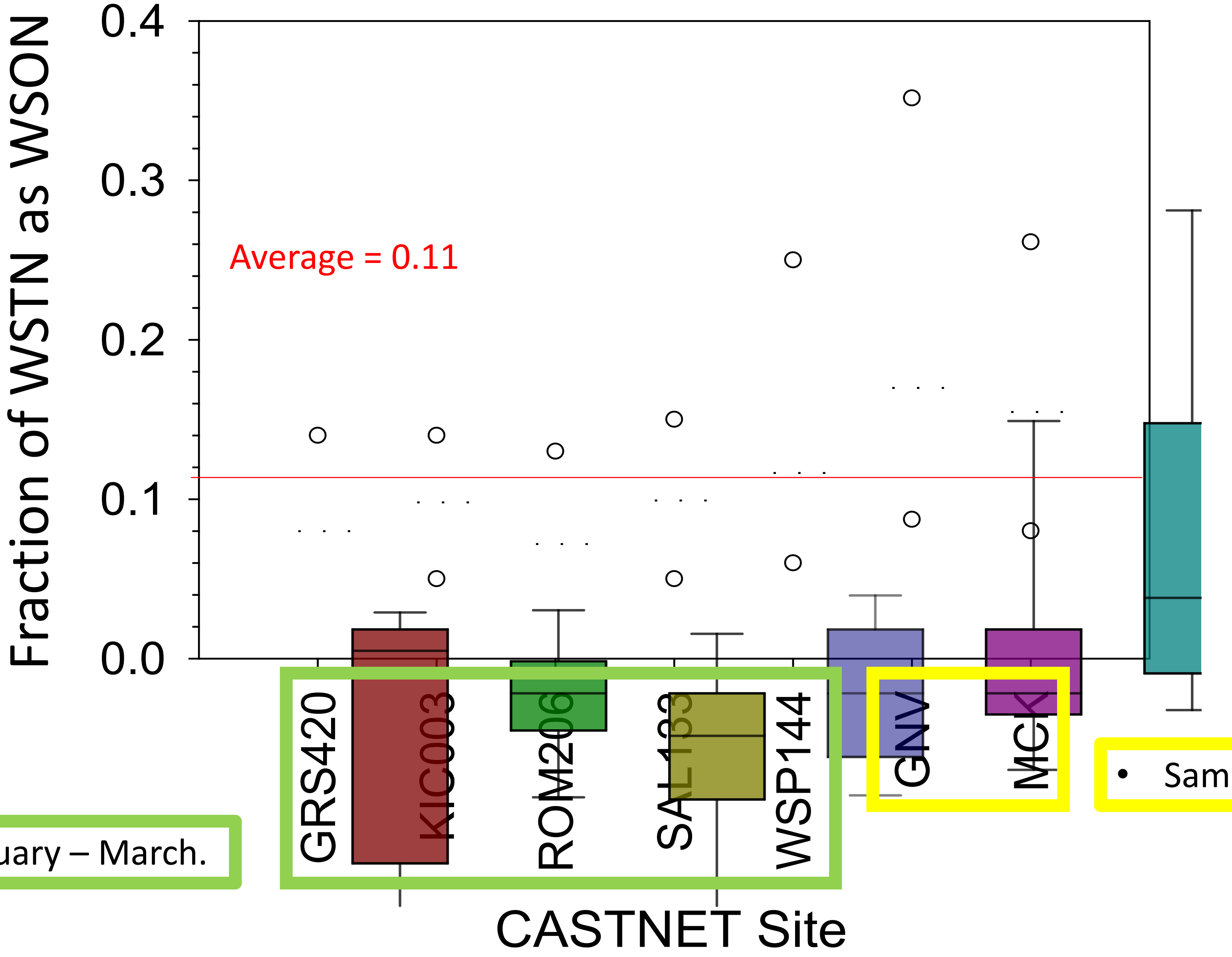




- Differences similar between refrigerating versus freezing samples.

Median % difference	
NH4N	1.8
NO3N	-0.2
TN	1.2
ON	-2.2

11% of WSTN as WSON on average at 7 sites



- Sampled January – March.

- Sampled March – June.

Conclusions and Improvements

- Further testing showed decreased TN (and ON) variability with the averaging of additional injections on the Shimadzu.
- Sample volume was limited due to analysis on multiple instruments, which restricted reruns and replicate injections.
- Overall, there is no reason to believe that CASTNET's standard storage methods significantly impact median WSON concentrations. By increasing replicate injections and/or reducing instruments used, precision could potentially be improved.

Addition of SEAL autoanalyzer simplifies analysis and should improve precision

Teflon

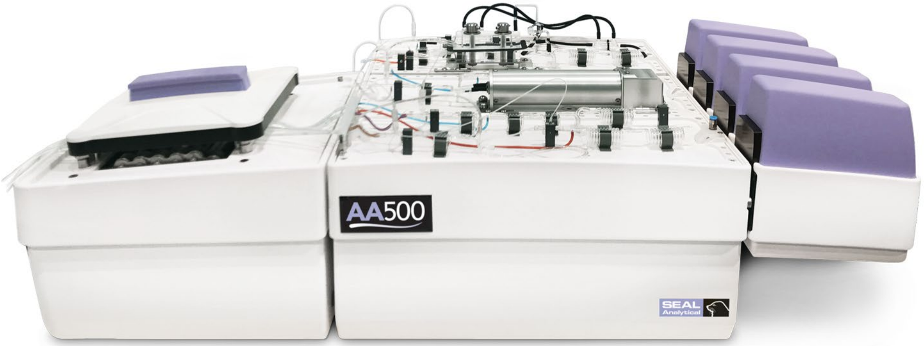
Nitrate (NO_3^-)

IC Dionex ICS-1600

$$WSON = TN - (NO_3^- + NH_4^+)$$

Ammonium (NH_4^+)

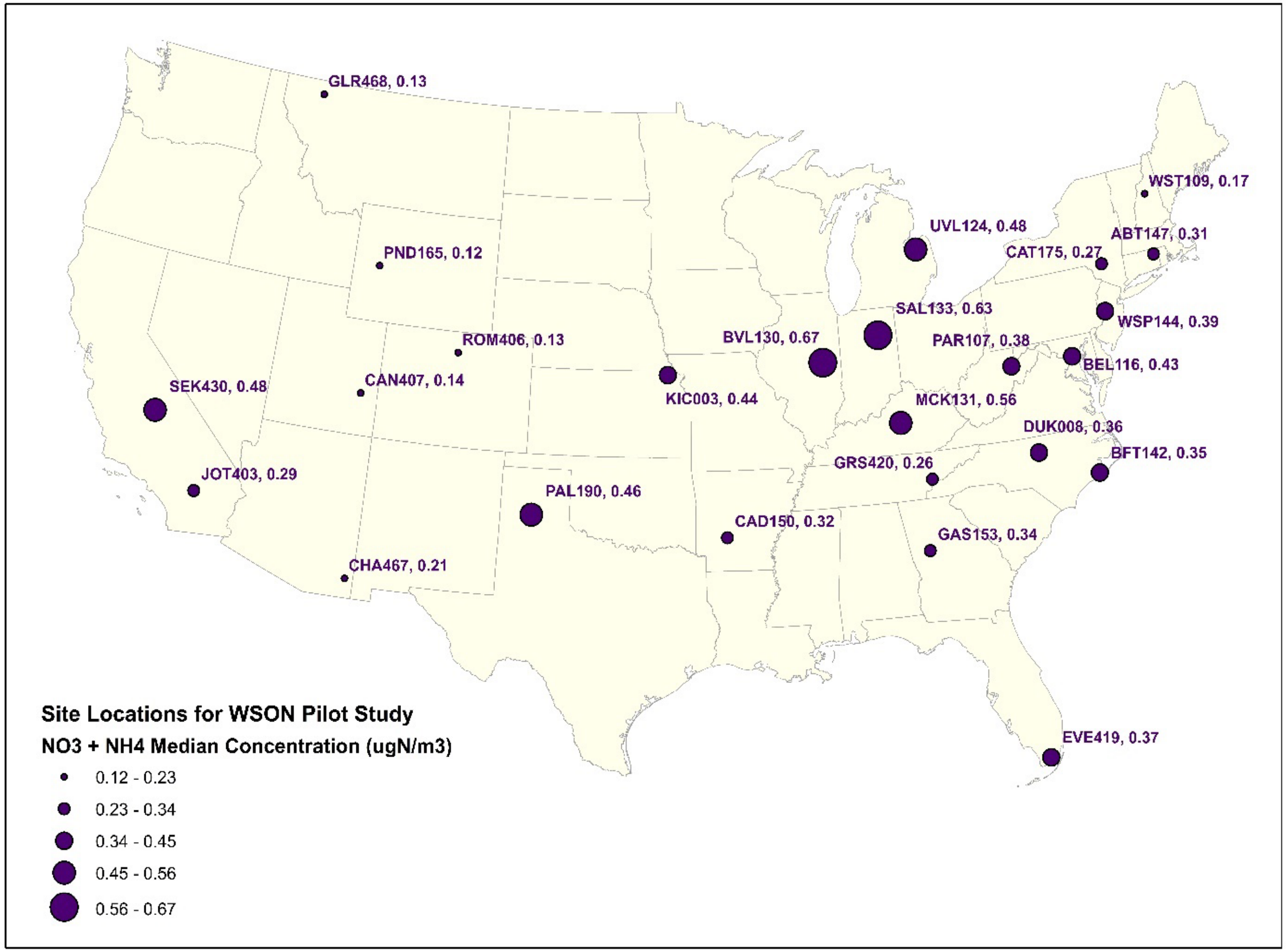
Total Nitrogen (TN)



SEAL AutoAnalyzer

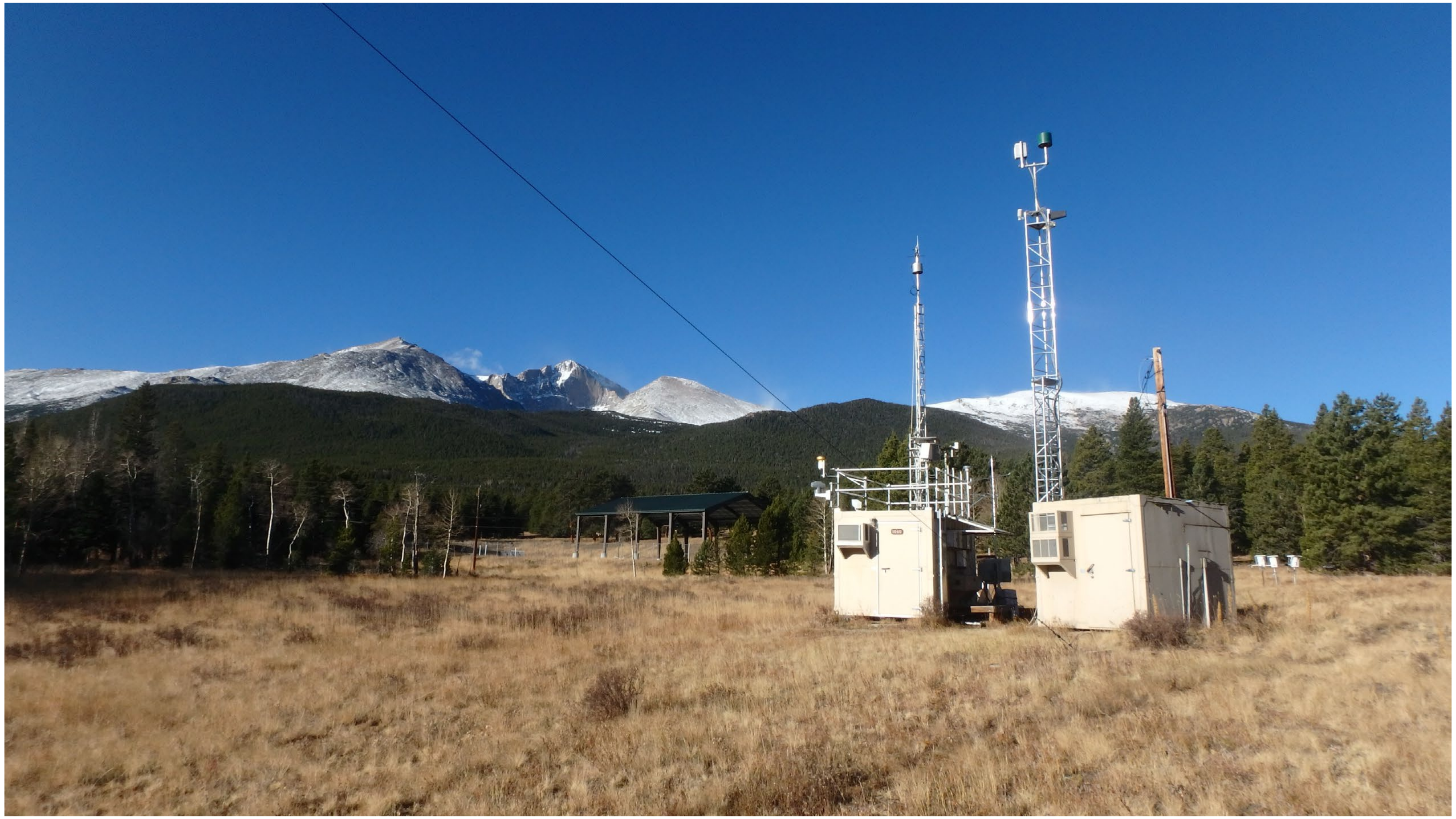
Next steps

- Assess performance characteristics of new autoanalyzer for TN and NH_4^+.
- Test cross-calibration procedure for TN, NH_4^+ and NO_3-
- Establish subset of proposed CASTNET WSTN measurement sites for NADP total N/P precipitation sampling (SNiPiT)
- Implement 12 months of monitoring at 27 CASTNET sites



CASTNET sites for 12-month monitoring study. Sites were chosen for geographical coverage, land-use diversity and range of particulate inorganic N (NH_4^+ + NO_3^-) concentration.

Any Questions?



Rocky Mountain National Park Co-located Site (ROM406/206)

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