CSN/IMPROVE NHx Study in the Southeastern United States

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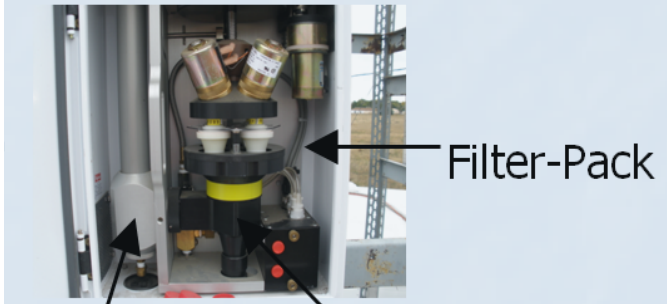
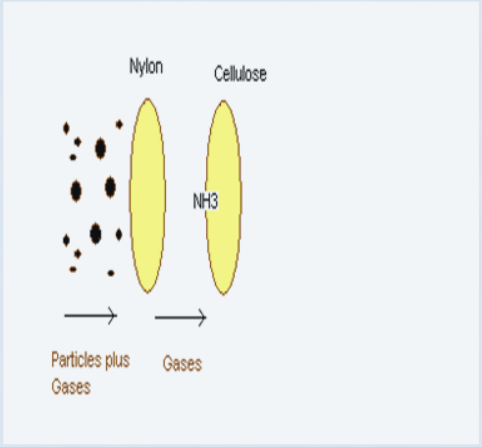
Recall the IMPROVE NHx Study

- Phosphoric acid impregnated cellulose backup filter to collect NH_3 and volatilized NH_3 from nylasorb filters
- Acid impregnated cellulose front filter to collect NH_3 + NH_4^+ and other gases e.g. methylamine

The IMPROVE Sampler utilizes a denuder to remove HNO3, a cyclone to limit sample collection to PM2.5 aerosol, and a filter-pack.



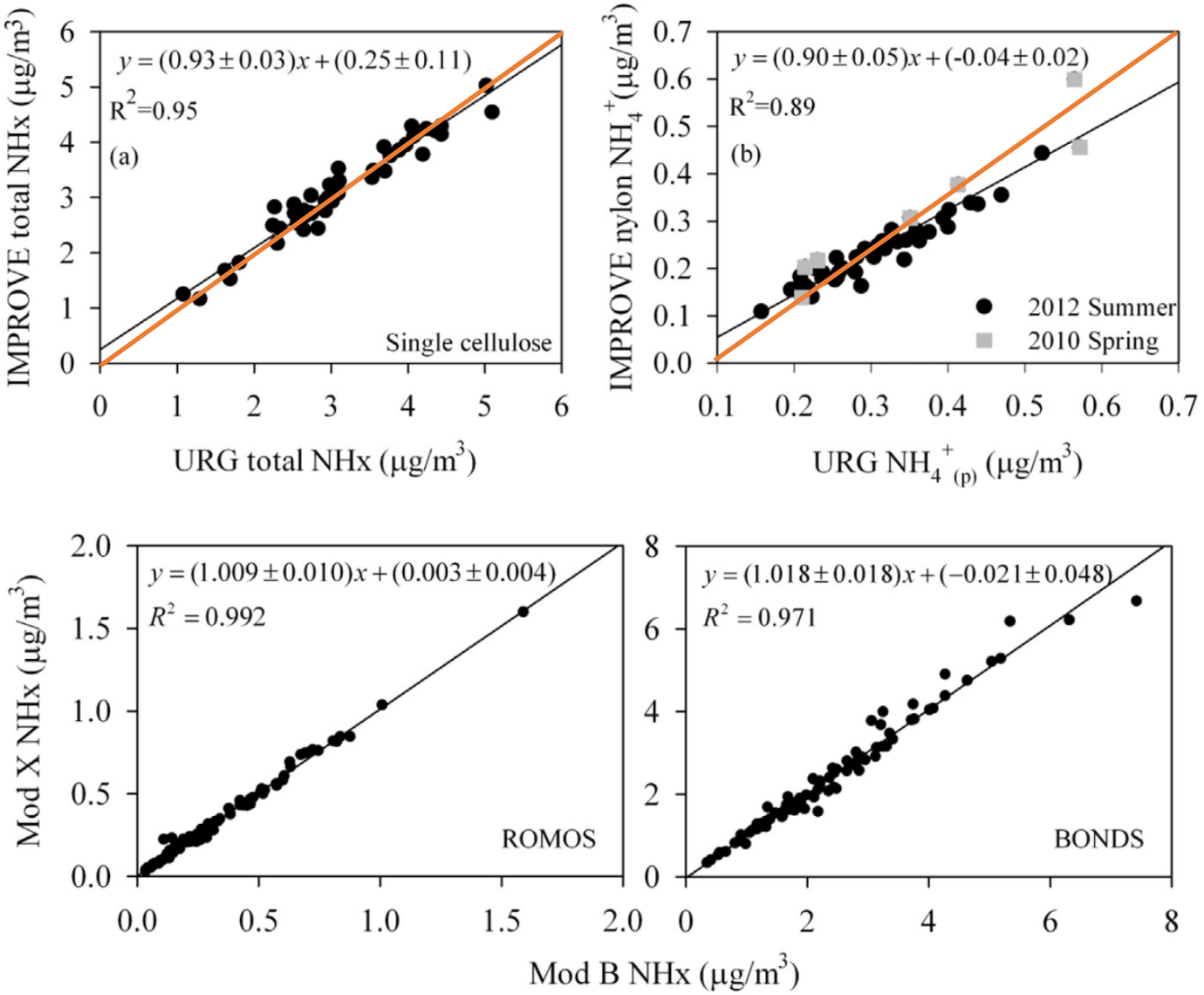


Schematic of filter-pack array

- IMPROVE samplers collects 24-h samples
- Filters analyzed for NH4+ and methylamine by ion chromatography

NHx IMPROVE Measurement Evaluation

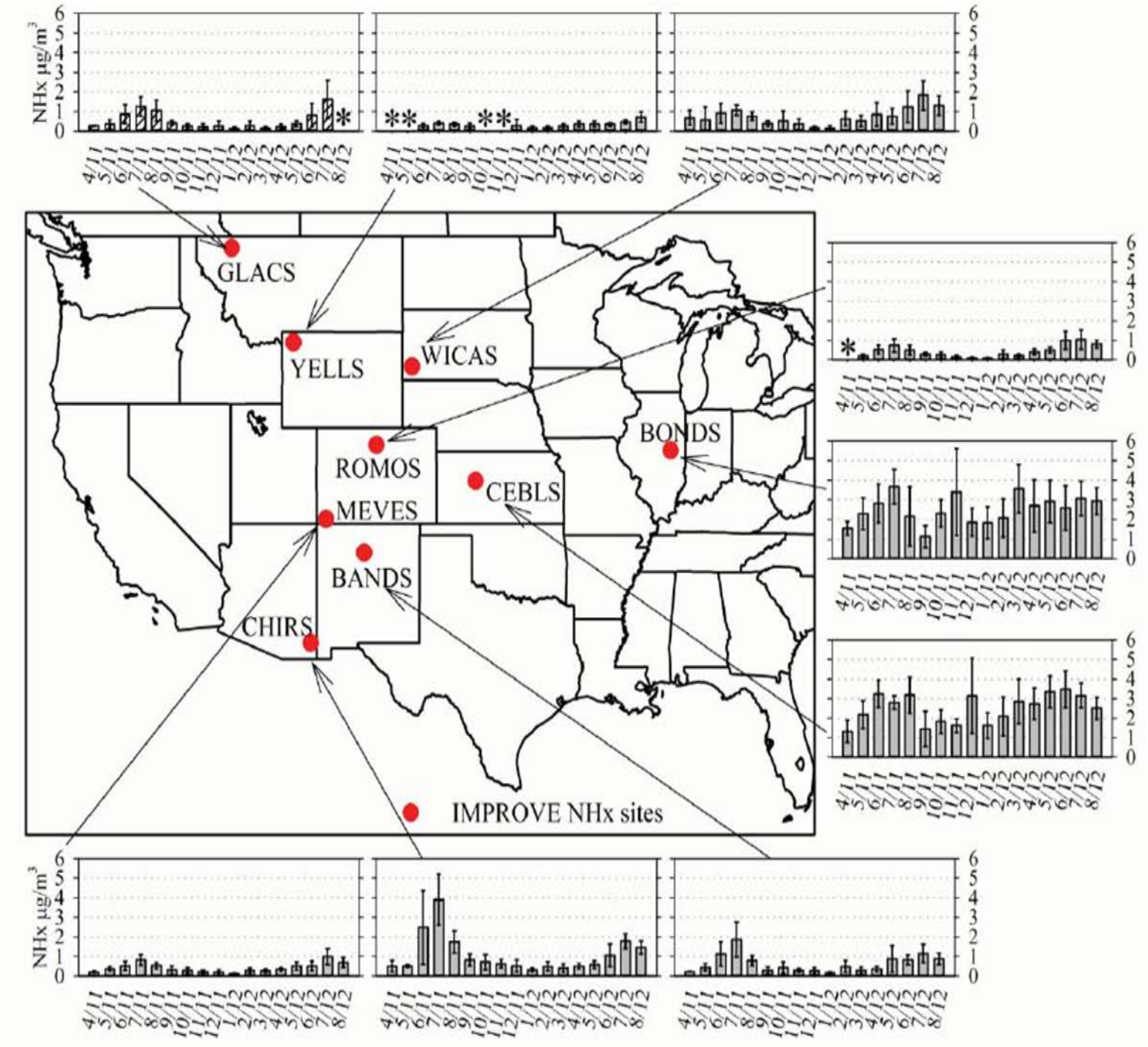
- Comparison with URG reference method at CSU
  - Good agreement between IMPROVE NHx and URG filter + denuder
  - Good agreement between IMPROVE nylon filter NH_4^+ and URG-NH_4^+
    - IMPROVE NH_4^+ low due to NO3-NH_4^+ loss
- Collocated NHx samplers
  - Good measurement precision



Chen et al. (2014)

IMPROVE NHx Pilot Study

- Monthly NH_x average concentrations ($\mu g/m^3$) measured from spring 2011 to summer 2012
- Note, that at mostly western low RH sites



Chen et al. (2014)

Southeastern US Study Design, May-Nov 2017

- Similar set up at Gainesville
- Gainesville is very humid

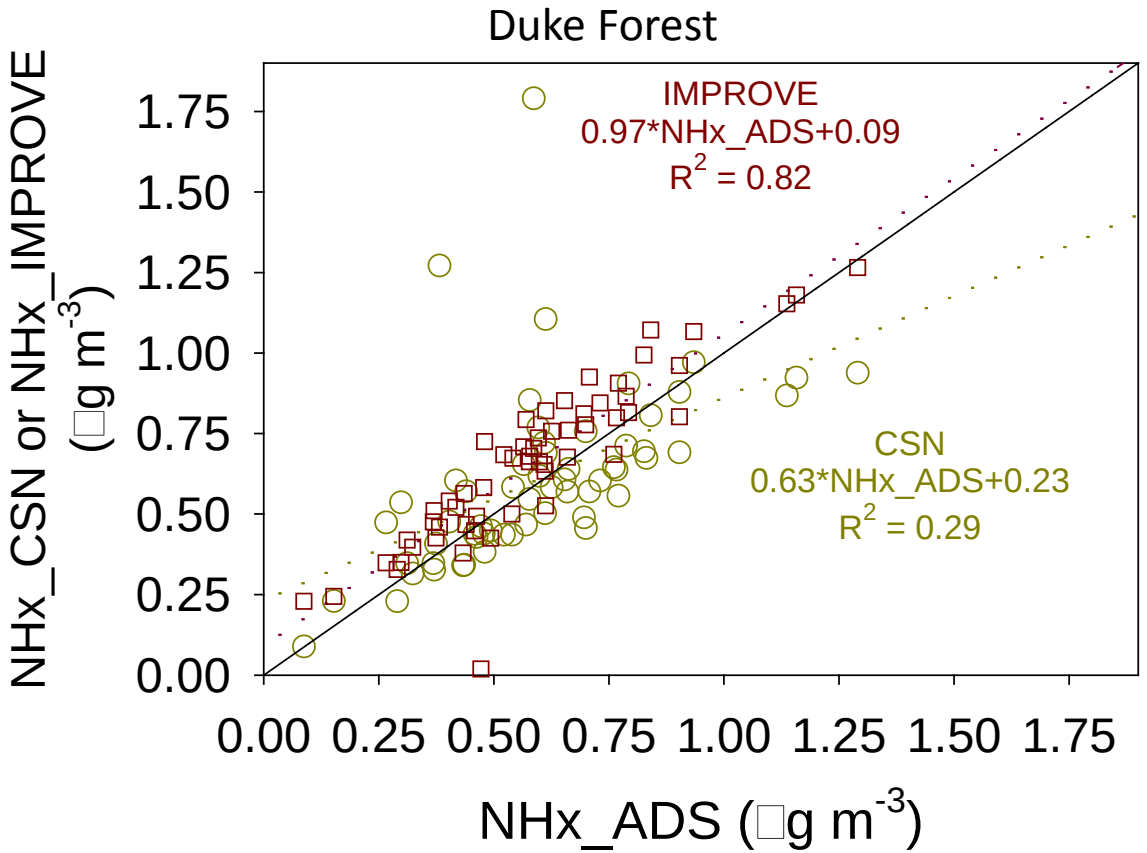
Duke Forest NHx study site

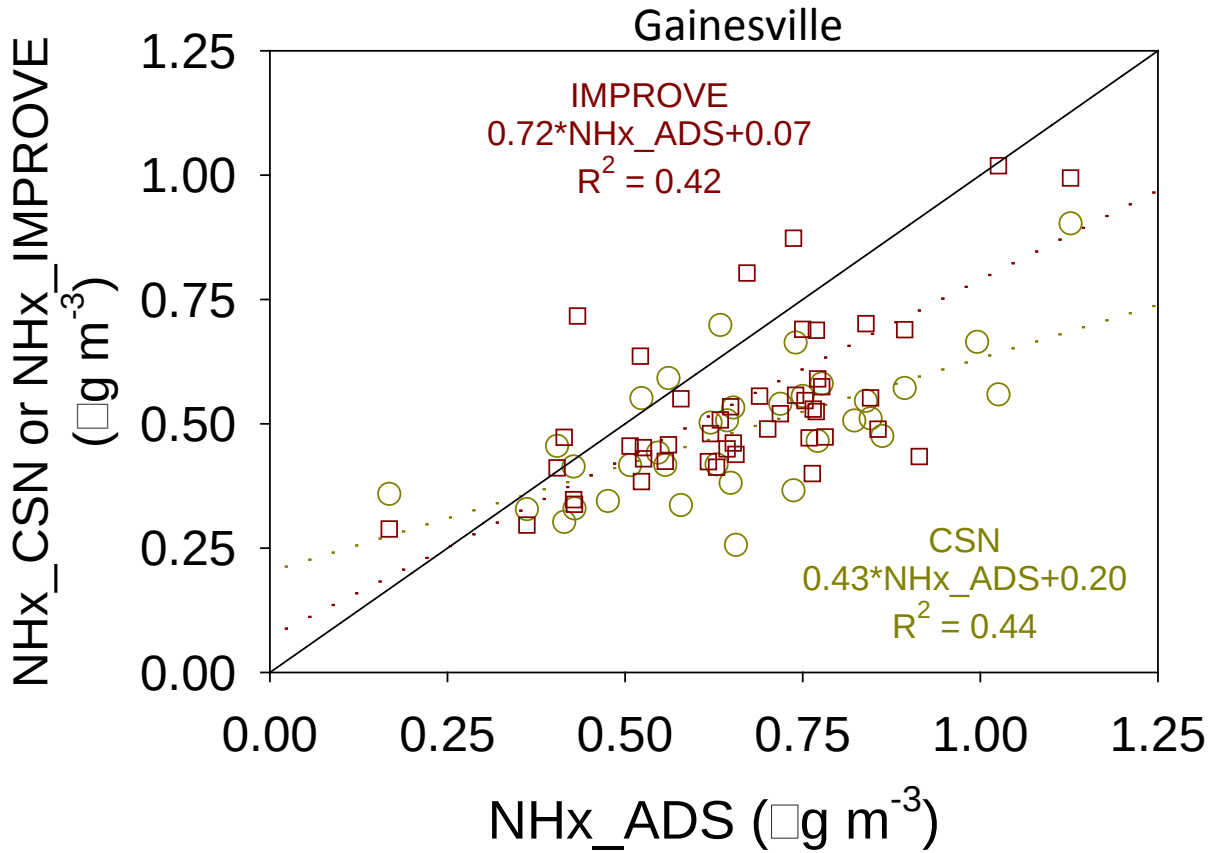
URG denuder/filter pack
- Separates NH_3 and NH_4^+
  - Acid coated denuder (NH_3)
  - Nylon filter (NH_4^+)
  - Backup denuder (volatile NH_3)
- Duplicates
- $PM_{2.5}$ inlet @ 10 Lpm

CSN
- One module collecting NH_4^+ on nylon filter
- 2nd module collecting total NHx on acid impregnated cellulose filter
- $PM_{2.5}$ inlet at 6.7 Lpm

IMPROVE
- Acid impregnated cellulose filter to capture total NHx
- $PM_{2.5}$ inlet @ 22.8 Lpm

Results

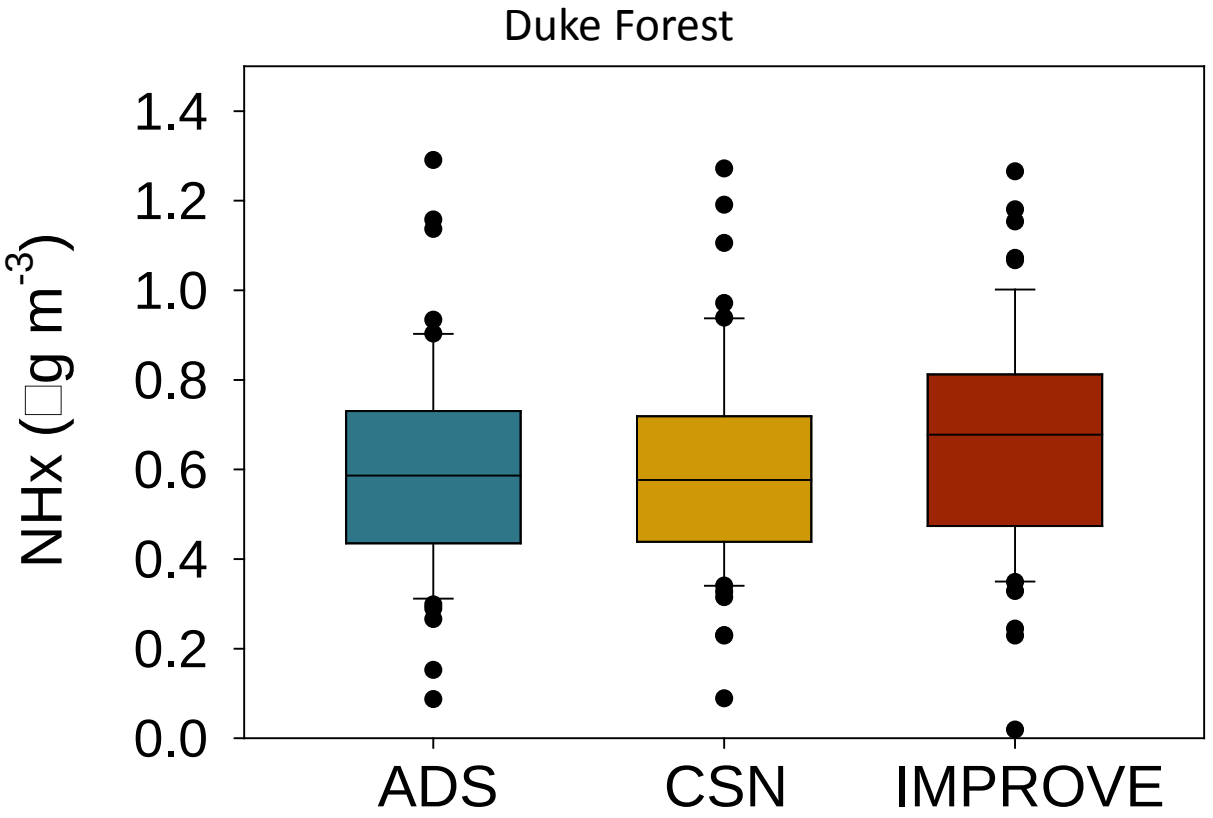


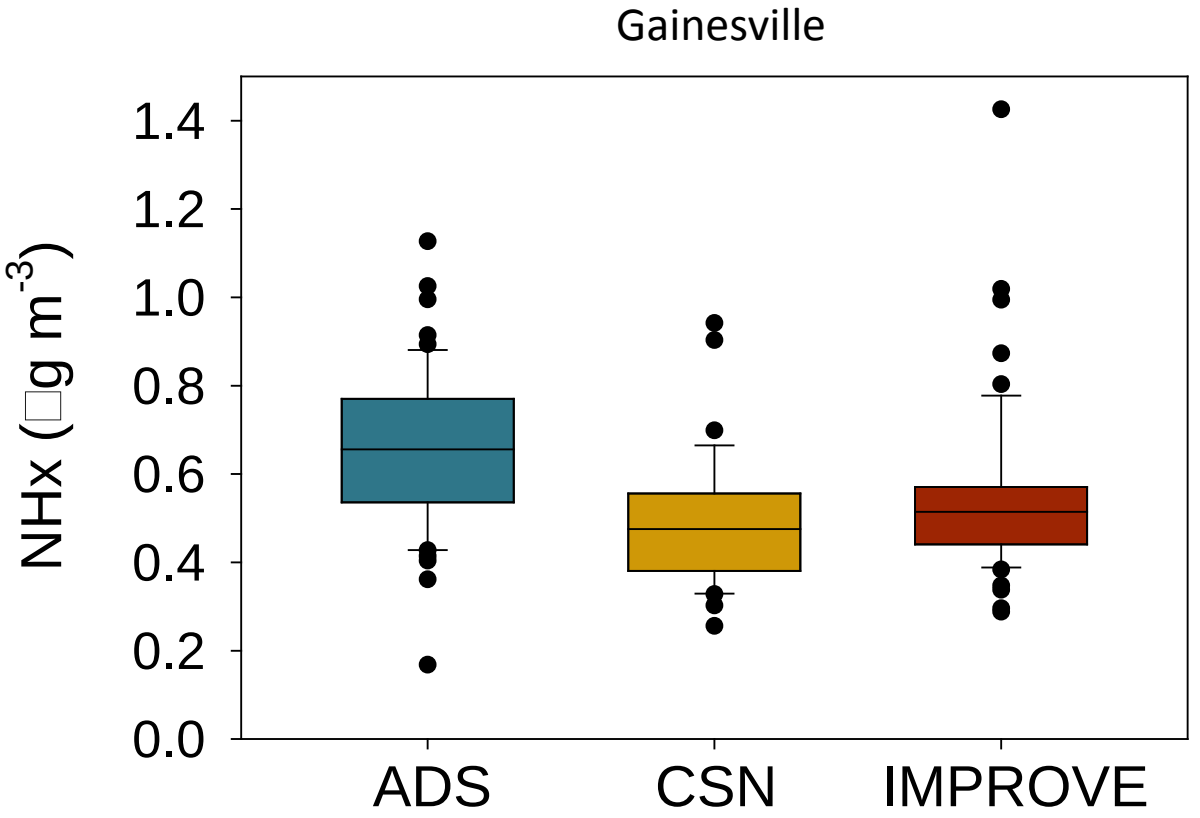


- High correlation between ADS and IMPROVE sampler
  - Similar performance to Chen at al 2014
- Moderate correlation between ADS and CSN
- CSN measures less NHx than ADS at higher concentrations

- Moderate correlation between methods
- Low variability
- Larger bias at higher concentrations for CSN

Results

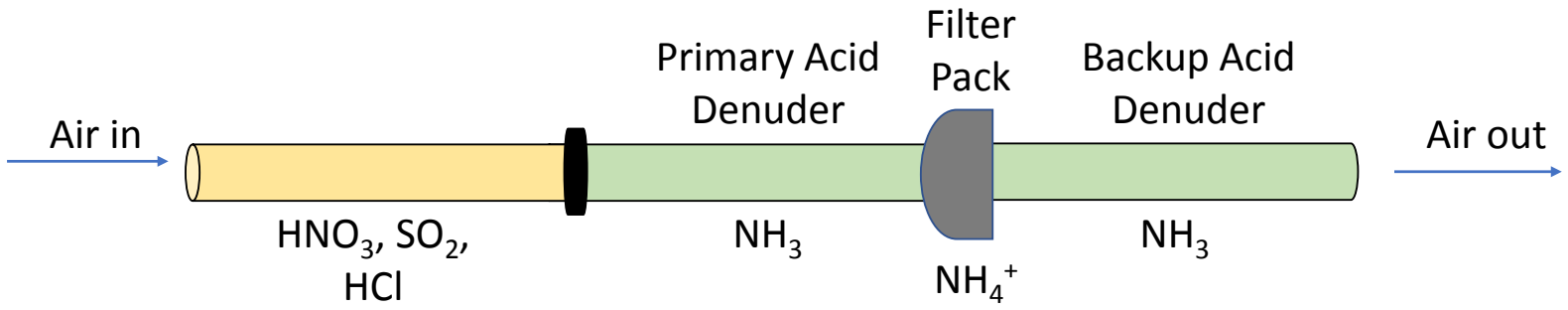




- Median concentrations are similar across methods
- CSN and IMPROVE measure less NHx than ADS

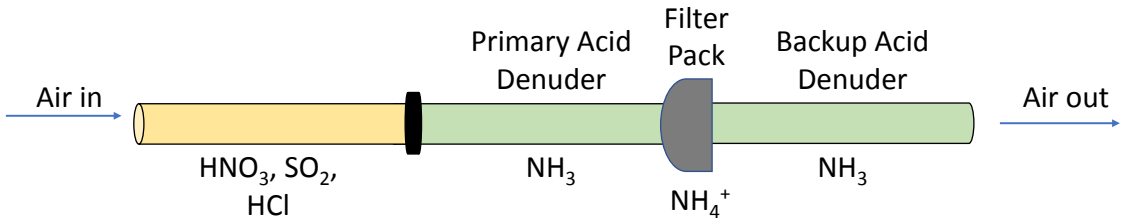
What is causing disagreement between methods?

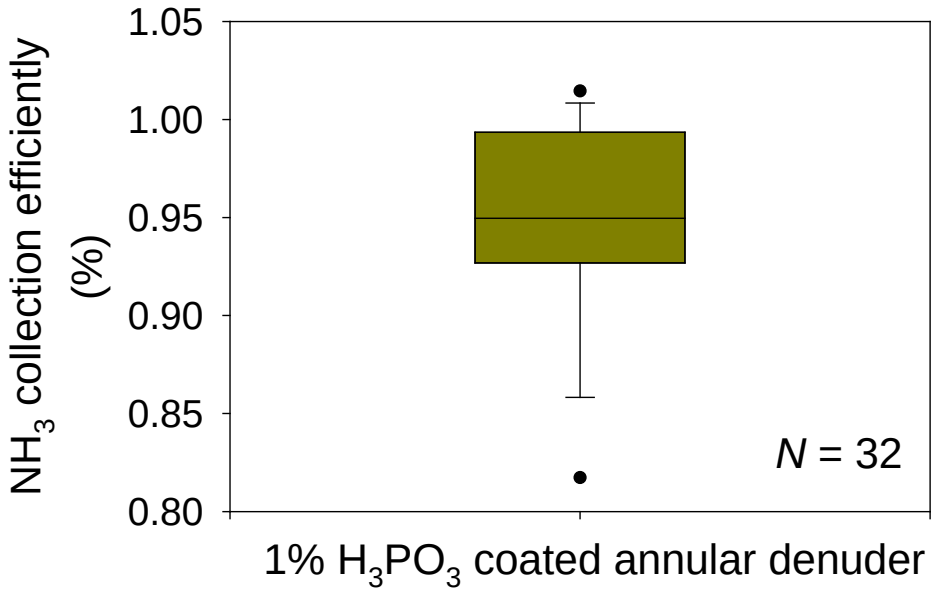
ADS performance?

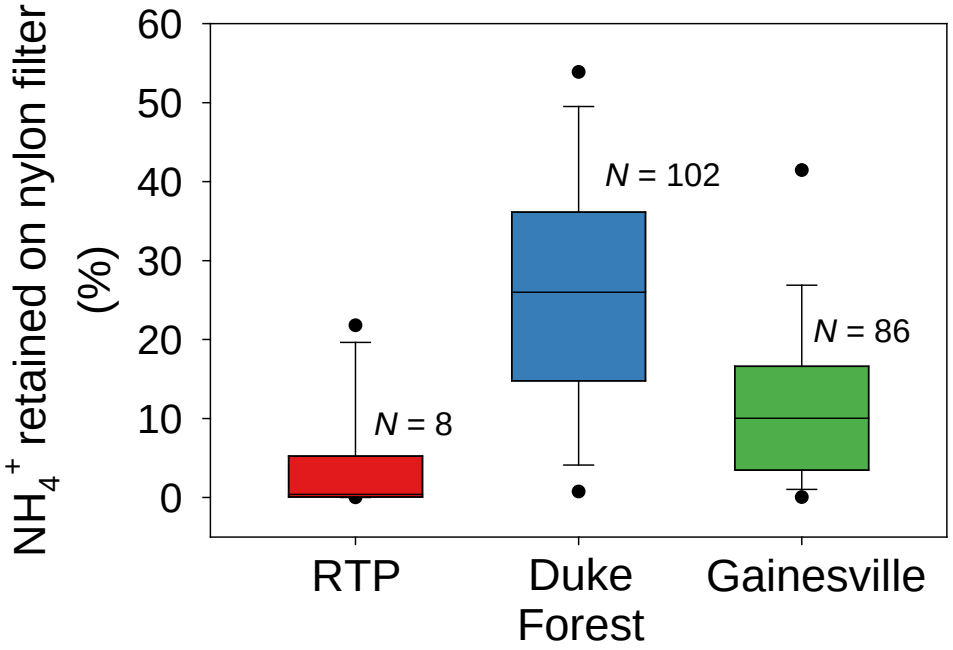


- ADS results showed a large fraction of NH_4^+ on the backup acid denuder (downstream of nylon filter).
- This could be caused by
  - NH_3 breakthrough on the primary acid denuder
  - NH_4^+ volatilization from the nylon filter
- Three 24 hour samples were collected at the end of the NHx study with additional denuders to test breakthrough on both the primary and backup acid denuder.
- These tests indicated breakthrough on the primary denuder.
- This motivated a follow up study in RTP to test the collection efficiency of the acid denuder.

ADS Performance





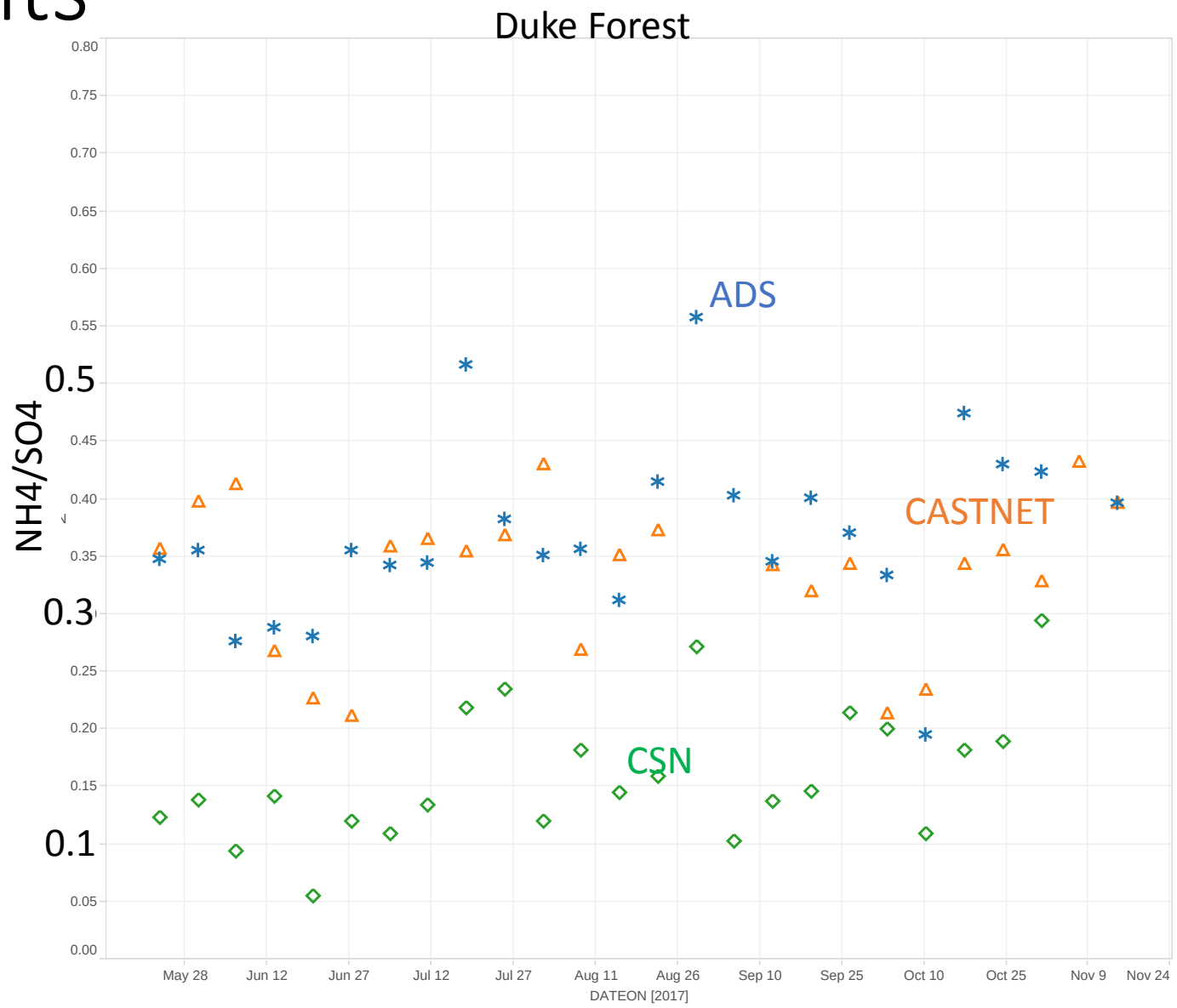


- RTP study showed good NH_3 collection efficiency.
- NH_4^+ being lost from nylon filter but captured as NH_3 in backup denuder
- Issue with nylon filter retaining NH4+ but total NHx captured with backup acid denuder.
- Anion analysis suggests filter issue related to chemistry not particle collection efficiency.

Supplemental Results

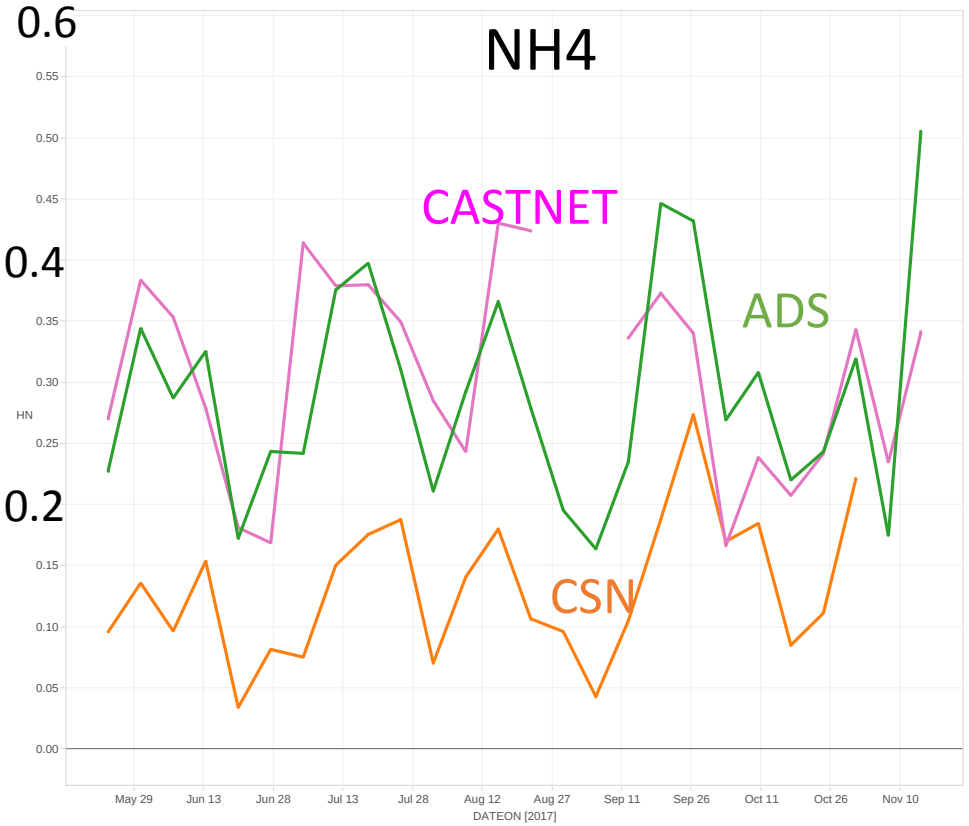
- Anion analysis
  - Wood analyzed extracts for NO3, SO4 from CSN and ADS nylon filters
  - NH4/SO4 ratio

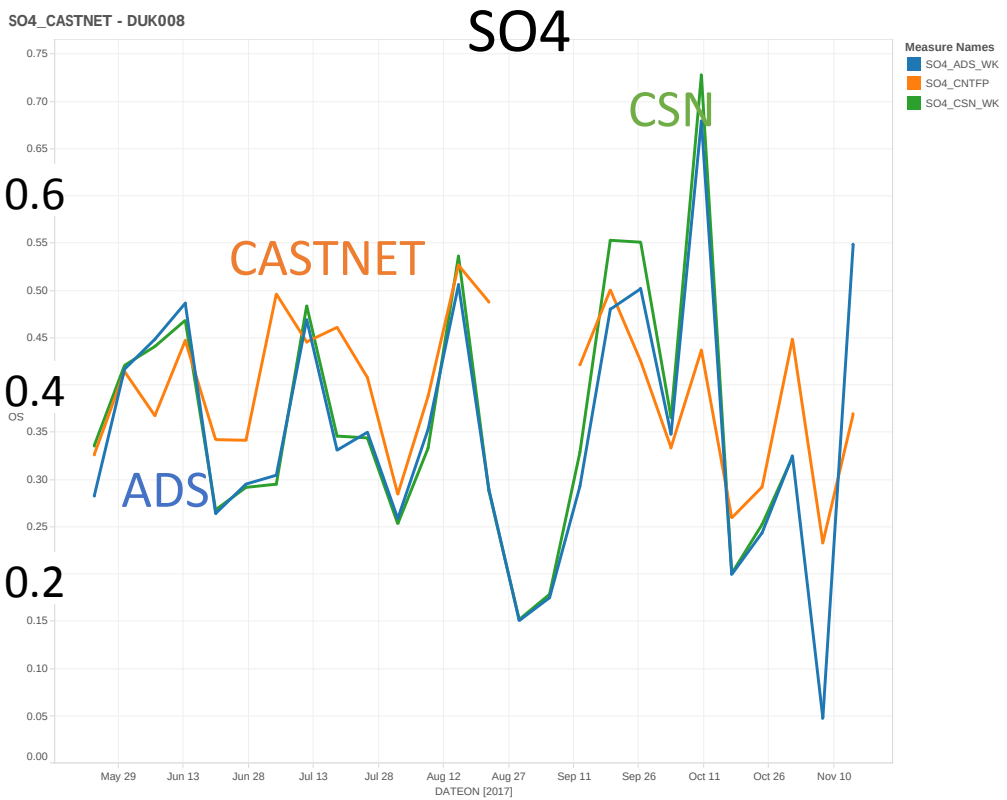
	Duke Forest	Gainesville
CASTNET	0.33	
ADS	0.41	0.40
CSN	0.16	0.12



Comparison with CASTNET – Duke Forest

- Evidence of Loss of NH4 associated with sulfate from nylon filters



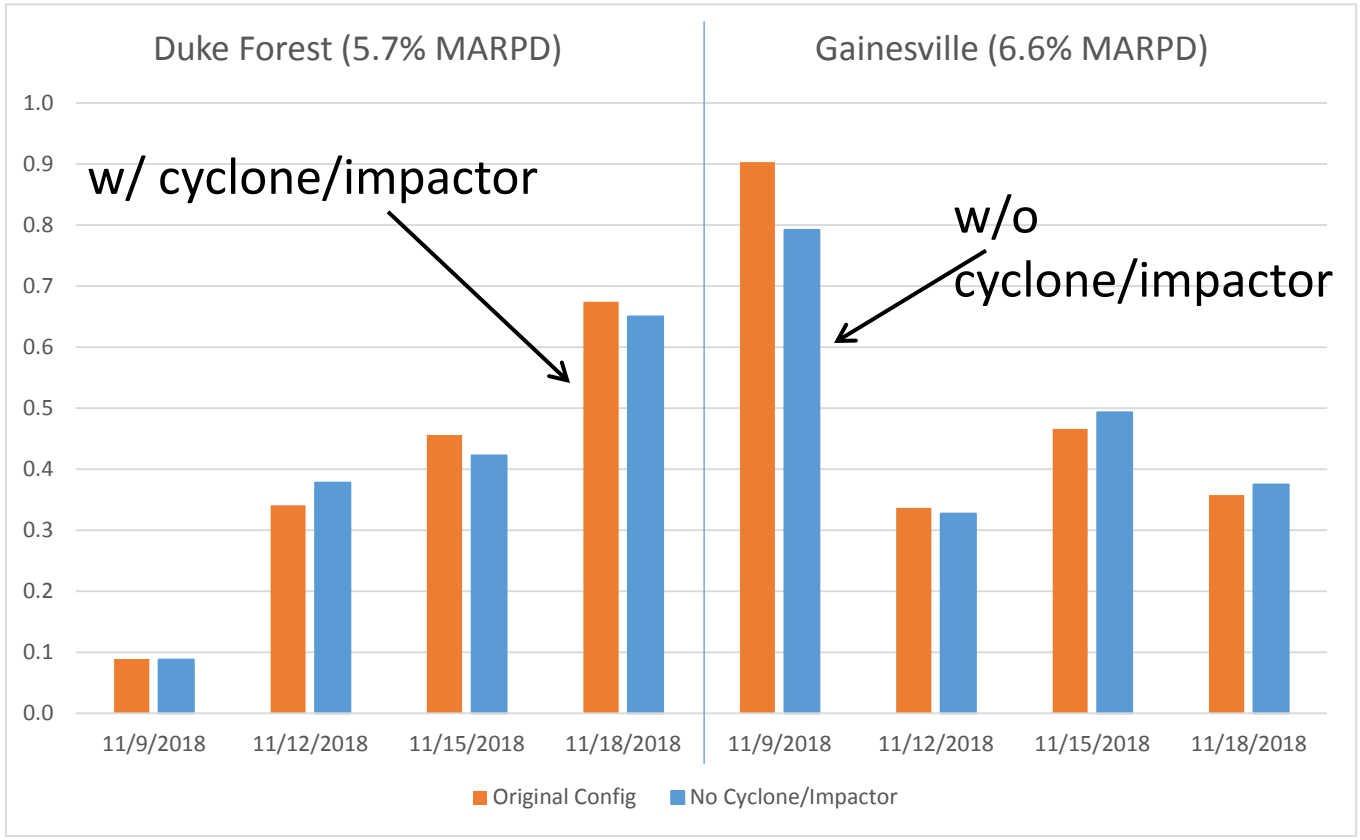


- CASTNET uses Teflon for NH4, SO4
- CSN using nylon filter for NH4, SO4
- ADS Nylon NH4 + backup denuder NH4

- Good agreement between methods for SO4
- Nitrate concentrations were very low
- Nylon and Teflon filters retain SO4, but nylon lost NH4

CSN performance?

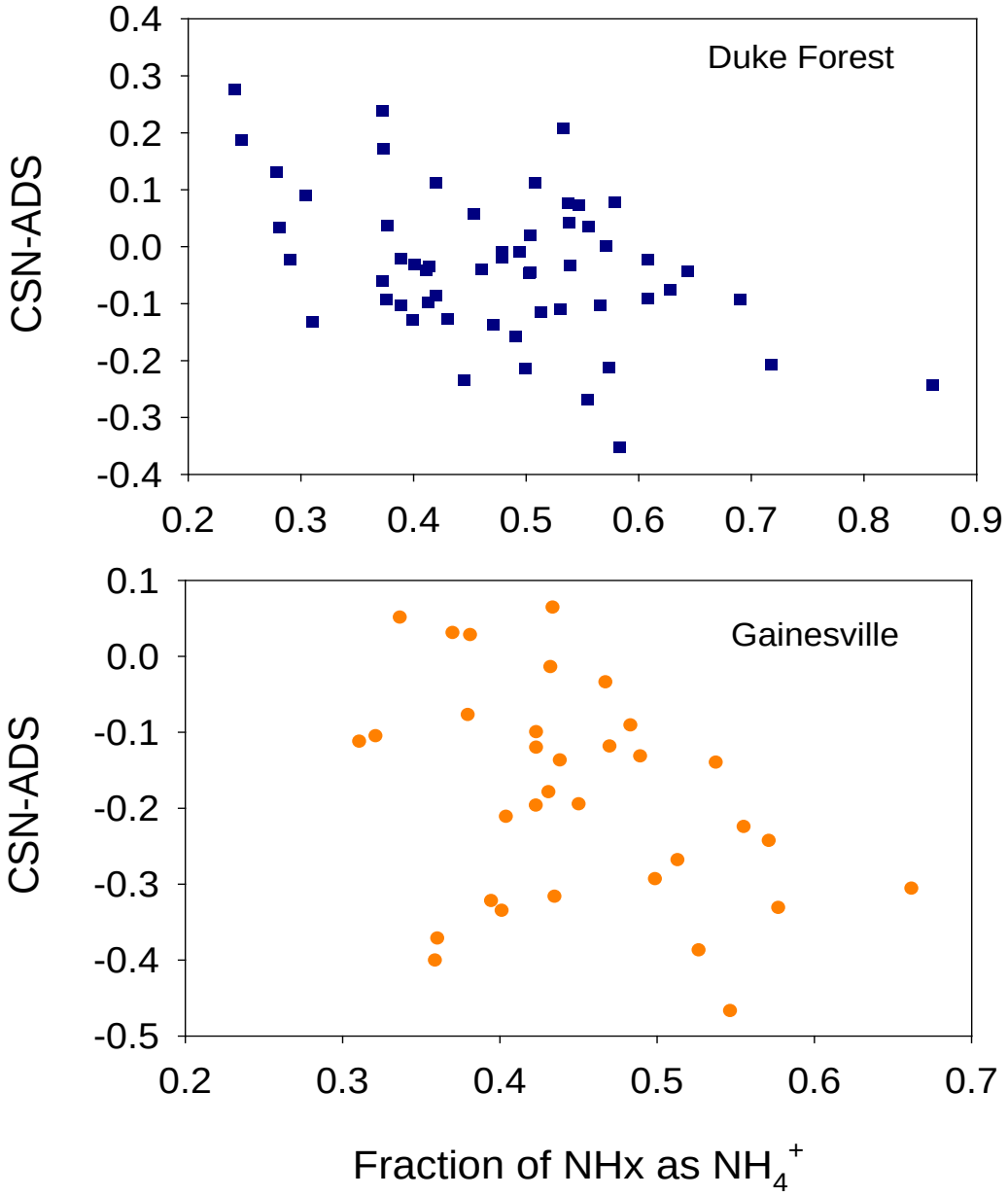
- Why does CSN measure less NH_x than ADS and IMPROVE?
- Is the CSN inlet scrubbing NH_3? - No



- Ran the CSN sampler with and without the cyclone/impactor
  - No change in NH4 concentrations

CSN performance?

- NHx bias increases with concentration at both sites
- Negative bias may become larger as NHx becomes dominated by aerosol NH_4^+ fraction
- Bias may be more related to NH4+ than NH3?
- IMPROVE
  - Type 40 cellulose filter
  - 98% retention of 8 um particles
- CSN
  - Type 41 cellulose filter
  - 98% retention of 20 um particles
- CSN cellulose filter collecting fewer NH4+ particles?

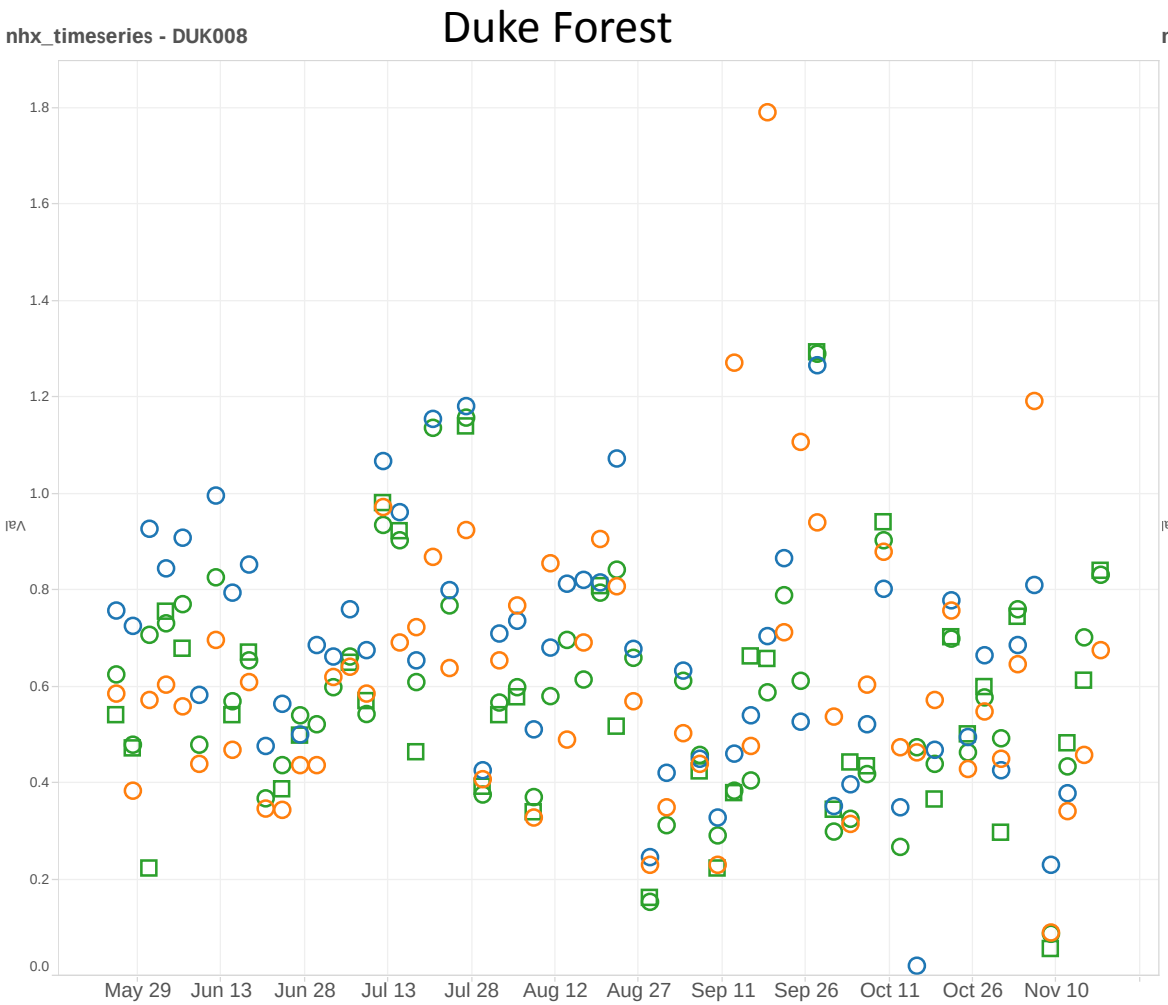


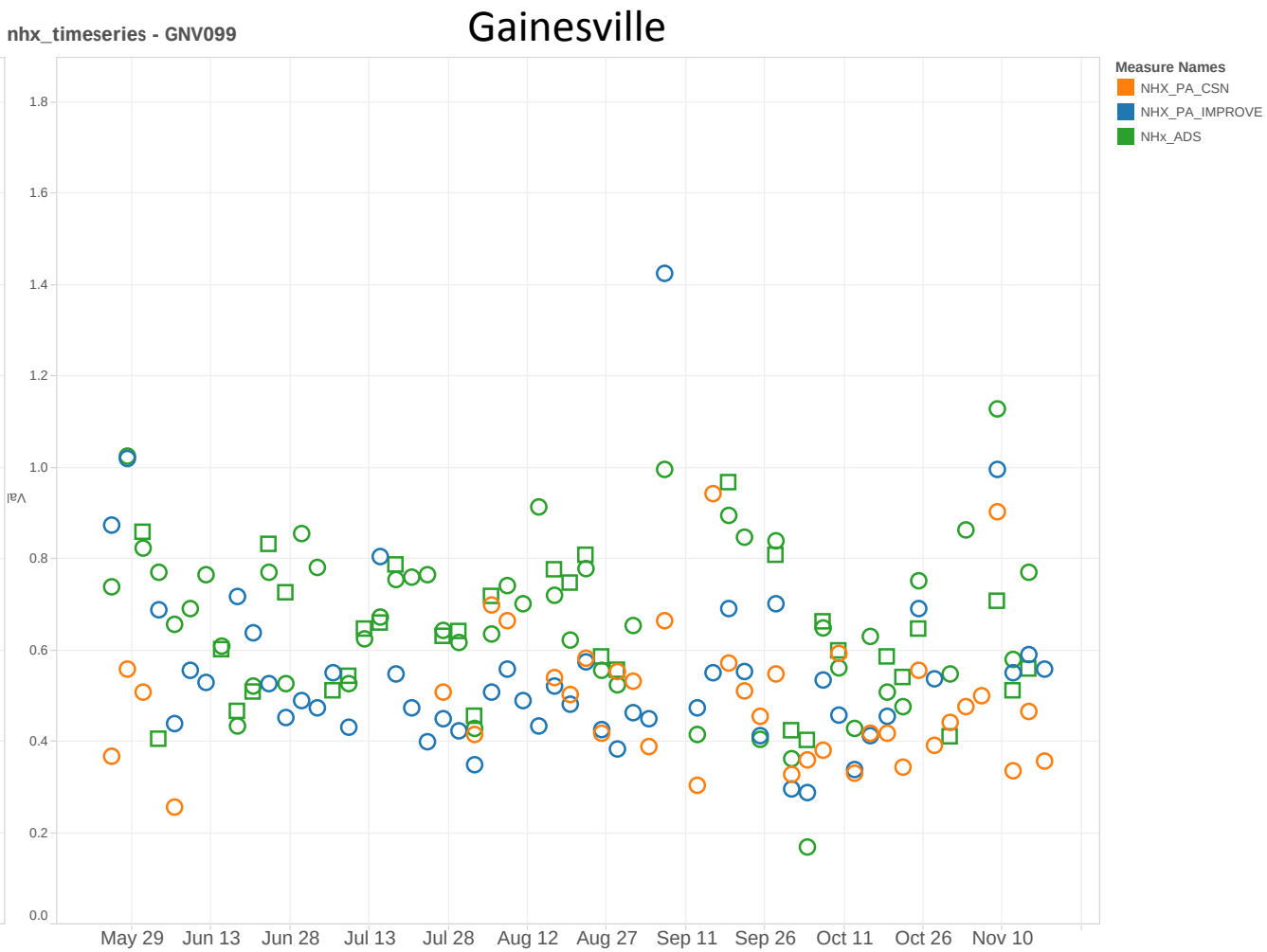
Recommendations and Next steps

- Is NHx sampling suitable for deployment in IMPROVE and or CSN networks?
  - Not in humid areas
  - Need to resolve CSN low bias
  - Need to develop filter handling protocols and procedures suitable for deployment in routine networks
- Interpret Gainesville/Duke Forest data in the context of meteorology (RH, dew, temperature)
- Run a comparison of the cellulose filters at Duke Forest or RTP to test particle collection efficiency
- Measure NHx at co-located CSN/IMPROVE sites to further test the method and develop protocols
- Would be interesting to understand how sulfate bound NH4 is lost from nylon filters

Results

- Very low concentrations of NHx at both sites





Next steps

- Further analysis ADS and CSN nylon filter extracts for anion concentrations (anion balance for NH_4^+)
- Analysis of NHx method differences versus meteorological variables
- Final summary report (Nov, 2018)
- Revisit other CASTNET studies to evaluate ADS versus CASTNET NH_4^+ aerosol
- Comparisons of other NHx methods at Duke Forest
  - CASTNET/AMoN total NHx
  - MARGA (online IC)
  - Nitrotrain (chemiluminescence)