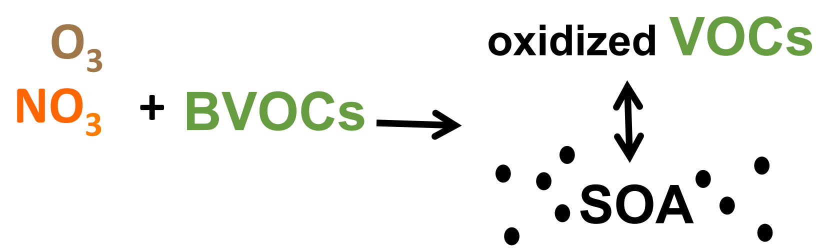
Size-dependent molecular-level characterization of secondary organic aerosol from O_3 vs. NO_3 oxidation of monoterpenes



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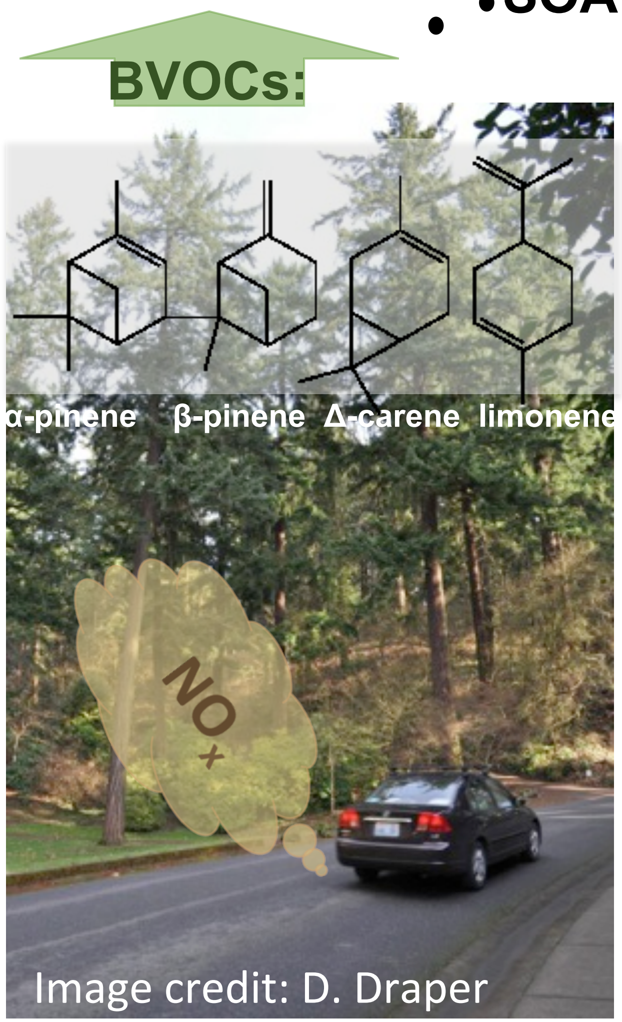
Reed College
Alex Laskin, Julia Laskin, Bingbing Wang, Peng Lin
Pacific Northwest National Lab
Pacifichem, Honolulu, HI, Dec. 19, 2015

Background: NO_3 and monoterpenes (C_{10} BVOCs)

O_3 / NO_3 / OH + BVOCs → oxidized VOCs ↕ SOA



$$\left[\begin{array}{l} NO_2 + h\nu \rightarrow NO + O \\ O + O_2 + M \rightarrow O_3 + M \end{array}\right]$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + hv \rightarrow NO_2 + O$$

*NO_3 is rapidly photolyzed and thus present primarily at night, in equil with N_2O_5:

$$NO_3 + NO_2 \leftrightarrow N_2O_5$$

Typical concentrations:
12 h nighttime avg [NO_3]: 5×10^8 #/cm^3
24 h avg [O_3]: 7×10^{11} #/cm^3
(Atkinson & Arey, 2003)

BVOC lifetimes w.r.t. each oxidant

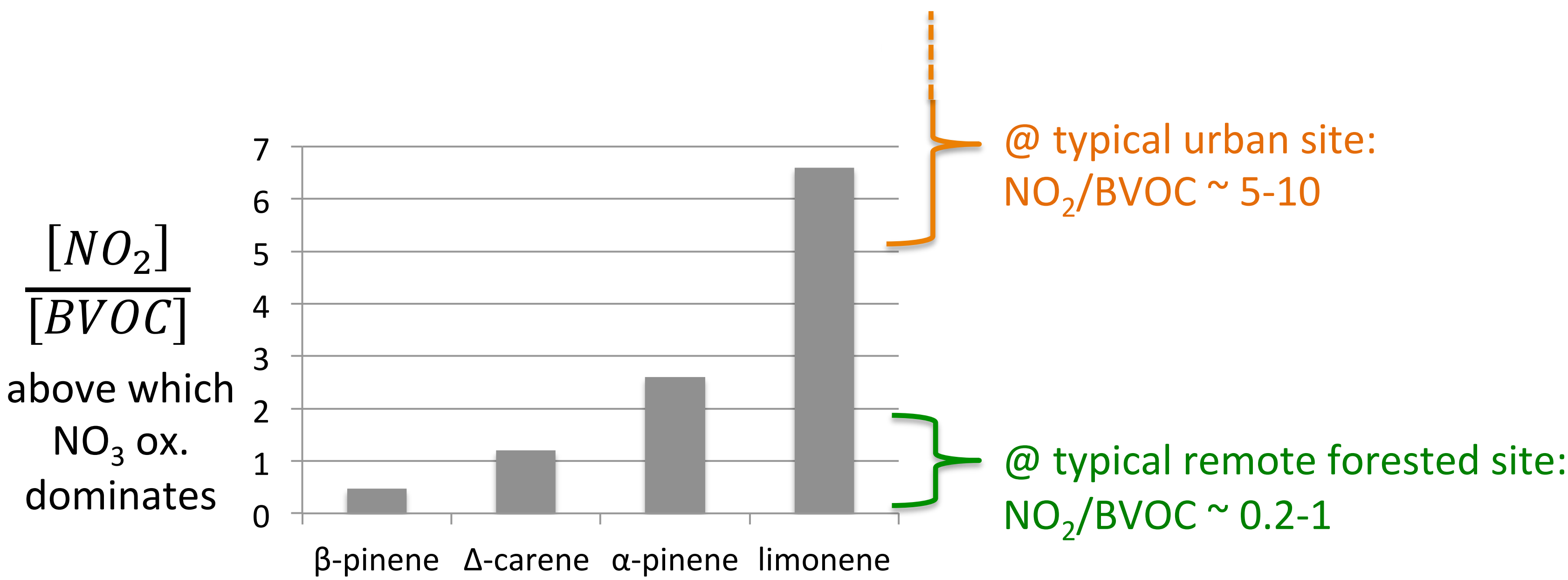
BVOC	O_3	NO_3
α-pinene	4.7 hr	5.4 min
β-pinene	1.1 day	13 min
Δ-carene	11 hr	3.7 min
limonene	1.9 hr	2.7 min

Background: NOx/terpene ratio at which NO_3 oxidation begins to dominate over O_3

Because NO_3 oxidation is so much faster than O_3, NO_3 oxidation dominates

Where $k_{O_3+NO_2}[O_3][NO_2] > k_{O_3+BVOC}[O_3][BVOC]$,

Critical ratio: $\frac{[NO_2]}{[BVOC]} > \frac{k_{O_3+BVOC}}{k_{O_3+NO_2}}$



=> β-pinene oxidation always more likely to be NO_3-dominated!

Draper et al., ACP 2015

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A qualitative comparison of secondary organic aerosol yields and composition from ozonolysis of monoterpenes at varying concentrations of NO_2

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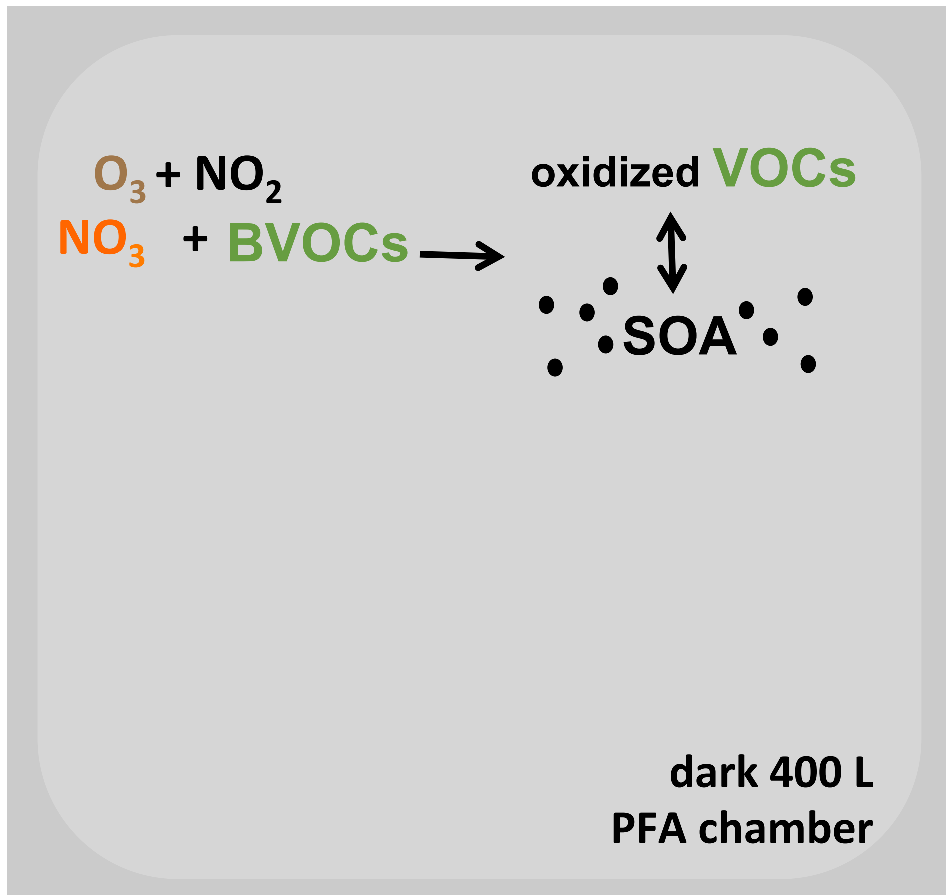
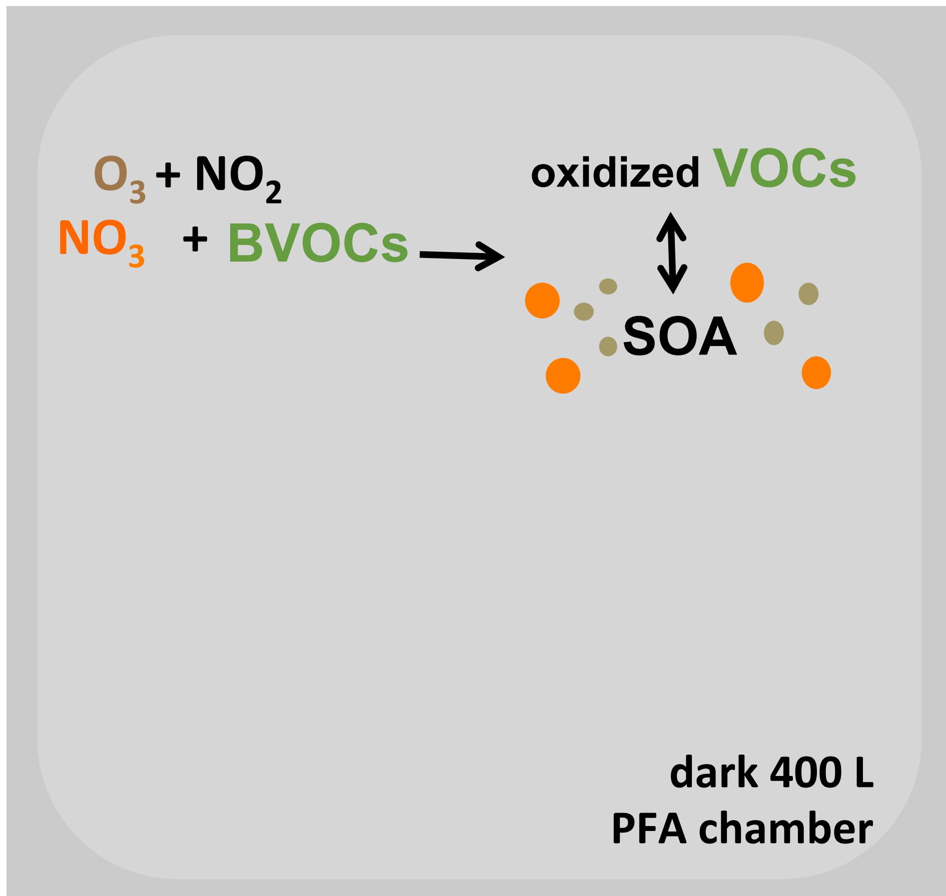
Draper et al., ACP 2015

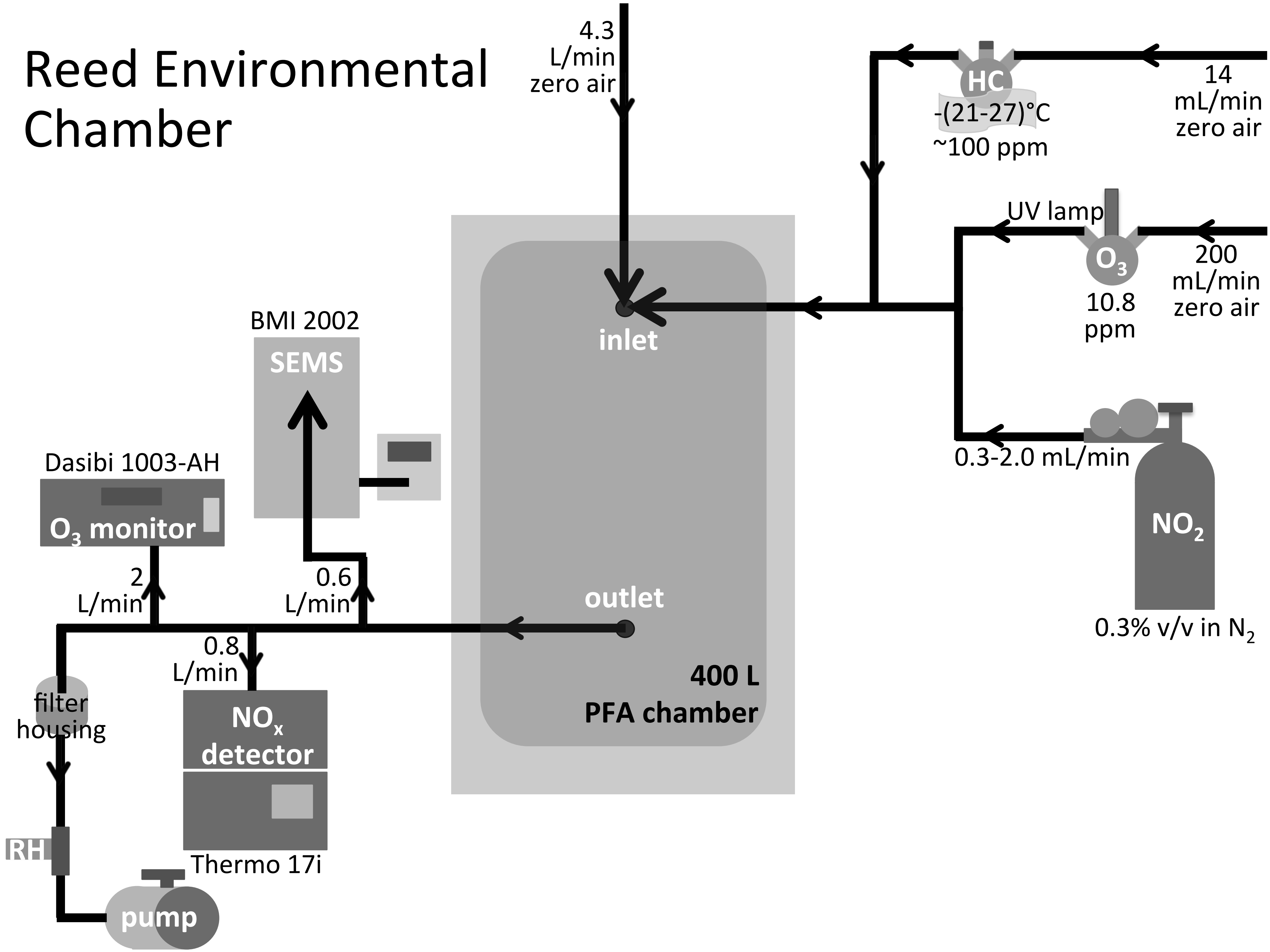
Chamber SOA experiments:



Chamber SOA experiments:
In mixed oxidant experiments, do O_3 and NO_3 form *separate* particle populations?



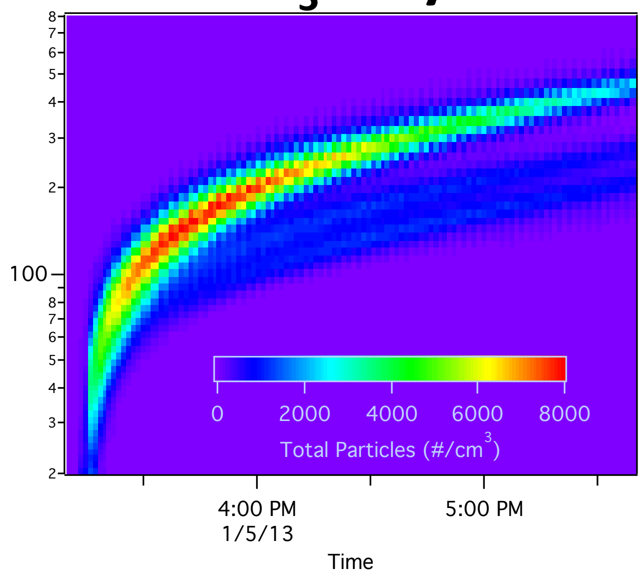
Reed Environmental Chamber

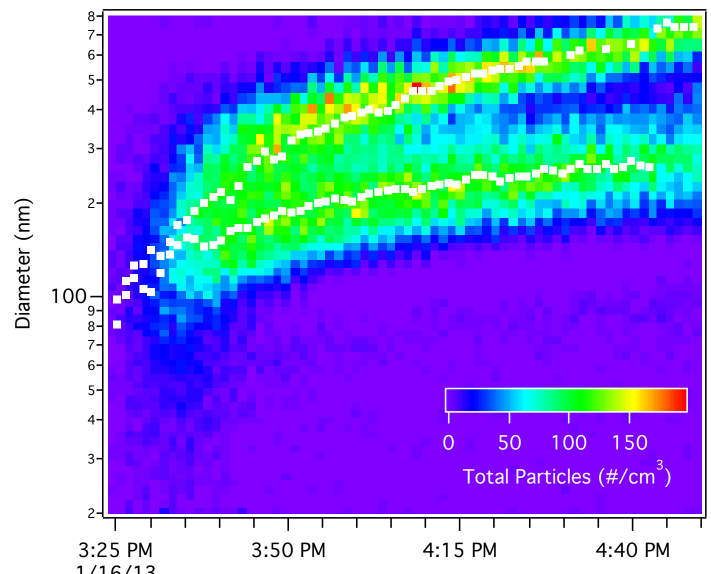


Impetus: In mixed oxidant (O_3 & NO_2) SOA experiments with various BVOCs, we frequently observe bifurcation of size distributions!

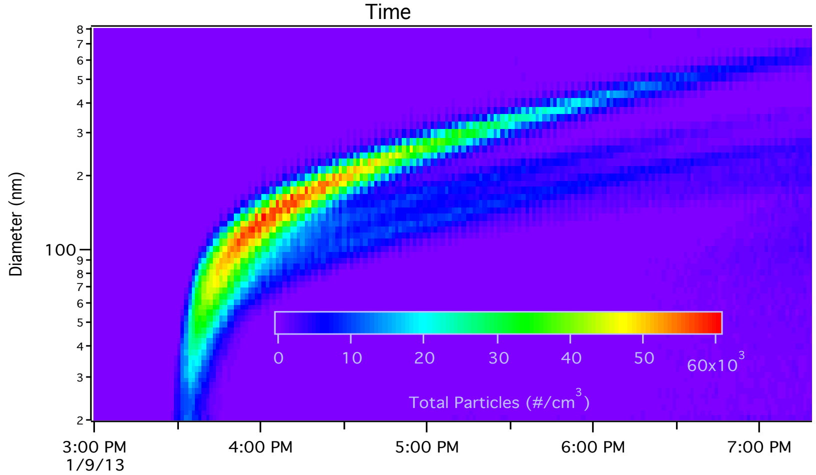
O_3 only | **$O_3 + NO_2$**

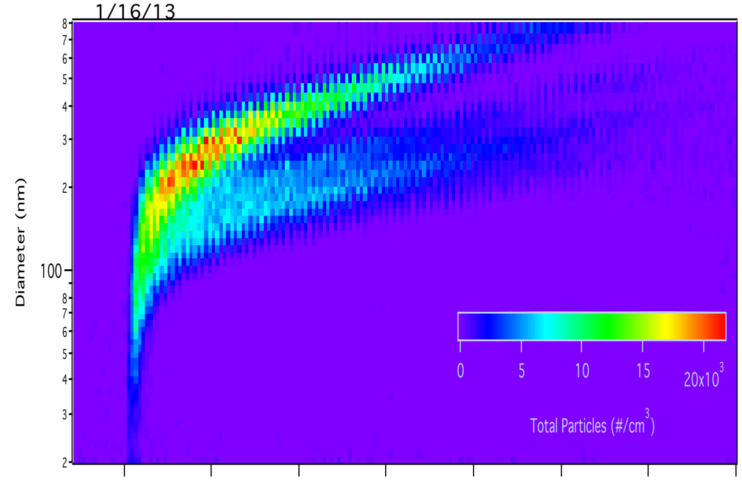
α-pinene



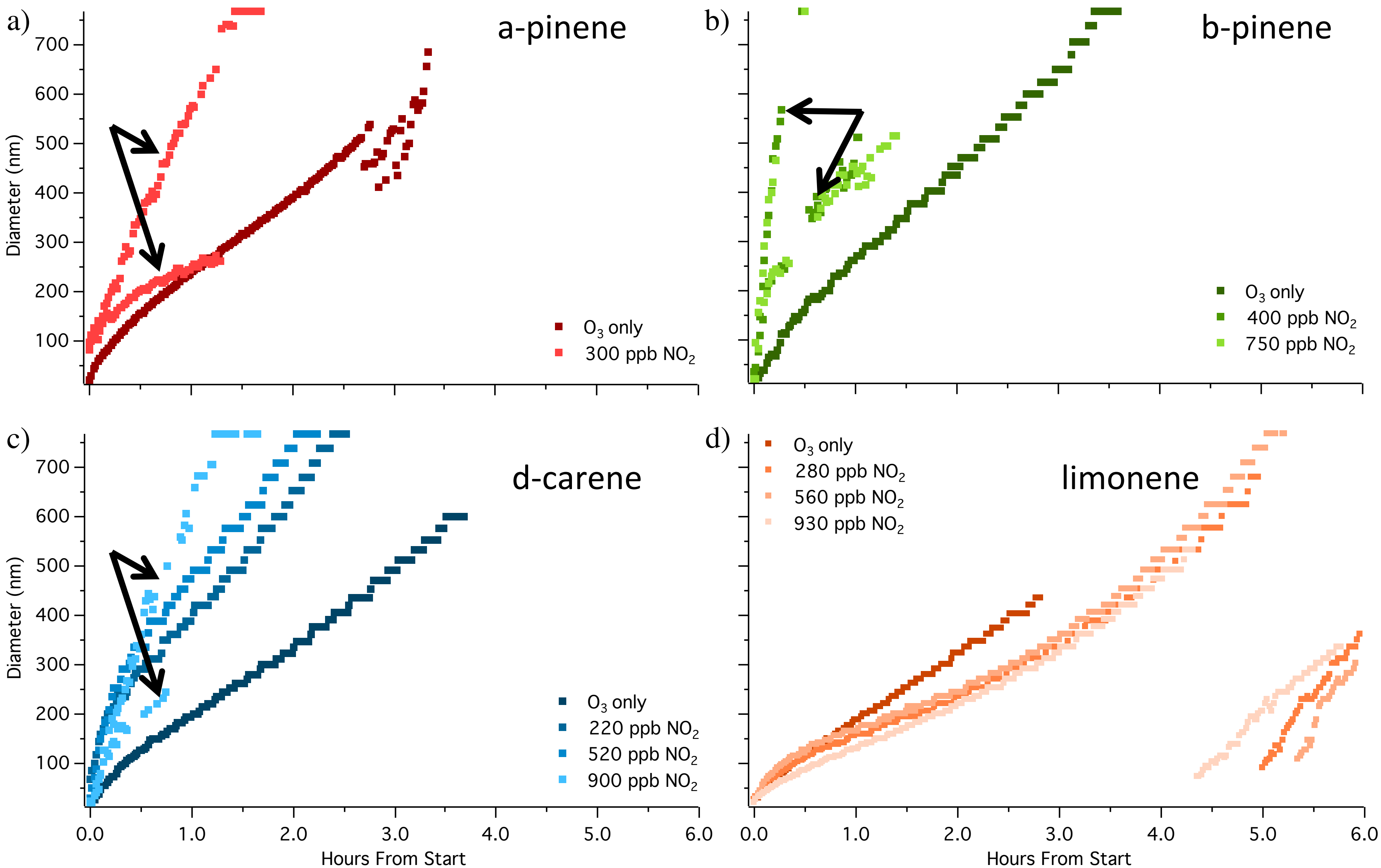


Δ-carene



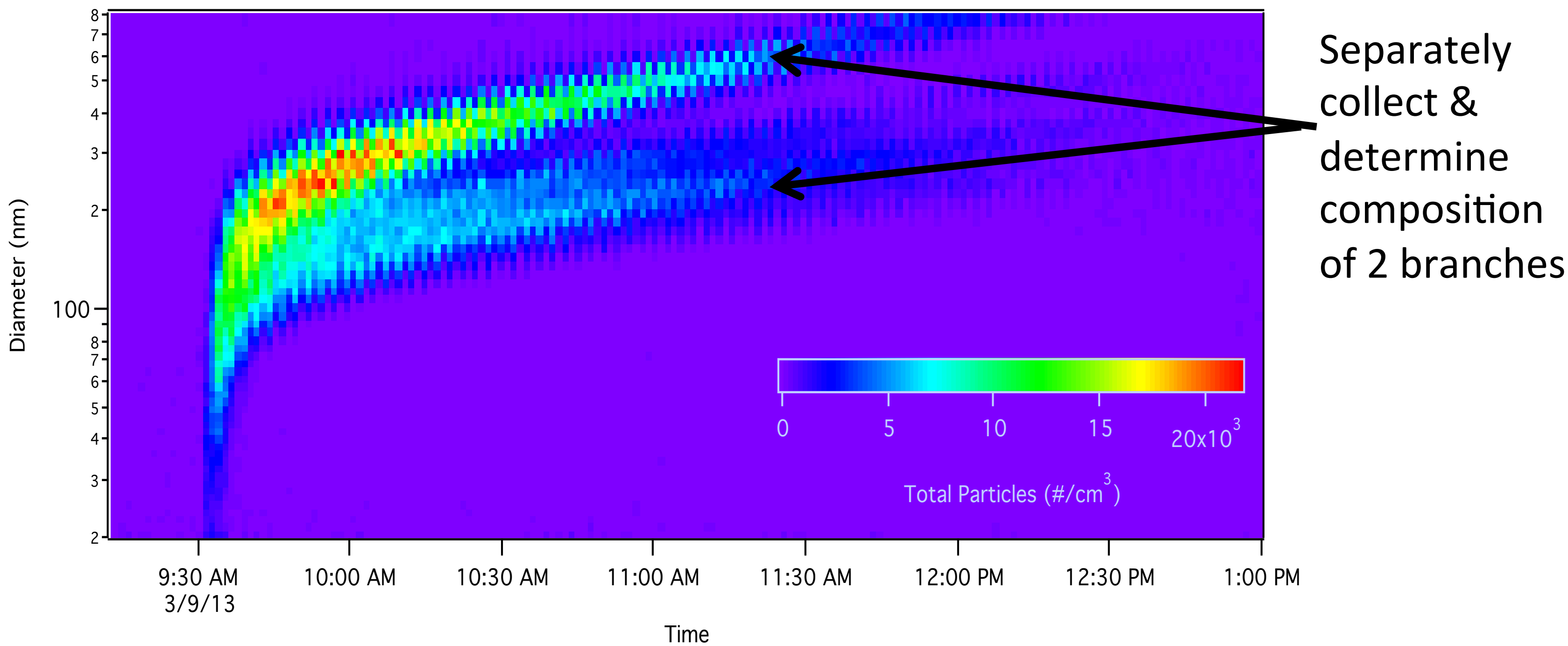


Growth curves: where bifurcation occurs, the slower branch grows at similar rate to O_3-only!



*also note: the slopes of the 2 branches are not different by a factor of 2, ruling out double-charging effects

Are NO_3-oxidized and O_3-oxidized Δ-carene SOA poorly miscible?

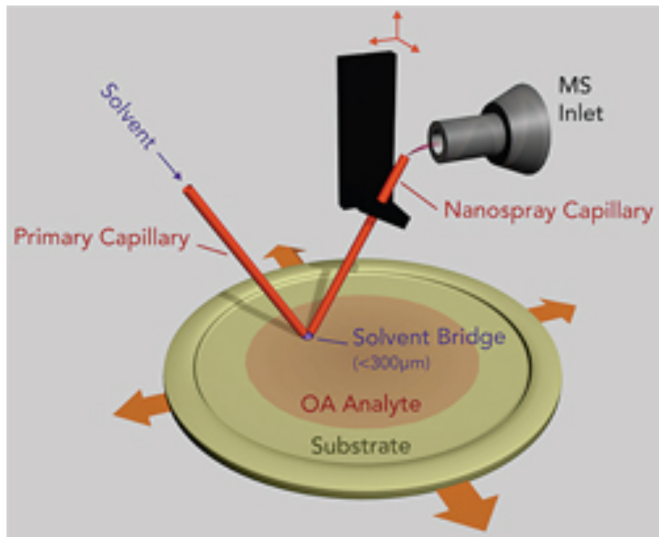


Analyzing size-segregated SOA by nano-DESI-MS at Pacific Northwest Lab EMSL

1. Size segregated collections @ Reed chamber:

2. Composition analysis at EMSL

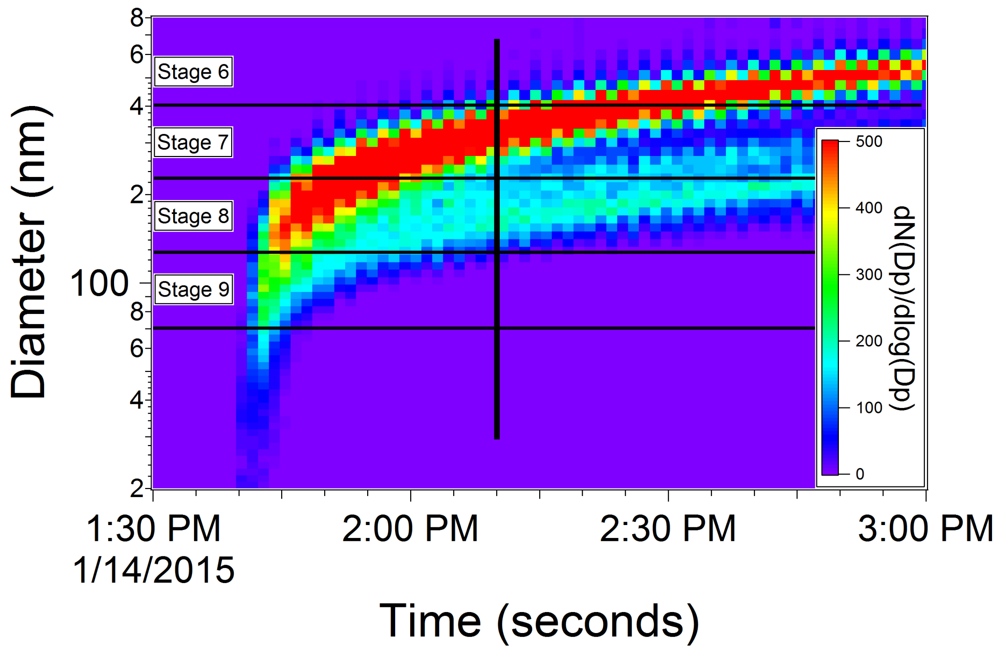
Micro-Orifice Uniform-Deposit Impactor (MOUDI)



Nanospray Desorption Electrospray Ionization High-Resolution Mass Spectrometry

Scanning Electron Microscope SEM

Measure size-segregated aerosol composition

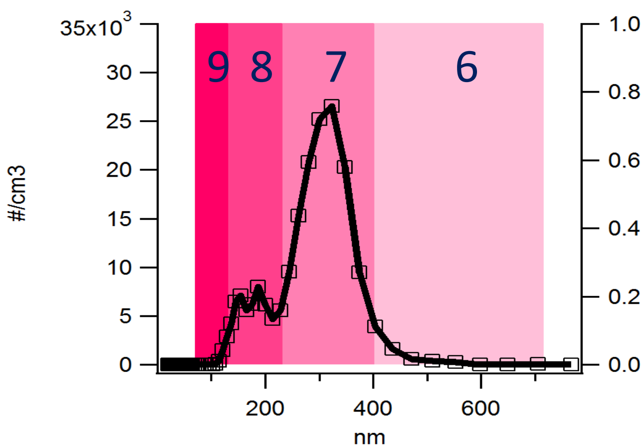


Procedure:

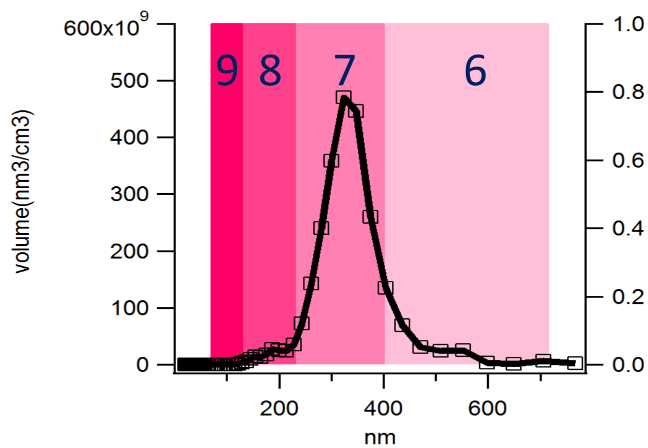
1. Inject O_3 until chamber concentration stabilizes.
2. Start injecting NO_2 to form NO_3. ($NO_2 + O_3 \rightarrow NO_3 + O_2$)
3. Start adding VOC.
4. Wait until bifurcation matches MOUDI size bins, then collect sample.

For stages 8 & 9, repeat this 6x onto same substrate

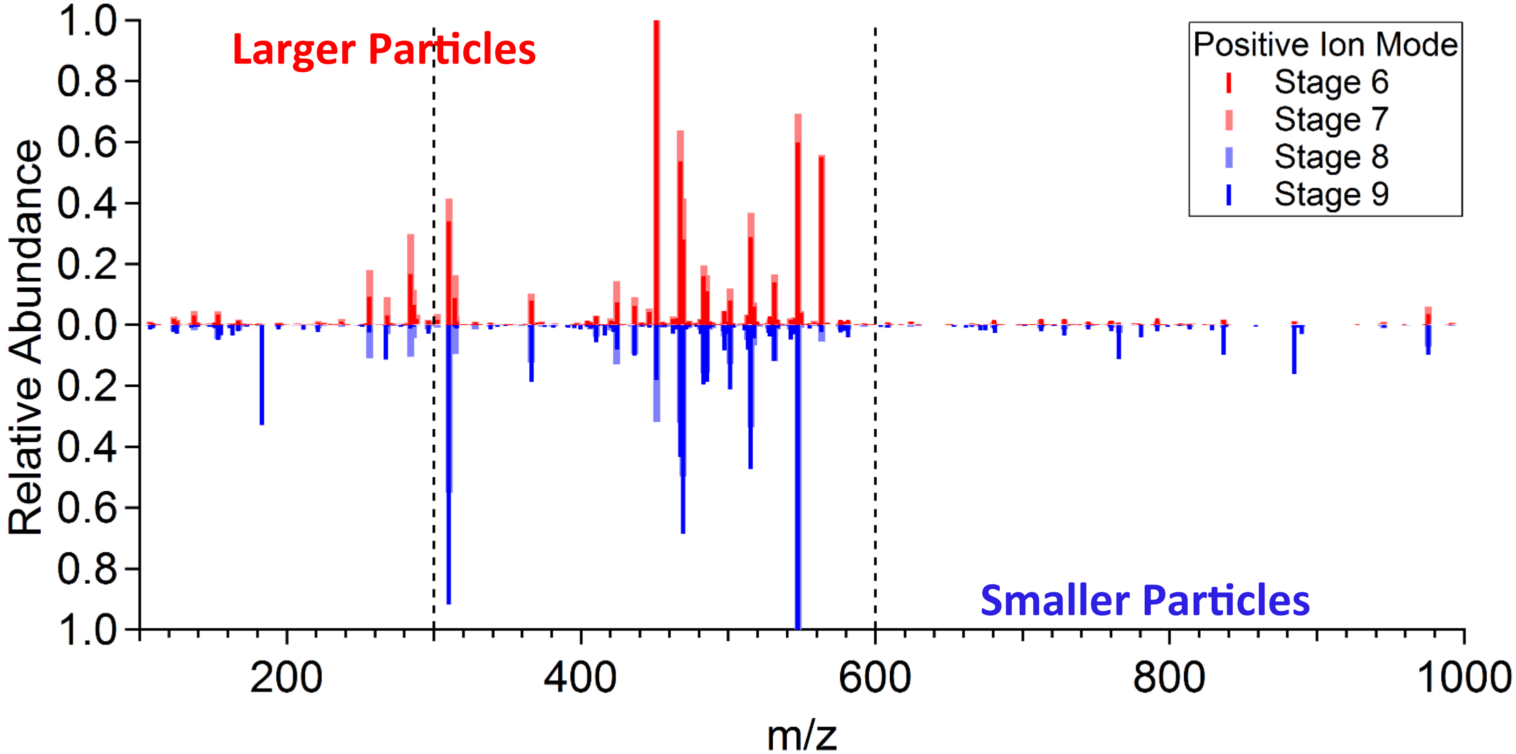
Particle Number Distribution



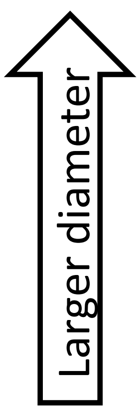
Volume Distribution



Average mass spectra for each size branch



Dashed lines: m/z=300 and 600: nominal cutoffs between monomers, dimers, and trimers



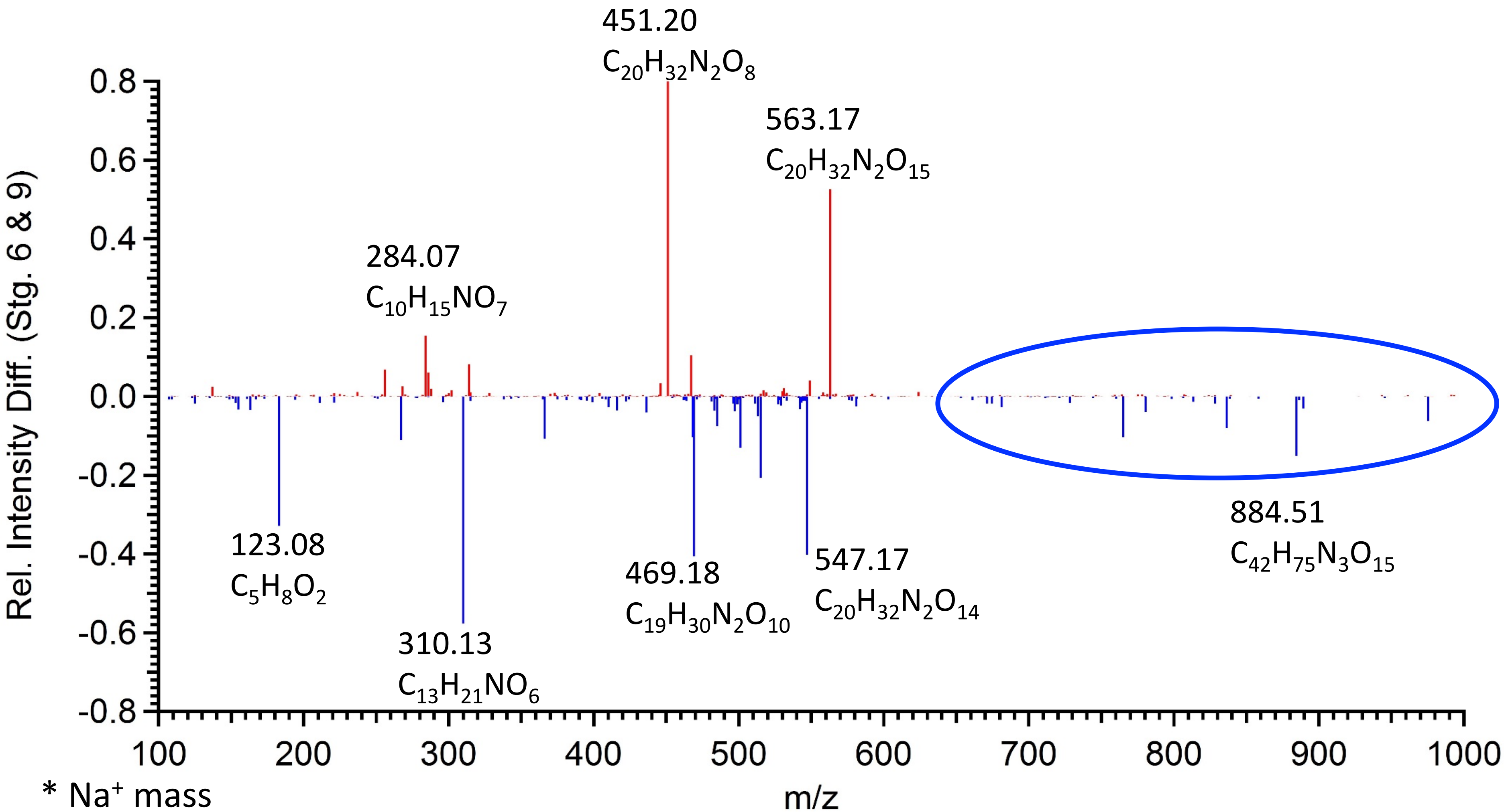
Positive mode*	Intensity-weighted average m/z
Stage 6	447
Stage 7	432
Stage 8	444
Stage 9	454

Negative mode	Intensity-weighted average m/z
Stage 6	337
Stage 7	344
Stage 8	382
Stage 9	439

* Na^+ mass removed from adducts

Difference mass spectrum (+ mode)

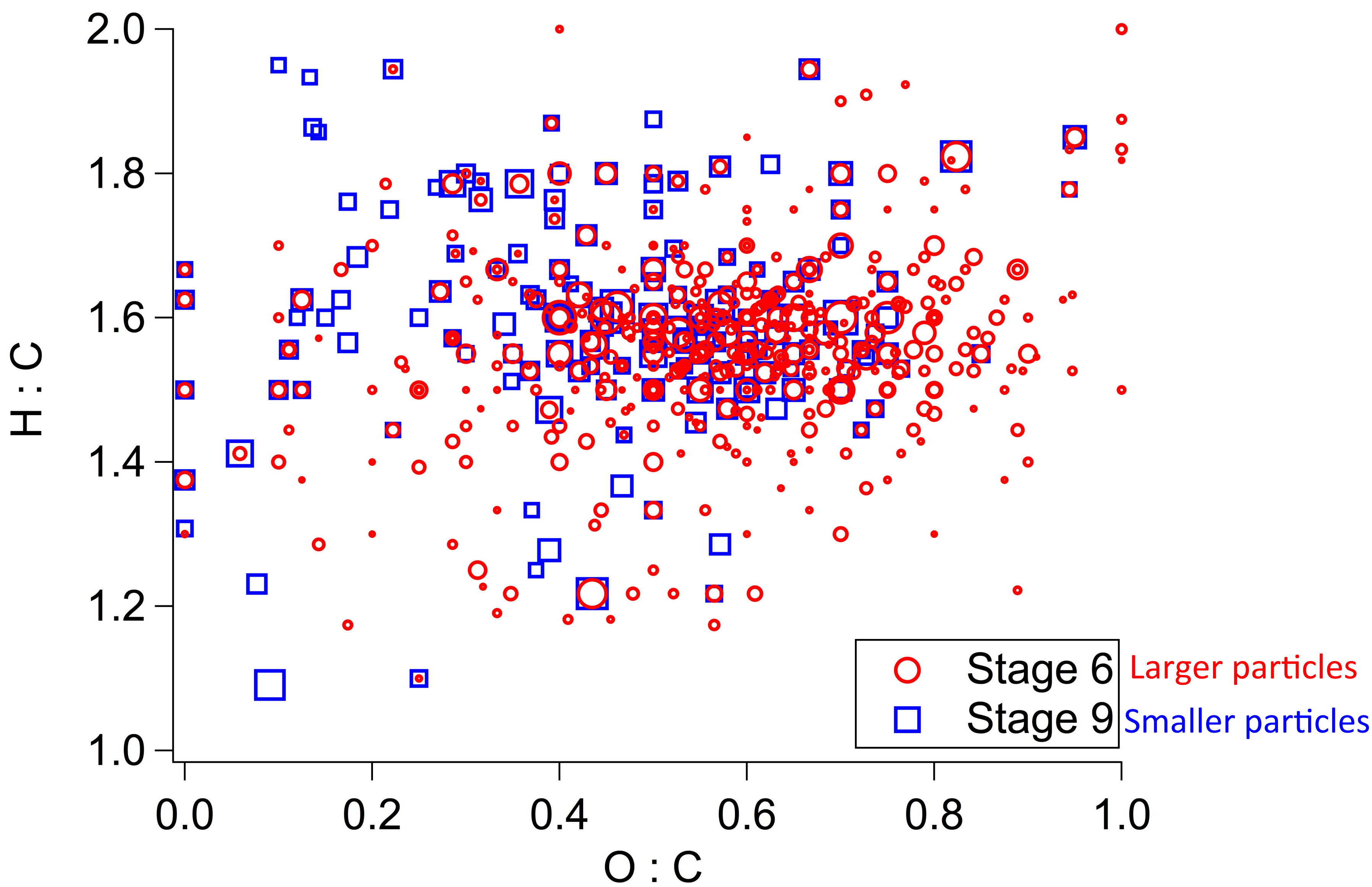
(Larger - Smaller Particles)



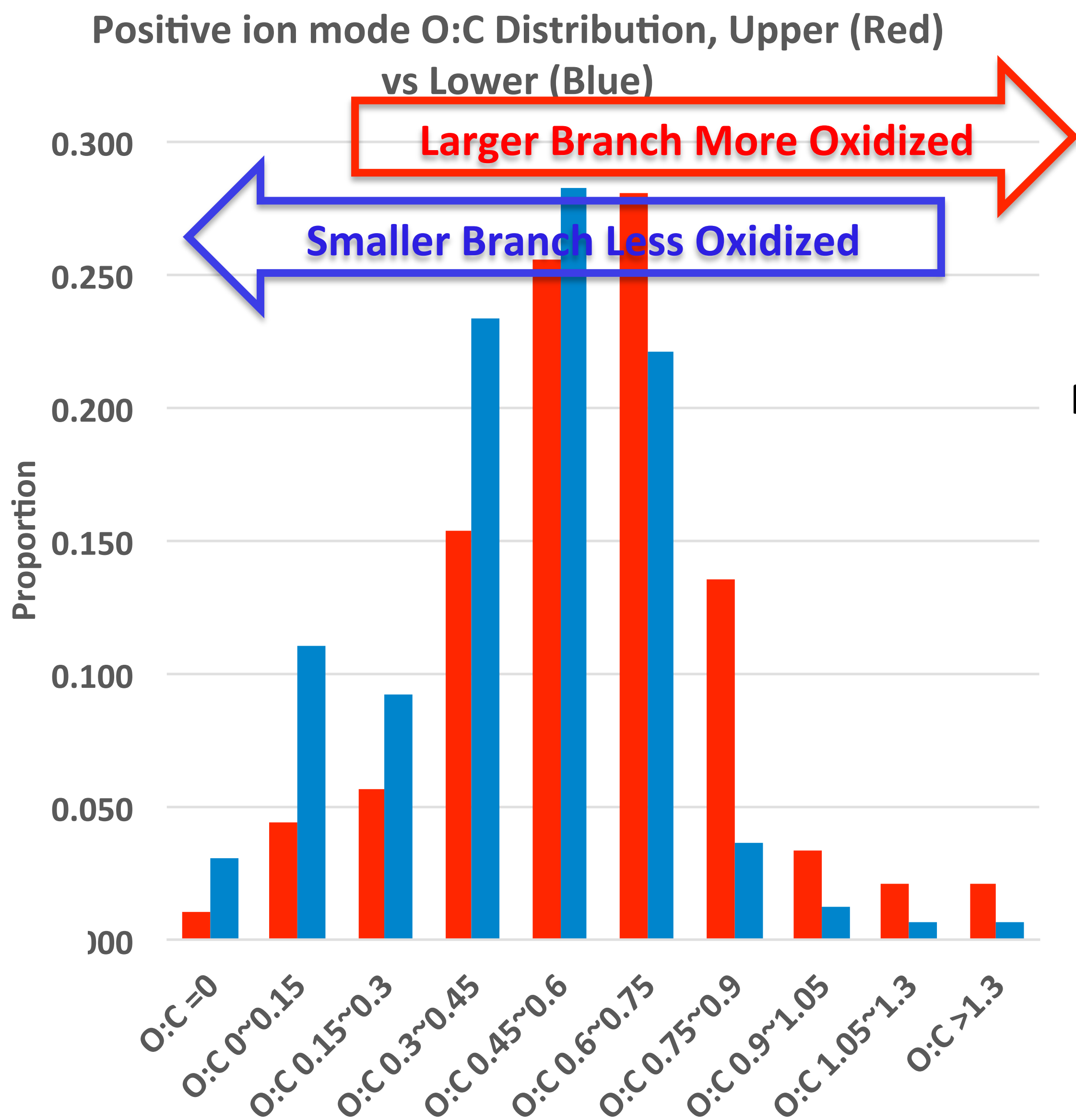
* Na^+ mass removed from adducts

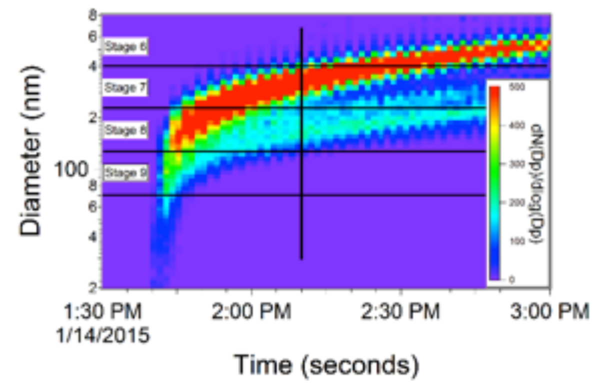
=> Smaller diameter branch has more high-m/z peaks!

H:C versus O:C for all identified molecules in each size branch



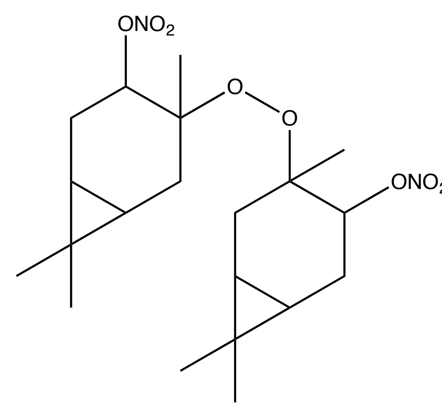
O:C distribution of molecules in each size branch





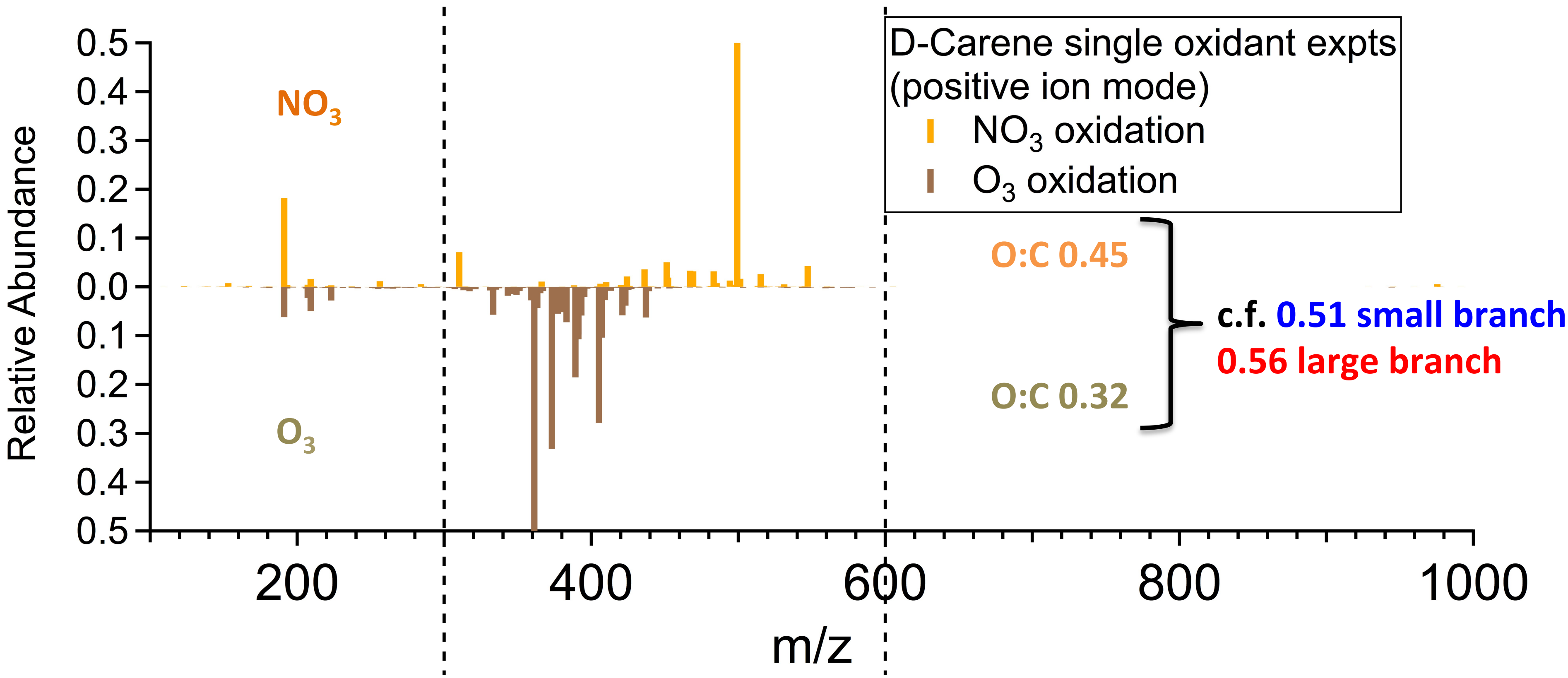
Note: these O:C include NO_3 group!

Example: below molecule (dominant peak in dimer region) has O:C = 8/20 = 0.4



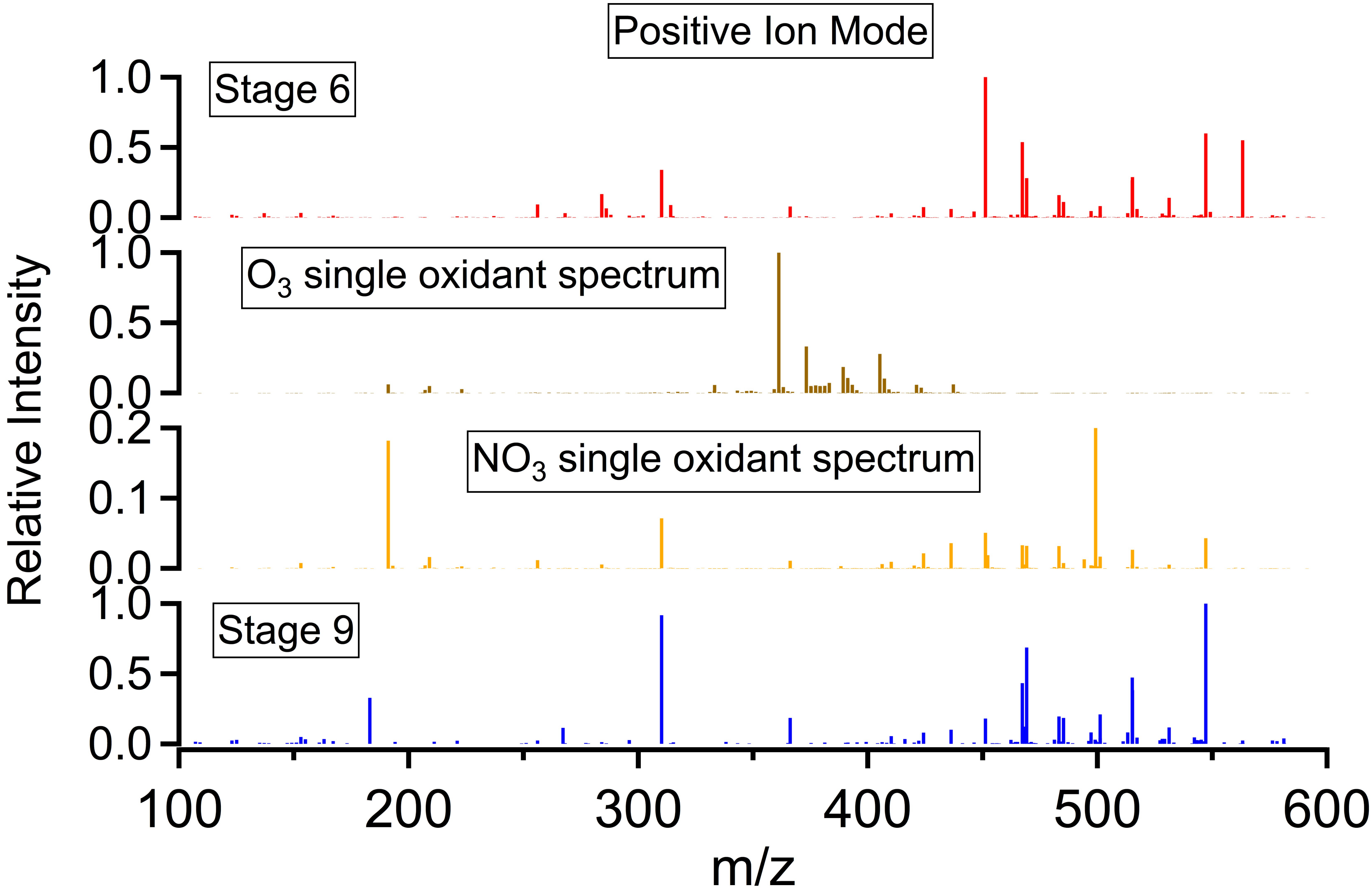
Chemical Formula: $C_{20}H_{32}N_2O_8$
Molecular Weight: 428.48

Pure NO_3 and O_3 initiated SOA composition measurements: preliminary results

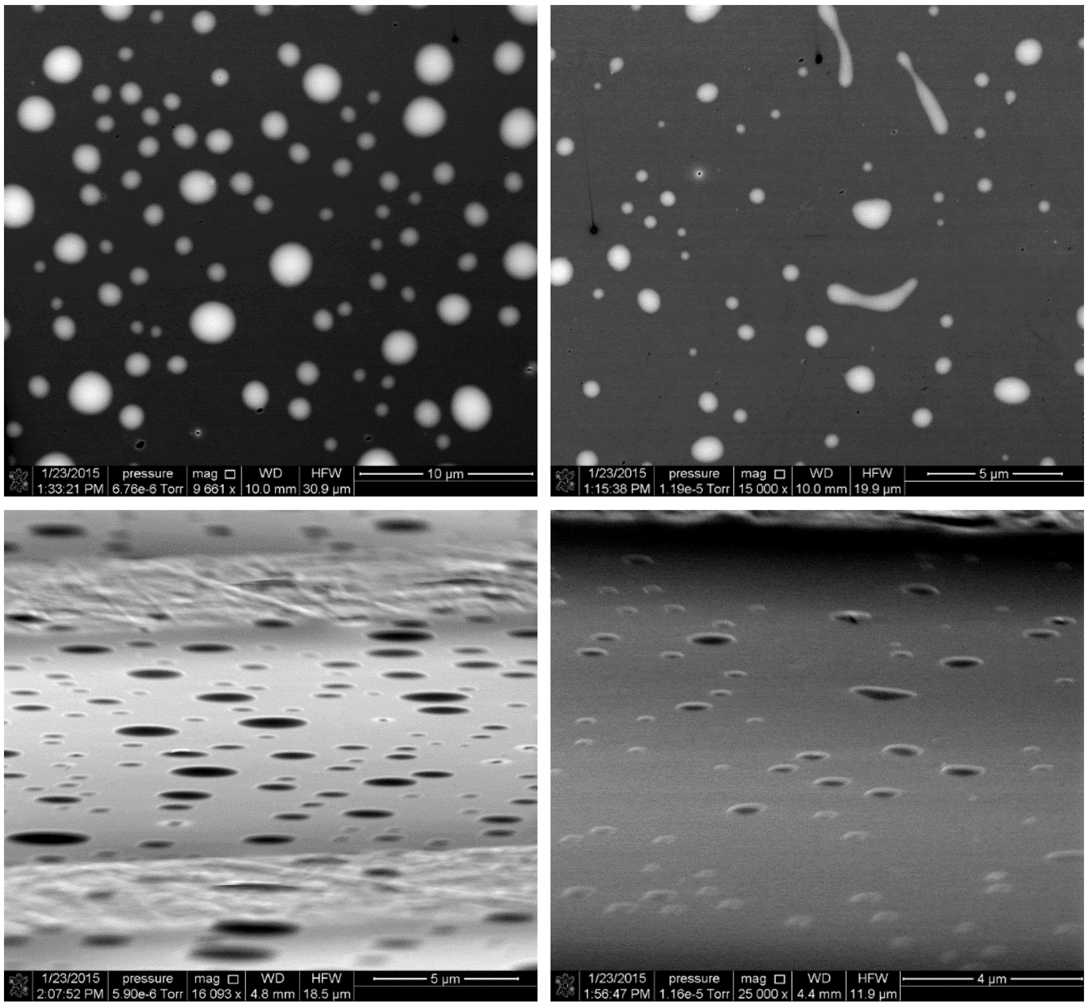


⇒ O:C of both branches apparently closer to that of NO_3 products

Pure NO_3 and O_3 initiated SOA composition measurements: preliminary results



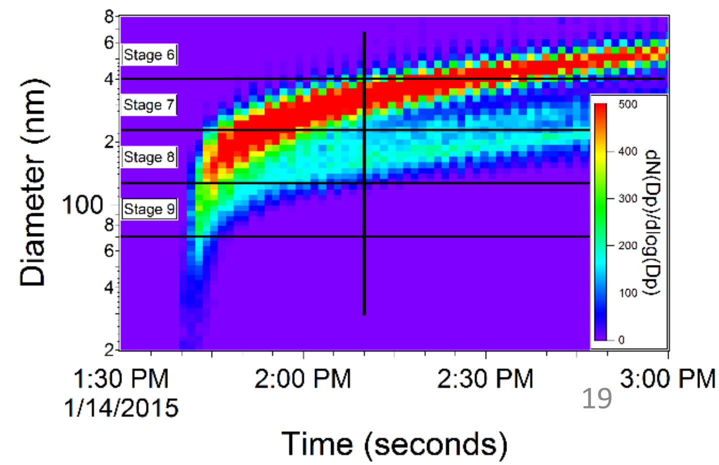
SEM impacted particles comparison (comparing smallest to largest stage)



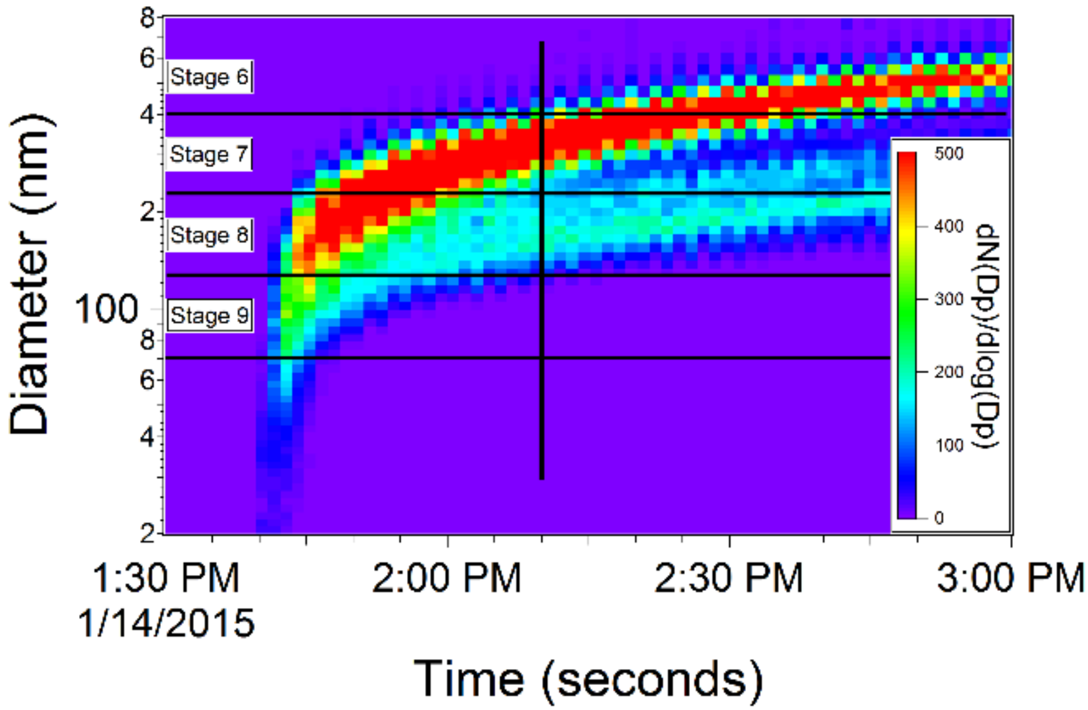
Large Particles | **Small Particles**

Positive	O:C (weighted)
Stage 6	0.564
Stage 7	0.571
Stage 8	0.572
Stage 9	0.505

Negative	O:C (weighted)
Stage 6	0.709
Stage 7	0.710
Stage 8	0.667
Stage 9	0.619



Conclusions



Larger diameter, faster-growing aerosol population is more **oxidized** on average, and appears more liquid-like

while

Smaller diameter, slower-growing aerosol population has **more high-MW** components and appears more solid

=> These composition differences may or may not map to O_3 vs. NO_3 oxidation sources!

Thanks!

- Funding:

  EMSL proposal #48347

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  Reed College Opportunity Grants

EMSL