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 HNO$_3$, a cyclone to limit sample collection to PM2.5 aerosol, and a filter-pack.

- IMPROVE samplers collects 24-h samples
- Filters analyzed for NH$_4^+$ 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 NO$_3$-NH$_4^+$ loss

• Collocated NHx samplers
  • Good measurement precision

Chen et al. (2014)
IMPROVE NHx Pilot Study

• Monthly NH$_x$ average concentrations (μg/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

**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
- 2$^{nd}$ 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.
• 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 NH$_4^+$ but total NH$_x$ 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

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Comparison with CASTNET – Duke Forest

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

CASTNET
CSN
ADS

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 NH$_4$ 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 NH$_4^+$ than NH$_3$?
- **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 NH$_4^+$ 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 $\text{NH}_4^+$)
• Analysis of NHx method differences versus meteorological variables
• Final summary report (Nov, 2018)
• Revisit other CASTNET studies to evaluate ADS versus CASTNET $\text{NH}_4^+$ aerosol
• Comparisons of other NHx methods at Duke Forest
  • CASTNET/AMoN total NHx
  • MARGA (online IC)
  • Nitrotrain (chemiluminescence)