Fast Submicron Aerosol Composition of Ambient & OH-Processed Air with the CU+HAIS AMS

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University of Colorado at Boulder

WINTER Science Meeting, NCAR
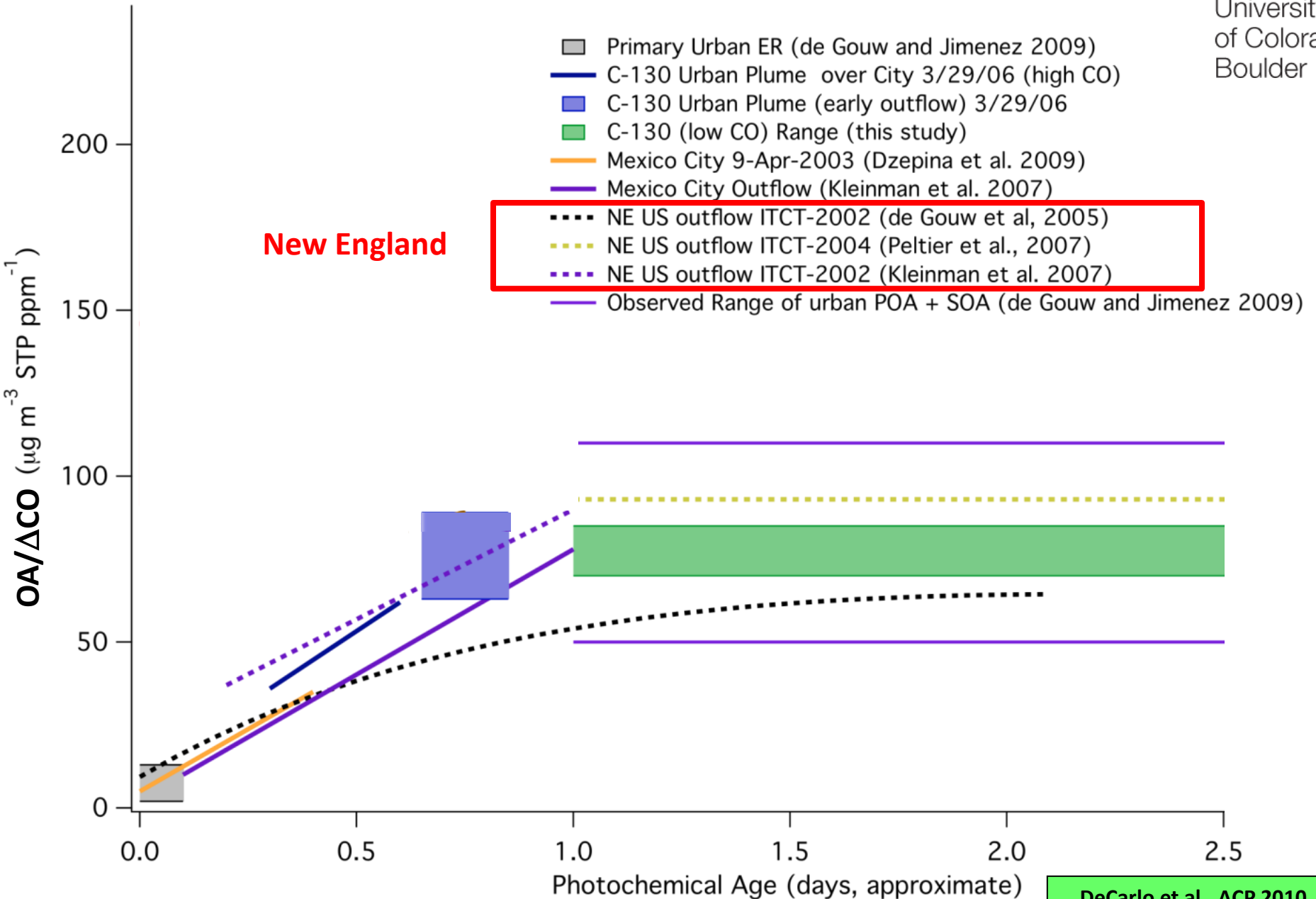Boulder, Nov 7th 2014

Outline

- **Scientific Goals**
  - **SOA Formation in polluted winter conditions**
    - **Ambient data vs. summer?**
    - **First aircraft deployment of OFR-AMS**
    - **Aerosol organic nitrate**
- Technical background
  - Summary of data products & capabilities
    - Lots of improvements over original HAIS AMS & AMSs flown by other groups
  - Gaps for a couple of reasons
    - Let us know when those would hurt, can skip them

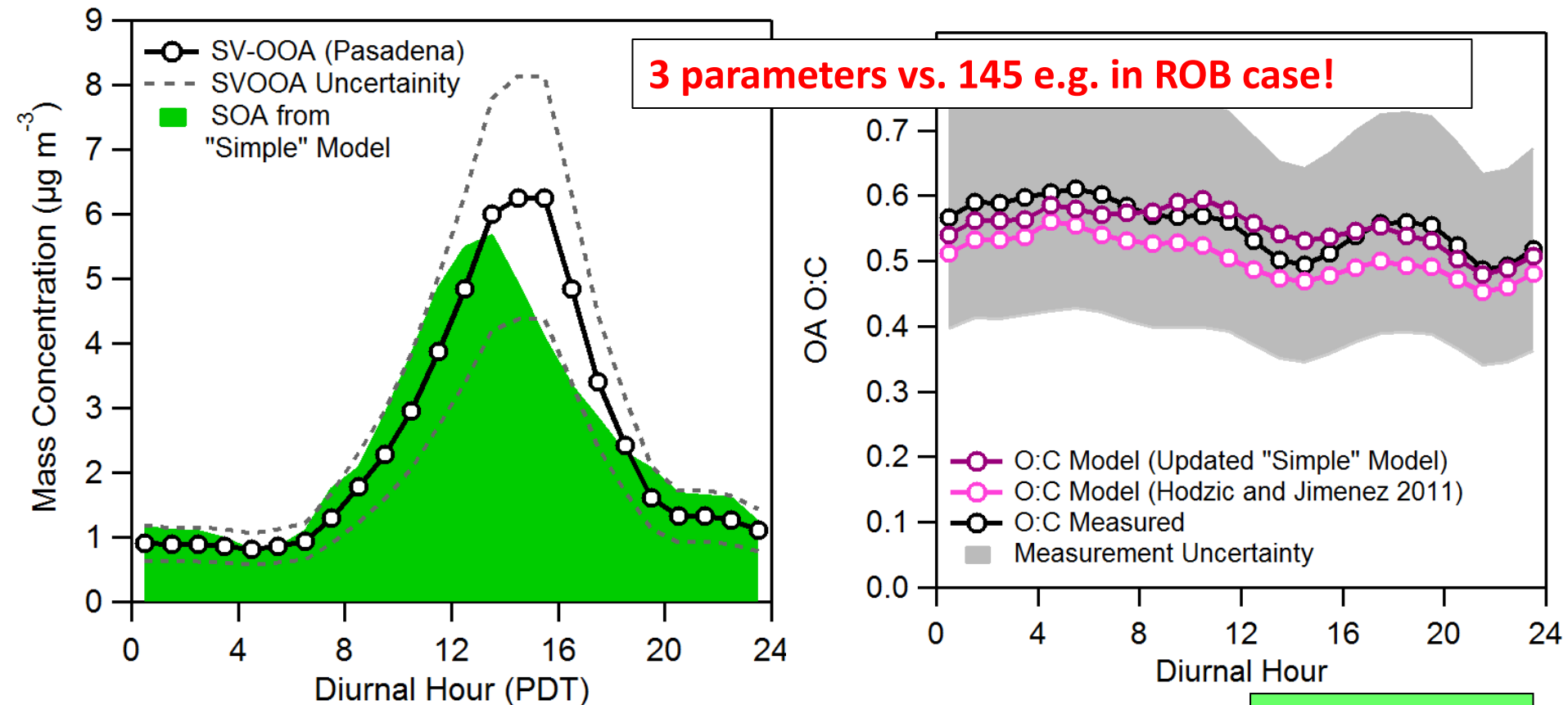# SOA in Polluted Air in Previous Studies

University of Colorado Boulder

Legend:
- ☐ Primary Urban ER (de Gouw and Jimenez 2009)
- C-130 Urban Plume over City 3/29/06 (high CO)
- ☐ C-130 Urban Plume (early outflow) 3/29/06
- ☐ C-130 (low CO) Range (this study)
- Mexico City 9-Apr-2003 (Dzepina et al. 2009)
- Mexico City Outflow (Kleinman et al. 2007)
- ···· NE US outflow ITCT-2002 (de Gouw et al, 2005)
- ···· NE US outflow ITCT-2004 (Peltier et al., 2007)
- ···· NE US outflow ITCT-2002 (Kleinman et al. 2007)
- Observed Range of urban POA + SOA (de Gouw and Jimenez 2009)

New England

Y-axis: **OA/ΔCO** ($\mu g\ m^{-3}$ STP ppm^{-1})

X-axis: Photochemical Age (days, approximate)

DeCarlo et al., ACP 2010

SIMPLE model of Urban SOA

- Precursor VOC* emitted prop. to CO = 80 μg m^{-3} ppmv^{-1}

- VOC* + OH → SOA, with k = 1.25 x 10^{-11}

- Similar parameters for Mexico City (Hodzic & Jimenez, GMD 2011) & LA (Hayes et al., ACPD2014)

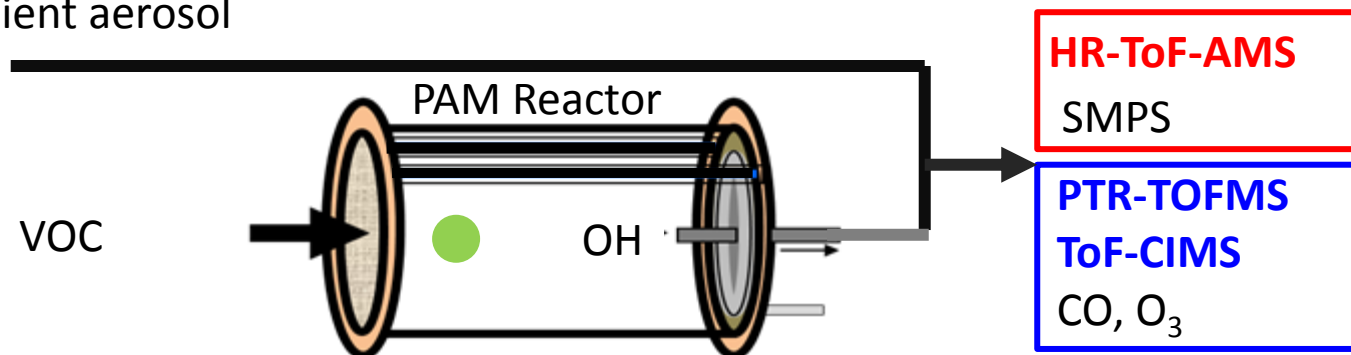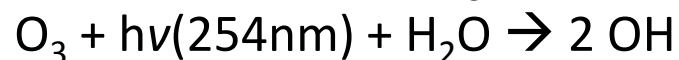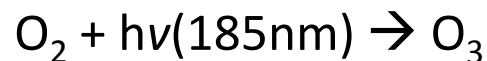**3 parameters vs. 145 e.g. in ROB case!**

Hayes et al., ACPD, submitted 2014

Oxidation Flow Reactor (OFR)

Ambient aerosol

PAM Reactor

VOC

OH

HR-ToF-AMS
SMPS

PTR-TOFMS
ToF-CIMS
CO, O_3

❑ OH Production:

$$O_2 + h\nu(185nm) \rightarrow O_3$$
$$O_3 + h\nu(254nm) + H_2O \rightarrow 2\ OH$$
$$H_2O + h\nu(185nm) \rightarrow OH$$

❑ OH exposure range: 0 up to 10^{10} - 10^{13} molec. cm^{-3} s

Ambient OH ~ 1.5×10^6 molec. cm^{-3}
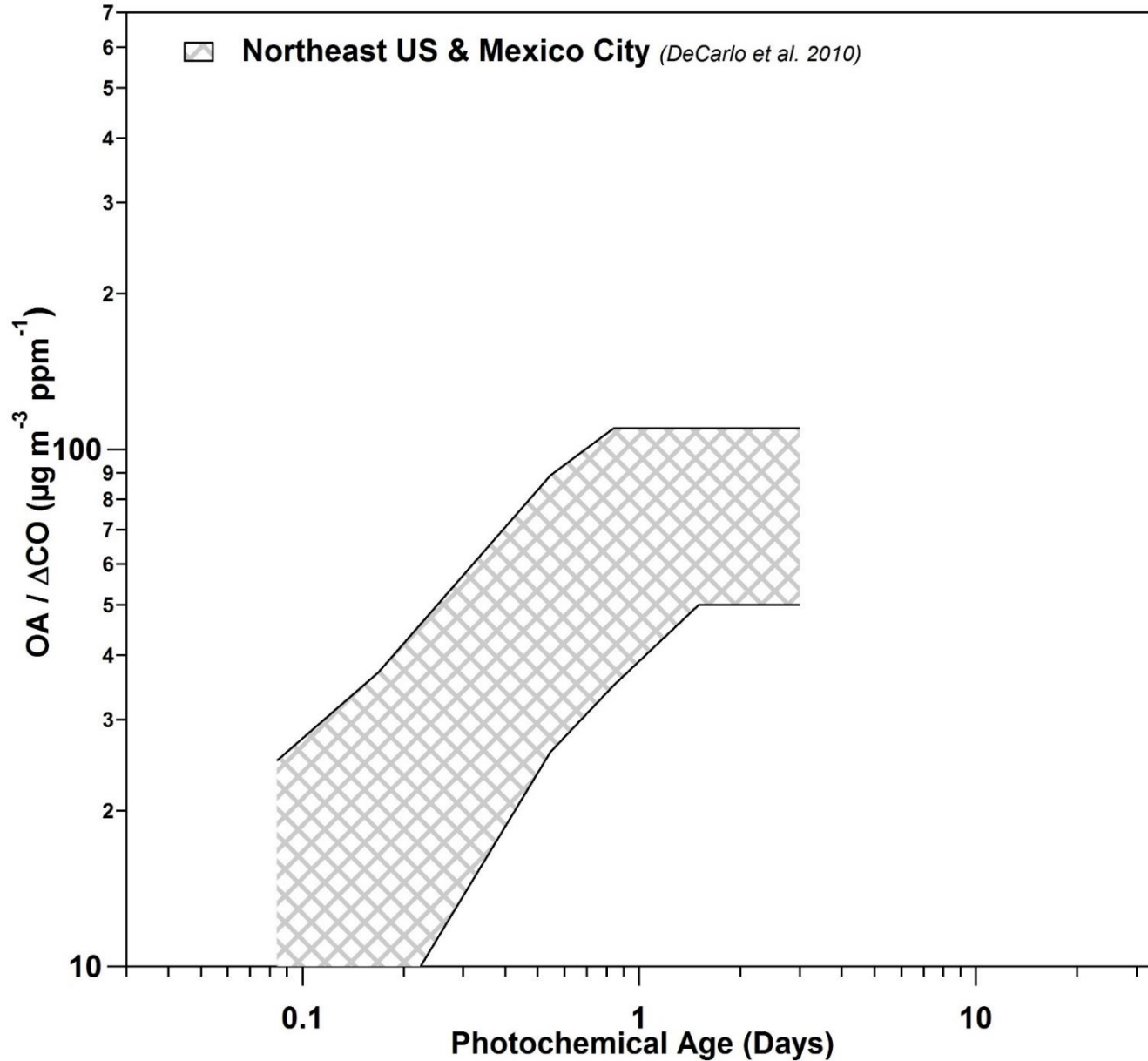
Photochemical aging: several hours to several weeks

❑ O_3 OFR: add O_3 w/o light

❑ NO_3 OFR: $N_2O_5 \rightarrow NO_2 + NO_3$

PAM reactor: **Kang et al., ACP 2007, 2011; Lambe et al., AMT 2011**

Our work: **Ortega et al. ACP 2013, Li et al. ES&T 2013; Li et al., JPCA submitted 2014; Palm et al., Li et al., Hu et al. Peng et al., Ortega et al., in prep.**
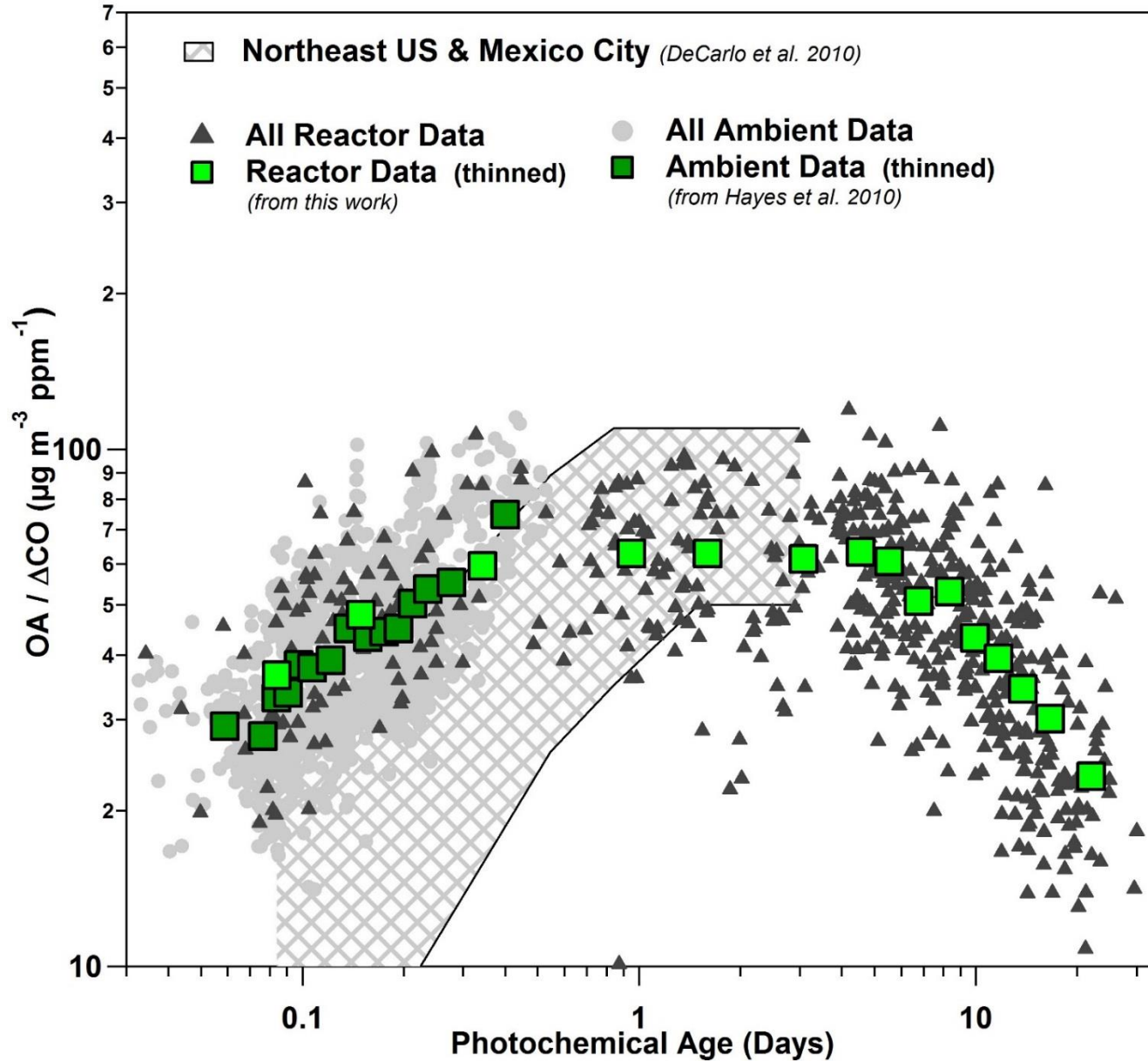
OFR: evolution of Urban SOA

Northeast US & Mexico City (DeCarlo et al. 2010)

y-axis: OA / ΔCO (μg m^{-3} ppm^{-1})

x-axis: Photochemical Age (Days)

OFR: evolution of Urban SOA

Northeast US & Mexico City (DeCarlo et al. 2010)

All Ambient Data

Ambient Data (thinned)
(from Hayes et al. 2010)
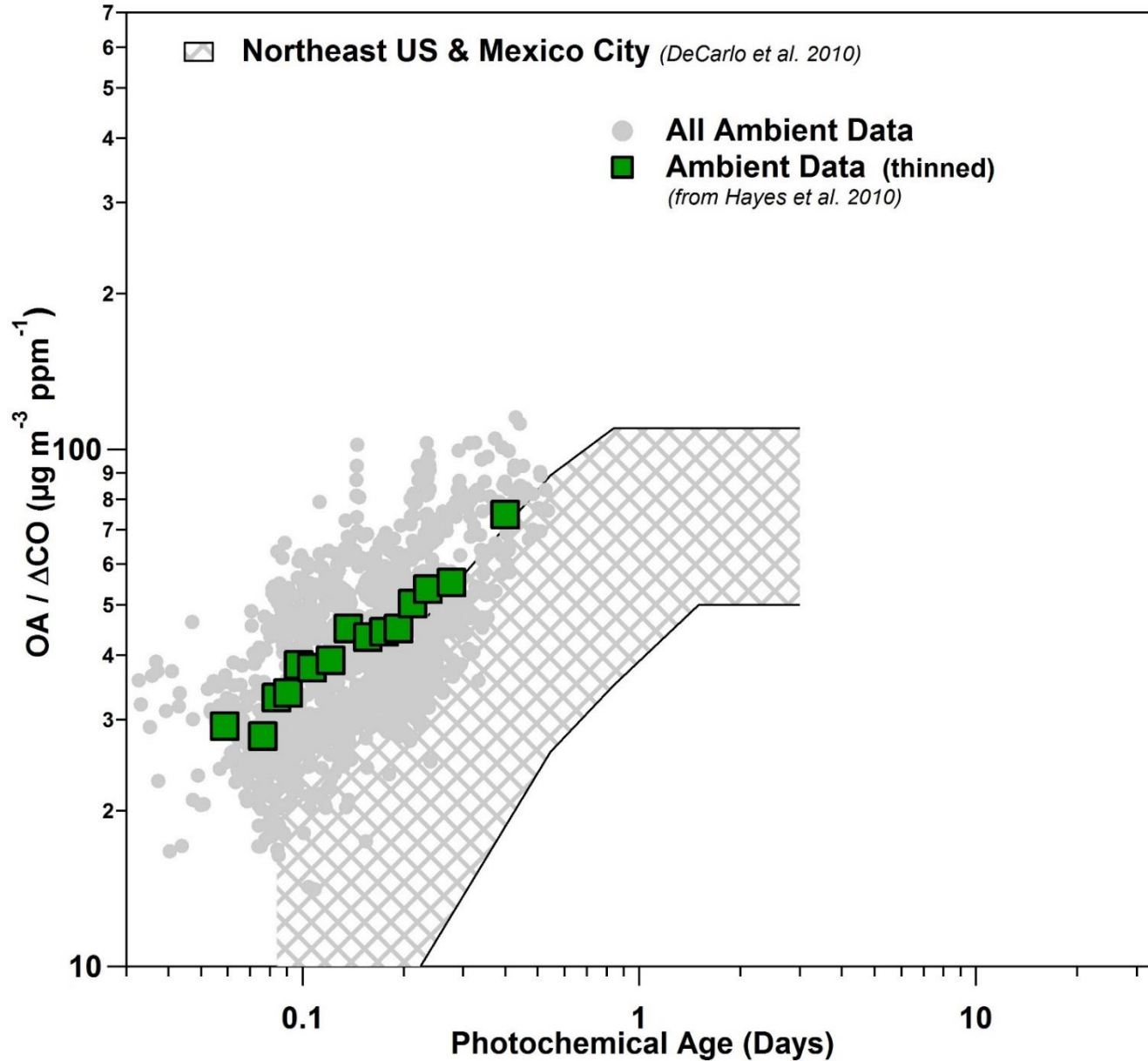
Hayes et al., JGR 2013;
Ortega et al., in prep.

OFR: evolution of Urban SOA

Organic Nitrate Fraction

- Aerosol RONO$_2$ at 1 min resolution.

- Based on calibration of NO$_2^+$/NO$^+$ ratios

- Validated in Fry et al (ACP 2013)

- Results from 4 campaigns confirm usefulness

- Interference if there is *submicron* NaNO$_3$ (reacted sea salt)
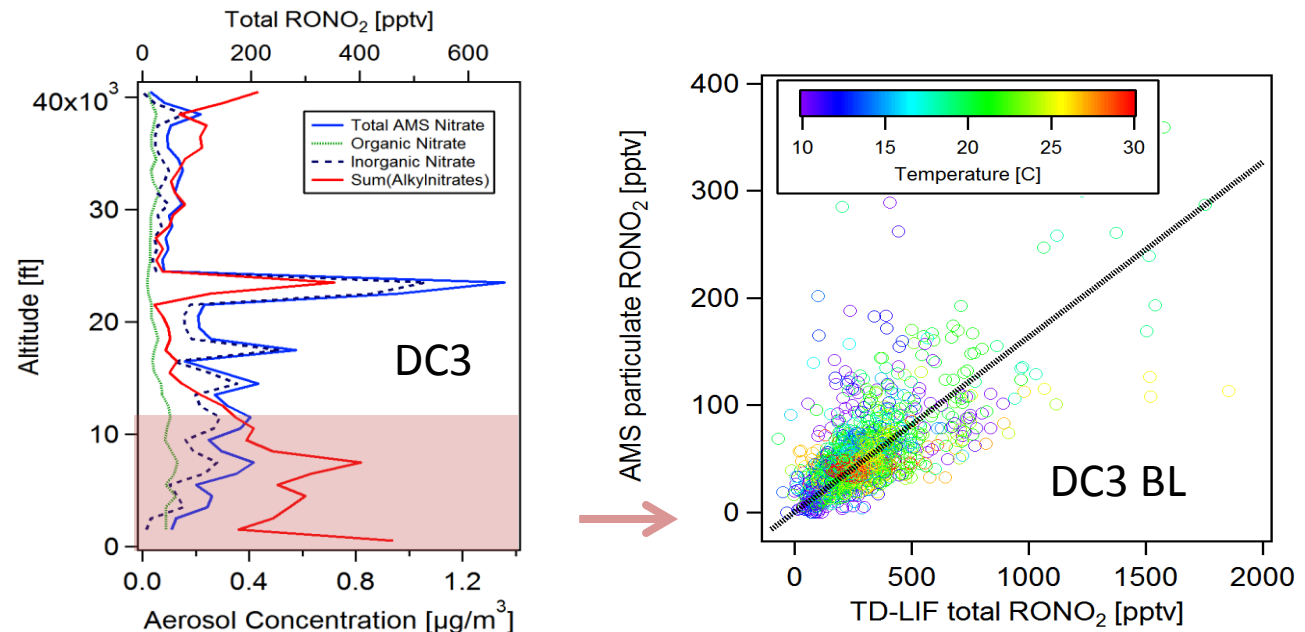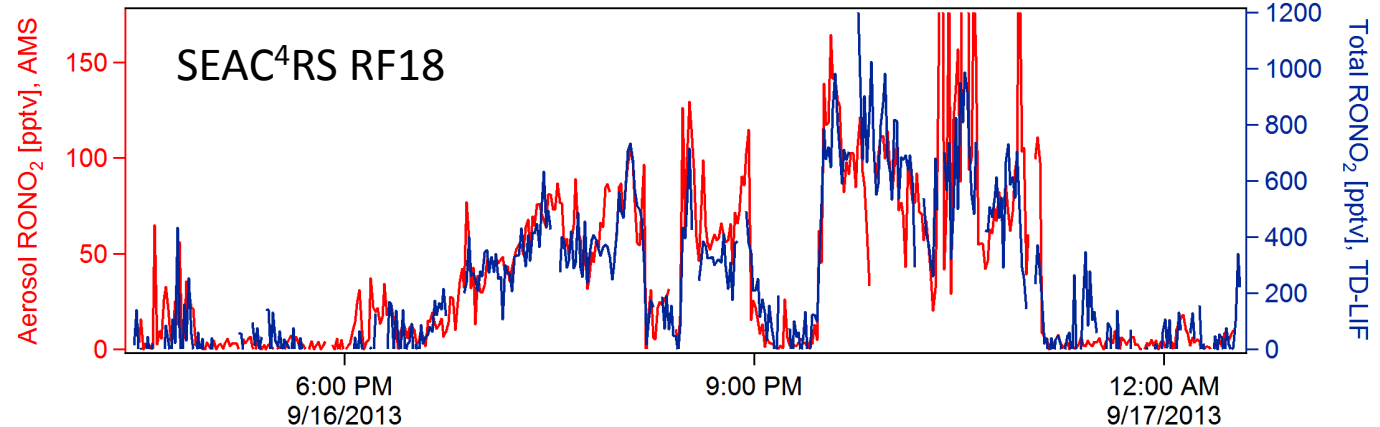
SEAC^{4}RS RF18

DC3

DC3 BL

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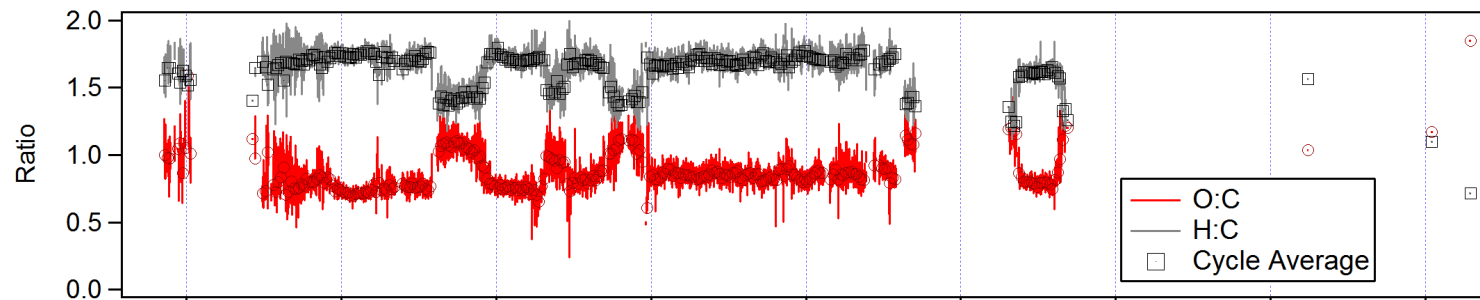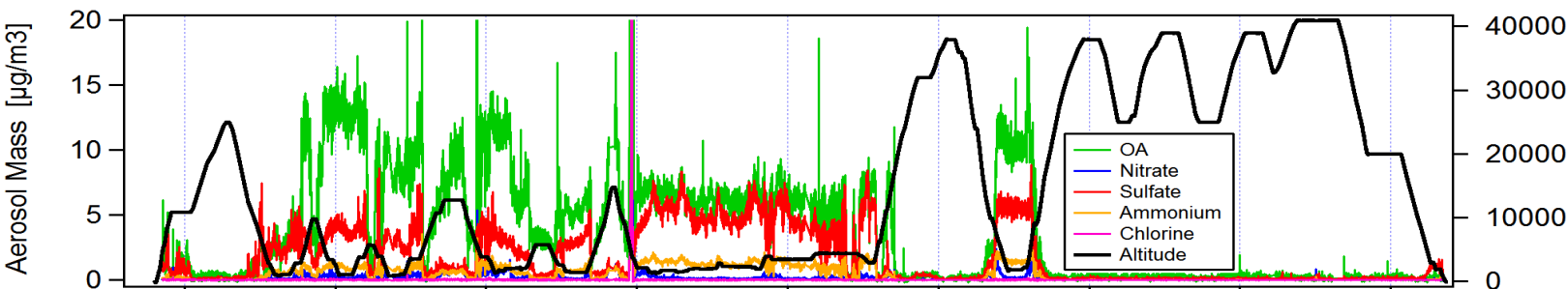   - • Let us know when those would hurt, can skip them

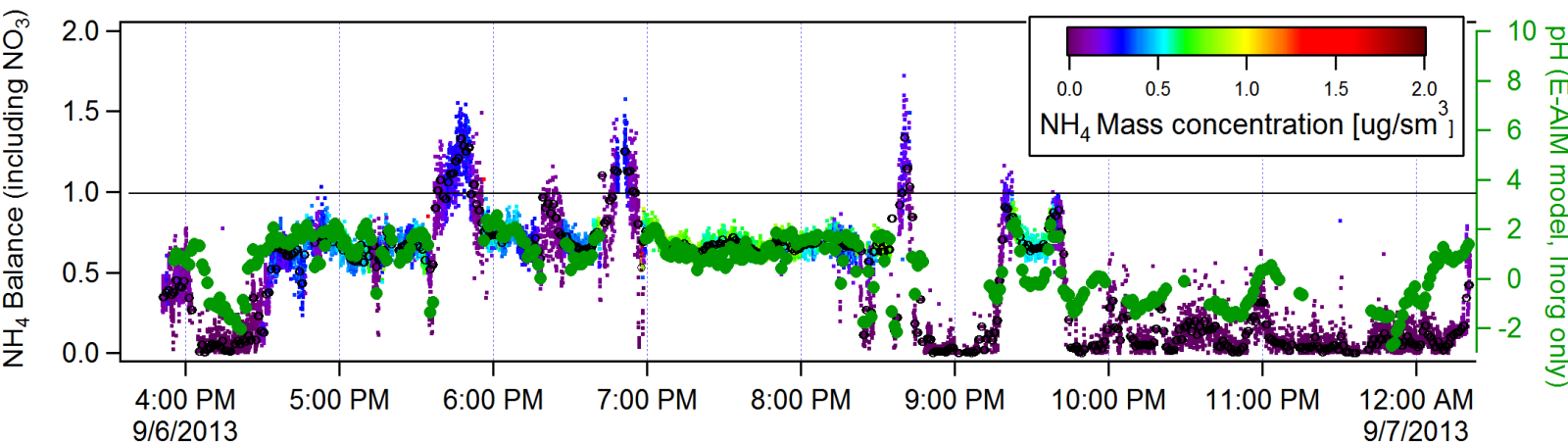# HAIS cToF vs CU HR-ToF AMS
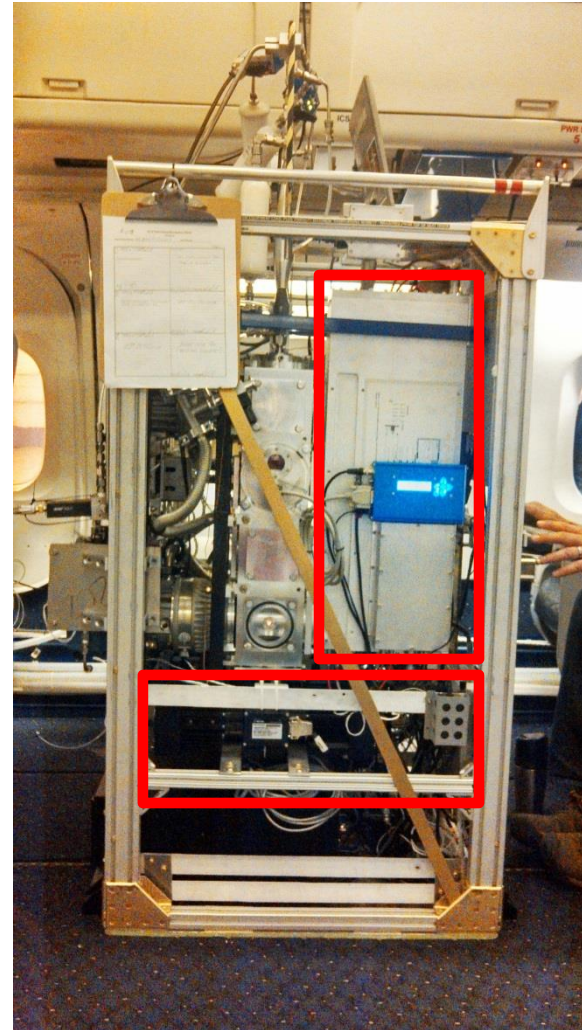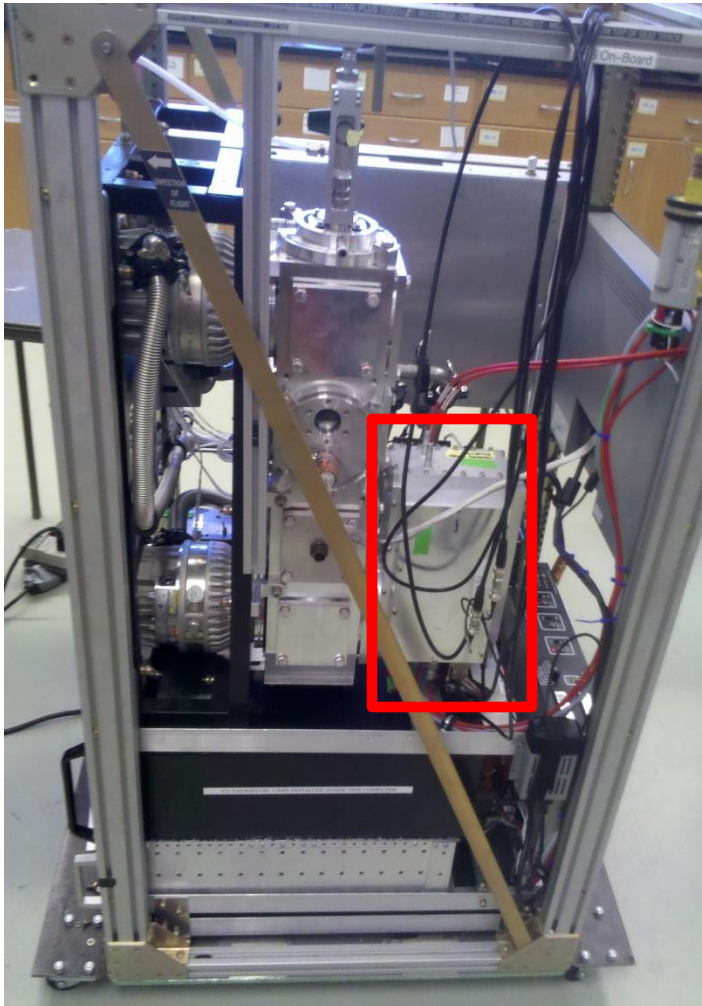
Standard AMS Data Products

University
of Colorado
Boulder

Aerosol
Species

OA Chemical
Age/Oxidation

Acidity

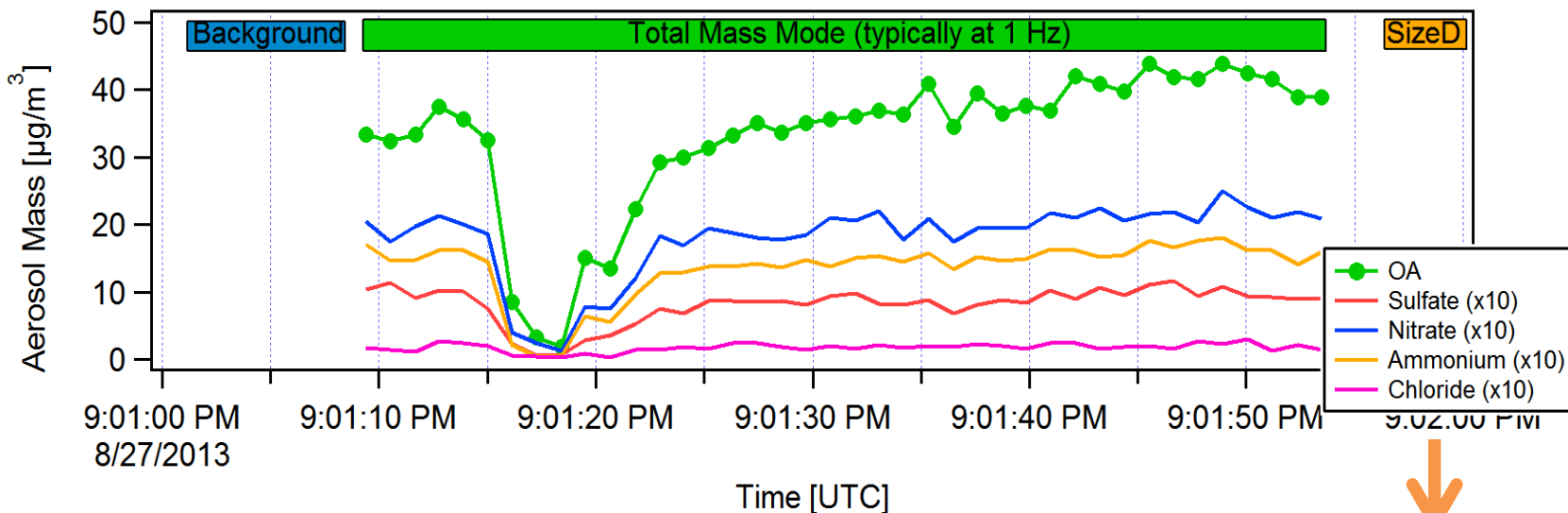Species and
markers are
available in RT
during flight!

Also reported: f_{43}, f_{44} (organic acids), f_{57} (HOA), f_{60} (BBOA), f_{82} (IEPOX-SOA)
PMF factors, while involved to derive, can be provided as well

AMS Data Acquisition

- 45 s out of every minute are spend in total mass mode
- Resolution is typically 1s, could be higher if desired
- 6 s background, can be suppressed if needed (NEW!)
- Data is analyzed AND reported for both 1 s and 1 min intervals

- 5 s are spend in size-segregated mode. S/N is typically too low for single run analysis, but acceptable over longer intervals (10-20 min)
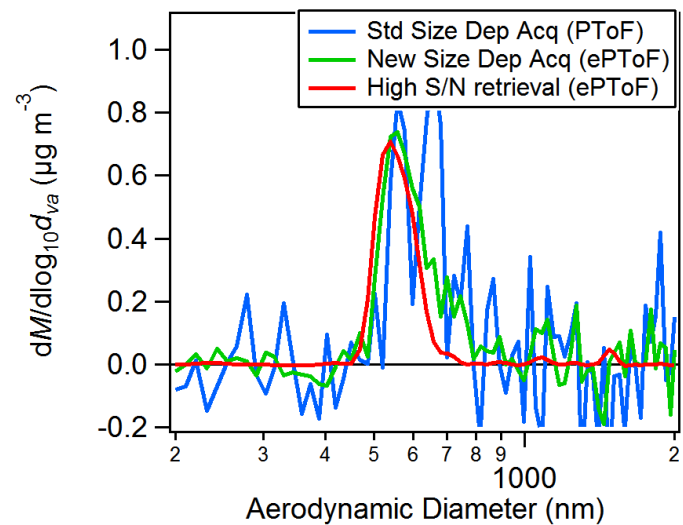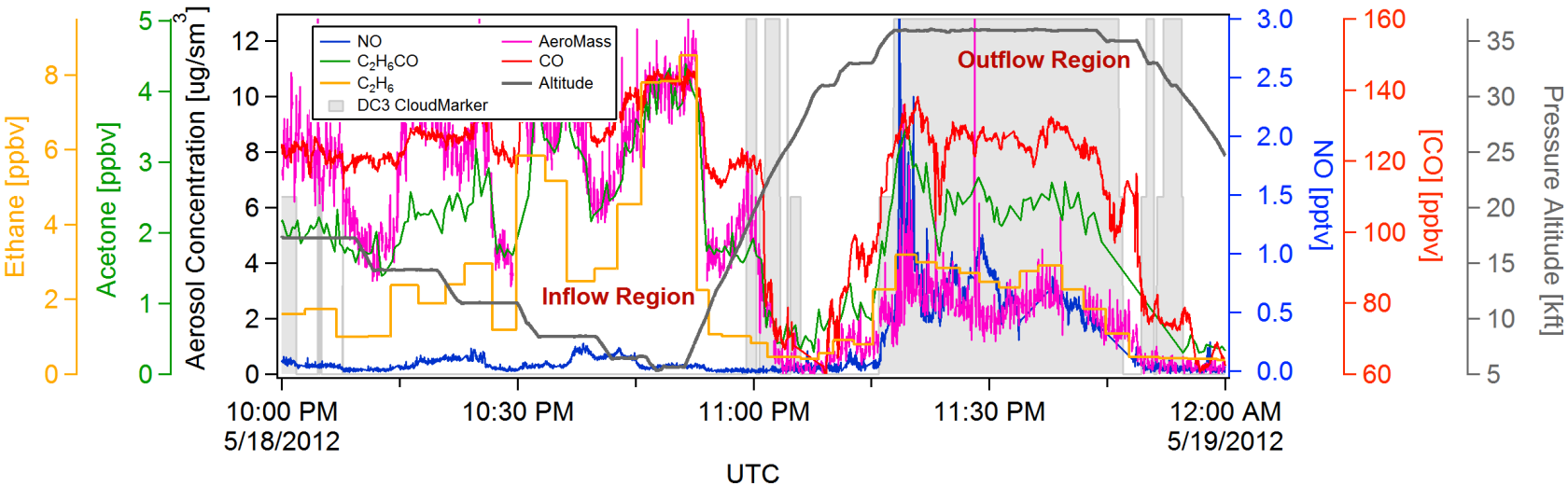
CU HR-TOF Detection Limits
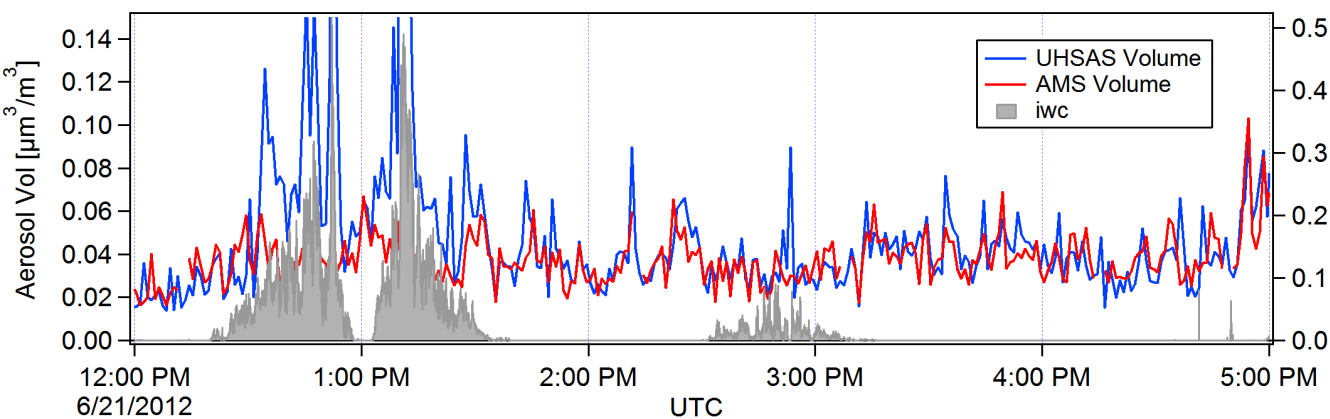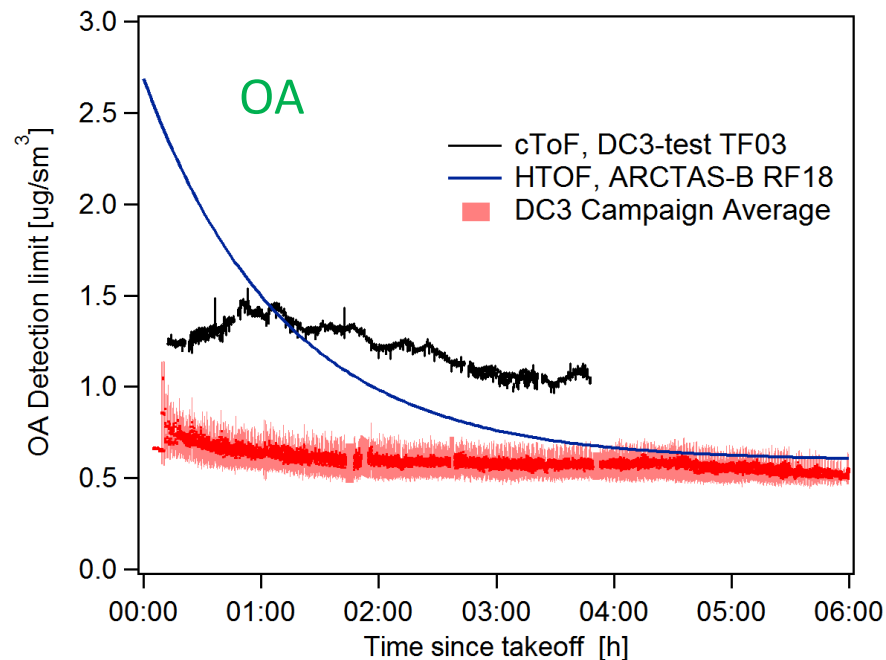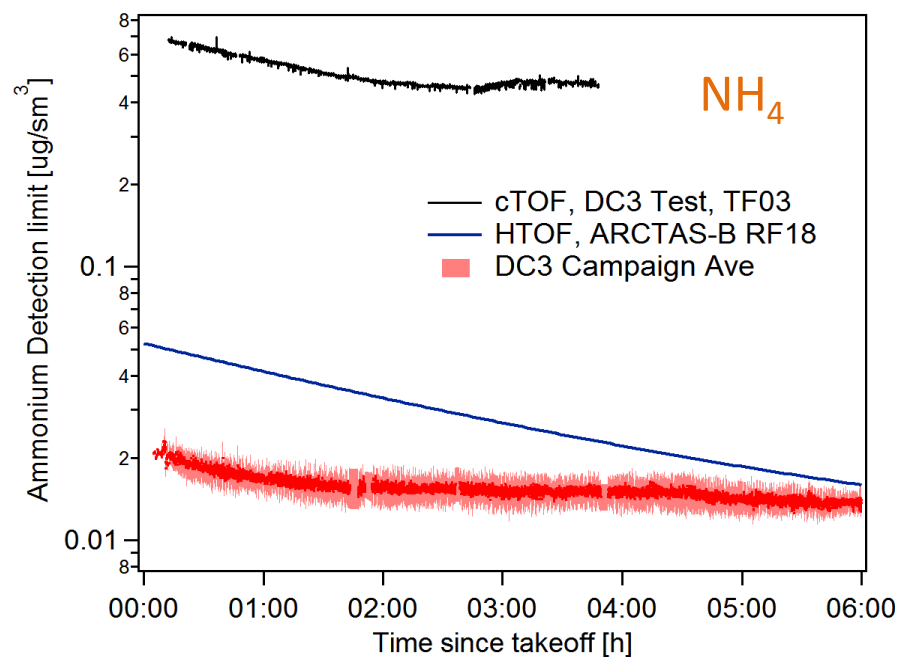
Typical detection Lim (1s, ug/sm³):

|	
Sulfate:	0.03
Nitrate:	0.06
Ammonium:	0.02
Chloride:	0.07
OA:	0.7

AMS measurements in ice clouds

The AMS is:

- Insensitive to metals and other refractory particles typically ablated from inlets in ice clouds
- Less prone to "single particle noise" due to the linear mass measurement (similar to nephelometer vs UHSAS data).

During DC3, 95% of measurements in clouds were unaffected by artifacts and tracked gasphase tracers well. We also provide an ice cloud marker (based on water and Zn ion signals) to flag such periods)

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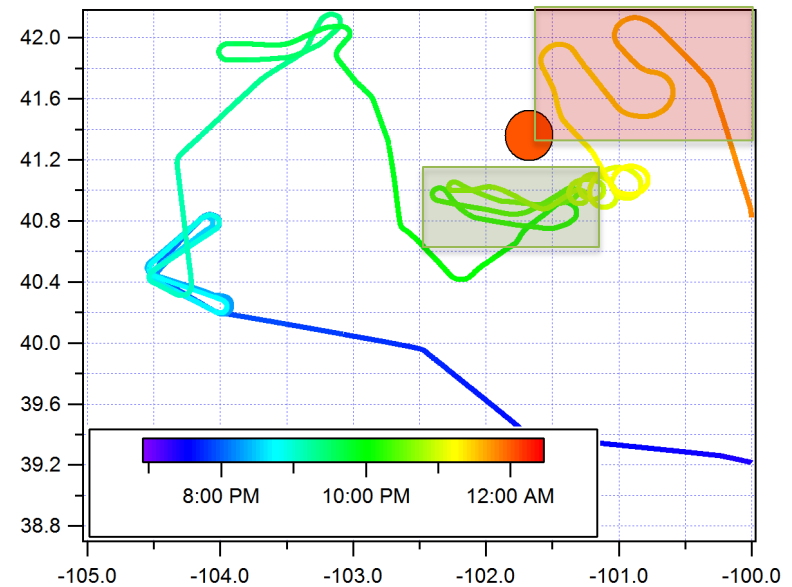
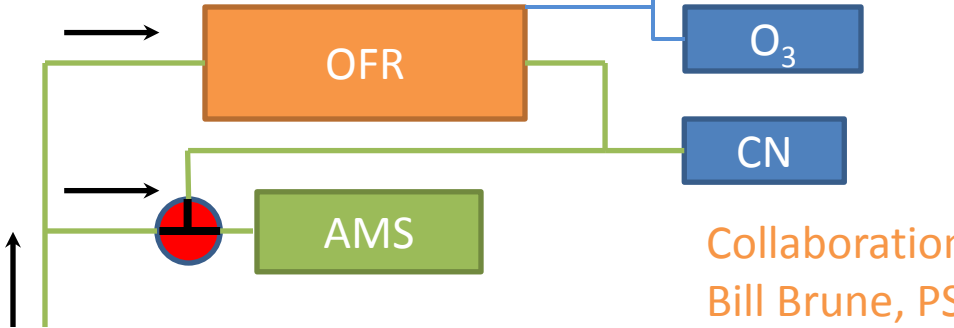# OFR aircraft deployment

Your instrument here!

OFR

O$_3$

CN

AMS

Collaboration with
Bill Brune, PSU

- 10 s / 2 min OFR sampling planned (~ residence time)
- About 1 day of summertime OH exposure expected in the BL for WINTER conditions

BEACHON

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