Insights into submicron composition during WINTER as measured by the AMS

WINTER Science Meeting

17-Sept to 18-Sept-2015

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University of Colorado Boulder

Road map

1. Data Overview
2. Instrument Comparisons
3. Campaign Averages
4. Organic Aerosol (OA)
5. Aging of OA – Case study
6. Oxidation flow reactor (OFR)
7. Biomass burning OA (BBOA)

Overview of Data:

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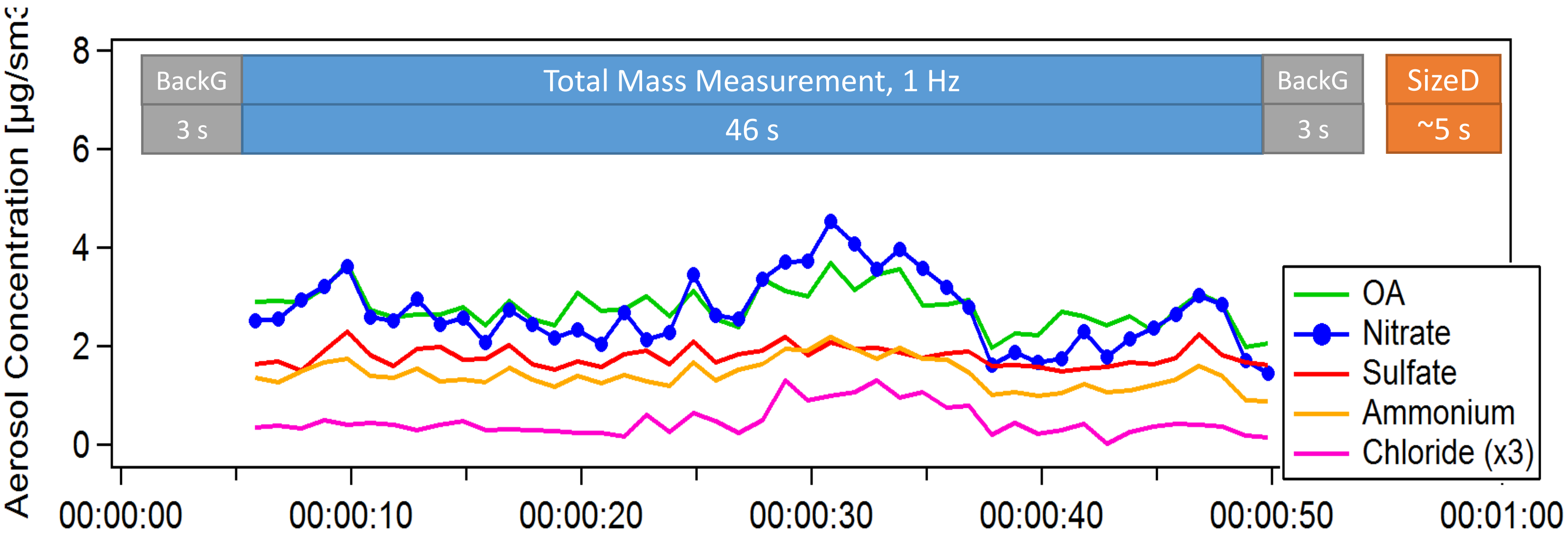
Close to final data:

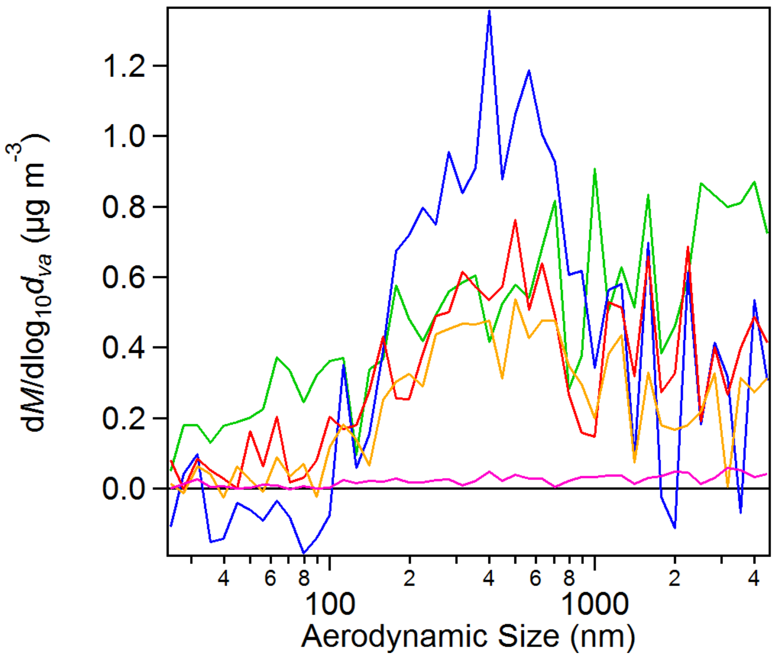
- Implement final calibrations
- Implement improved background interpolation method
- Finish working out kinks for size distributions

Issues:

- Down for RF05
- Not yet reporting organic nitrate when sampling marine environment due to potential interference of $NaNO_3$
- Still investigating spikes for RF01, could be HOA, could be radio towers

Some notes on size distributions

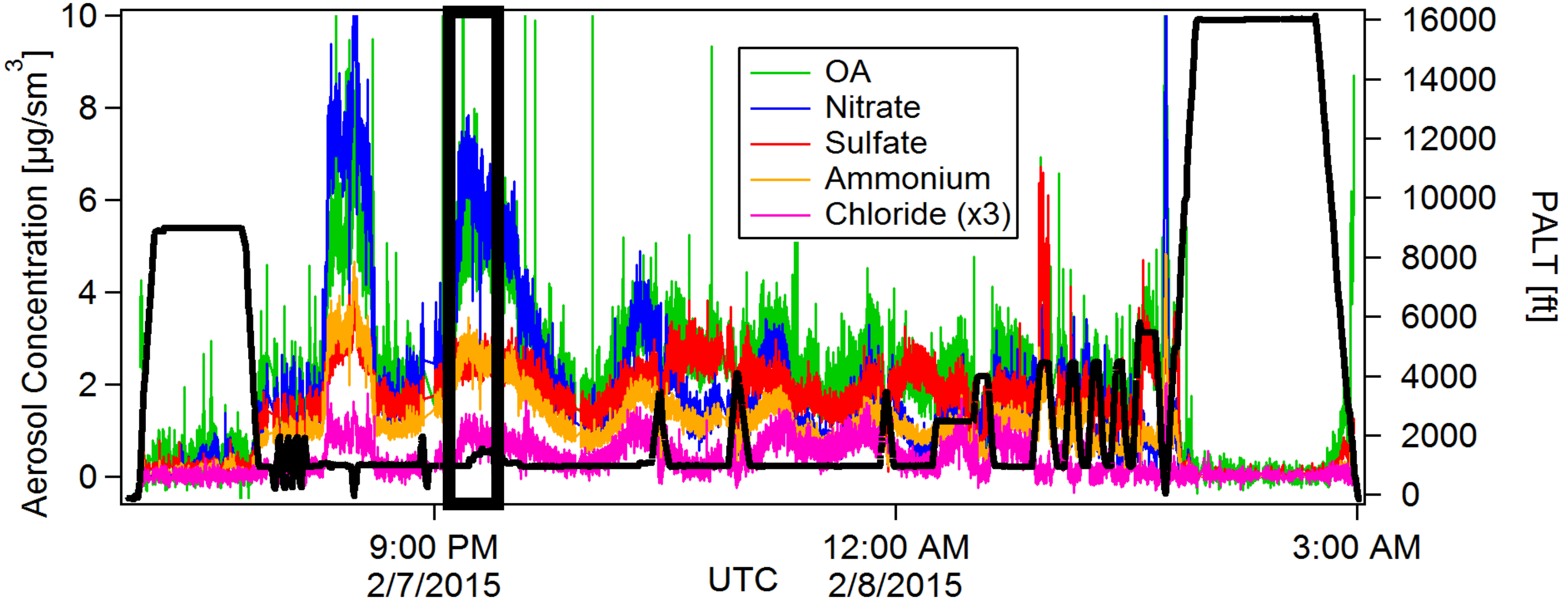


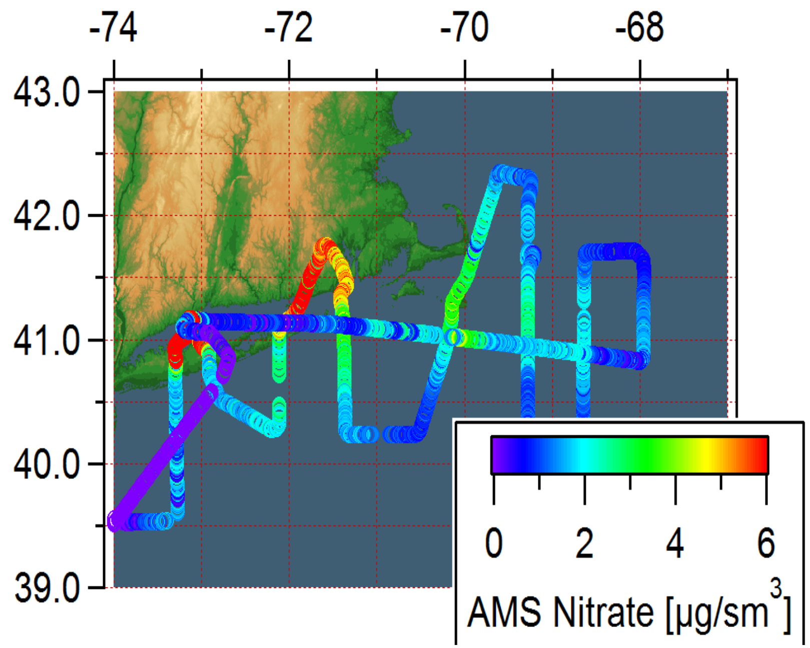


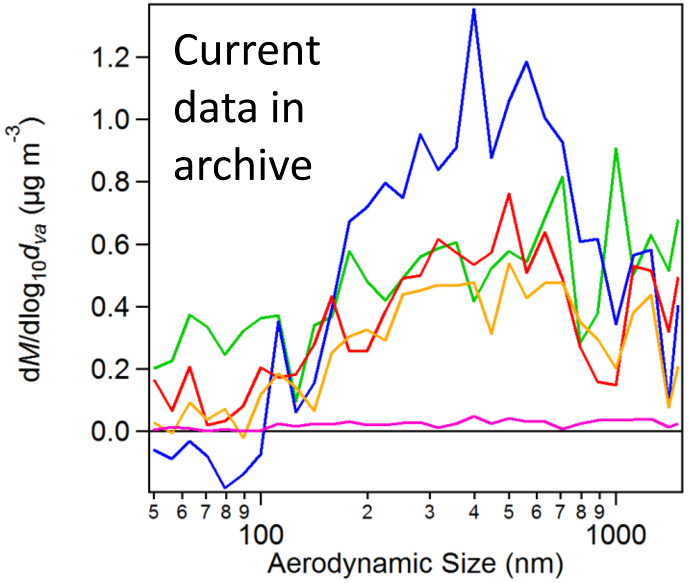
- Currently there are speciated size distributions files in the archive under the DataID “AMSSD”
- All these are using a new, experimental mode to acquire size distributions with 50% dutycycle (instead of 2%)
- Data needs to be normalized to account for slow vaporization
- Currently reported distributions are noisier than they can be

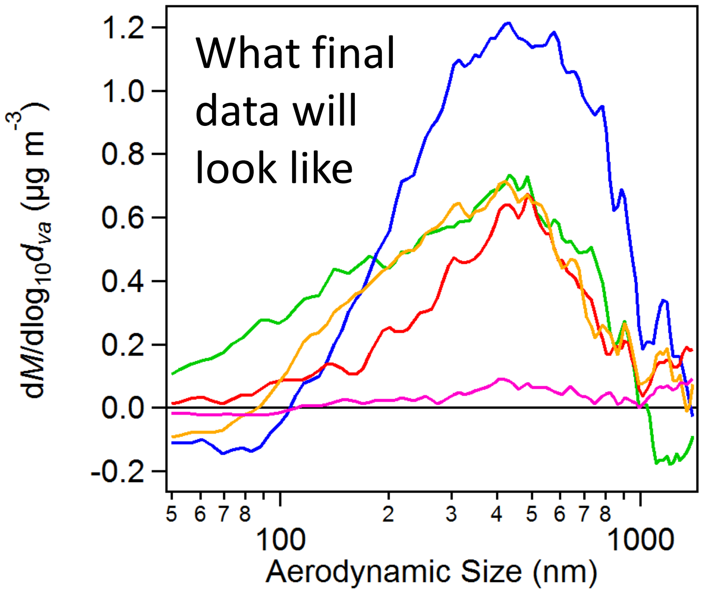
- New size calibration, new normalization method implemented in the last few months, indicating no major problems.
- Still need to work on the inversion algorithm, but current results are encouraging

An example from RF03:









- More validation work needed on the new inversion algorithm, especially performance at low concentrations
- AMS software needs a sizeable overhaul for this to work.
- Non-linear inversion poses some data reporting challenges
- Need to decide what time resolution(s) are useful for this group

Instrument Comparisons: AMS Volume VS PCASP Volume

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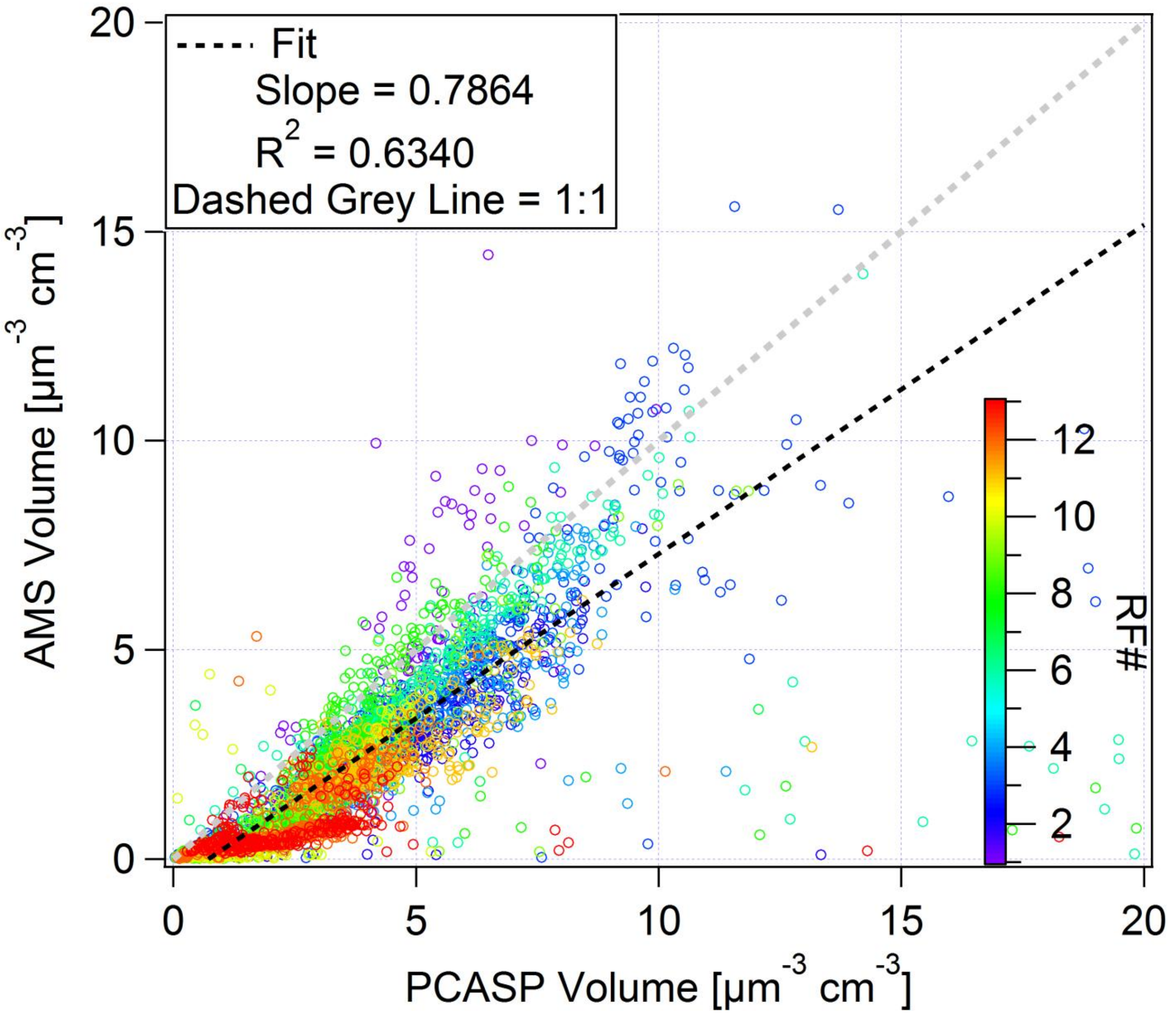

Don't expect perfect agreement

- **PCASP is wet, AMS is dry**
- **PCASP includes supermicron**
- **PCASP > 300 nm, AMS > 60 nm**

Once I get a hold of the final UHSAS data I can make a more fair comparison

Instrument Comparisons: AMS & SAGA & PILS

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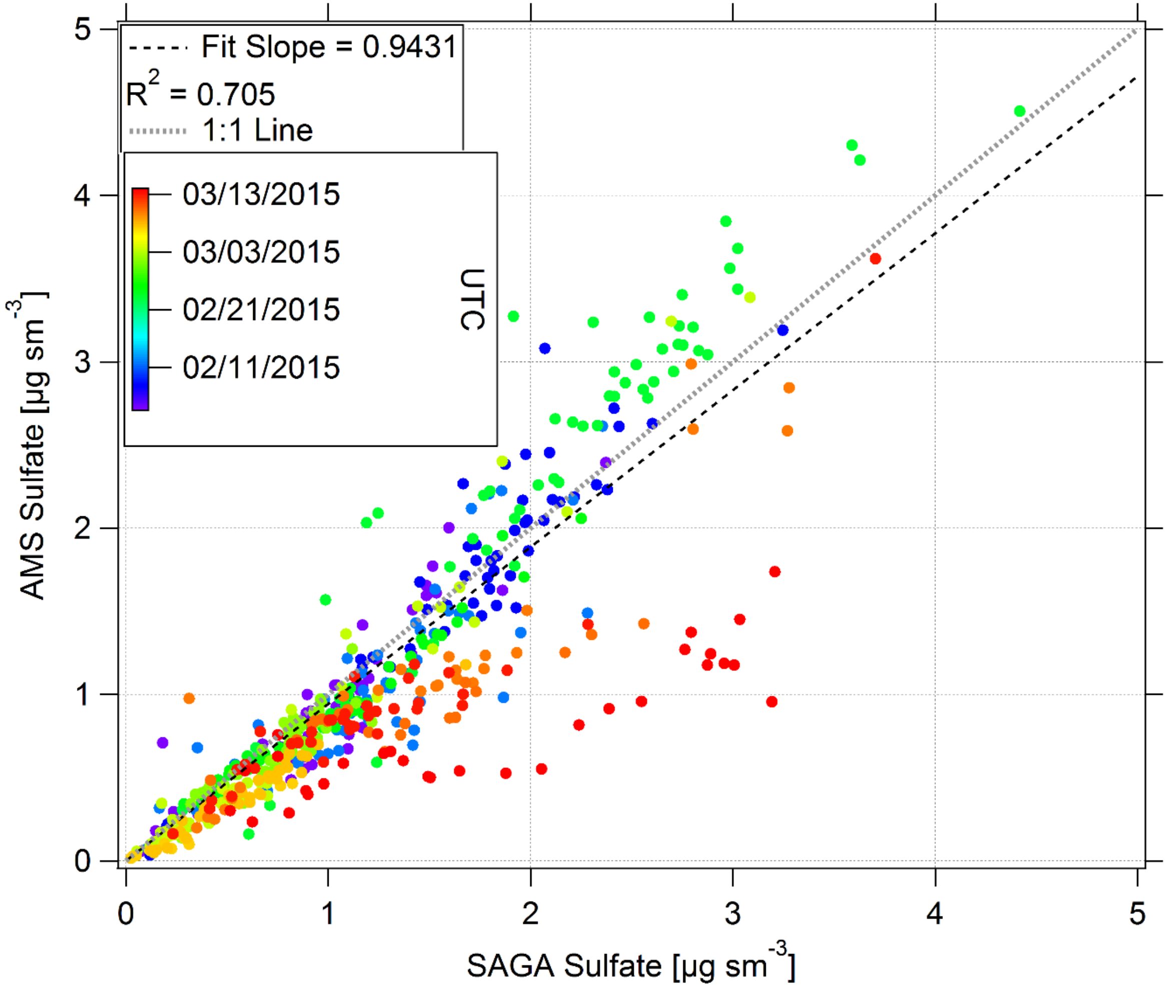

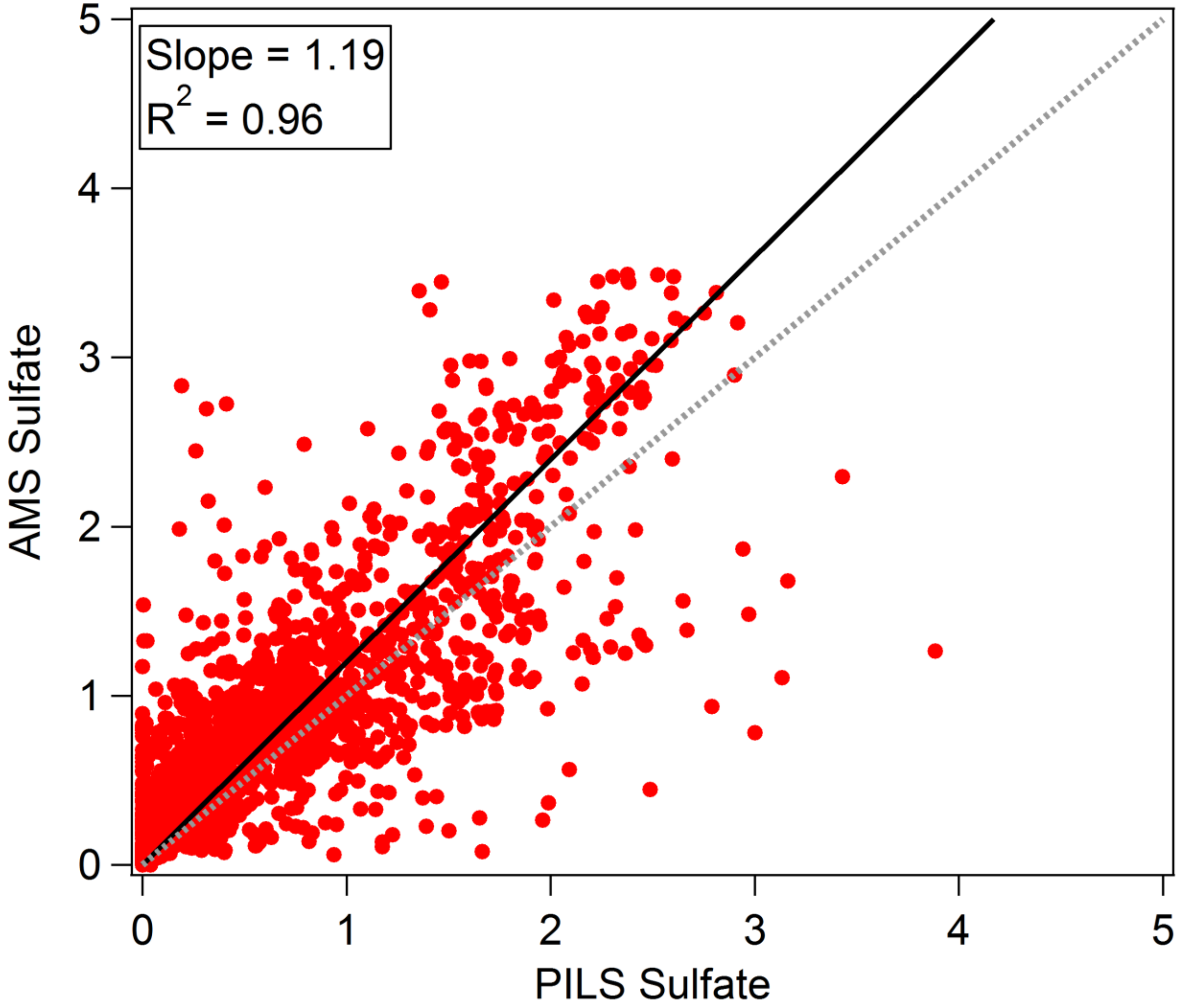

Instrument Comparisons: AMS & SAGA & PILS

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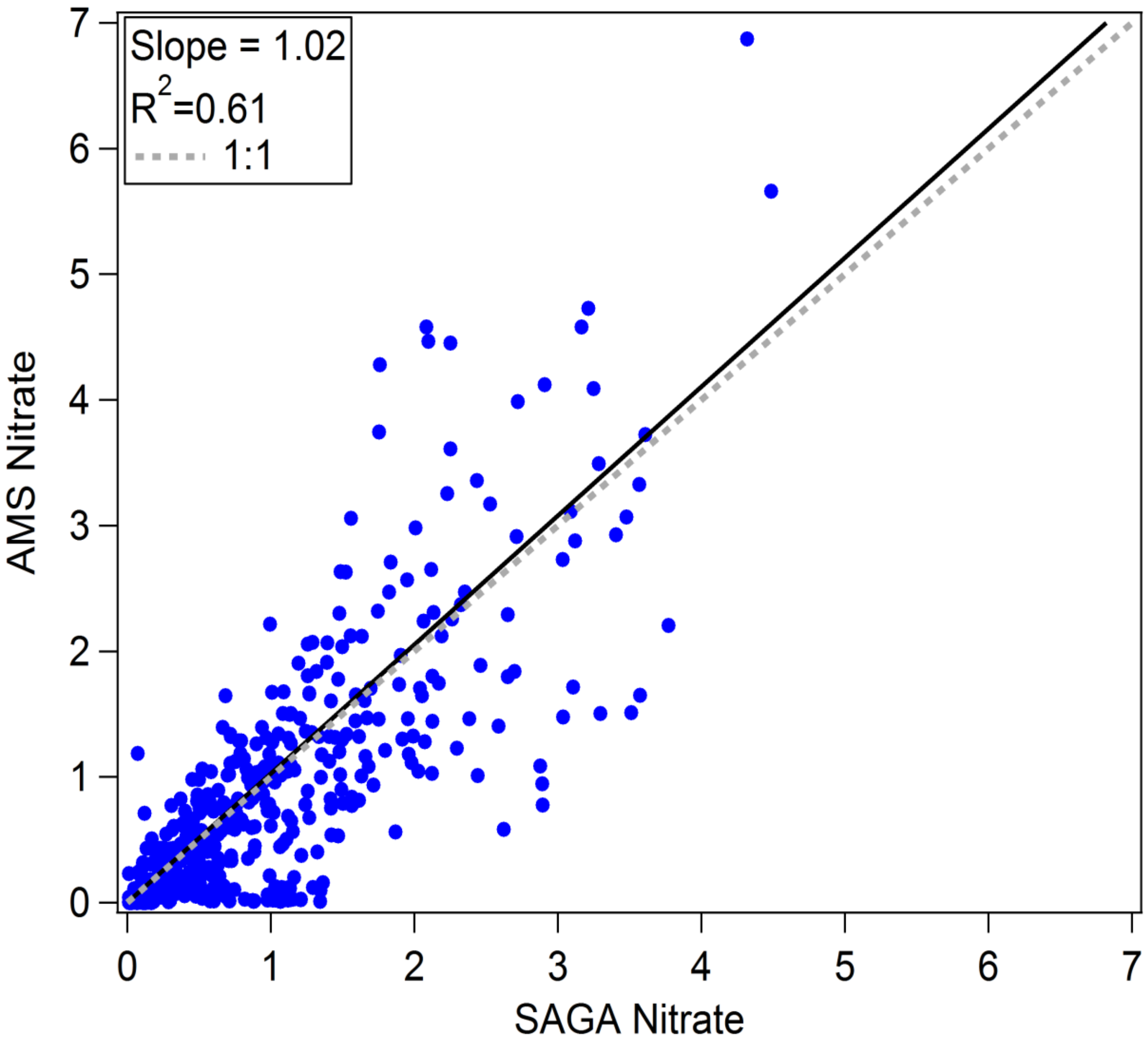
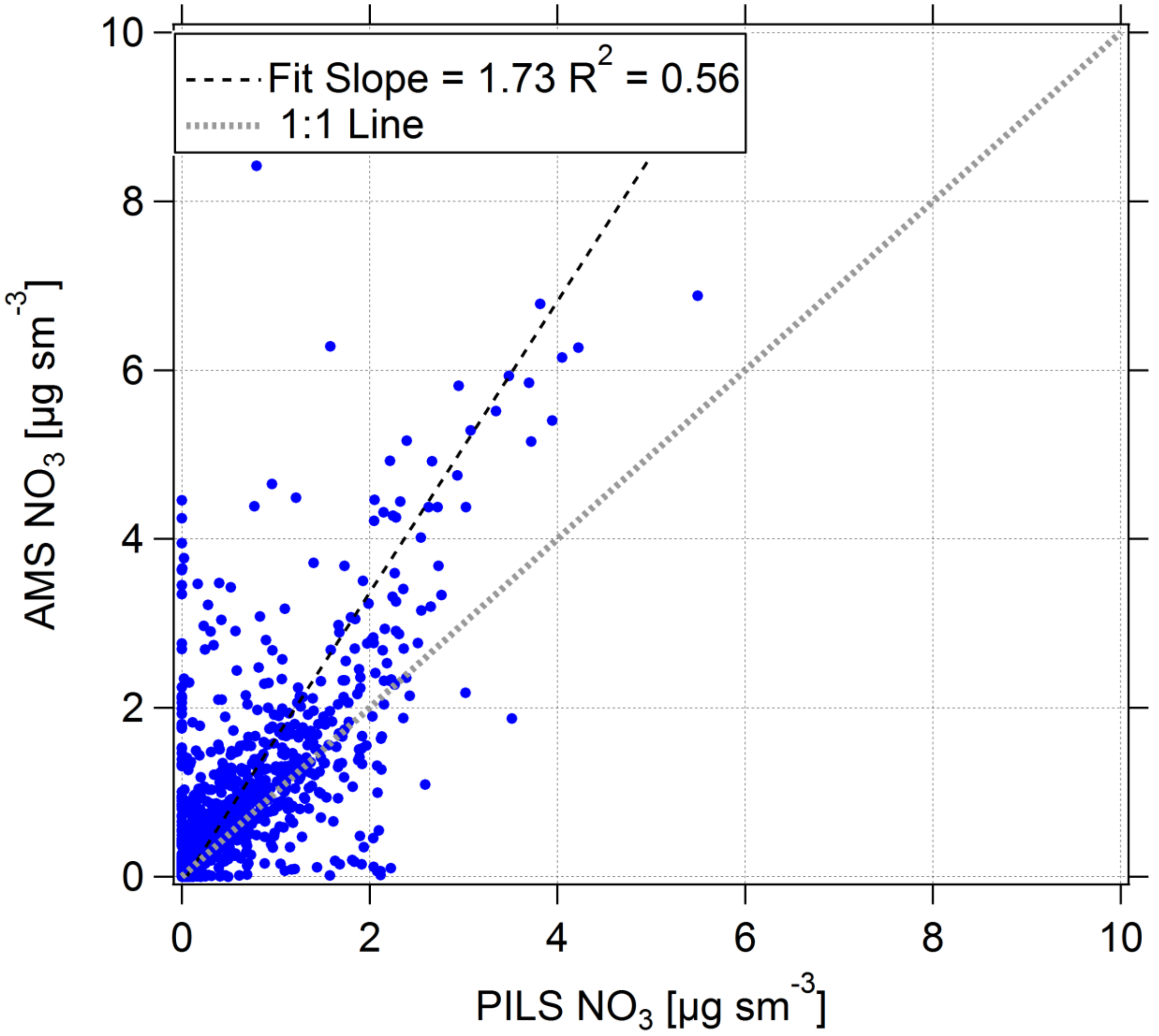
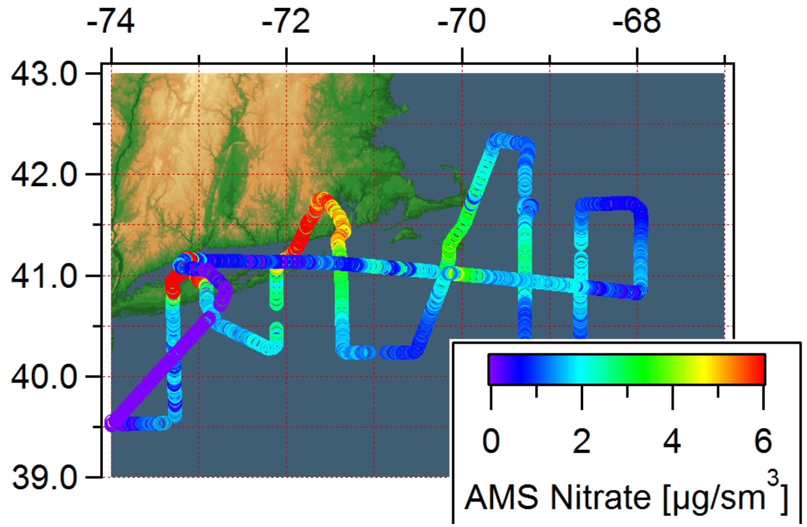


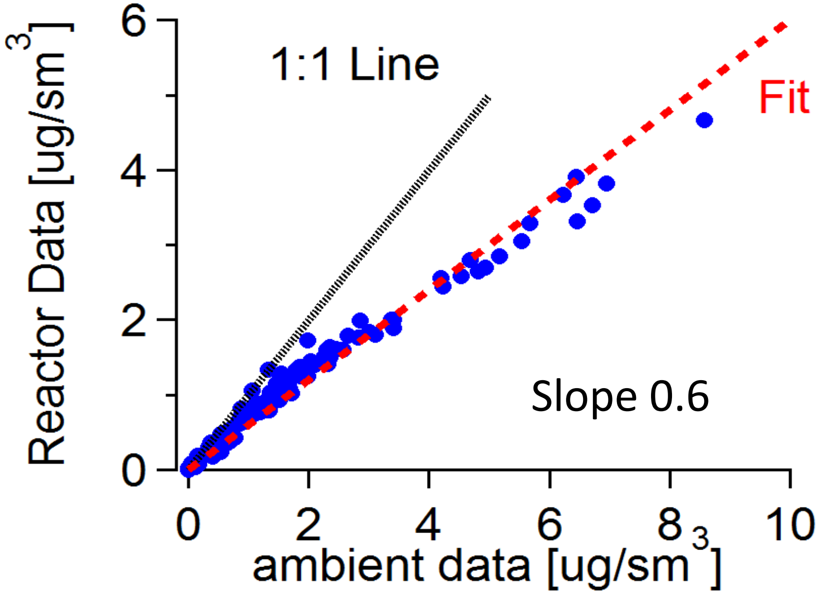


Some observations of nitrate volatility

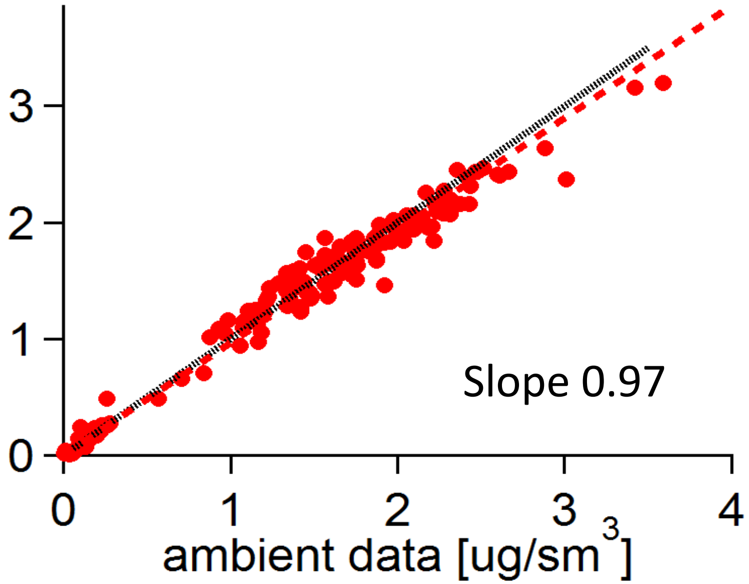


- Residence time in the AMS inlet is 0.4 s in the BL (inlet tip to vacuum chamber), ~~> 1 min~~ 1.6 s for the PILS (SAGA filters sample typically 3-5 min)
- Residence time in the Oxidation Reactor (OFR) is 66 s on average
- No oxidation going on (reactor lights *off*)
- This allows us to look at NH_4NO_3 volatilization in real time
- Results are consistent with substantial volatilization over 1 min timescales

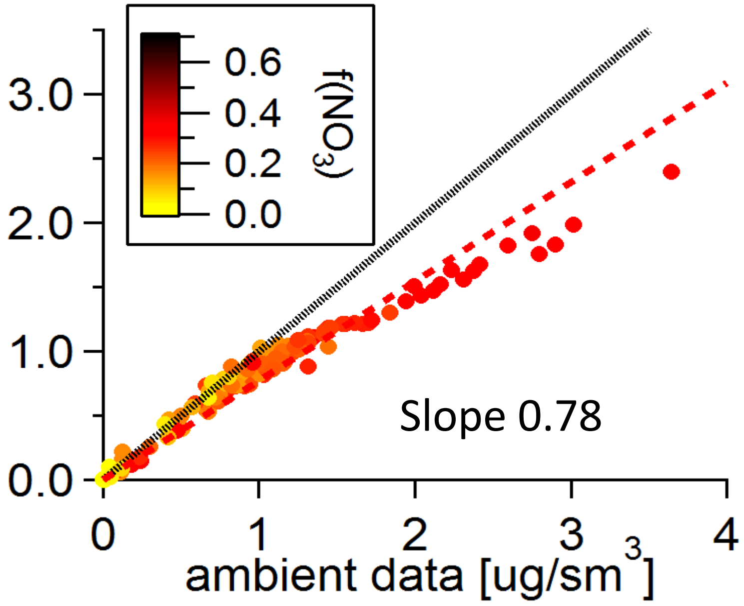
Nitrate



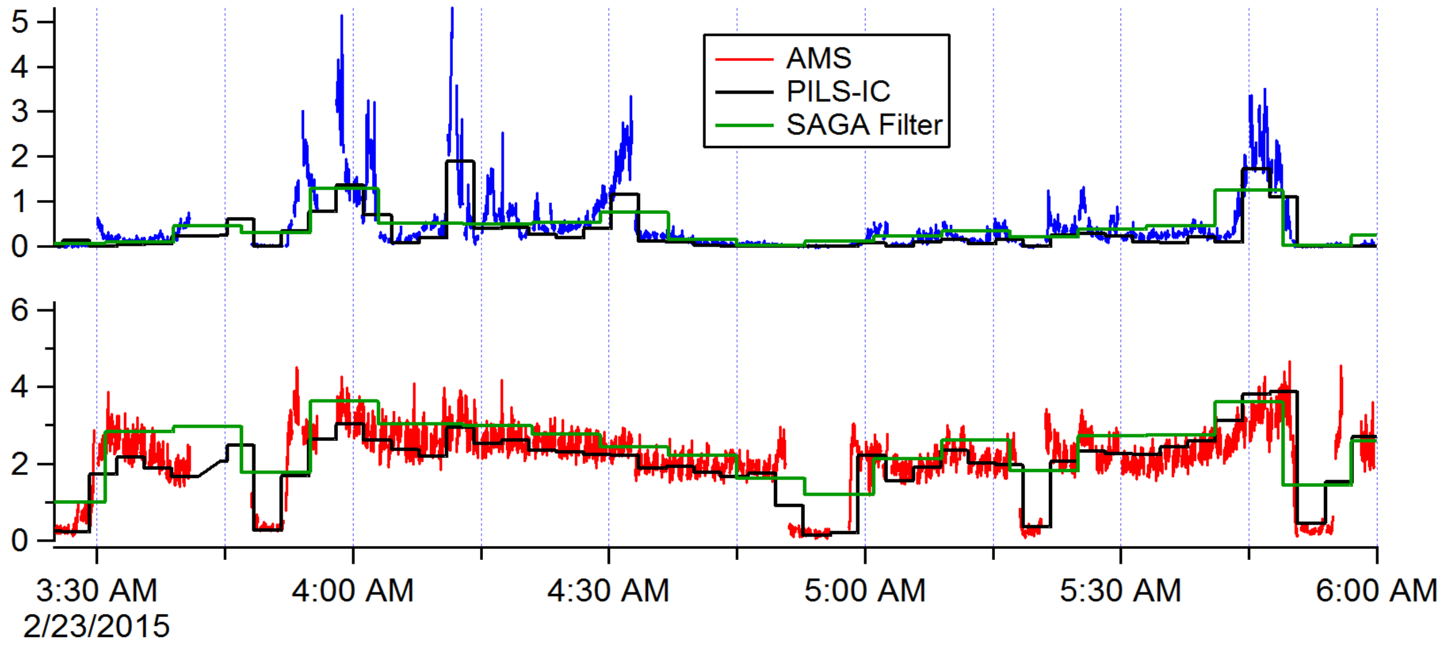
Sulfate

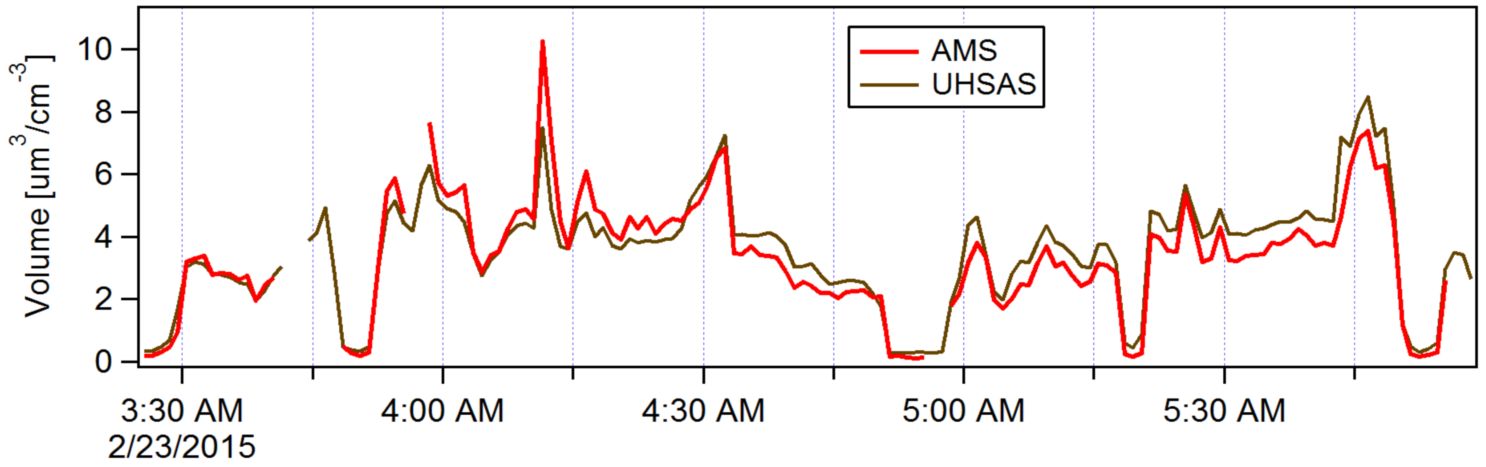


Ammonium



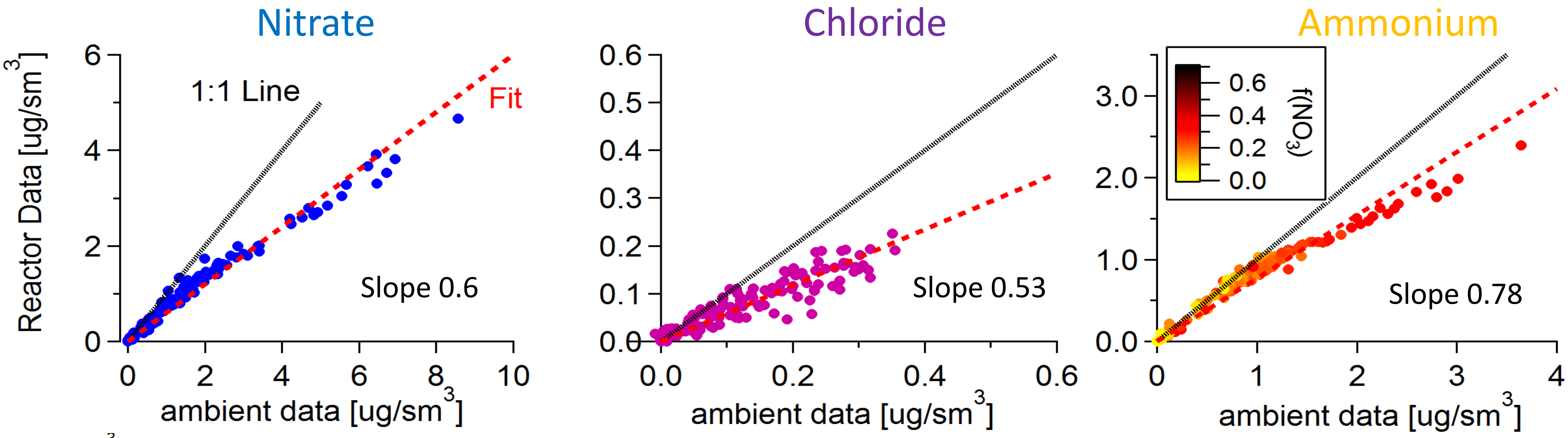
Intercomparison on RF06

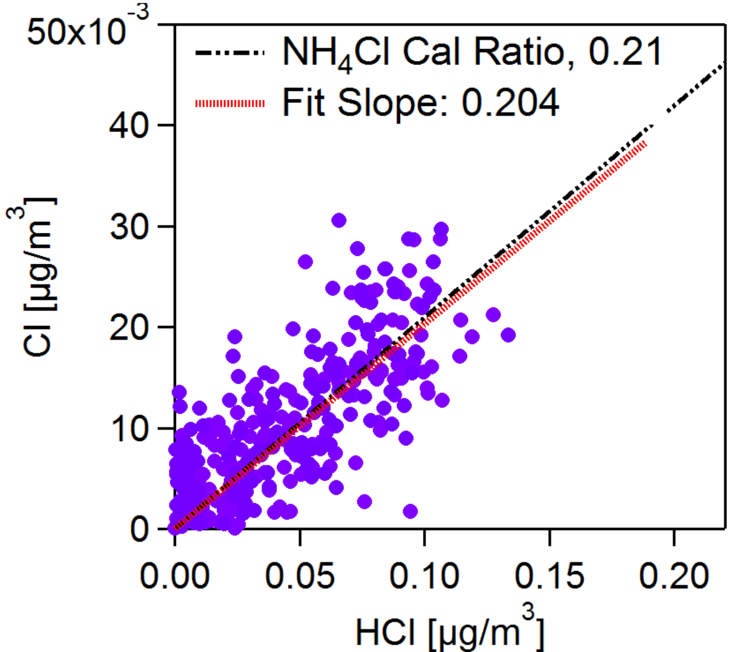




- Biggest discrepancy seen in thin NH_4NO_3 layers
- Preliminary evidence suggest that the UHSAS (outside the plane) and the AMS Volume agree very well during these events

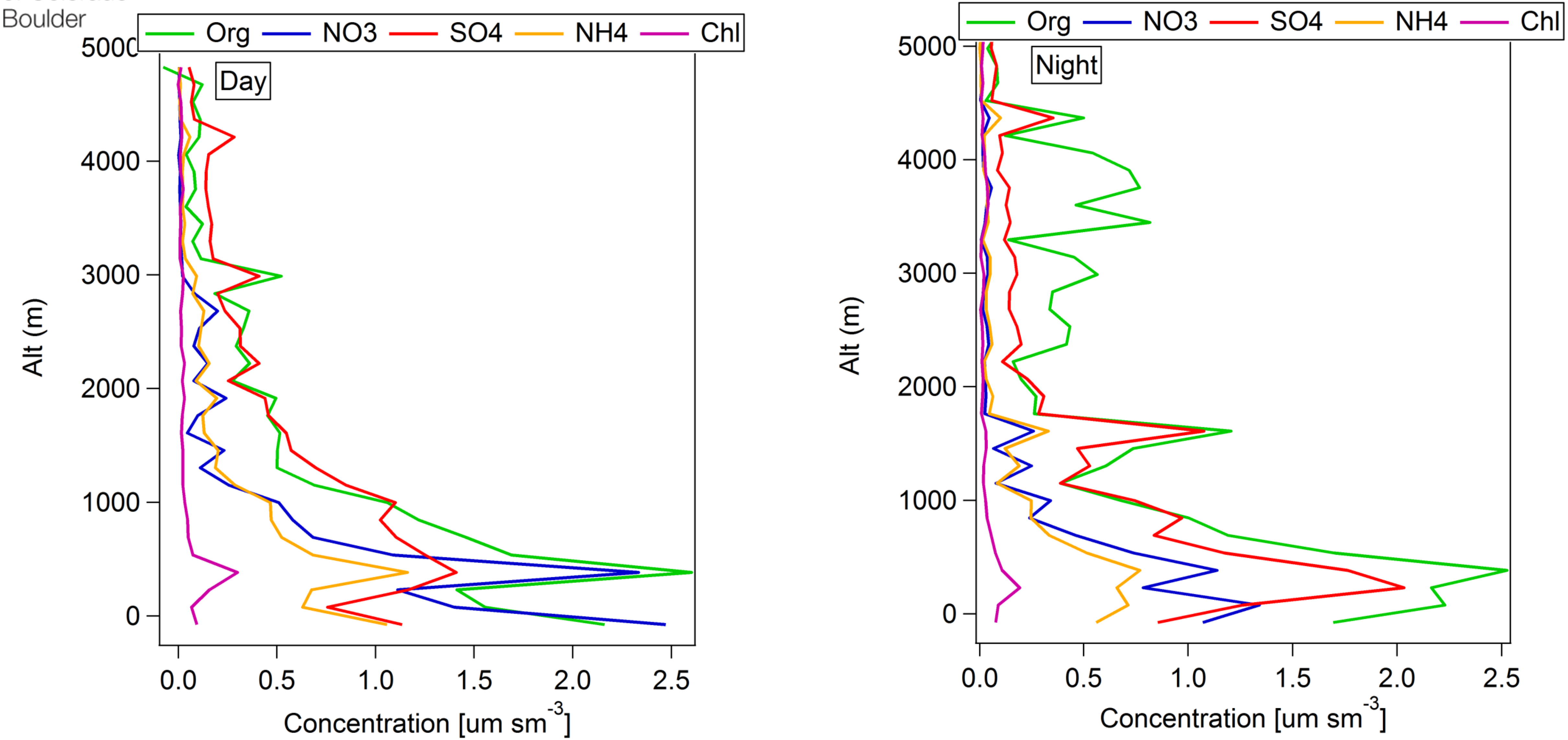
Chloride: also semivolatile, consistent w/ NH_4Cl





- Volatility of chloride
- Roughly tracks ammonium nitrate, and suggest NH_4Cl
- The ratio of the main ions Cl^+/HCl^+ is consistent with in-field calibrations of this ratio conducted with NH_4Cl

Campaign Averages



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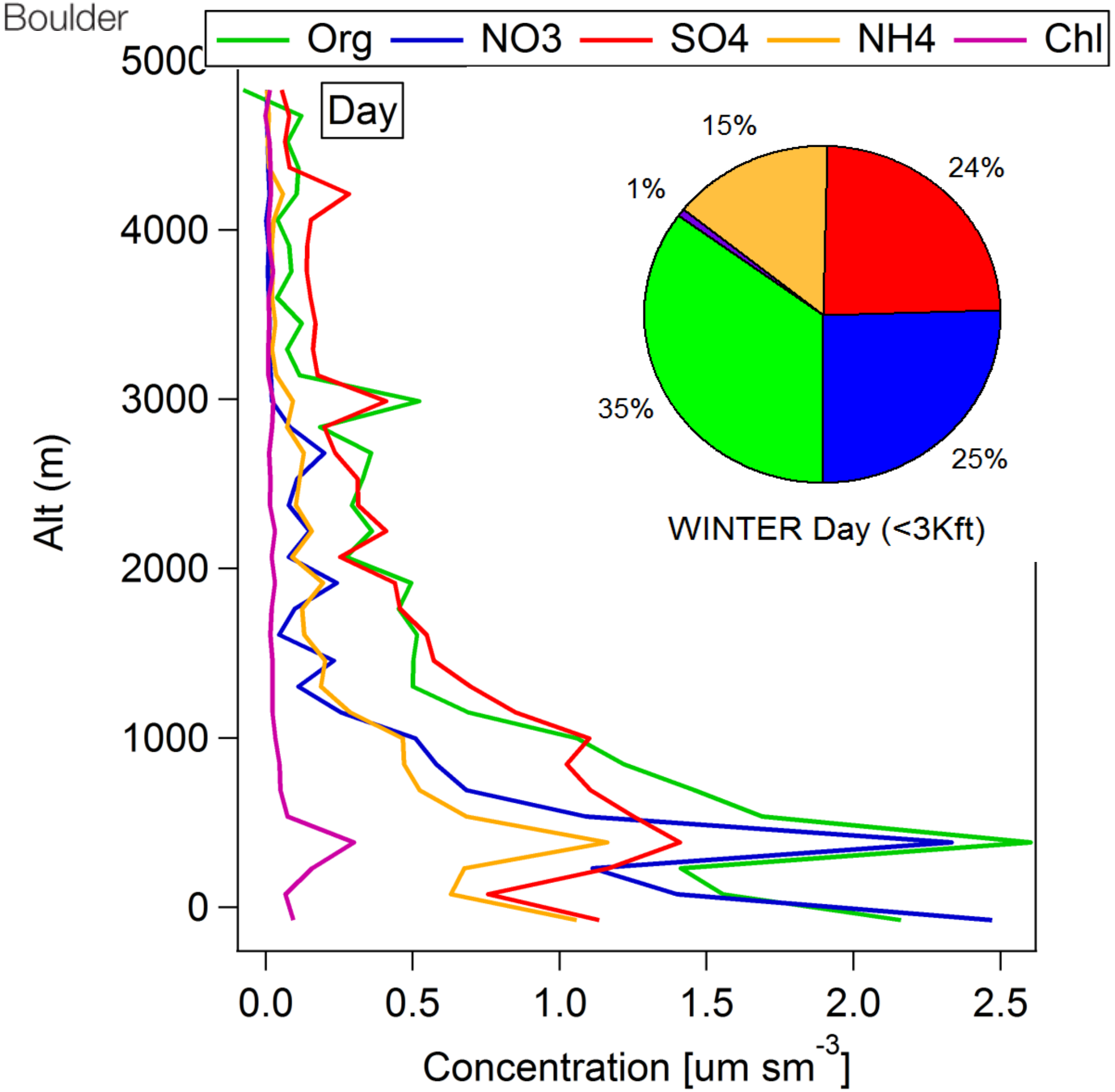

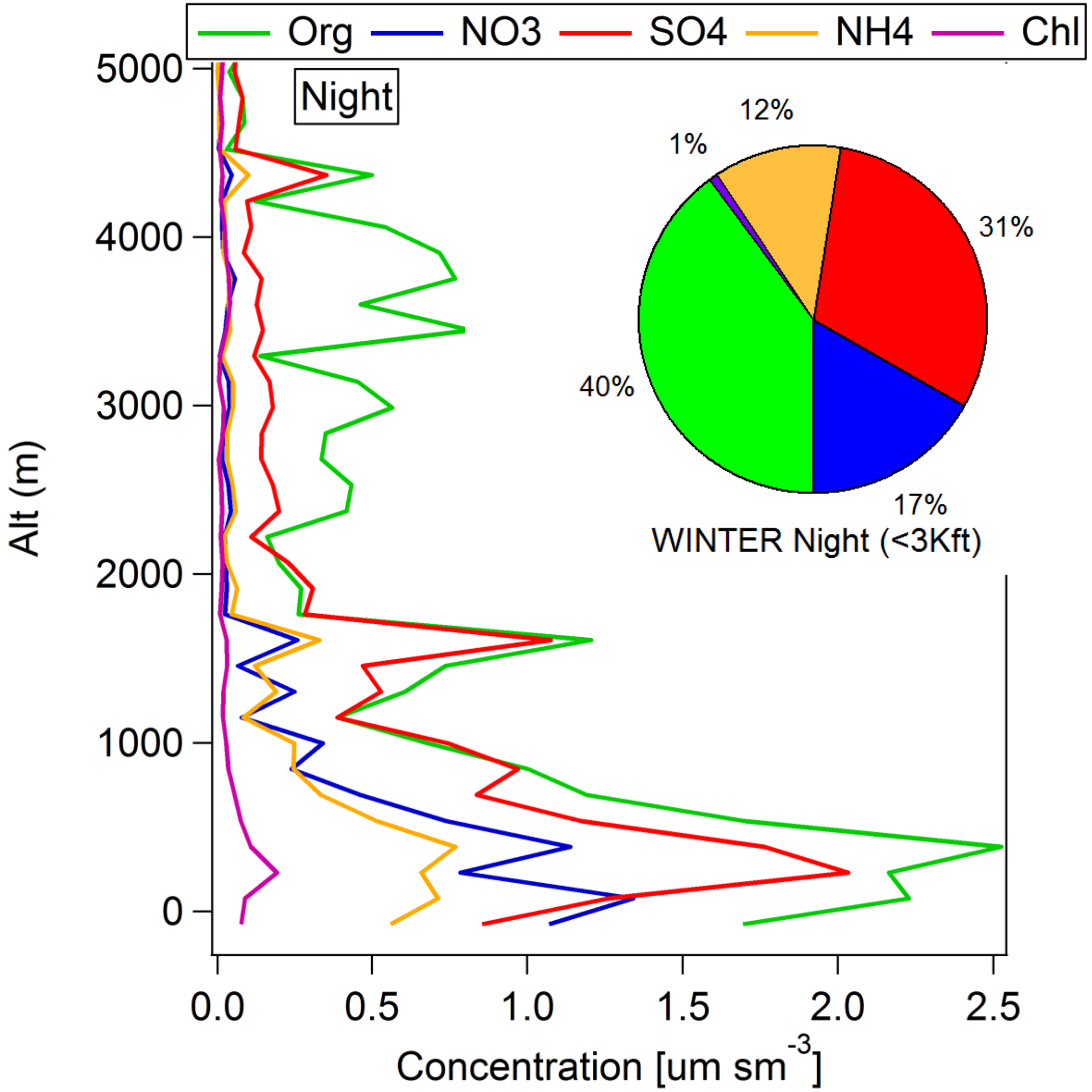

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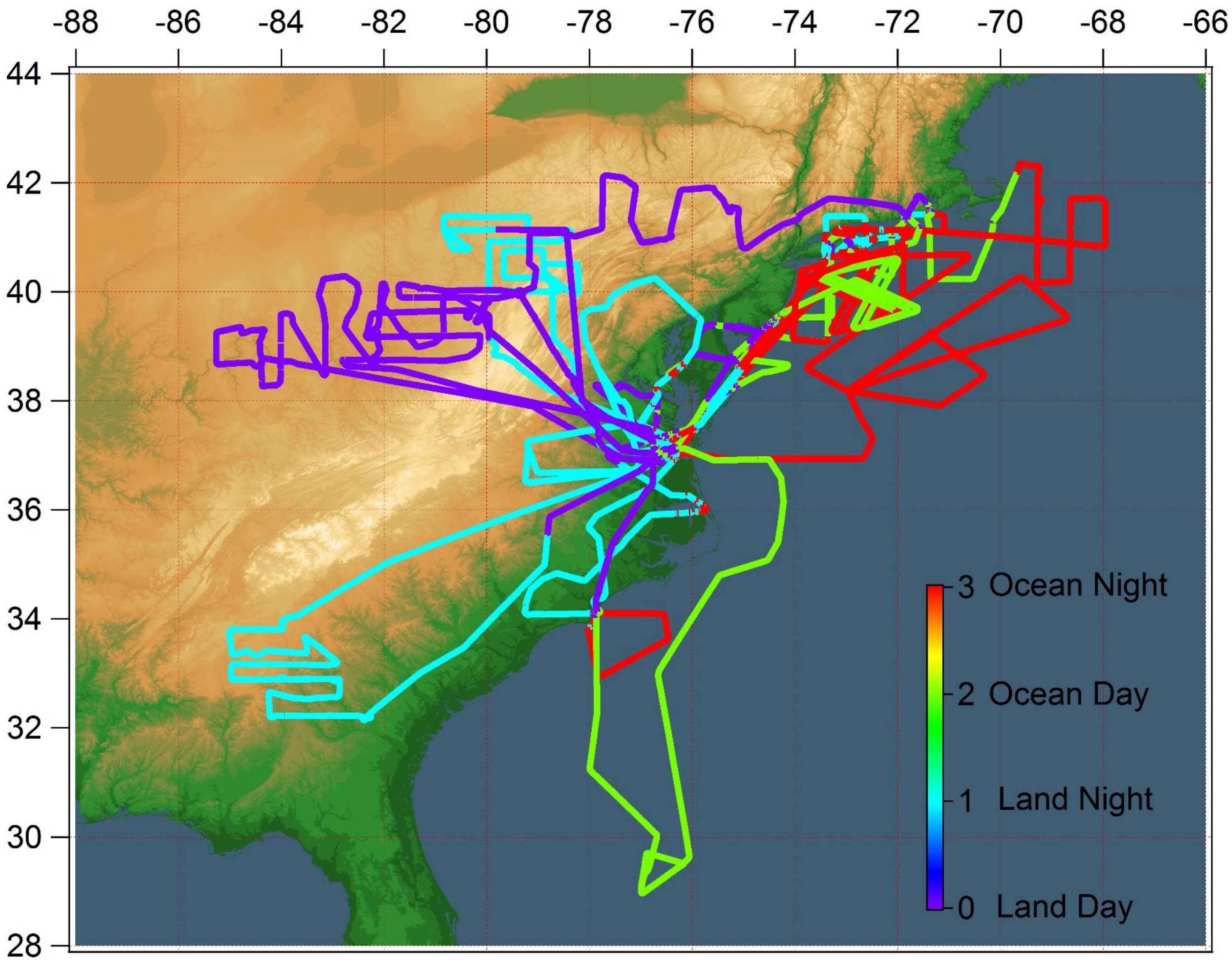
Campaign Averages – Flight by Flag

	% of Time
Land – Day	29
Land – Night	31
Ocean – Day	17
Ocean - Night	23



Campaign Averages - AMS Species By Flag

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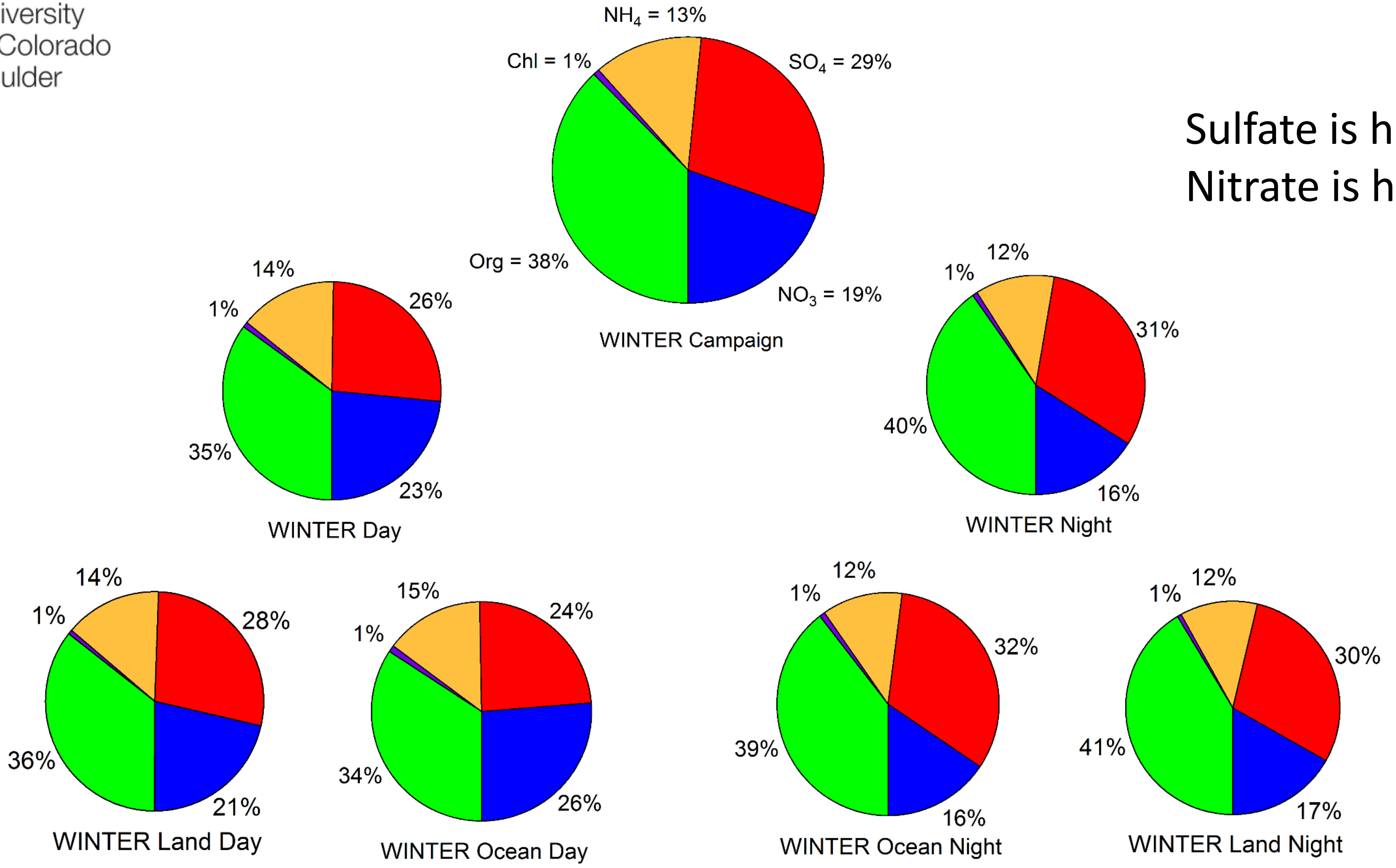

Sulfate is higher at night
Nitrate is higher during the day

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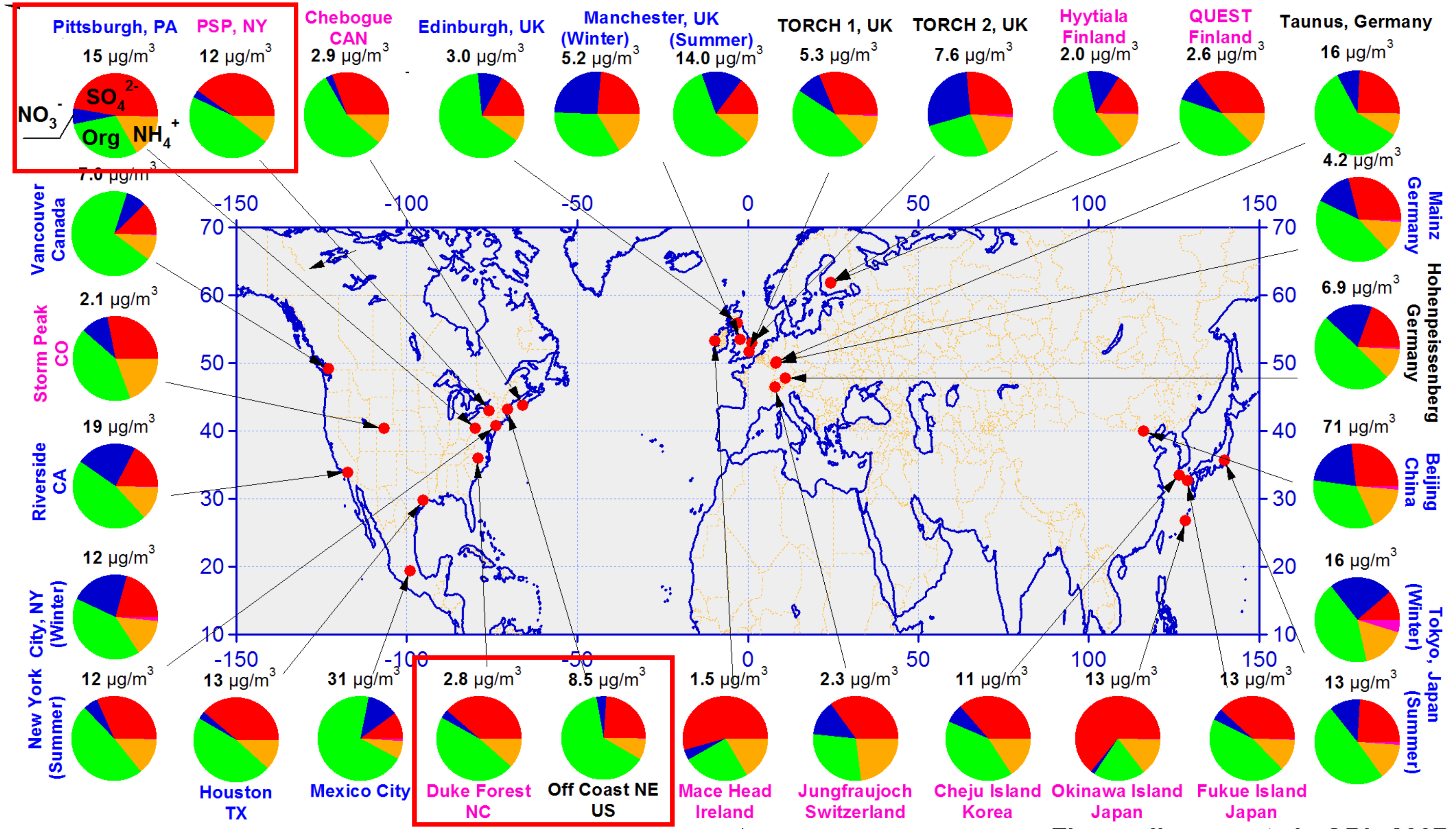
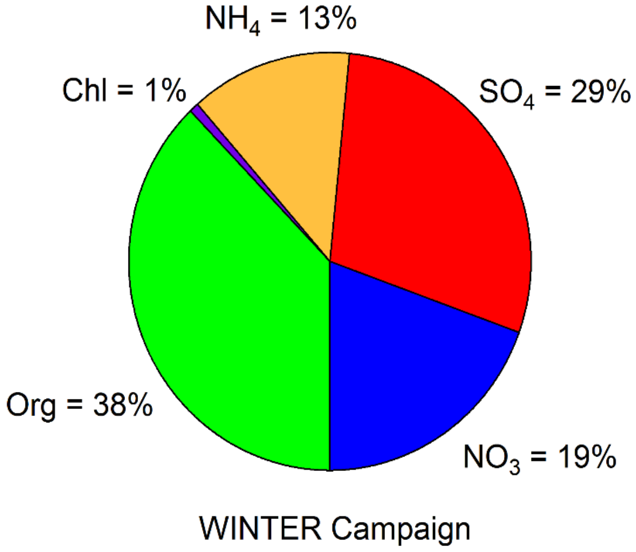
Campaign Averages - Comparison

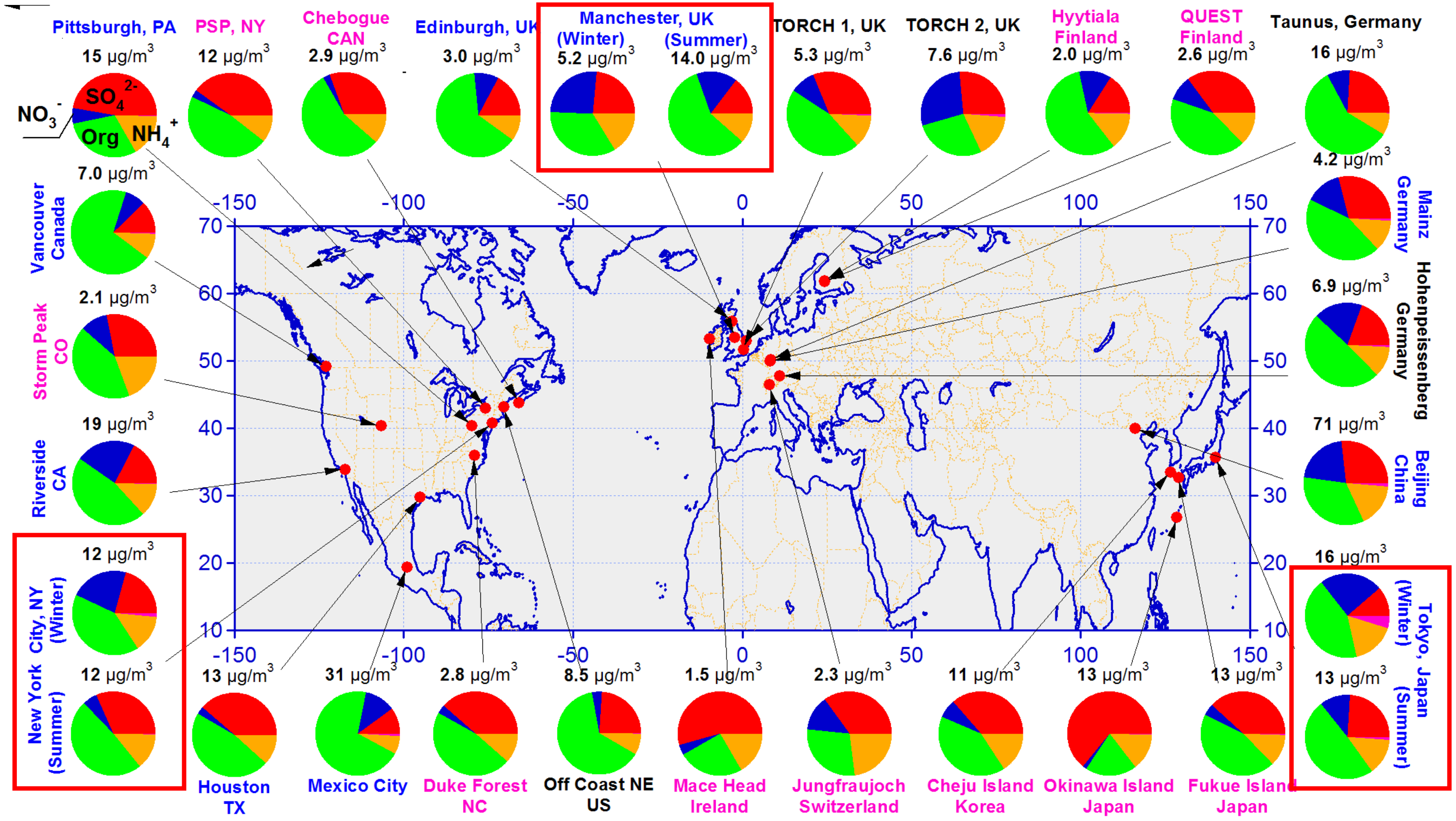


Zhang, Jimenez et al., *GRL*, 2007



- Lower organic and higher nitrate, compared to summer
- Consistent with other wintertime studies

Campaign Averages - Comparison



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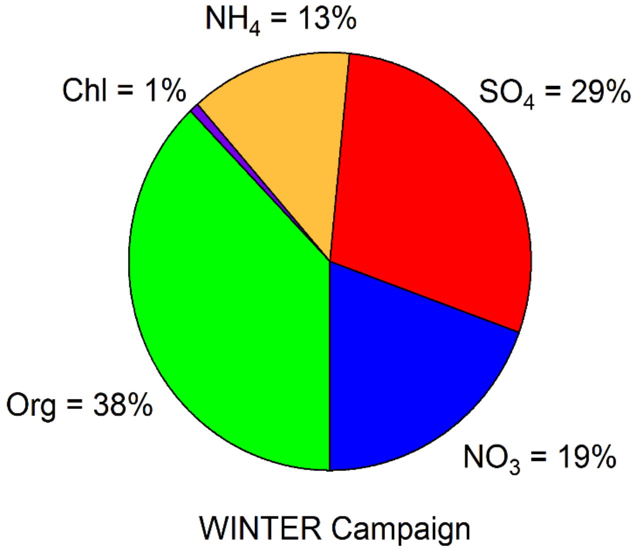

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Organic Aerosol – Campaign Flight Track

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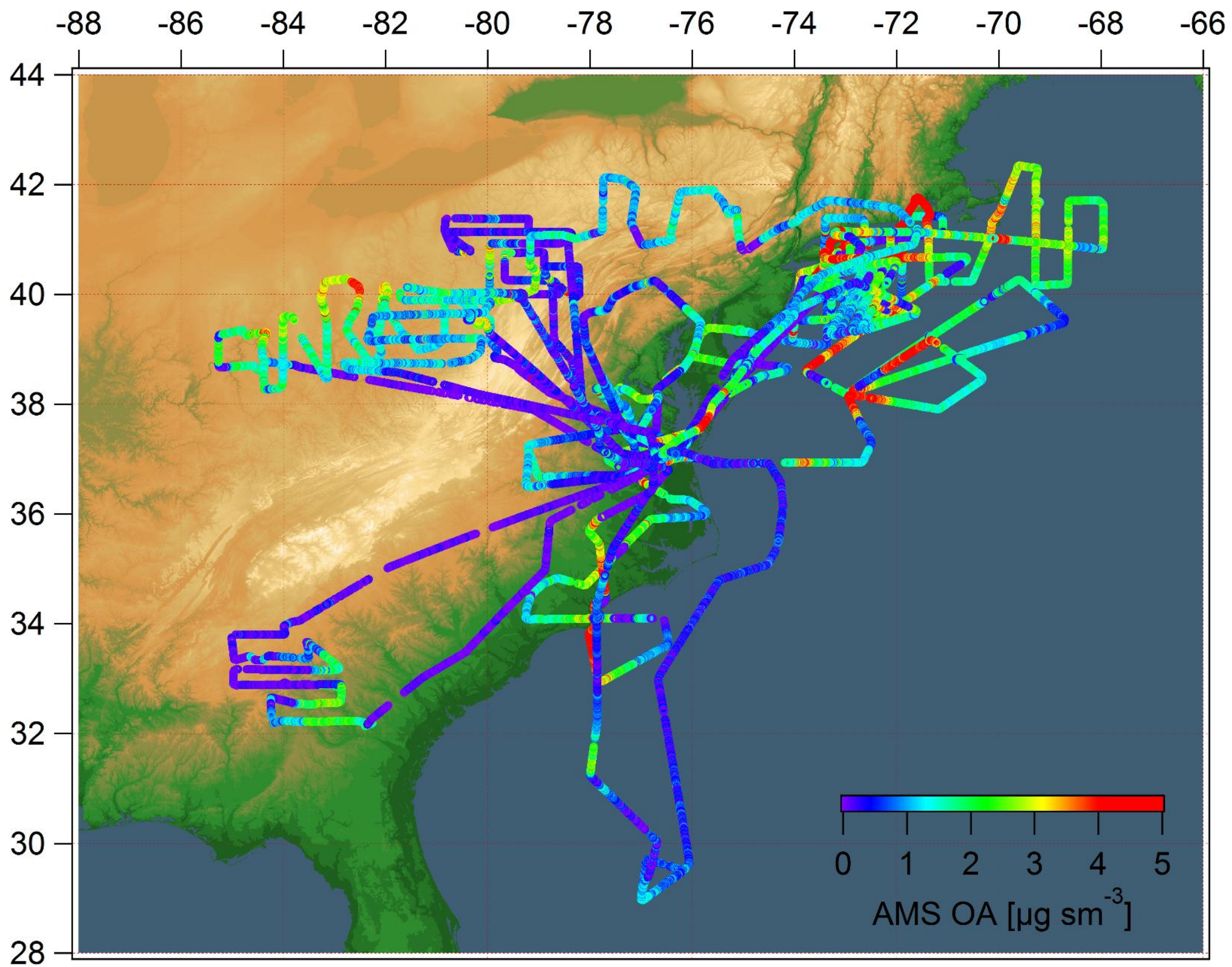

Organic Aerosol – O/C

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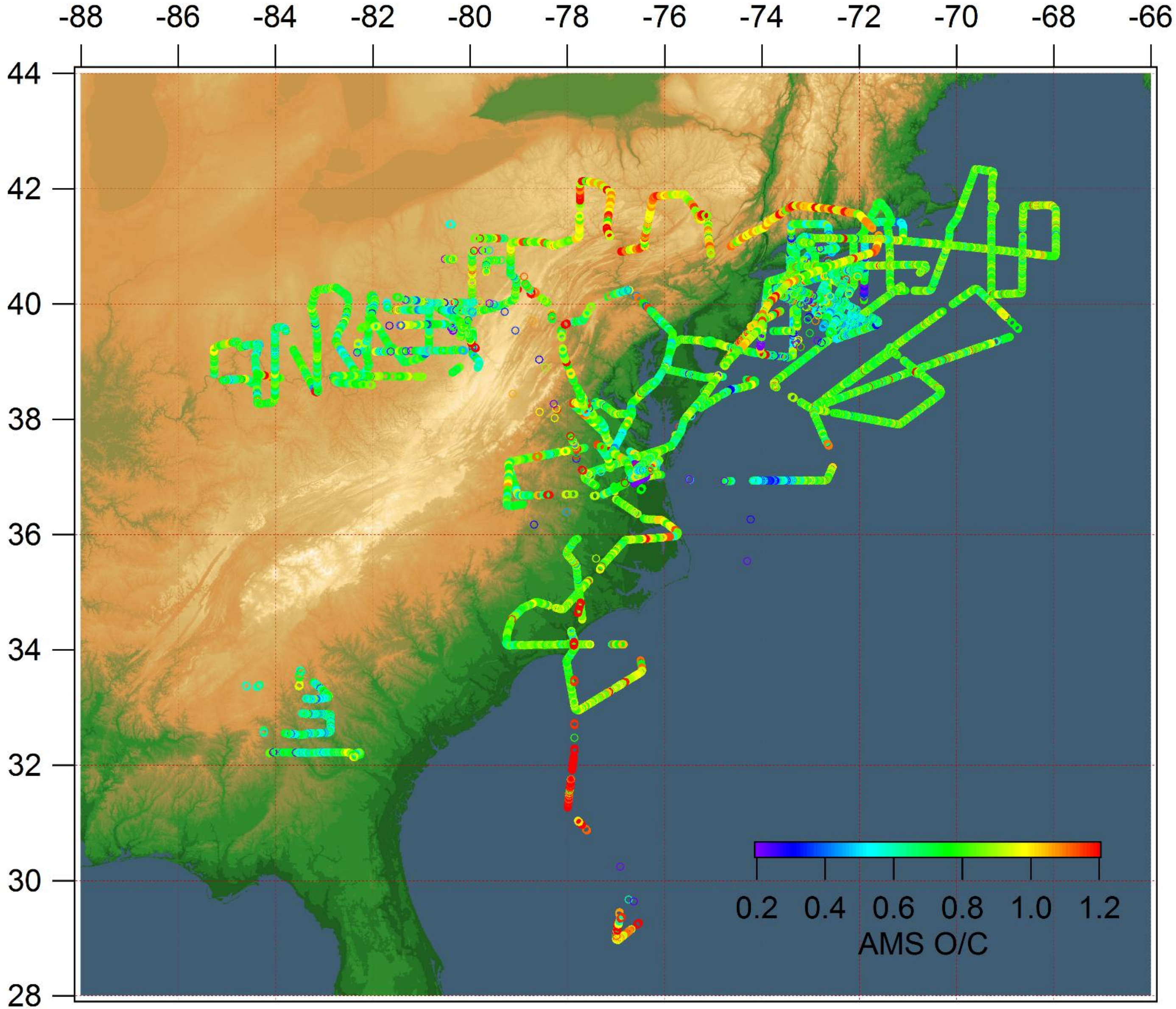
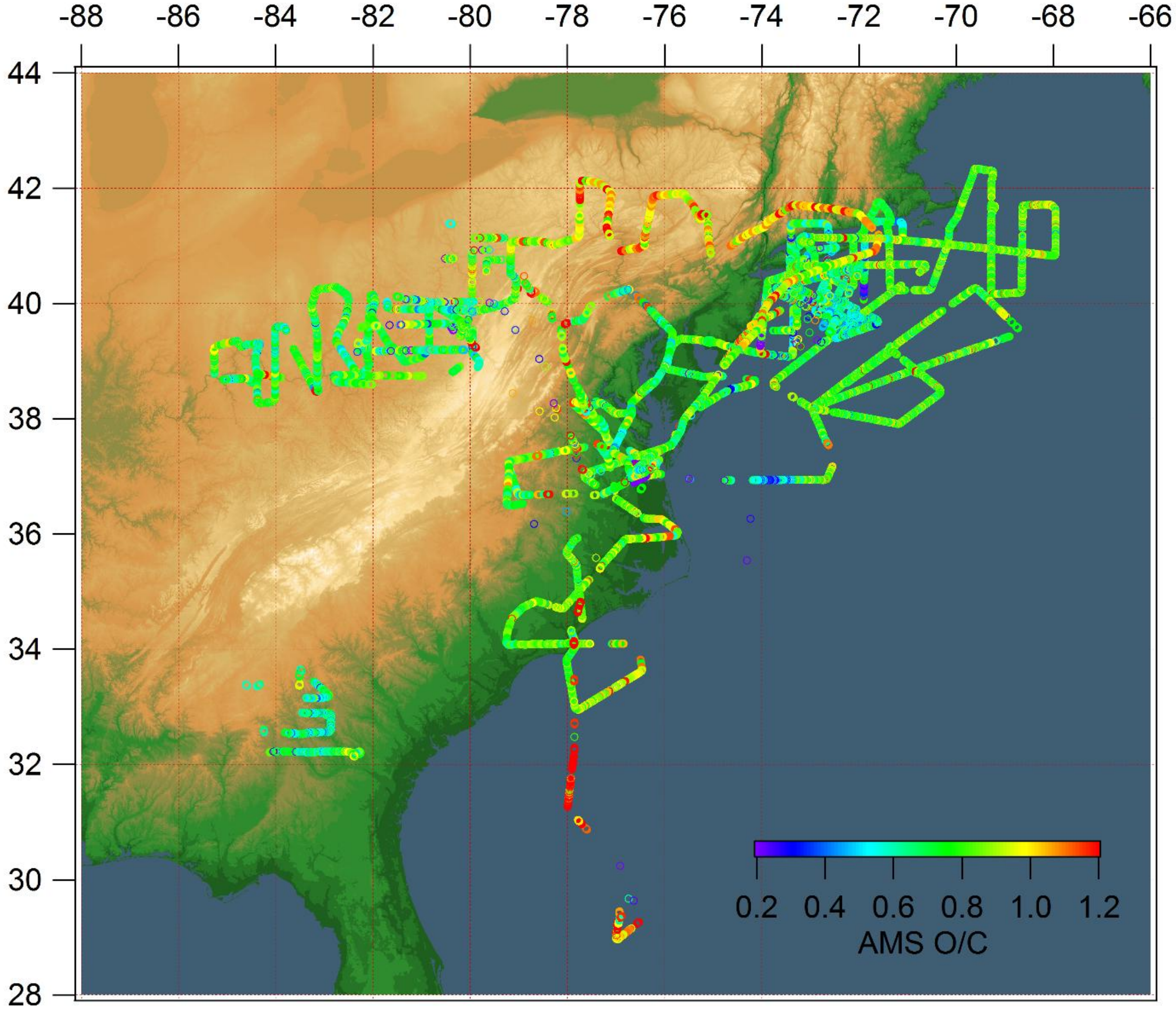
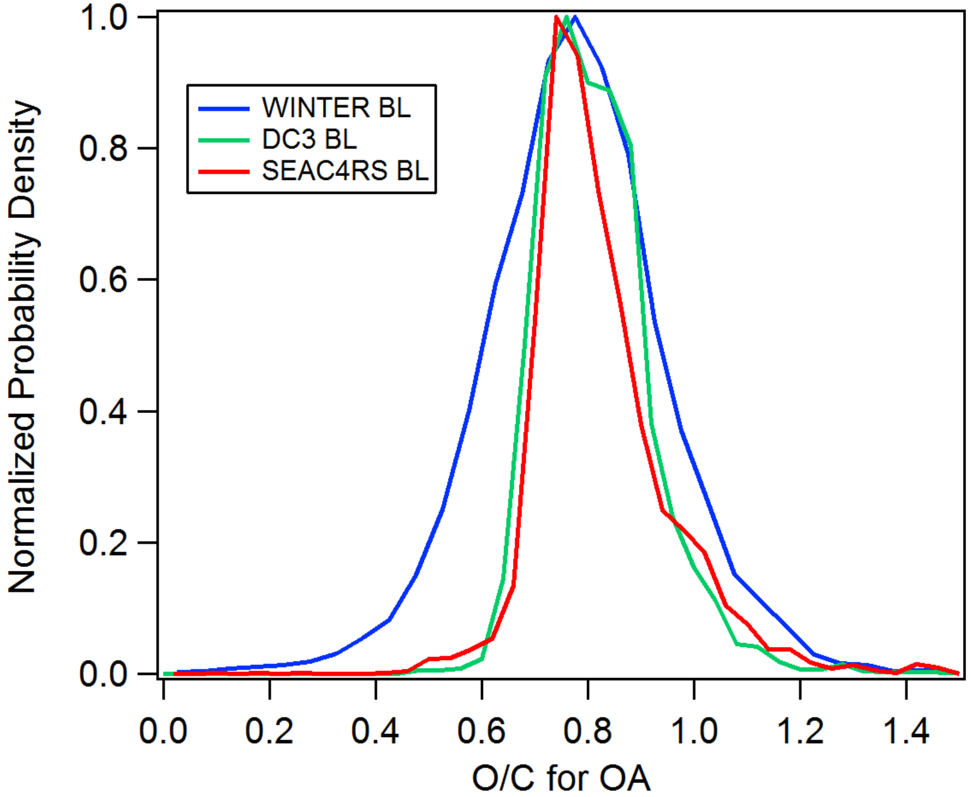


Organic Aerosol – O/C

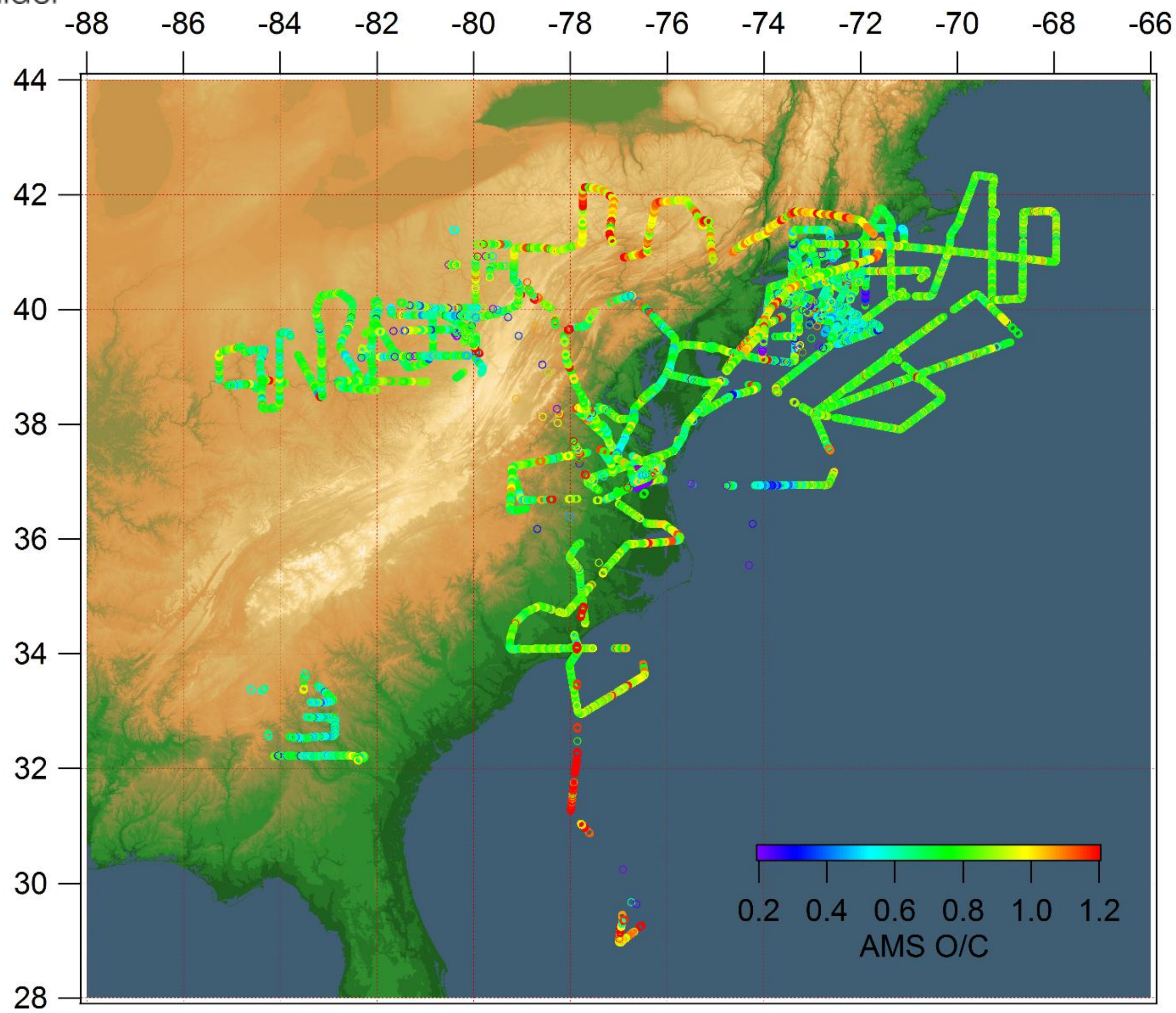
DC3 = Midwest, Spring
SEAC4RS = SE US, Summer





- The WINTER distribution is broad
- Reaches similar ratios for aged particles

Organic Aerosol – O/C



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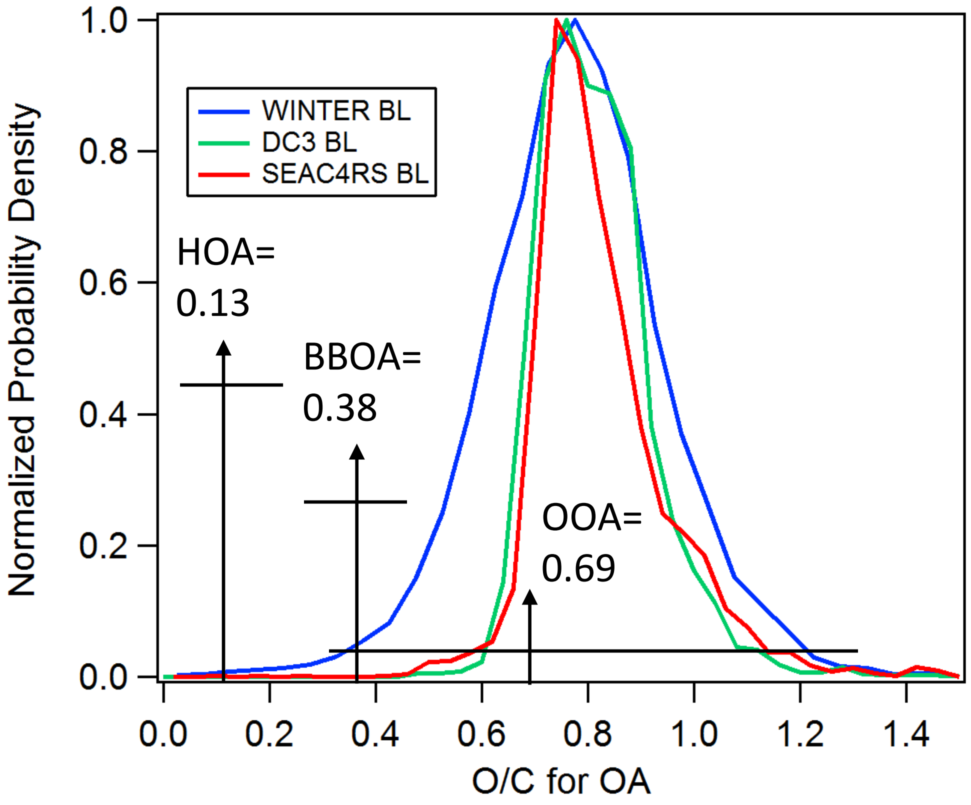
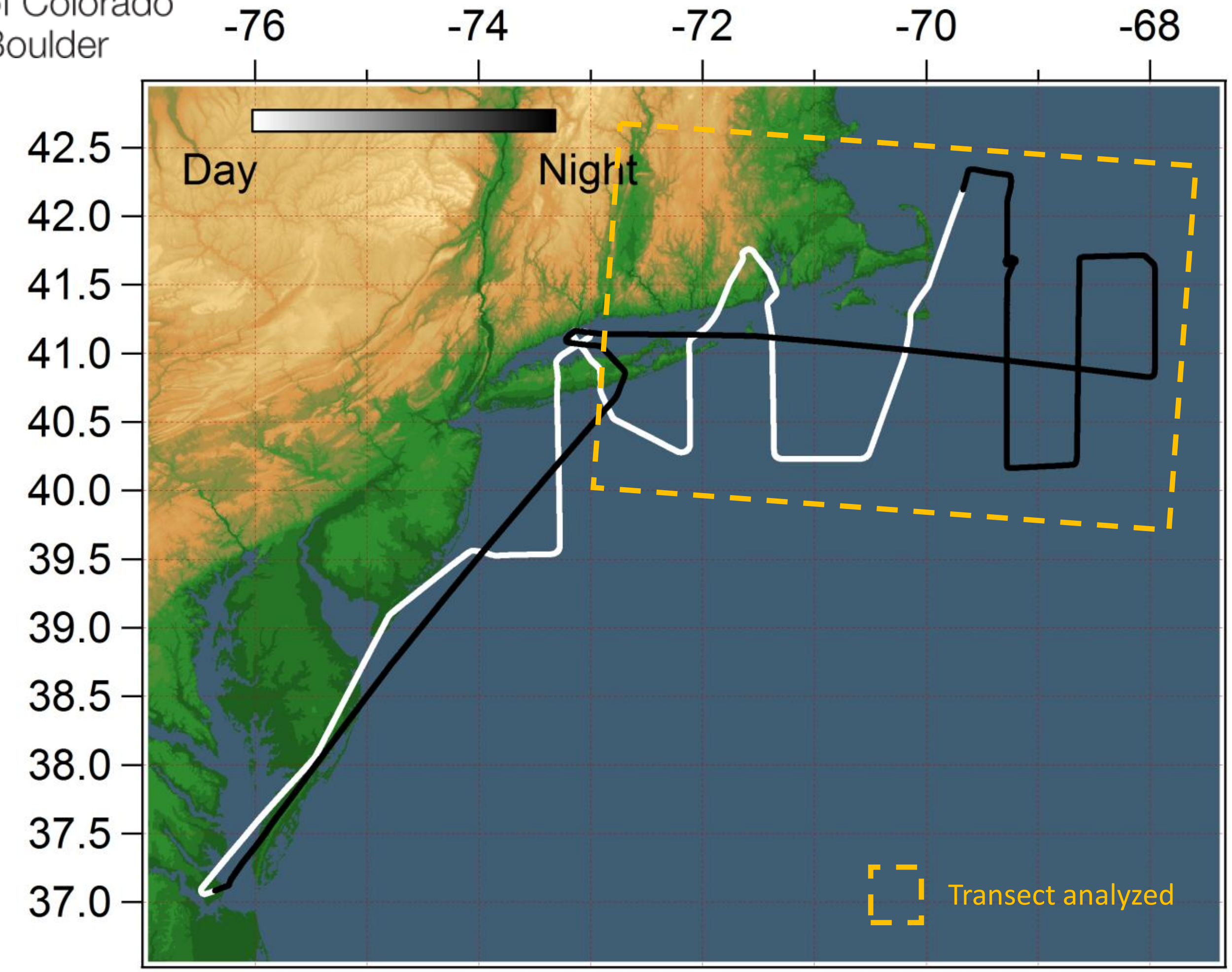
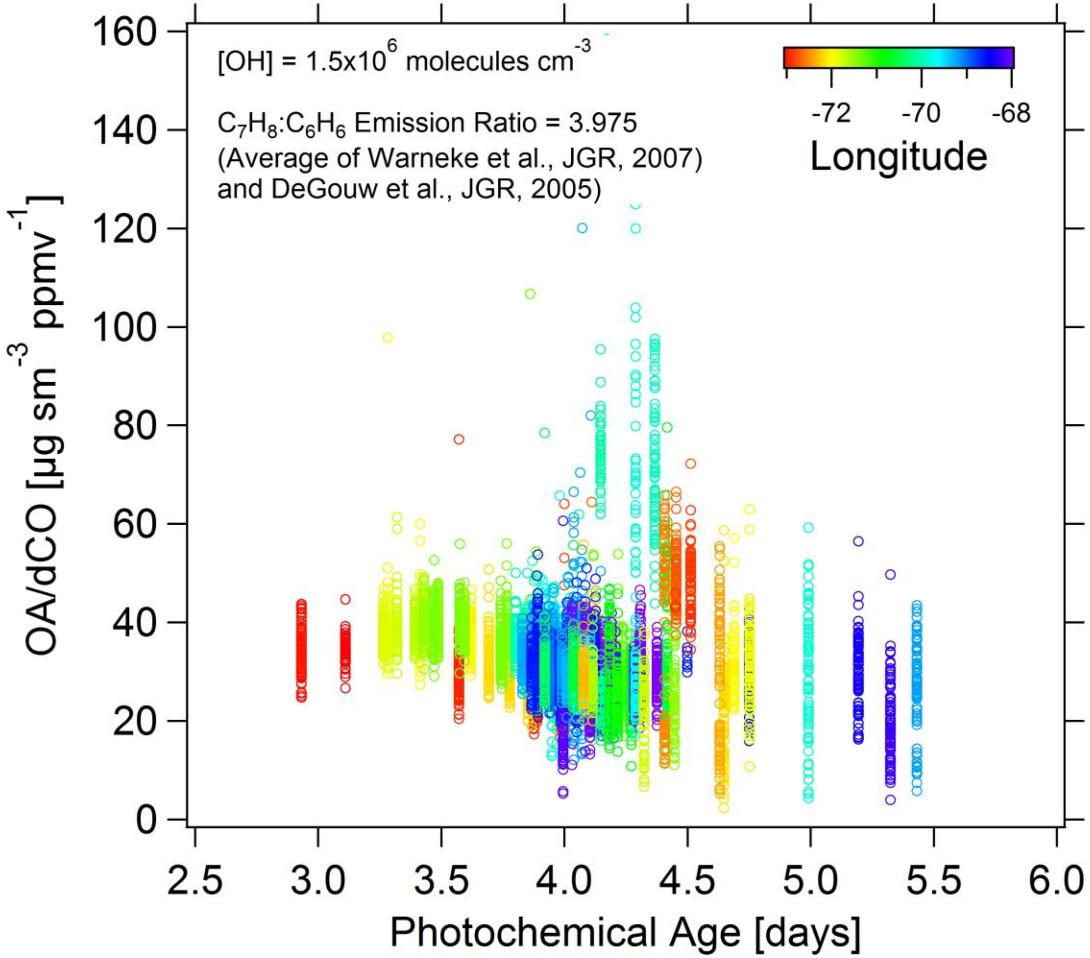


- The WINTER distribution is broad
- Reaches similar ratios for aged particles
- Doesn't look like HOA primary urban emissions
- Very aged POA + aged BBOA + SOA ?
- OA oxidation in clouds?

Averaged O/C from Canagaratna et al., ACP 2015

Photochemical Age – “NYC” Plume Transect RF03





$$Age_{VOC} = \left(\frac{1}{OH*(k_{Tol}-k_{Ben})}\right) * \left[ln(emmision\ ratio) - ln\left(\frac{Tol}{Ben}\right)\right]$$

Warneke et al., JGR 2007

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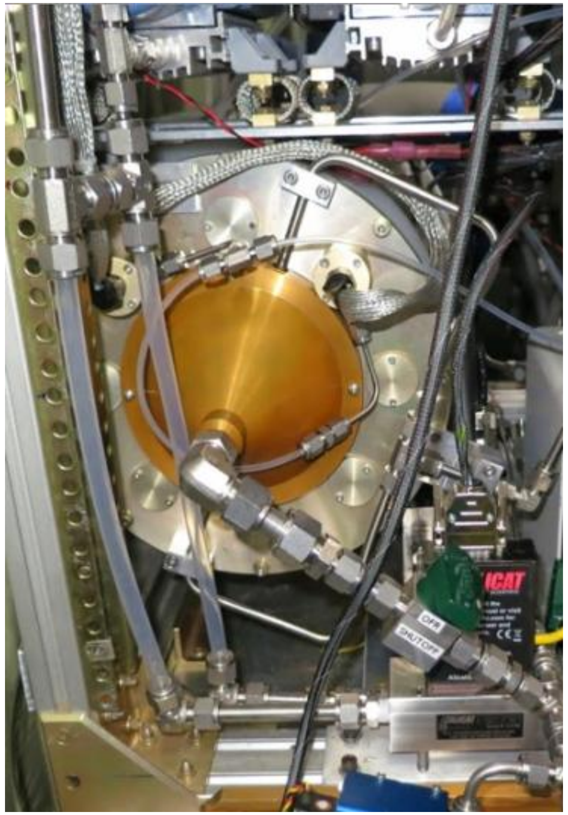
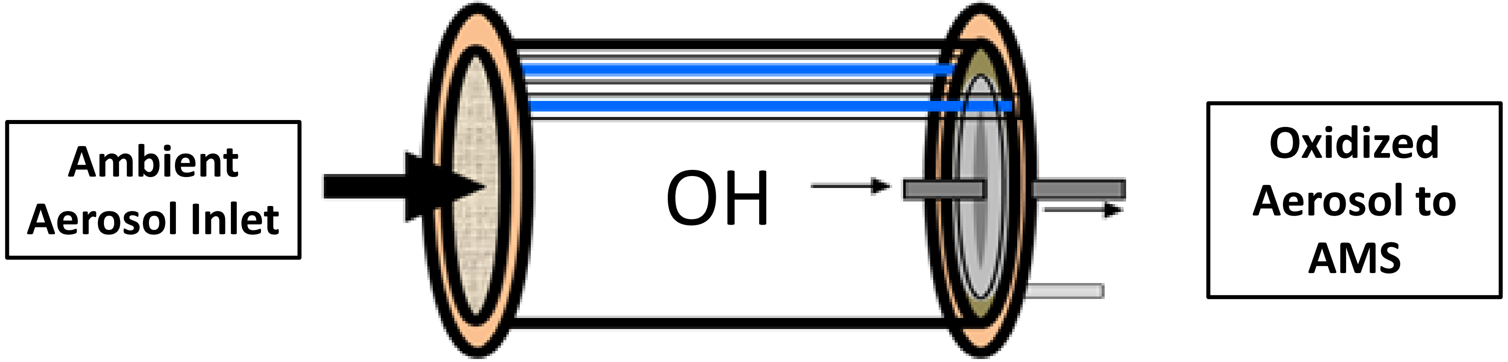
Oxidative Flow Reactor (OFR)





OH Production in OFR at l= 185nm:

$H_2O + h\nu\ (185nm) \rightarrow OH$

$O_2 + h\nu\ (185nm) \rightarrow O_3$

$O_3 + h\nu\ (254nm) + H_2O \rightarrow\rightarrow 2\ OH$

Oxidation Flow Reactor (OFR)

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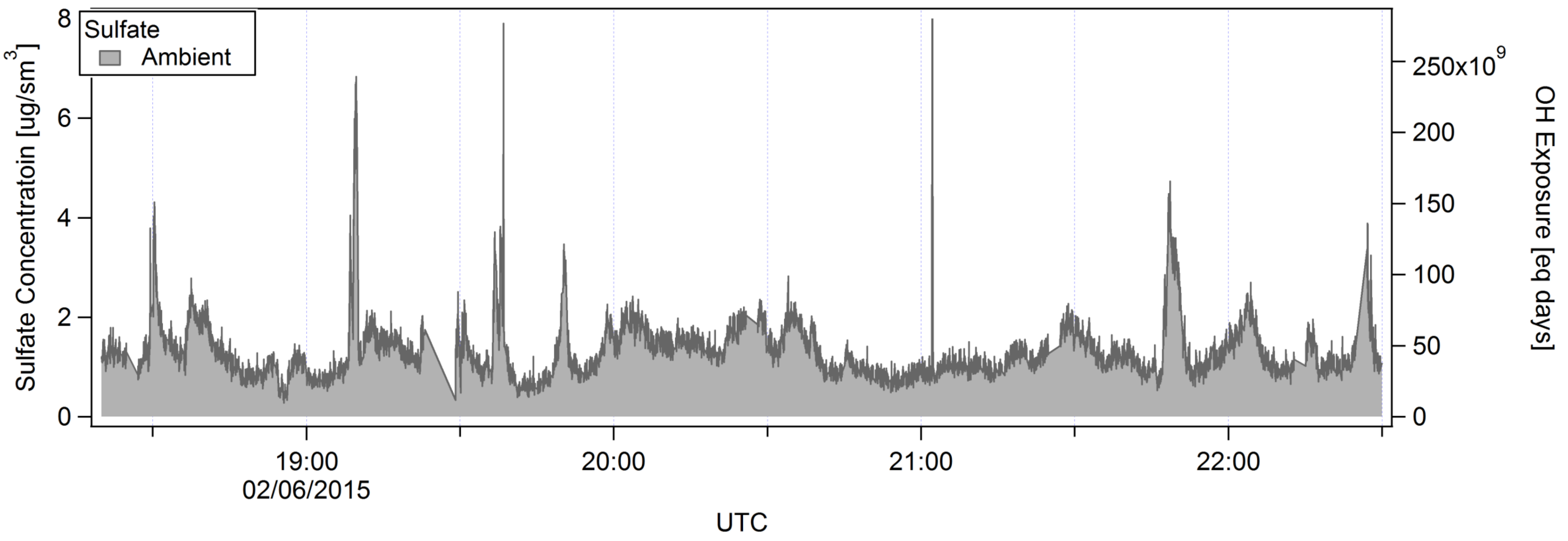
RF02



Oxidation Flow Reactor (OFR)

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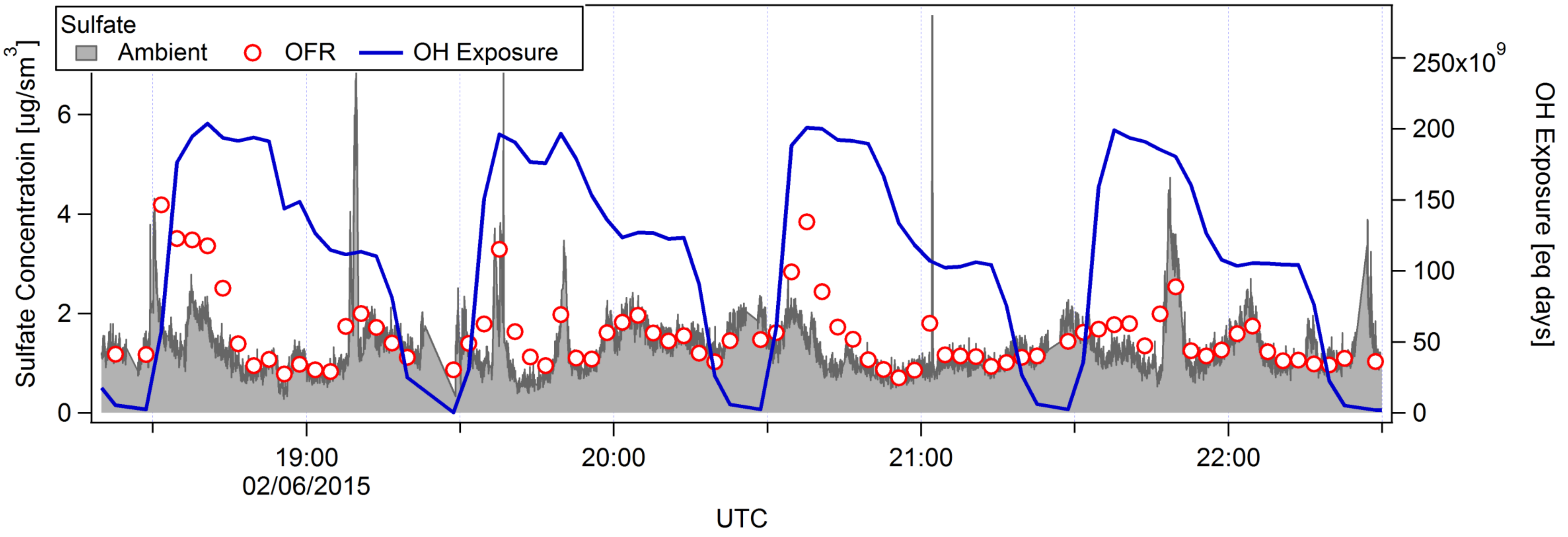
RF02



Oxidation Flow Reactor (OFR)

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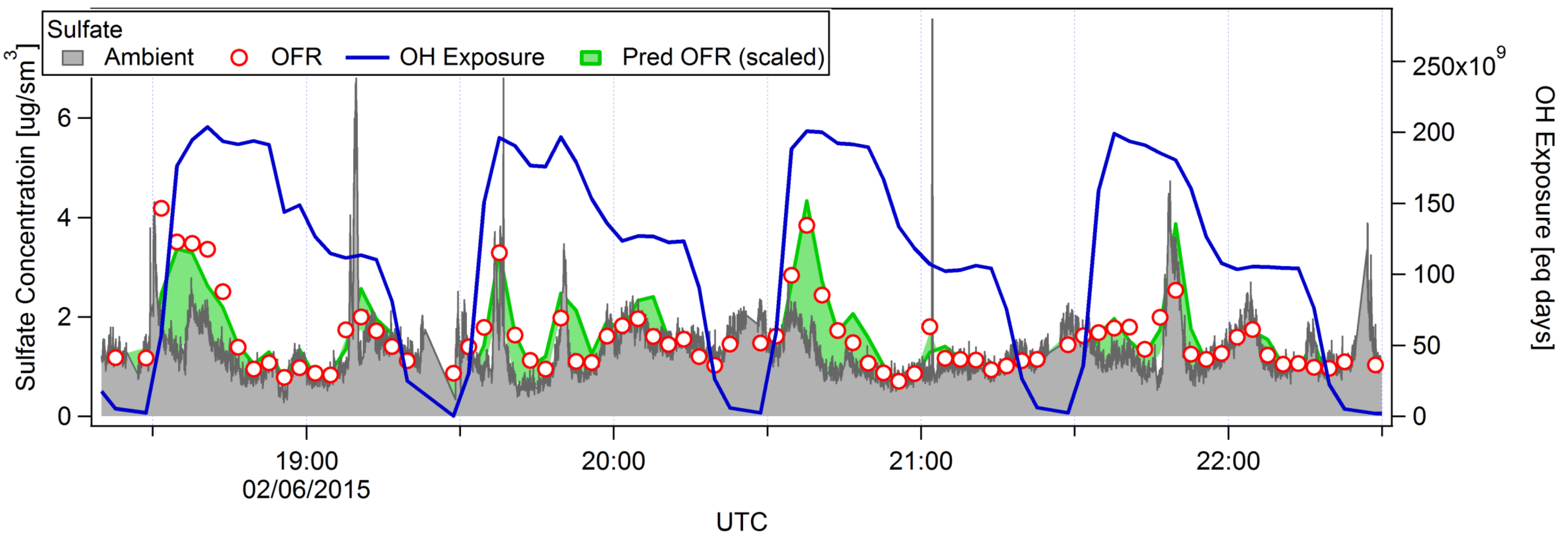
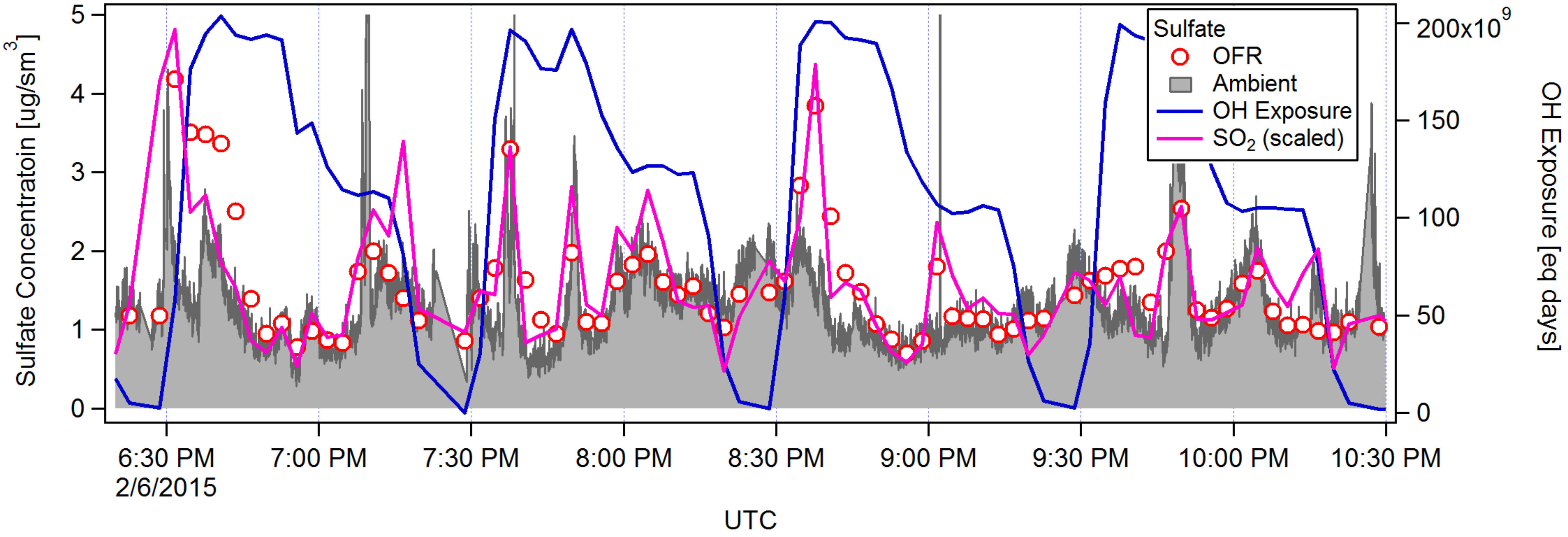


Oxidation Flow Reactor (OFR)

University of Colorado Boulder

RF02



Oxidation Flow Reactor (OFR)

University of Colorado Boulder

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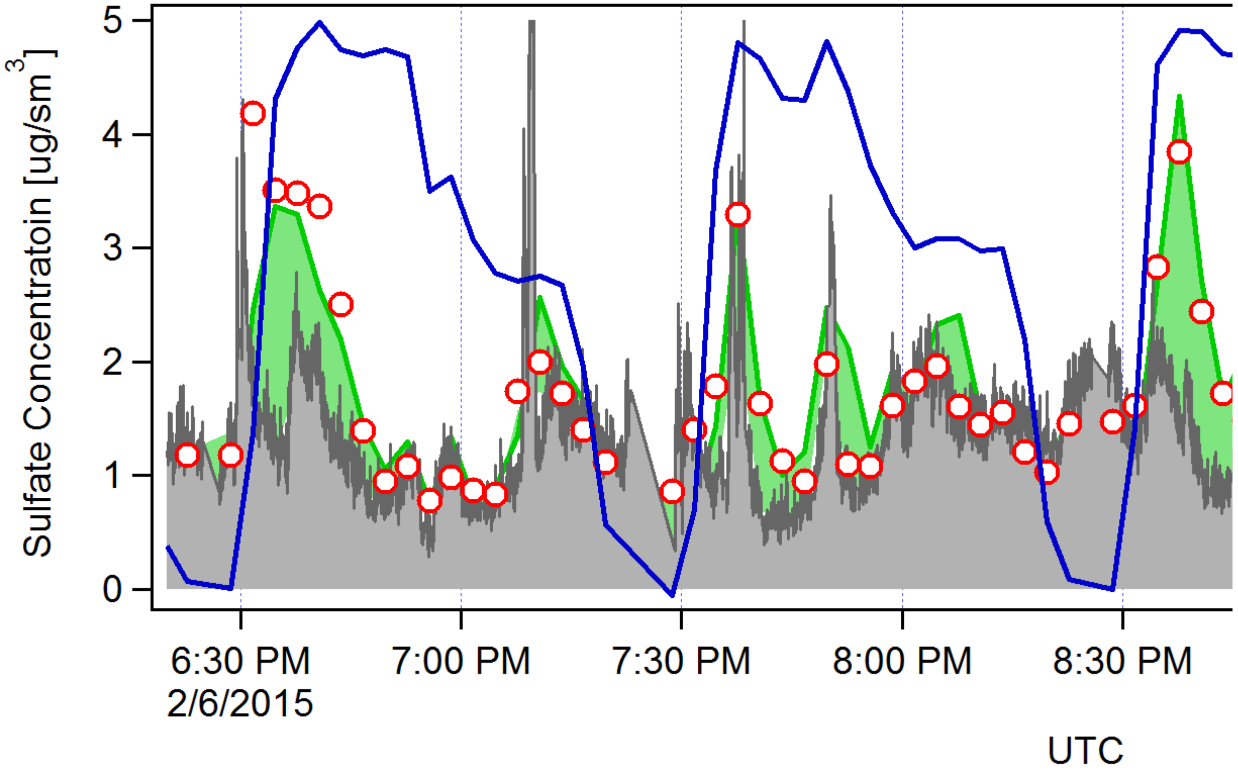

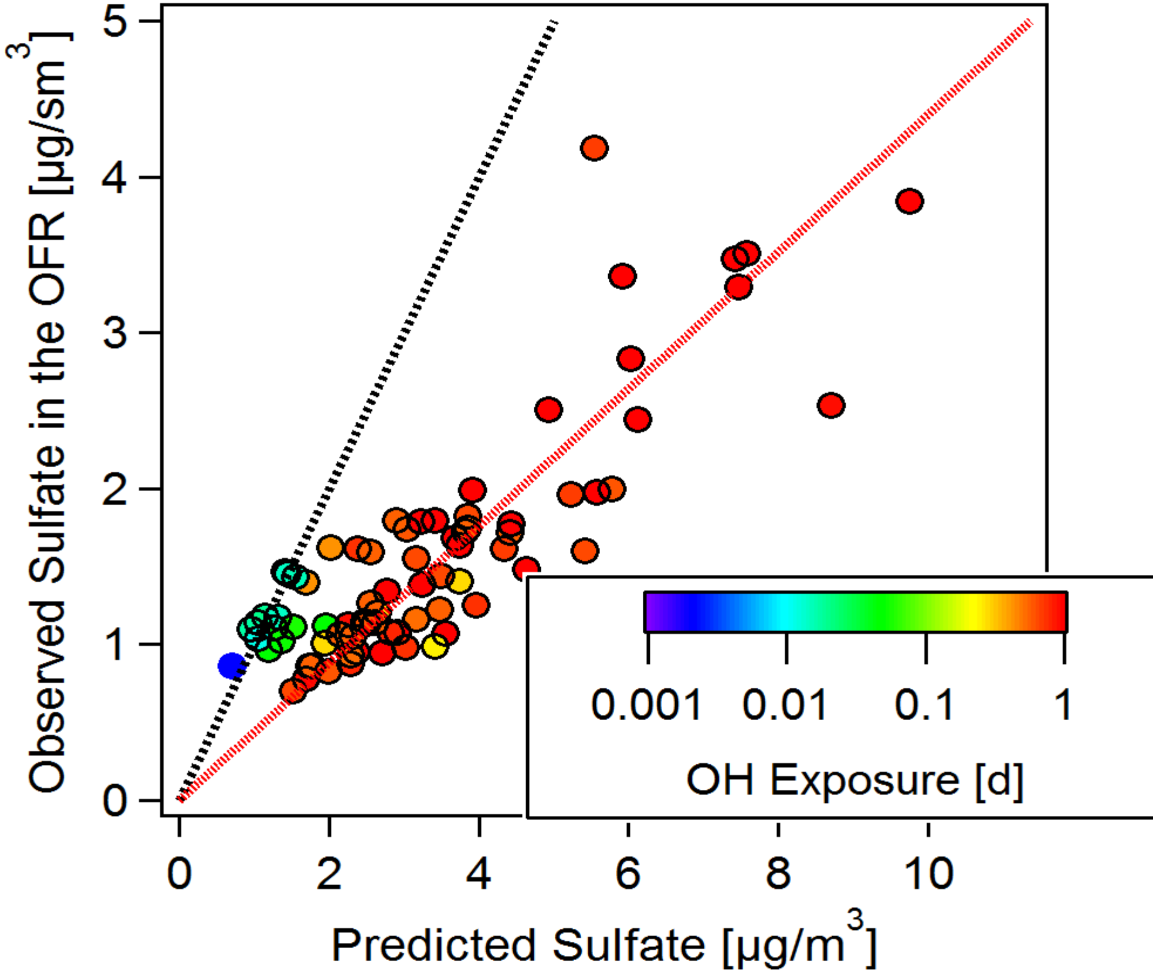

Biomass Burning Organic Aerosol

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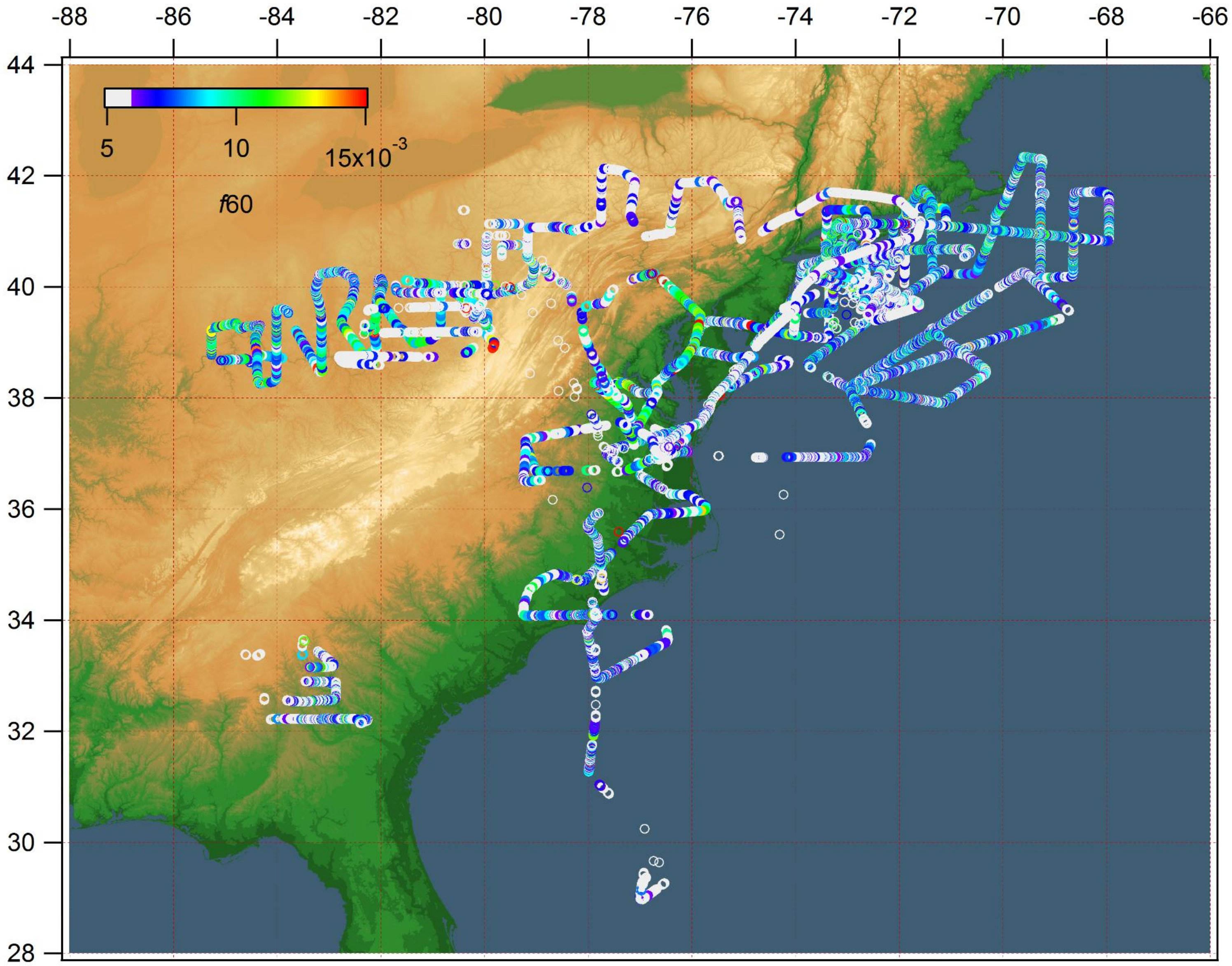

Fresh Biomass Burning Organic Aerosol?

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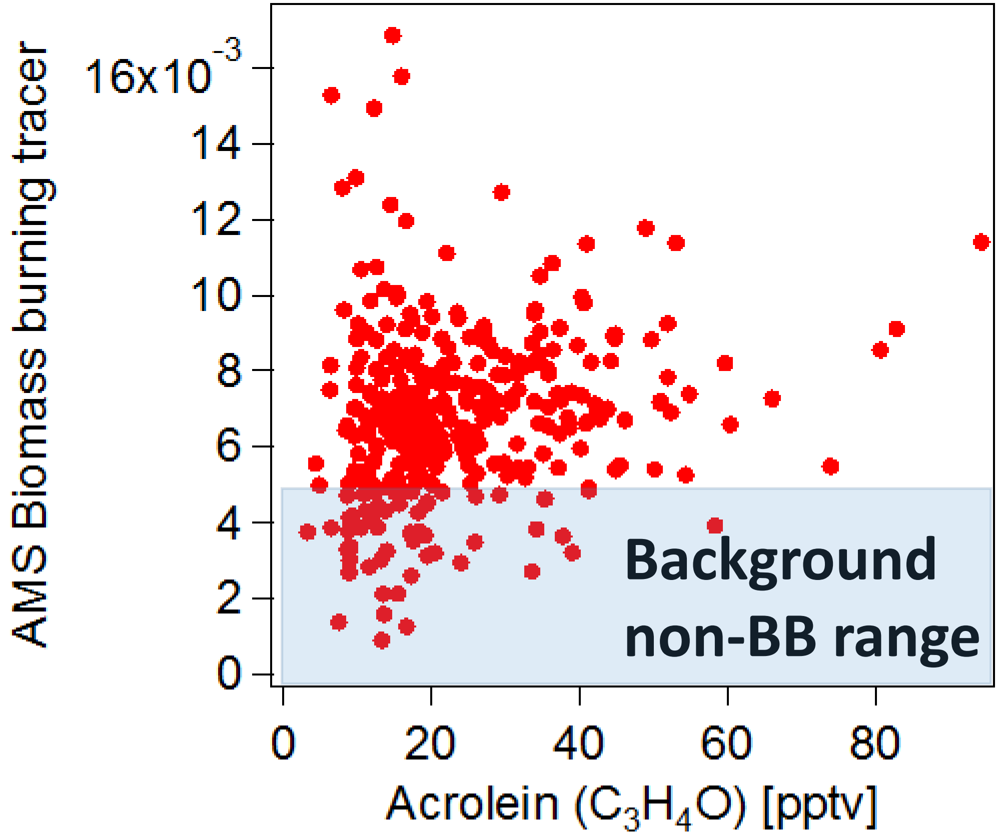

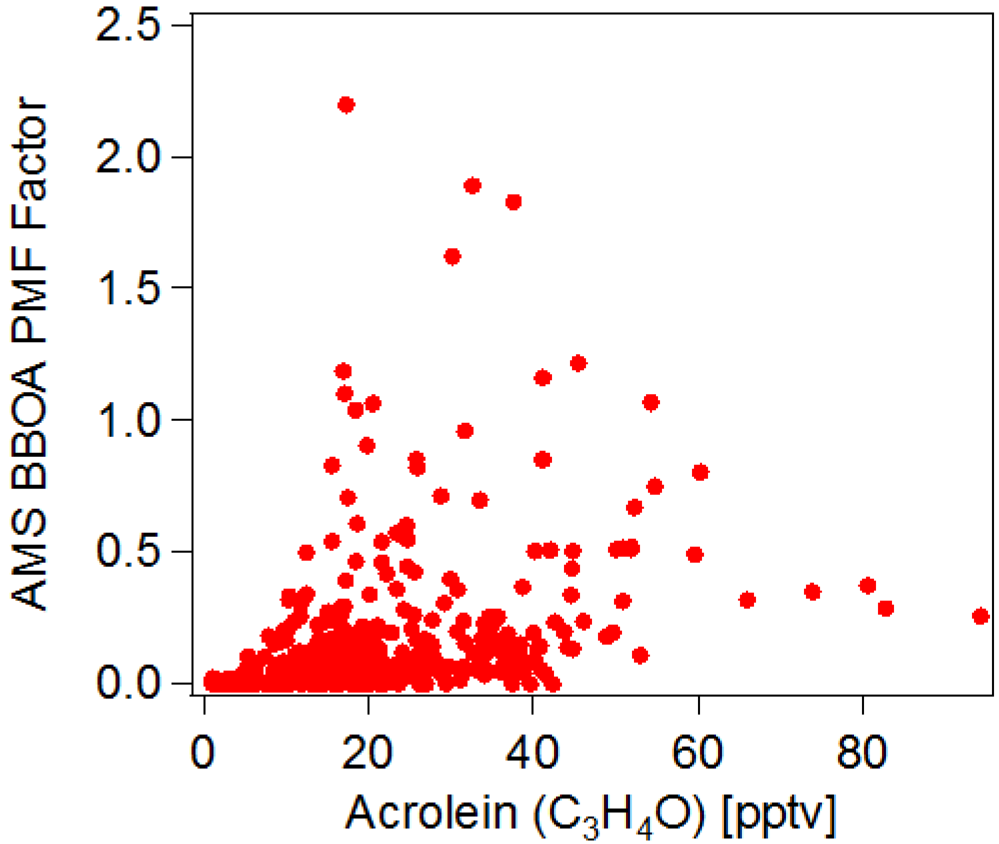

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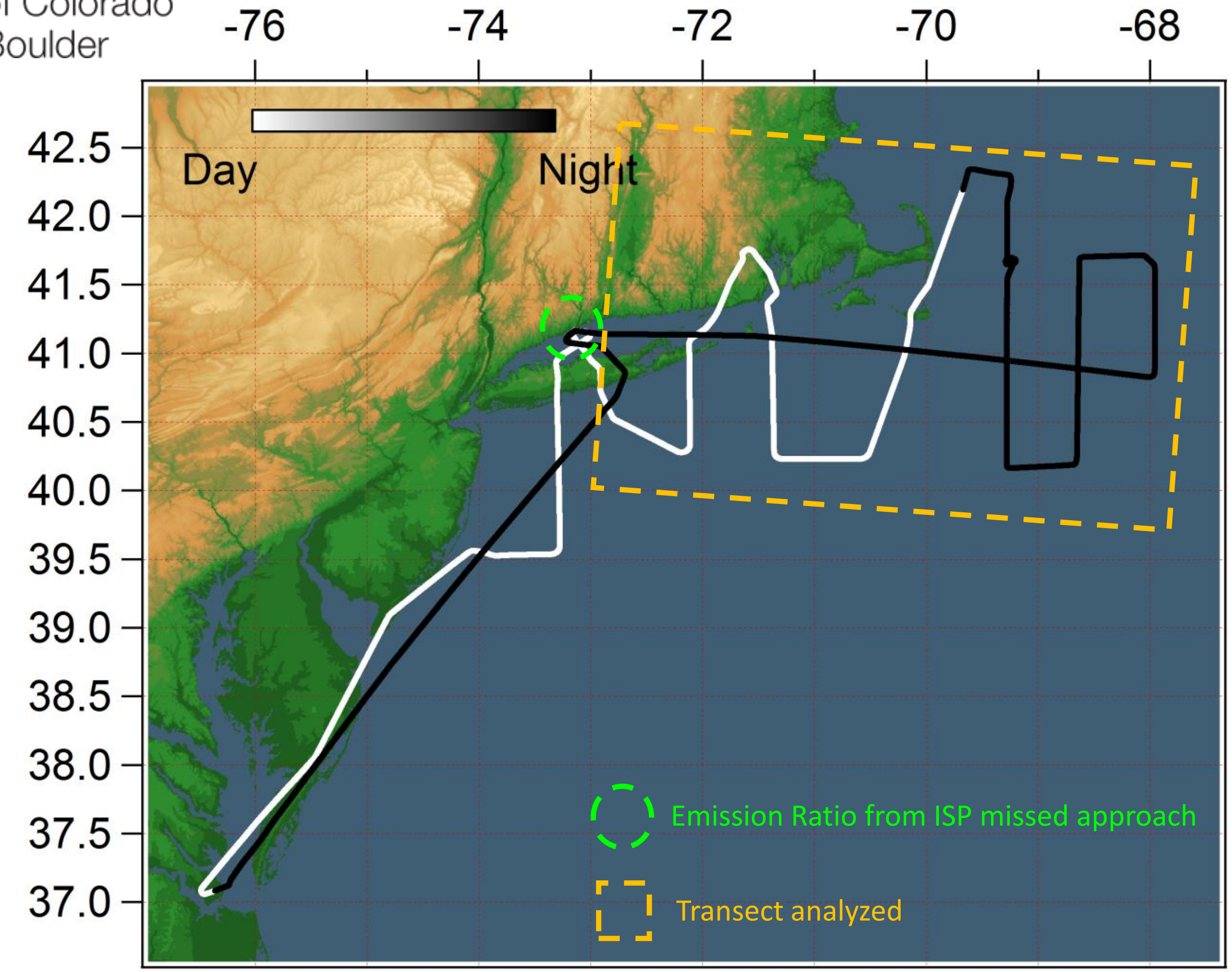
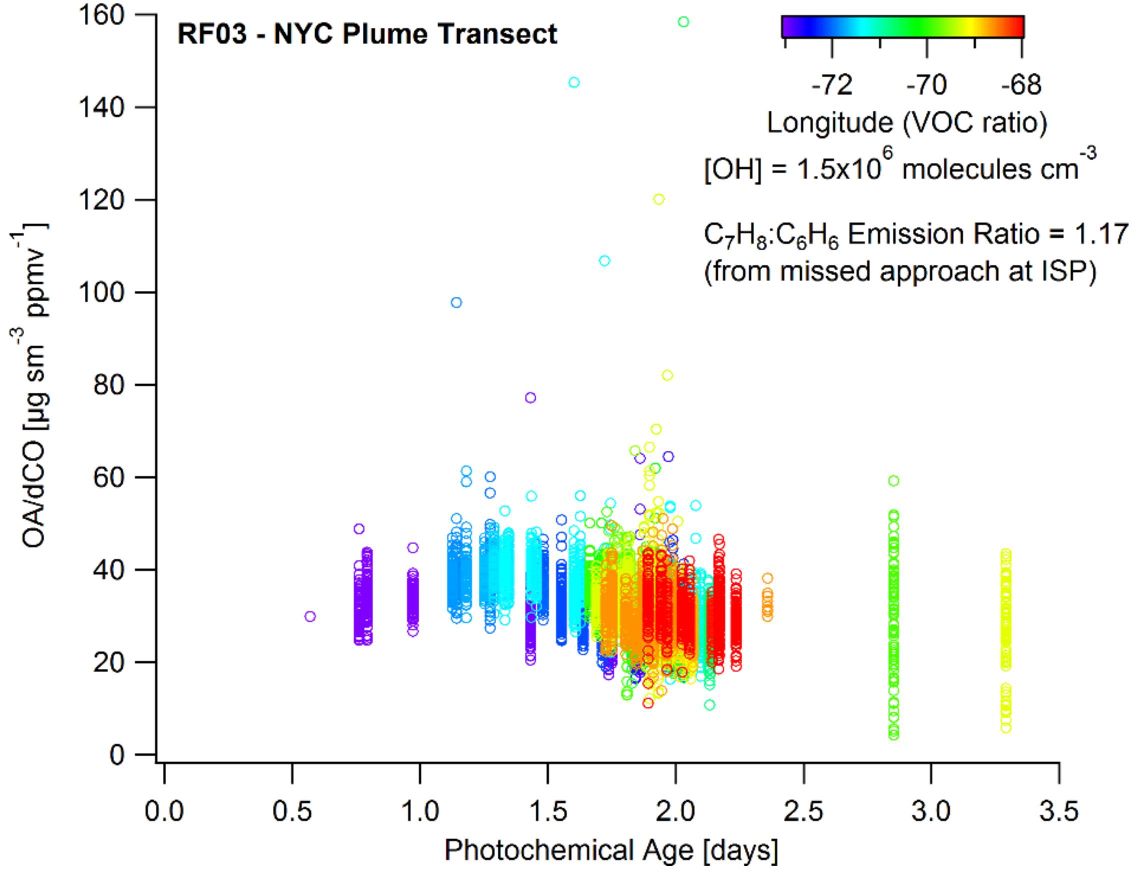
Moving Forward

- Why is OA/ΔCO lower in the winter?
  - Lack of SOA formation due to low radicals?
    - Is estimated photochemical age wrong?
  - Differences in mix of anthropogenic SOA precursors?
  - Higher losses? SV dry deposition? Wet deposition?
- Why is OA so oxidized, if radicals are low?
  - Very oxidized primary BBOA?
  - Look into timescales of OA oxidation near urban sources
  - OA oxidation in clouds?
- Look into measures of acidity downwind of power plant plumes

Thanks!

Photochemical Age – "NYC" Plume Transect RF03





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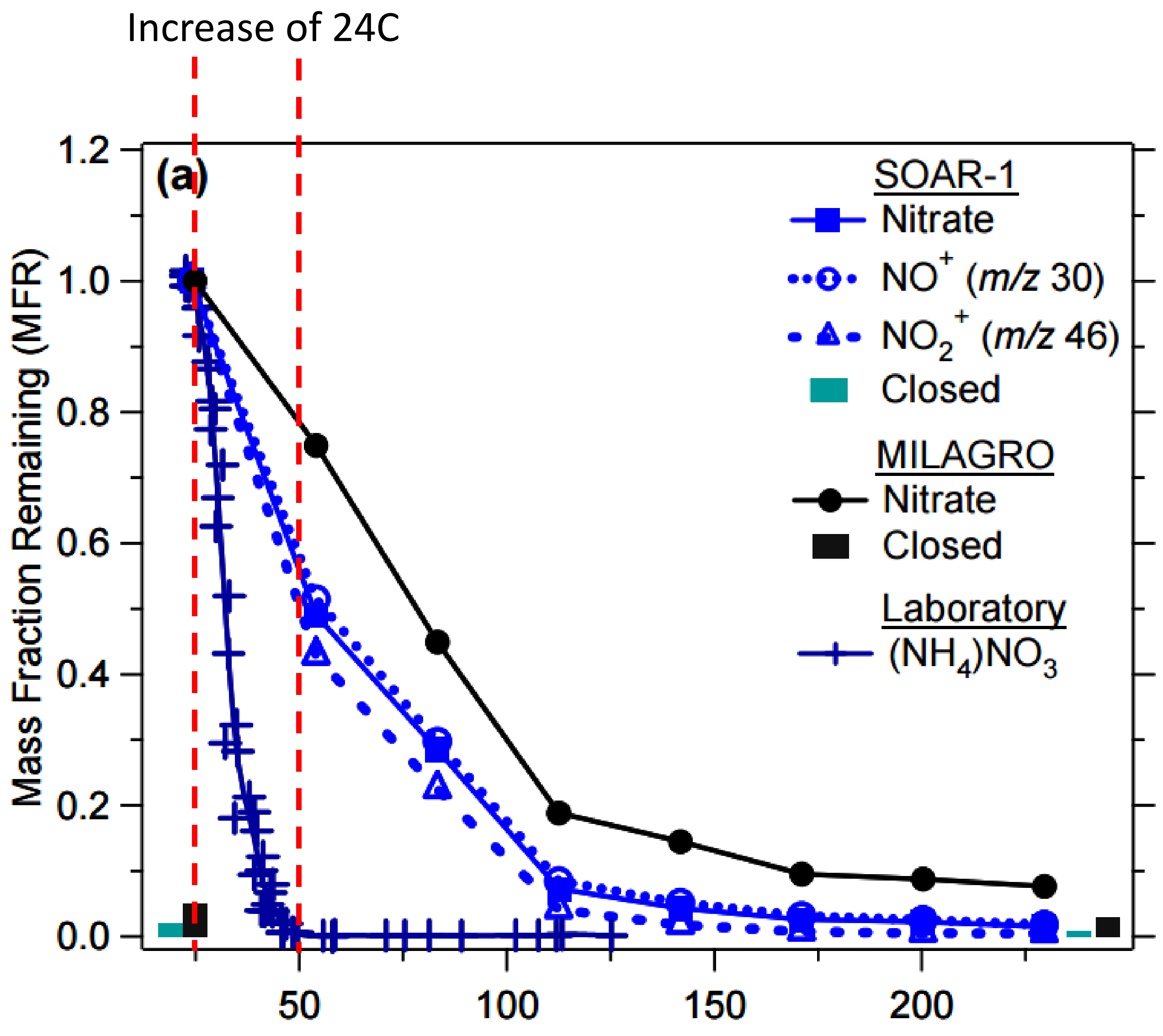
Warneke et al., JGR 2007

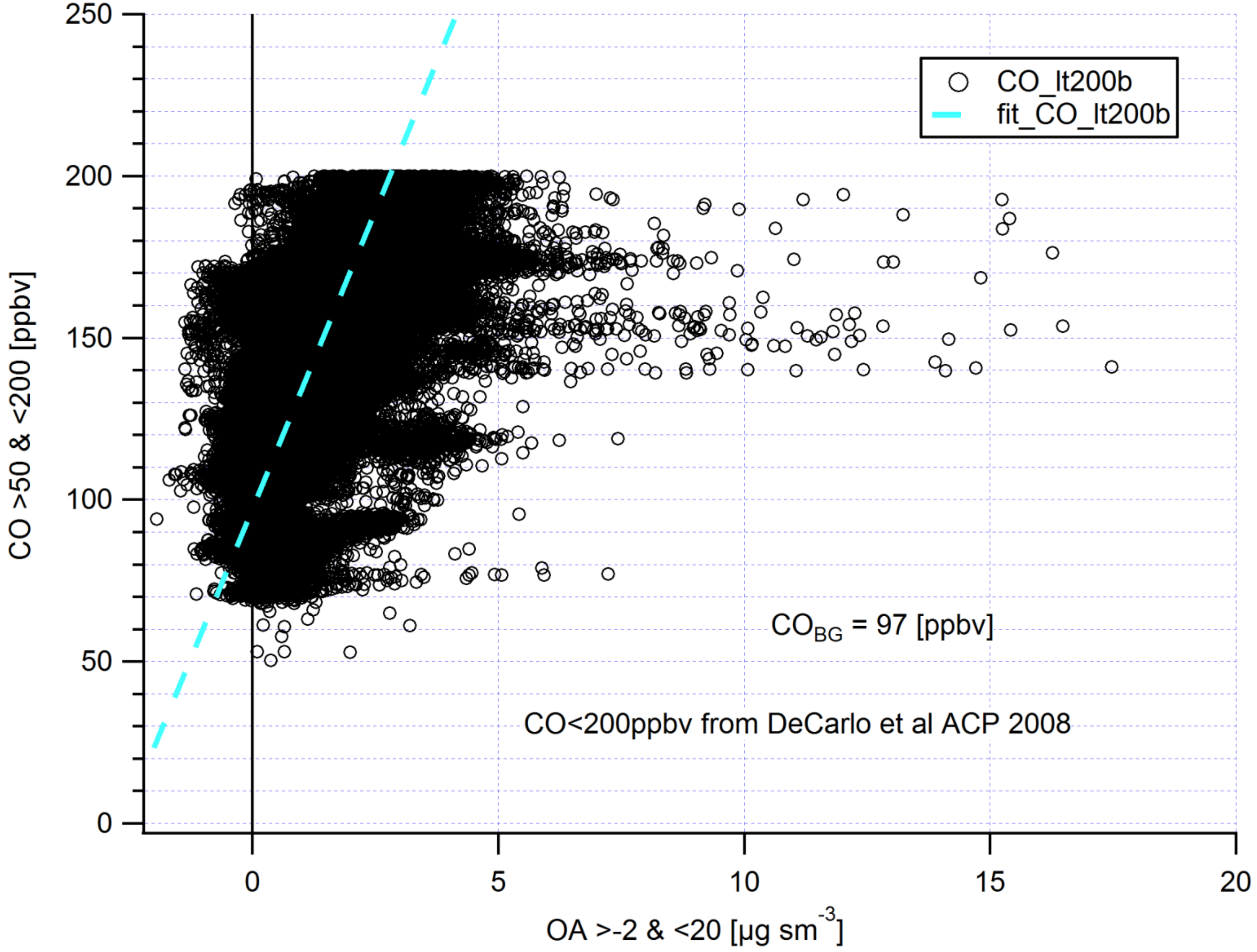
Nitrate evaporation in thermal denuder (~14 s)



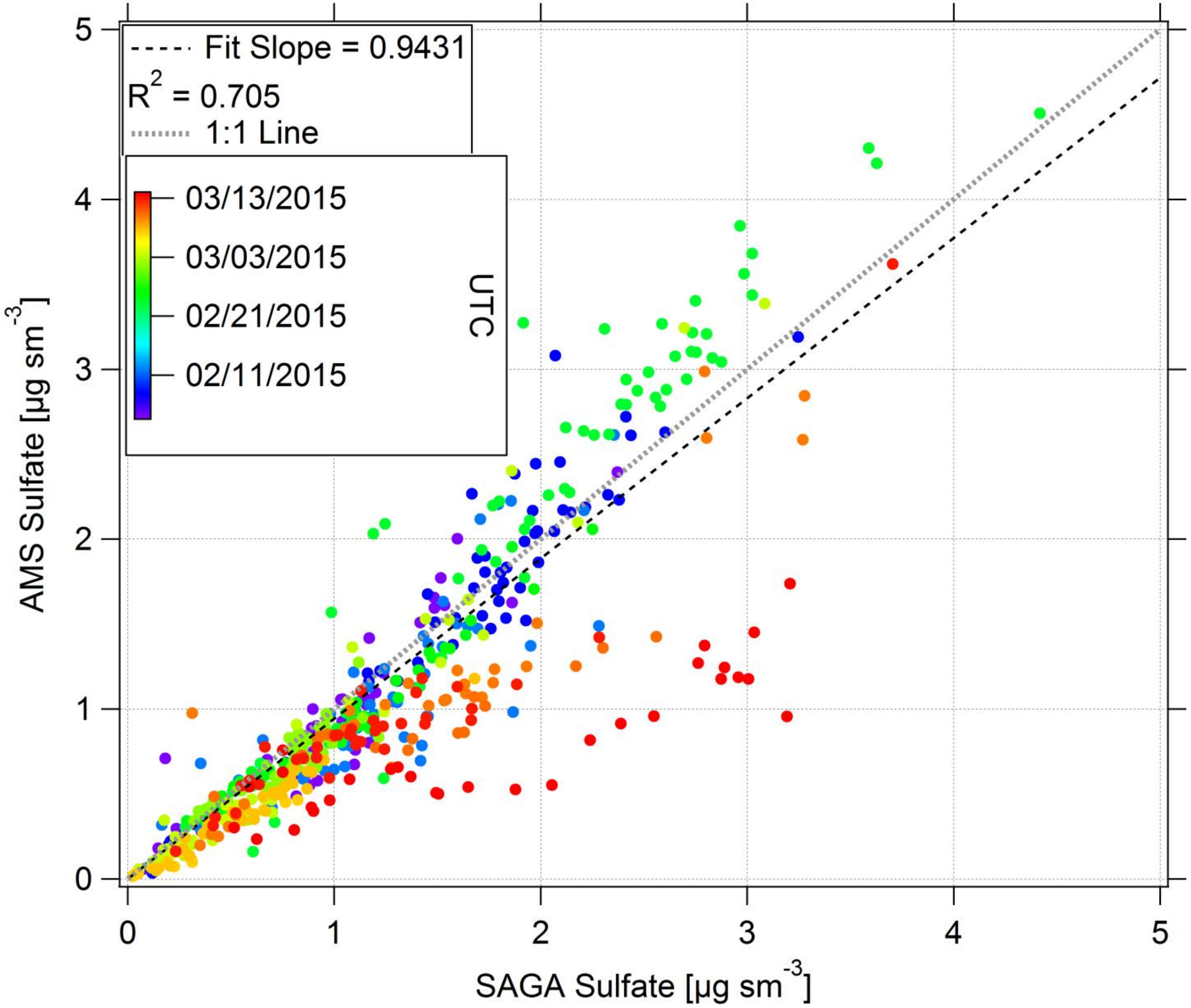
- Can lose 30-100% of nitrate in 14 s upon heating 25 C
- But different starting conditions than WINTER

Huffman et al., ACP 2009

Extra Slides:


250
200
150
100
50
0
CO >50 & <200 [ppbv]
0
5
10
15
20
OA >-2 & <20 [µg sm^{-3}]
CO_lt200b
fit_CO_lt200b
CO_{BG} = 97 [ppbv]
CO<200ppbv from DeCarlo et al ACP 2008

Instrument Comparisons: AMS & SAGA



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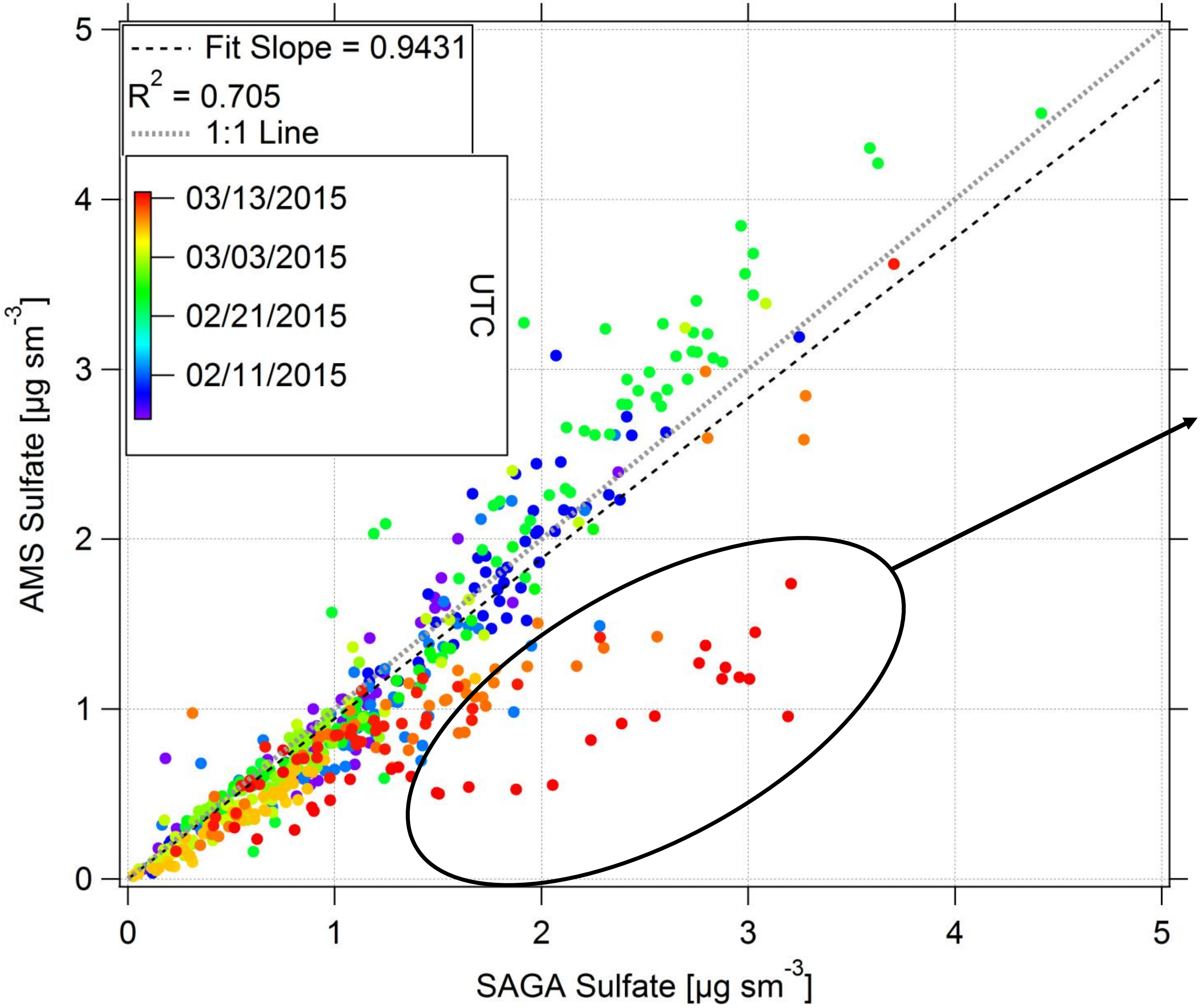
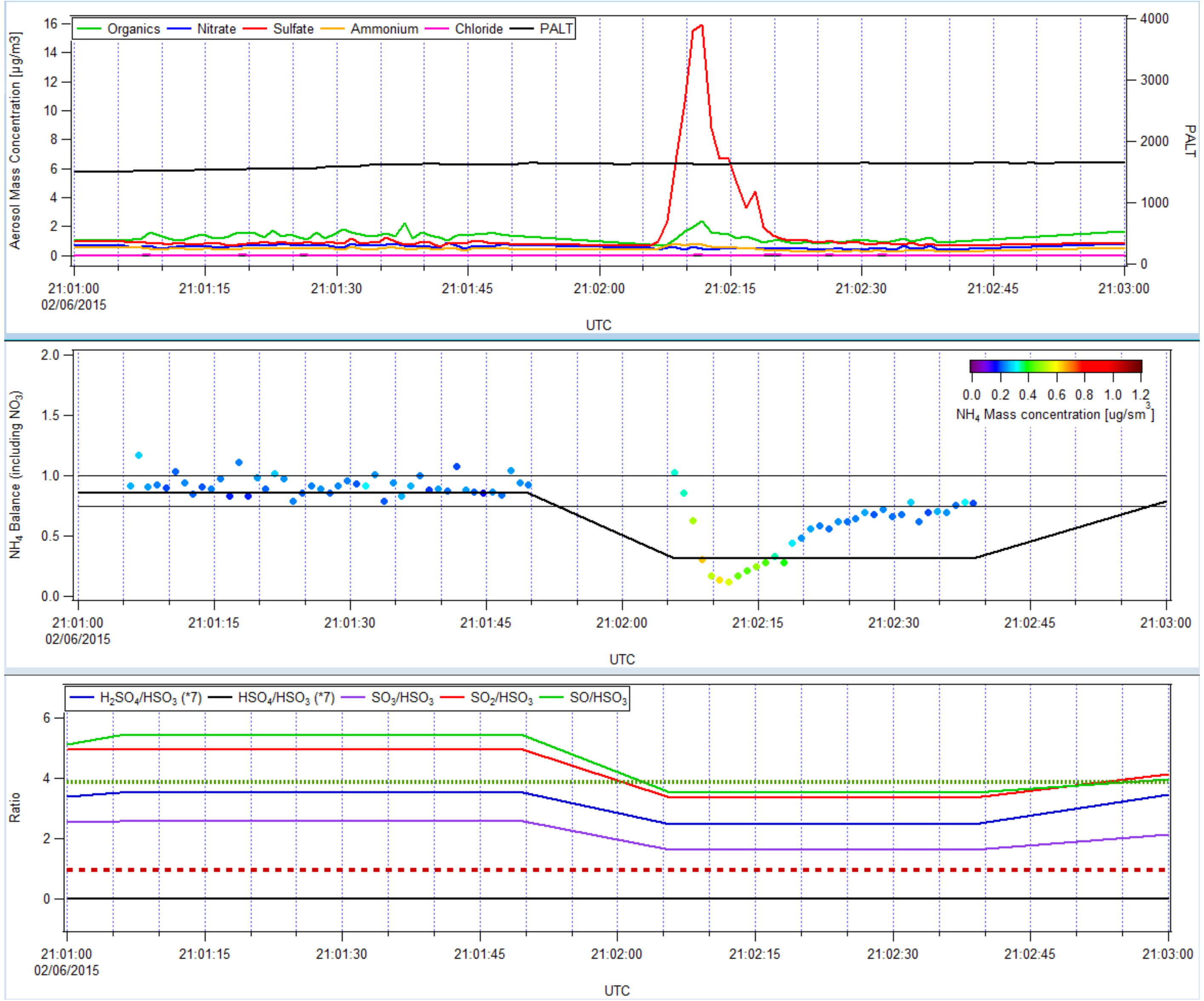
Instrument Comparisons: AMS & SAGA



- RF13 when over the ocean
- Per Jack: sea salt sulfate

Point Sources – Power Plants (RF02)



Point Sources – pH

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Insert Pedro’s new pH plots

Need to get him fresh data (waiting for NH_3 order)

Flight Summary

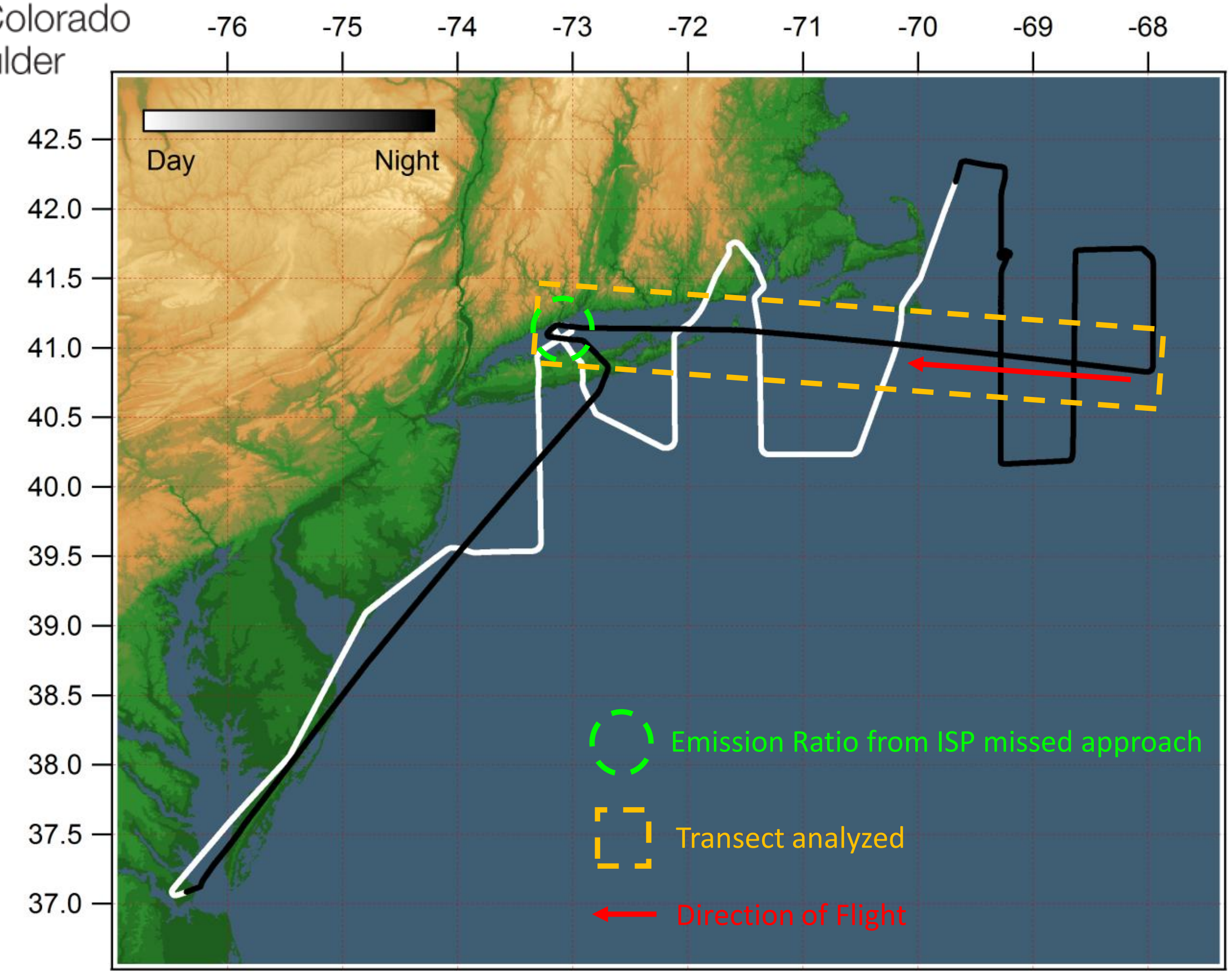
D2N = Day into night N2D = Night into Day

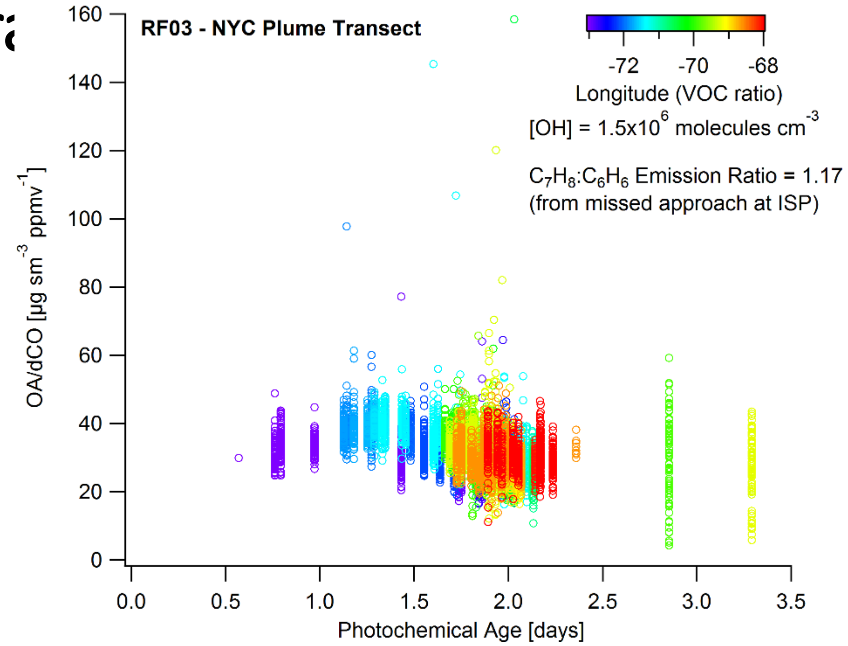
RF #	Flight Type	% Over Water	% Over Land	Approx. Hours After Sunrise	Approx. Hours After Sunset	Location
1	D2N	60	40	3	4.5	Long Island, Atlantic City
2	D2N	0	100	6.5	1	Ohio River Valley
3	D2N	98	2	3.5	4.5	Long Island and East
4	D2N	5	95	2.5	4.5	Crisscross eastern seaboard
AMS Down						
6	N2D	99	1	0.5	8.5	Offshore plumes
7	Night	1	99	0	7.5	Urban/Power plant PA to VA
8	N2D	97	3	5	3.5	Long Island (bow-ties)
9	N2D	0	100	6.5	2	PA (Urban and power plant)
10	N2D	0	100	0.5	7.5	Atlanta
11	D2N	20	80	5.5	1	Shale fields-> around Long Island
12	Day	0	100	7	0	Ohio River Valley
13	Day	95	5	6.25	0	Bermuda Triangle

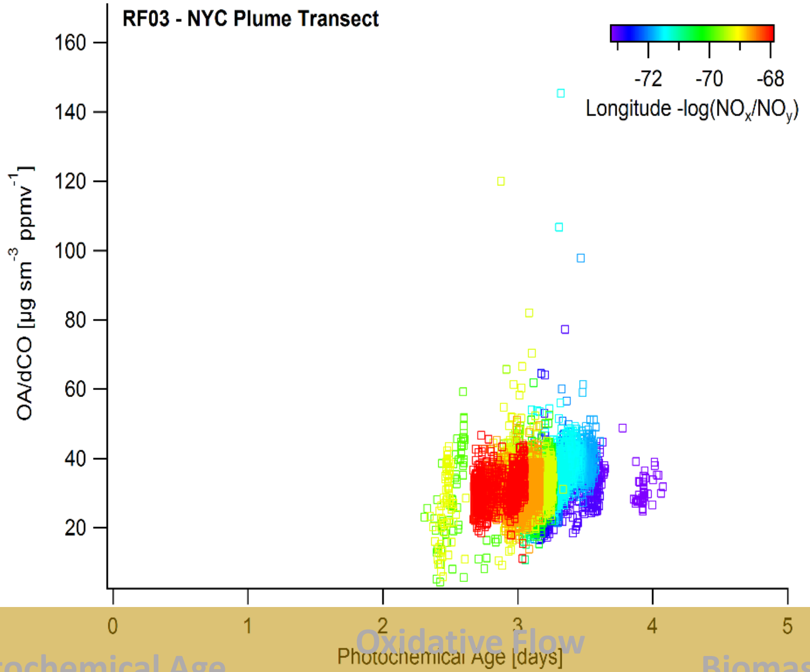
Total hours **55.25 hrs** **37 hrs**

Photochemical Age – NYC Tra

University of Colorado Boulder



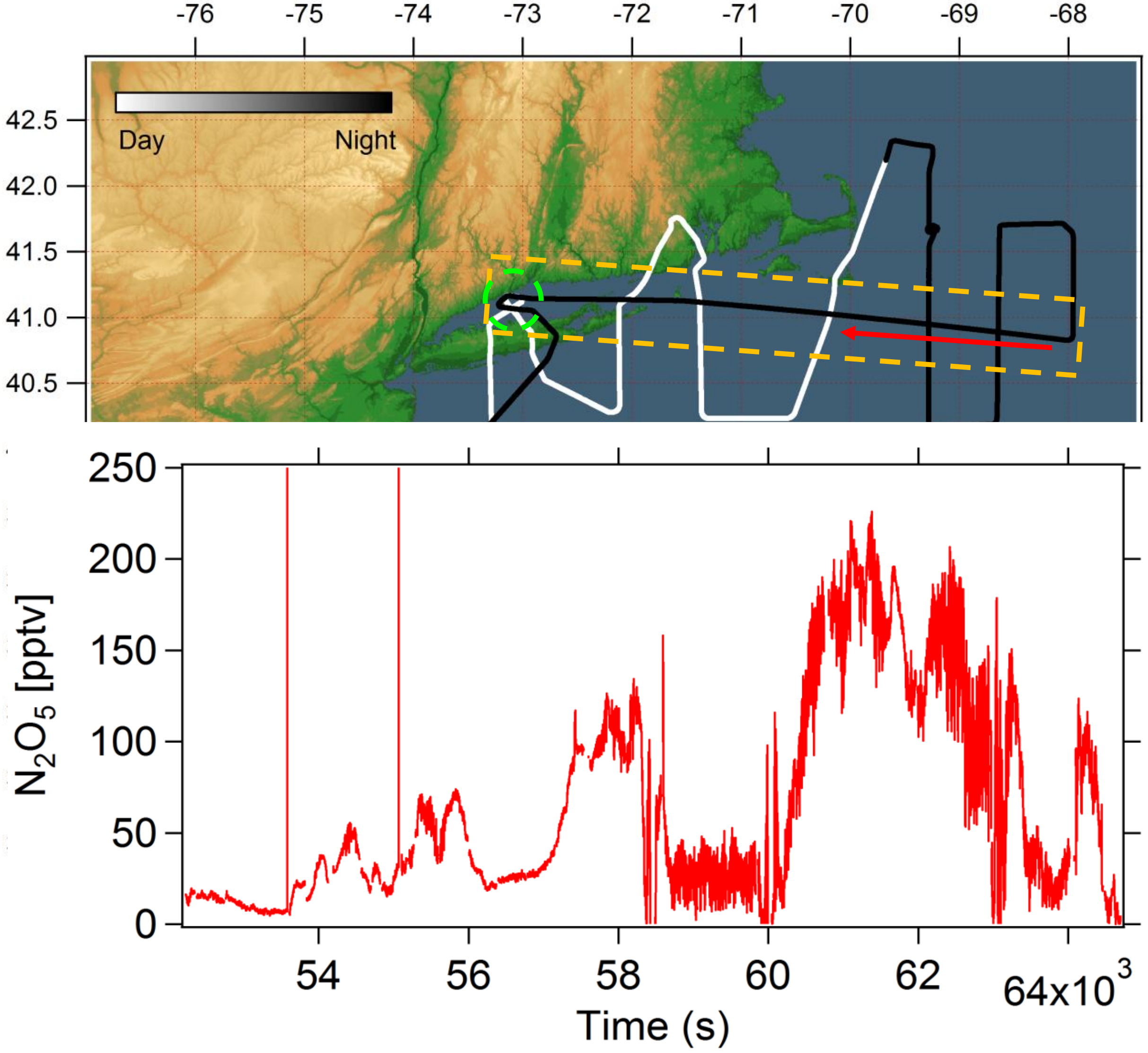


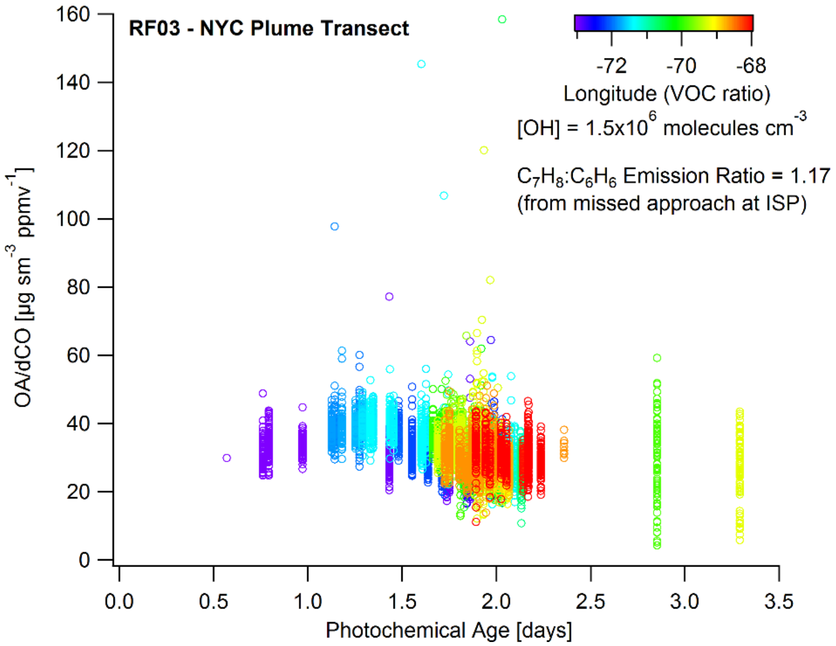


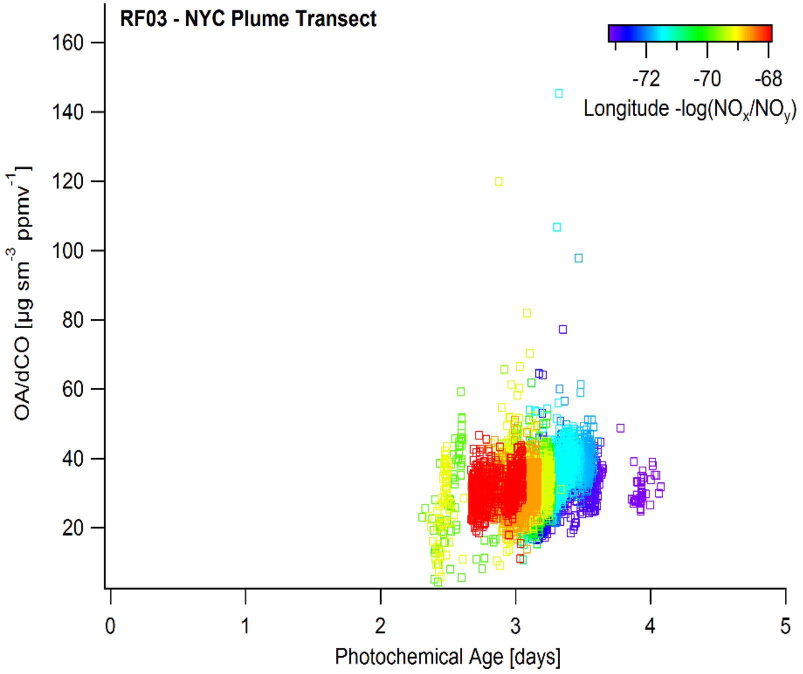
$$Age_{VOC} = \left(\frac{1}{OH*(k_{Tol}-k_{Ben})}\right) * \left[ln(emmision\ ratio) - ln\left(\frac{Tol}{Ben}\right)\right]$$

Warneke et al., JGR 2007

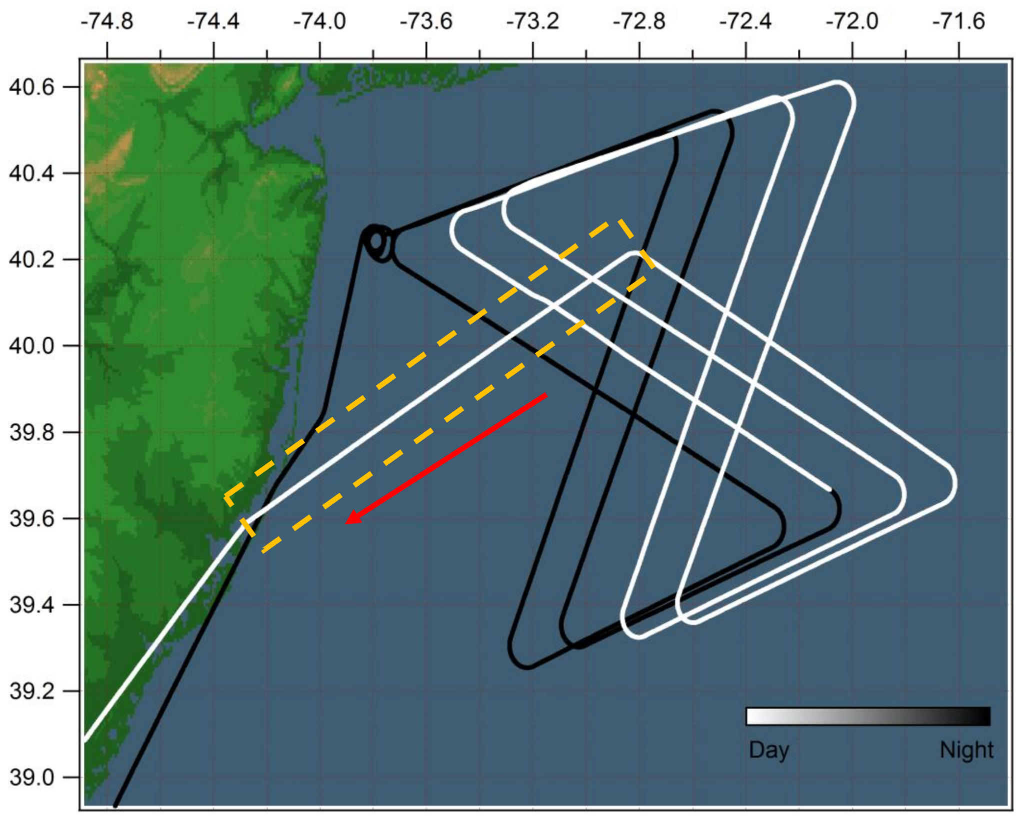
Photochemical Age – NYC Transect RF03

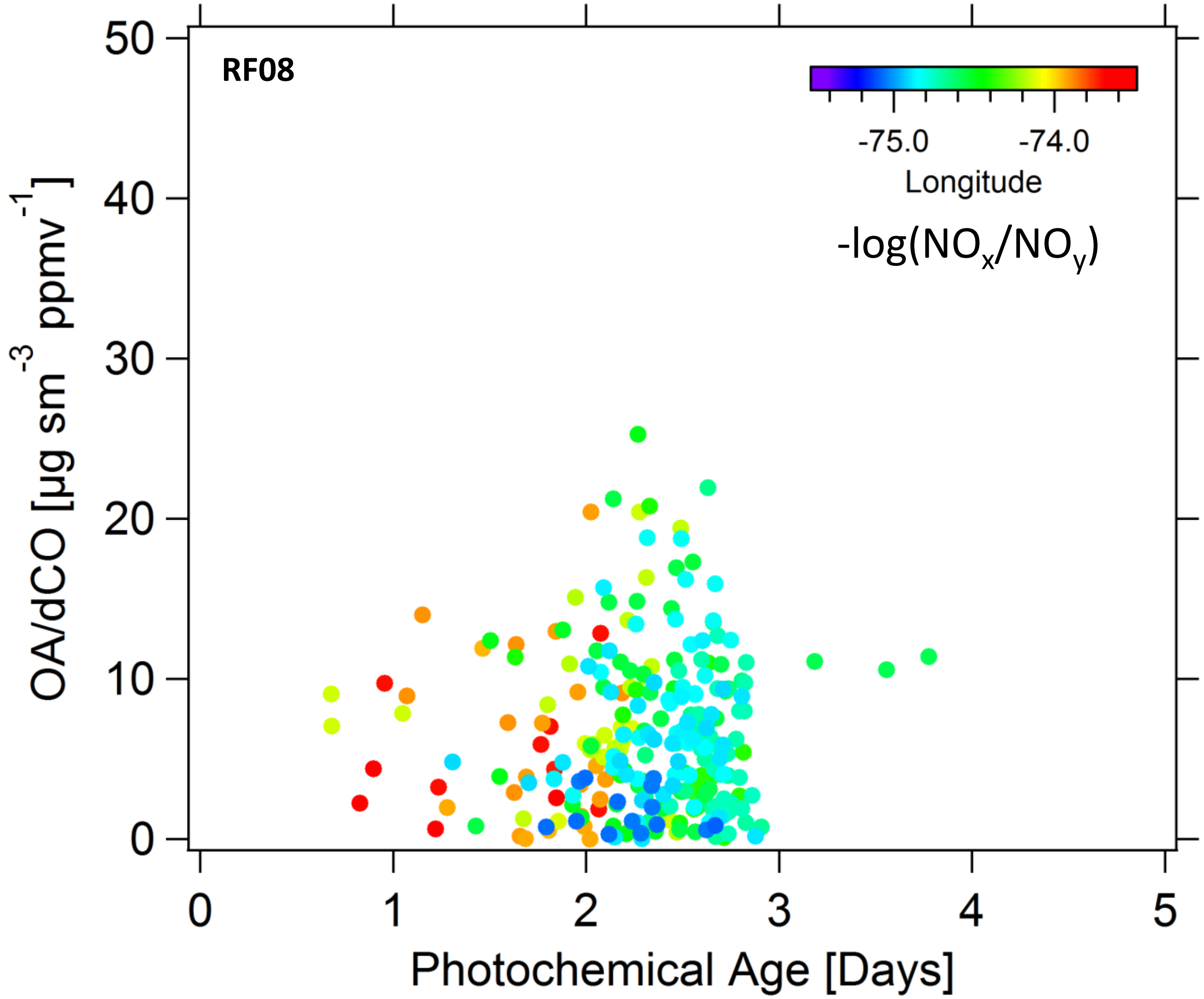




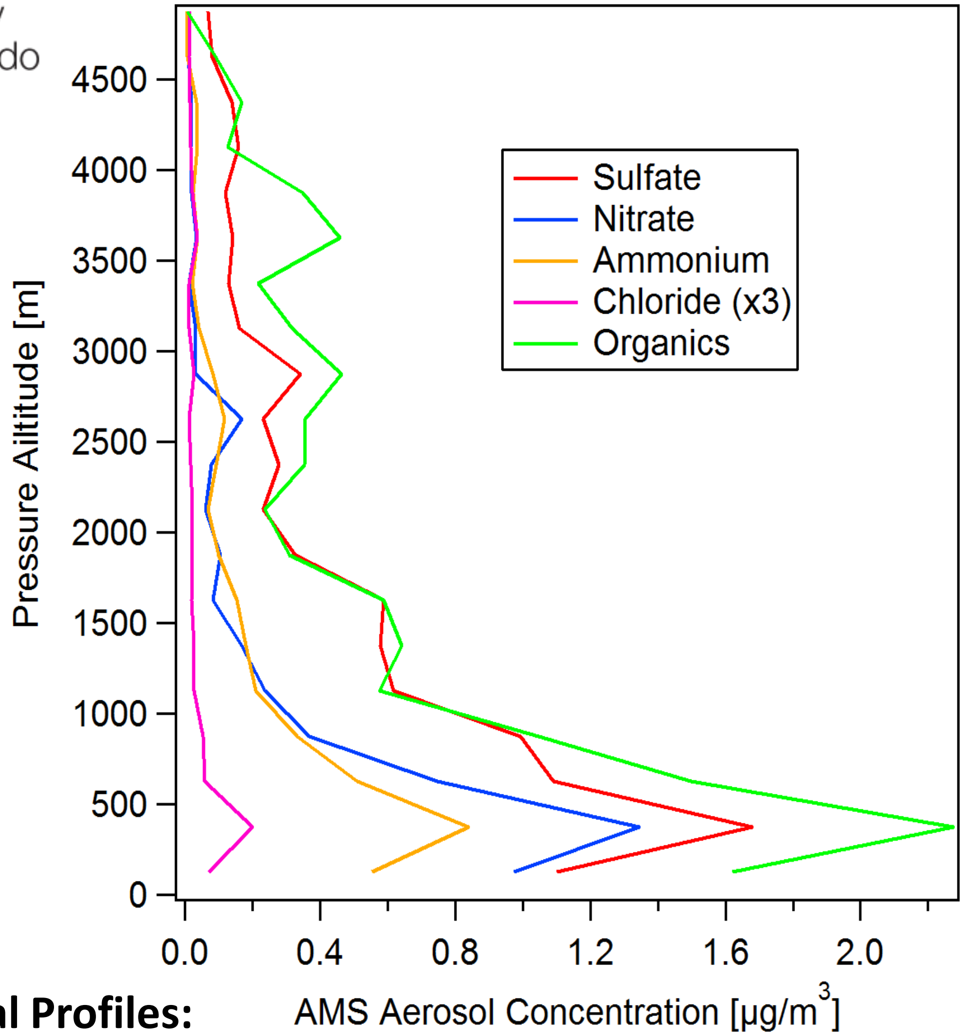


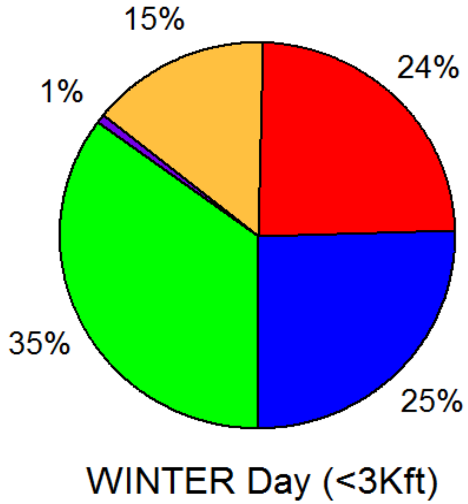
Photochemical Age - More NYC Outflow?

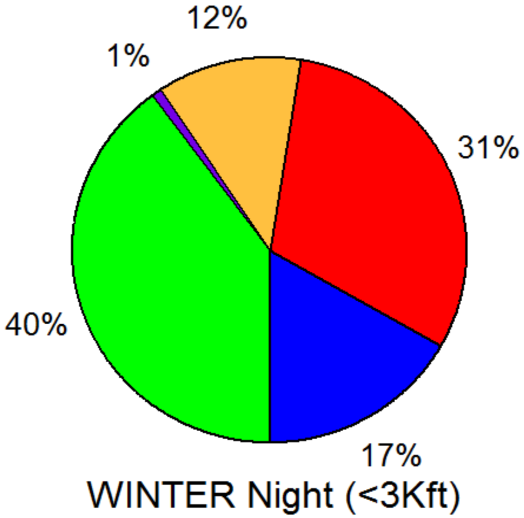




Campaign Averages







Fraction of OA and Inorganic Species:

- Larger fraction of NO_3 during the day
- Larger fraction of OA and sulfate at night

Vertical Profiles:

- Shows decreased boundary layer height
- Predominately regional background species (OA & Sulfate)
- Nitrate in shallower layer