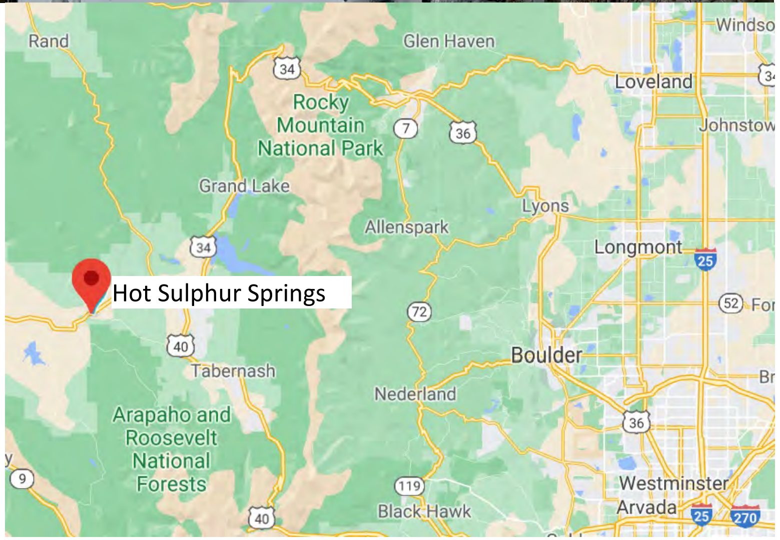
# FIREX-AQ Chem Otter Science Meeting

**1. Updates:**
AGU December 1-17
AMS January 10-15
Anything else?

**2. Zach Decker**

**3. Felipe Rivera**






**Audience assignment for this meeting:**
Have you looked at the flights that Felipe and Zach are analyzing?
Do you have information or measurements that could help their analyses?

26 October 2020

# Box Model Analysis of Wildfire smoke at sunset- when all oxidants are at play

Zachary C.J. Decker

CIRES

NOAA
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
U.S. DEPARTMENT OF COMMERCE

Thanks to

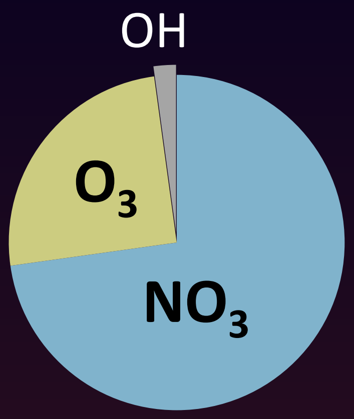
Michael Robinson, Kelley C. Barsanti, Ilann Bourgeois, Matt Coggon, Frank Flocke, Ale Franchin, Carley Fredrickson, Alan Fried, Jessica Gliman, Samuel Hall, Christopher Holmes, Aaron Lamplugh, DeeDee Montzka, Richard Moore, Andy Neuman, Brett Palm, Jeff Peischl, Dirk Richter, Claire Robinson, Andrew Rollins, Tom Ryerson, Kevin Sanchez, Rebecca Schwantes, Lee Thornhill, Joel Thornton, Geoff Tyndall, Kirk Ullmann, Paul Van Rooy, Patrick R. Veres, James Walega, Petter Weibring, Andy Weinheimer, Elizabeth Wiggins, Edward Winstead, Caroline Womack, Steven S. Brown

# Dark Smoke Plume Chemistry is an Open Science Question

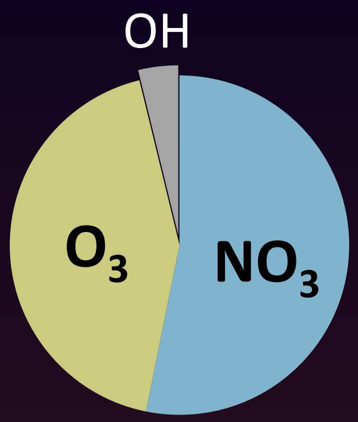
- Nighttime smoke is difficult to study
- Nighttime smoke involves reactions with OH, $O_3$ and $NO_3$
- $NO_3$ radical is produced within a plume
  - $NO_x$ from the plume + background $O_3$
- Under sunlight $NO_3$ is rapidly destroyed by photolysis and NO ($\tau$<10s)
- $NO_3$ is very reactive with biomass burning VOCs (BBVOCs)

# Dark Smoke Chemistry is $NO_3$ and $O_3$ Chemistry

Fraction of mass oxidized by **$NO_3$**, $O_3$ and OH over a 10 hour night (box model)



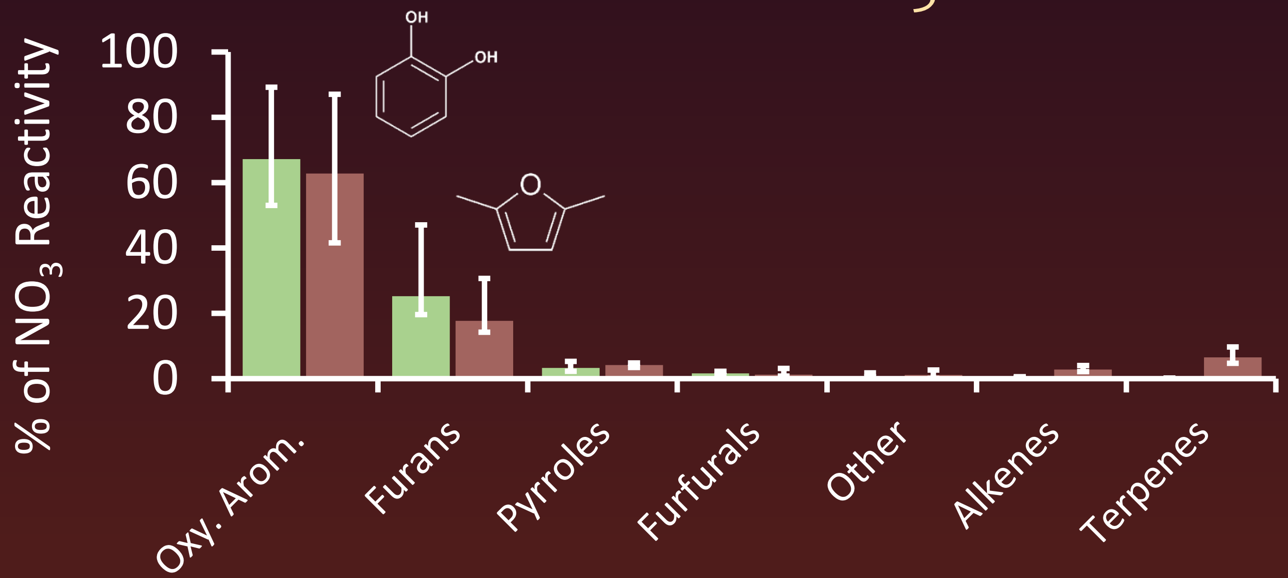

Rice Straw



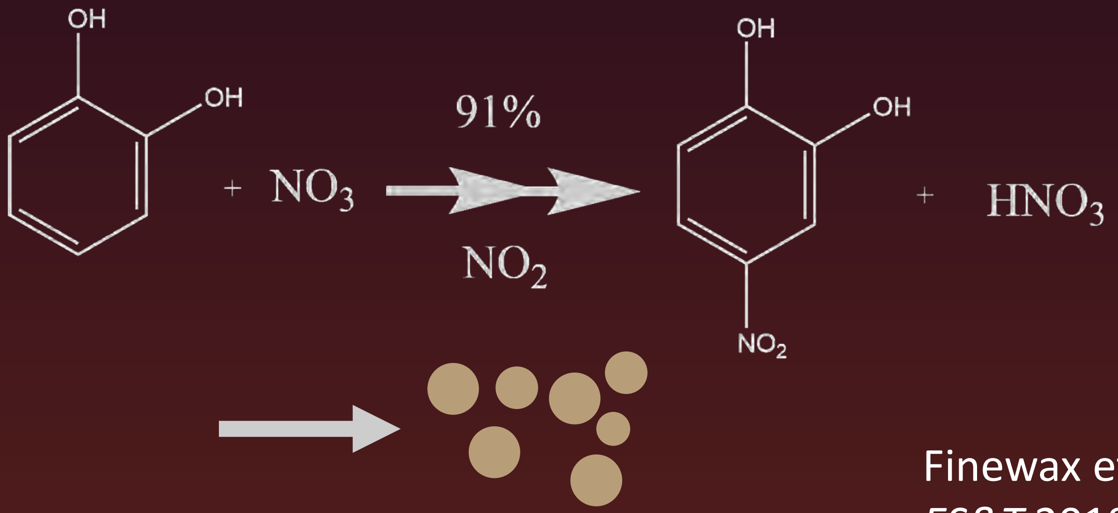

Ponderosa Pine

Decker et al. *ES&T* 2019

## Phenolics and Furans are Most Reactive with $NO_3$




## Many $NO_3$ + BBVOC products lead to BrC




Finewax et al. *ES&T* 2018

# We Investigate Five Plumes

## Castle Fire

Northern Arizona

Tiny plume
(1.7 ppmv CO)

## Williams Flats Fire (x2)

Eastern Washington

Big plume
(8 ppmv CO)

## 204 Cow Fire

Eastern-central Oregon

Medium plume
(2.6 ppmv CO)

## “Dark”

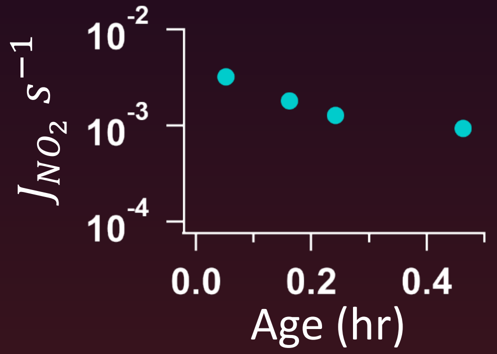
Thought Experiment

Big plume
(8 ppmv CO)

# We Investigate Dark Five Plumes

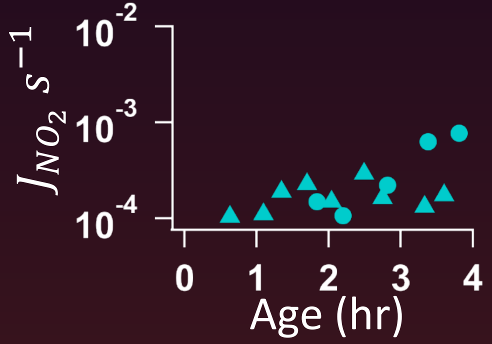
## Castle Fire
Northern Arizona

Tiny plume
(1.7 ppmv CO)




## Williams Flats Fire (x2)
Eastern Washington

Big plume
(8 ppmv CO)




## 204 Cow Fire
Eastern-central Oregon

Medium plume
(2.6 ppmv CO)

Emitted before sunset
Sampled after sunset

## "Dark"
Thought Experiment

Big plume
(8 ppmv CO)

# All Plumes Have Potential for Dark Chemistry

## Castle Fire
Northern Arizona

Tiny plume
(1.7 ppmv CO)

## Williams Flats Fire (x2)
Eastern Washington

Big plume
(8 ppmv CO)

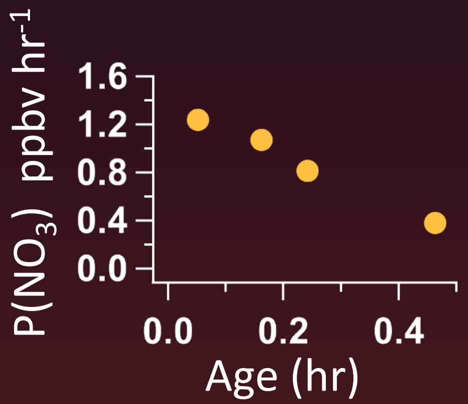
## 204 Cow Fire
Eastern-central Oregon

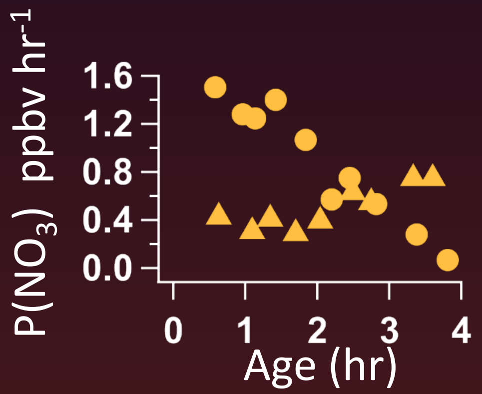
Medium plume
(2.6 ppmv CO)

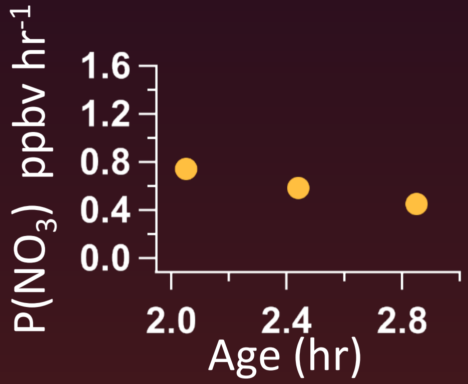
## "Dark"
Thought Experiment

Big plume
(8 ppmv CO)

$P(NO_3)$ = instantaneous production rate for $NO_3$ from $NO_2$ and $O_3$.

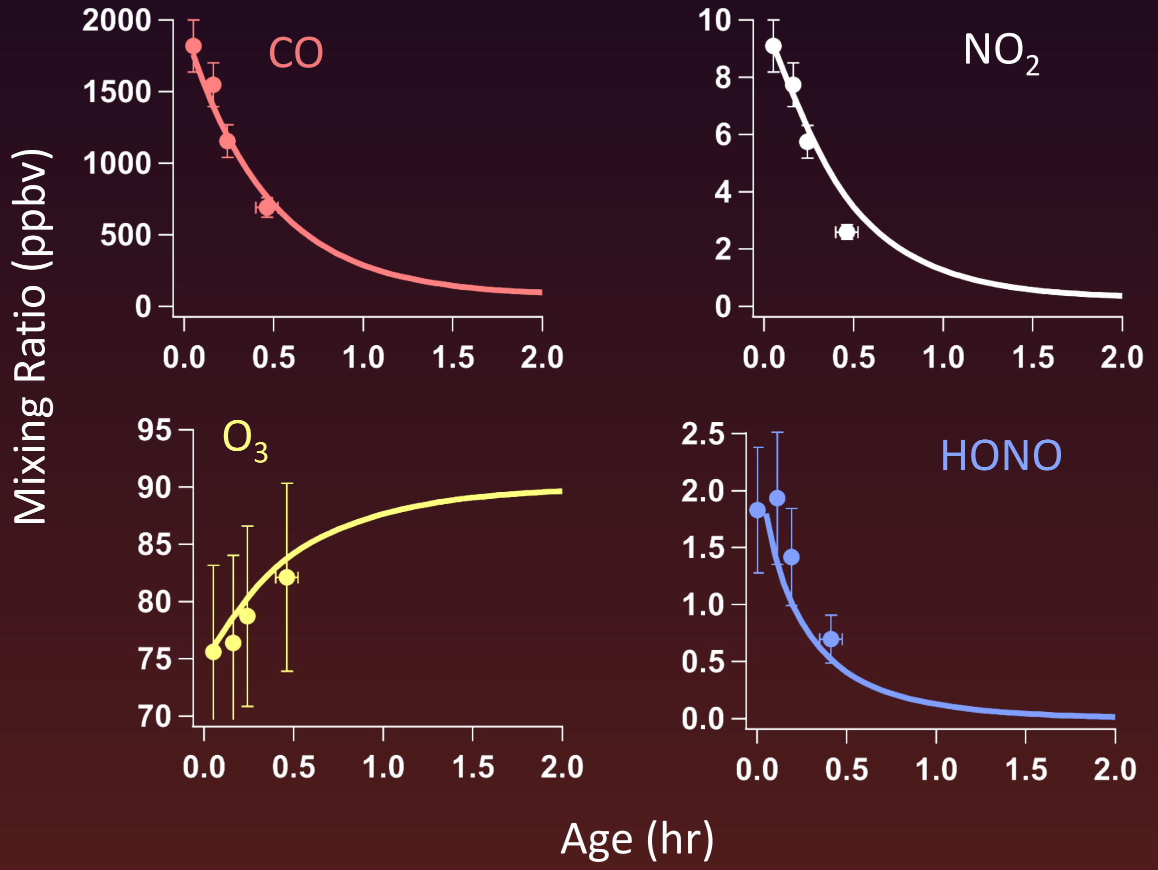


# We Use a Chemical Box Model to Tease Apart the Chemical Details of Overnight Evolution

- Using the Framework for 0-D Atmospheric Modeling (F0AMv4).
- Using a new "NOAA BB" mechanism (with the Master Chemical Mechanism)
  - Plus expanded reactions for phenolic compounds



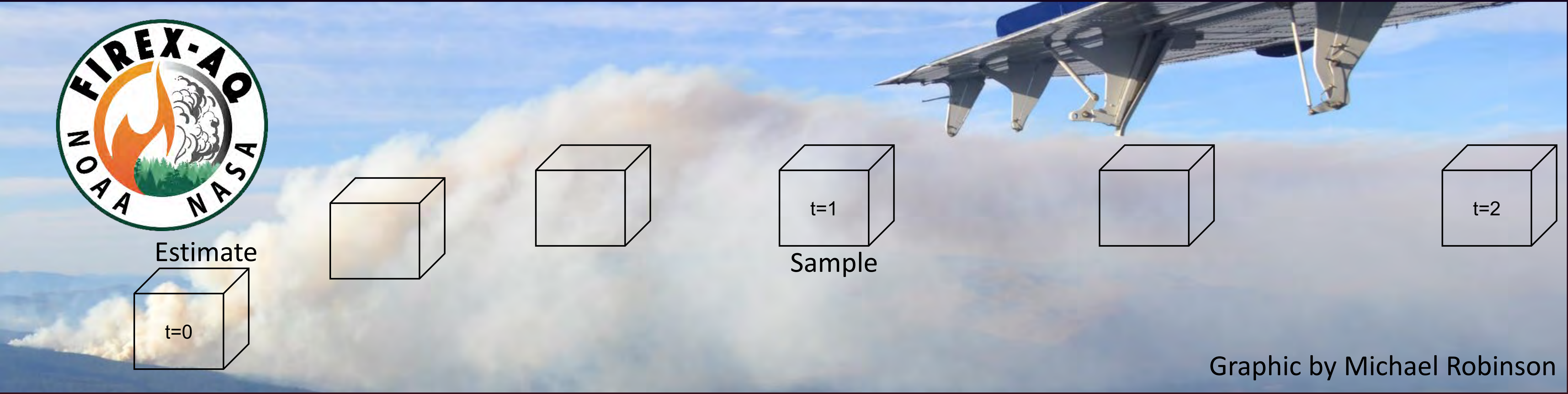

- Using field observations for dilution and chemical emissions.
  - CO, $NO_x$, $O_3$, HONO, and photolysis rates
- Using an aggregated biomass burning emissions and kinetics database of 300 BBVOCs

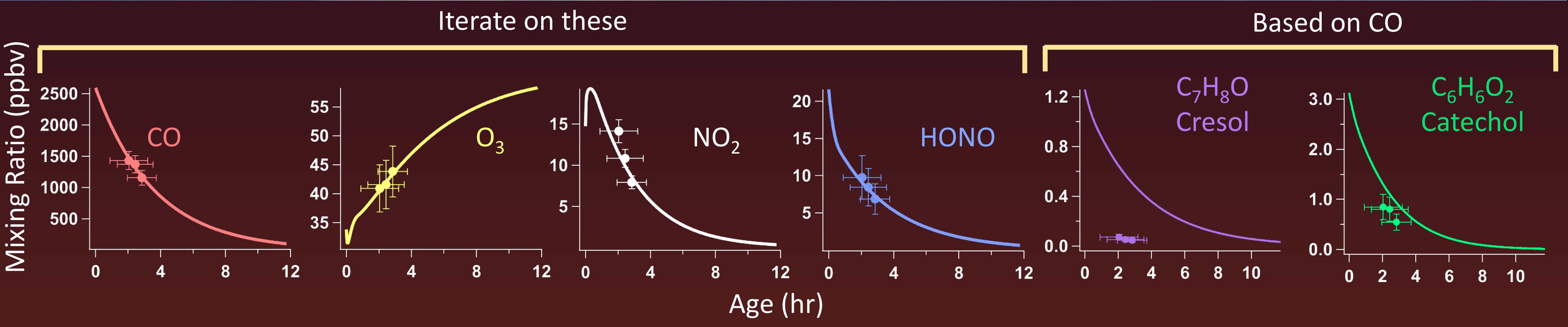
*Decker et al. ES&T 2019.*

*G. M. Wolfe, et al. Geoscientific Model Development, 2016.*

# Out Models are Constrained to Observations

We use an iterative 0-D box model to estimate initial emissions

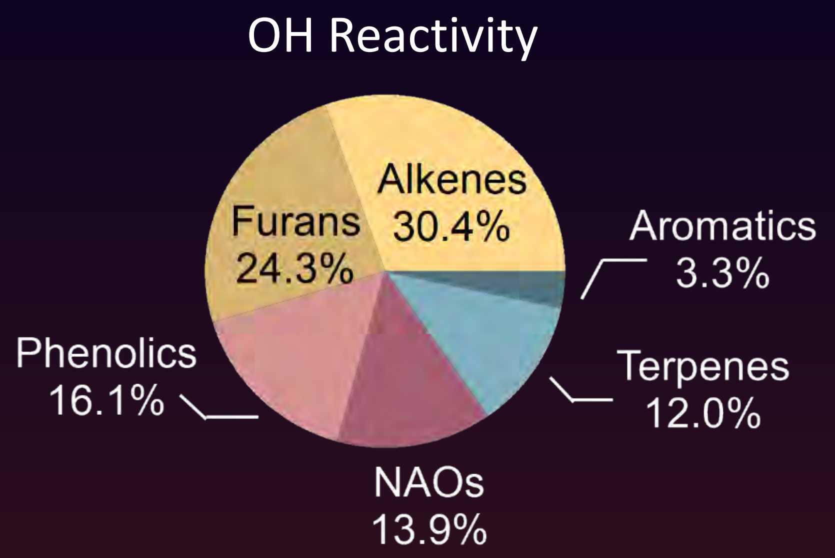


# We Model the Plumes Forward into the Night

- At sunset, all oxidants are present ($NO_3$, OH, and $O_3$), which oxidants are most important and when?
- What is the reactivity at emission and through the night for different BBVOC groups?
  - Phenolics, alkenes, and furans
- Understand $NO_x$ lifetime throughout the night.
- How much and which BBVOCs remain at sunrise?
- What can we learn about overnight BrC formation?

# OH Reactivity is Spread Over Many Groups

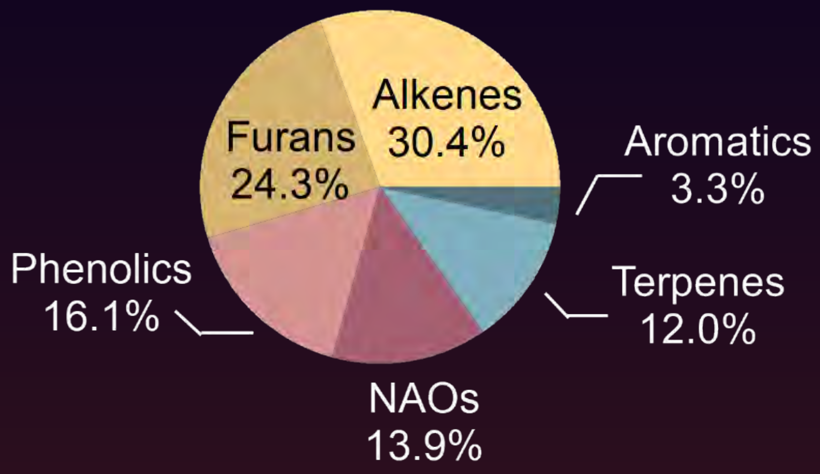



- Caveat: we don’t include alkanes in our BBVOC emissions inventory
  - We undercount OH reactivity.

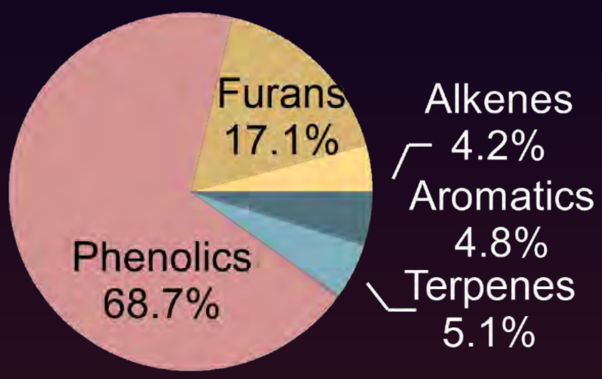
Decker et al. in prep

# $NO_3$ Reactivity is Dominated by Oxy. Aromatics

OH Reactivity




$NO_3$ Reactivity

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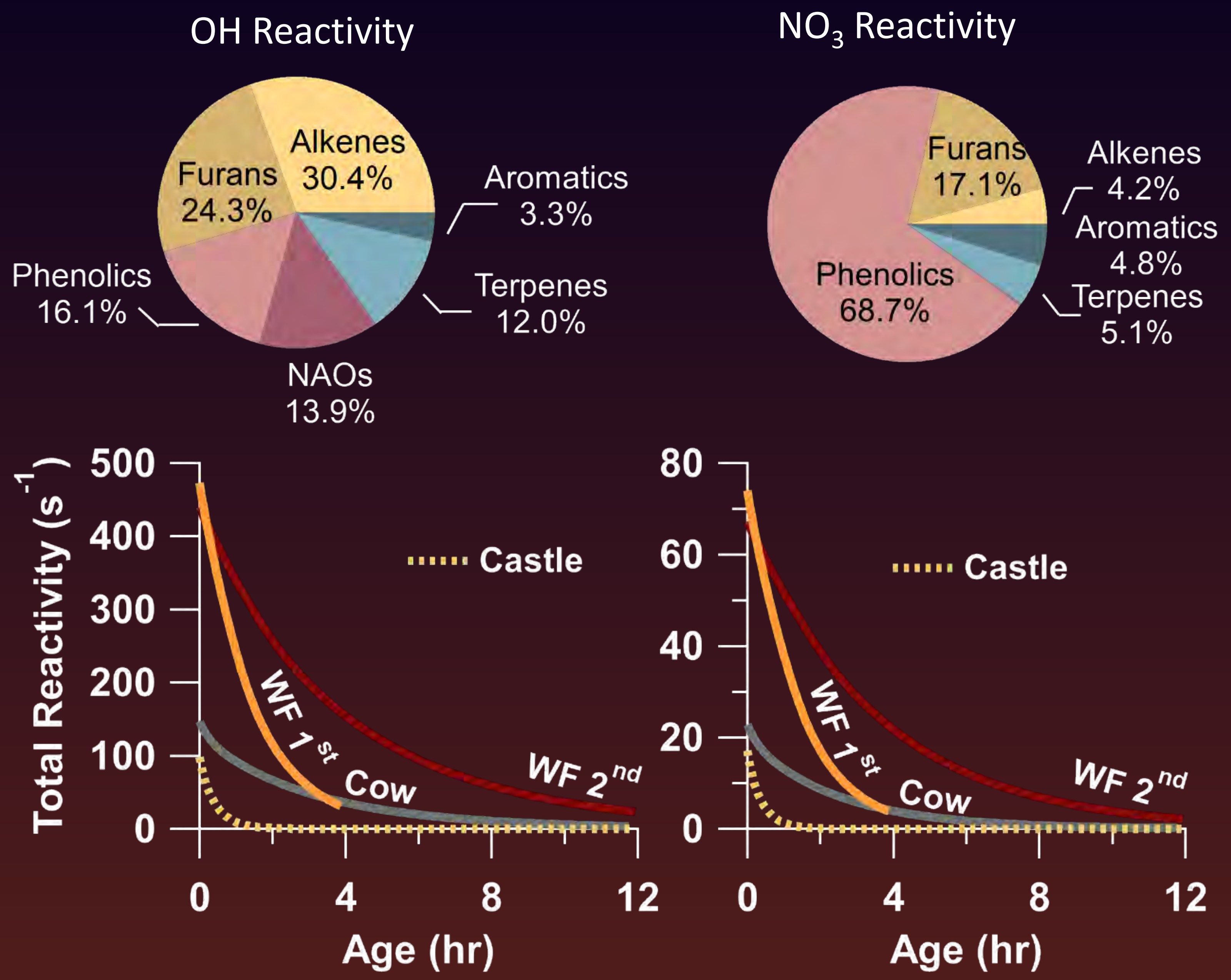
Decker et al. in prep

# For Most Fires Reactivity Nears Zero by Sunrise

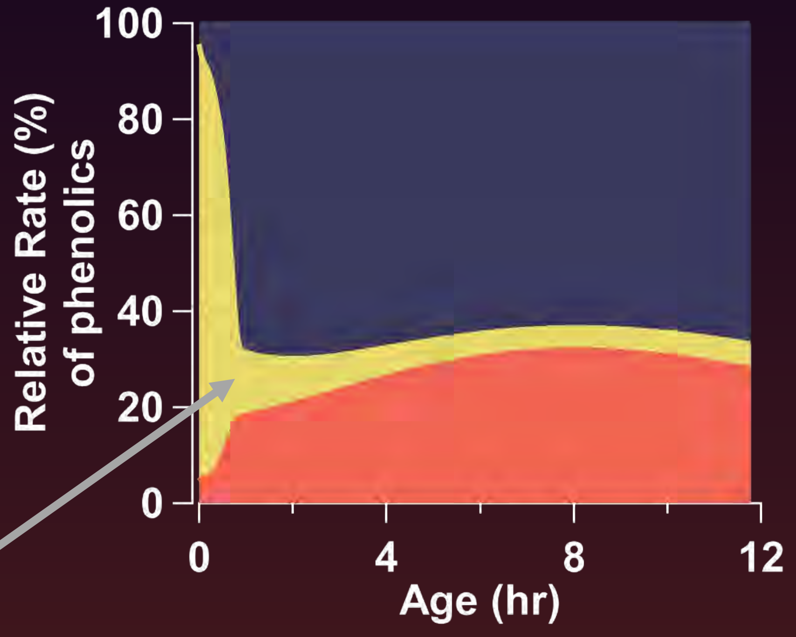



- Caveat: we don’t include alkanes in our BBVOC emissions inventory
  - We undercount OH reactivity.

- OH reactivity is near 450 $s^{-1}$ at emission
  - Spread over many groups
- $NO_3$ reactivity is mostly oxygenated aromatics

Decker et al. in prep

# OH Dominates Phenolic Oxidation Early

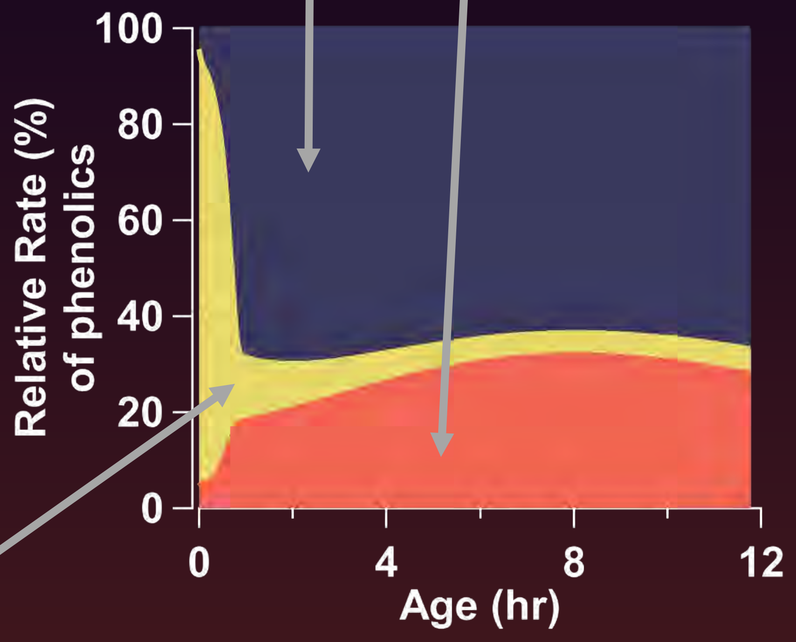



OH dominates phenolic oxidation early

Decker et al. in prep

# $NO_3$ and $O_3$ Dominate After Sunset

$NO_3$ and $O_3$ dominate after sunset



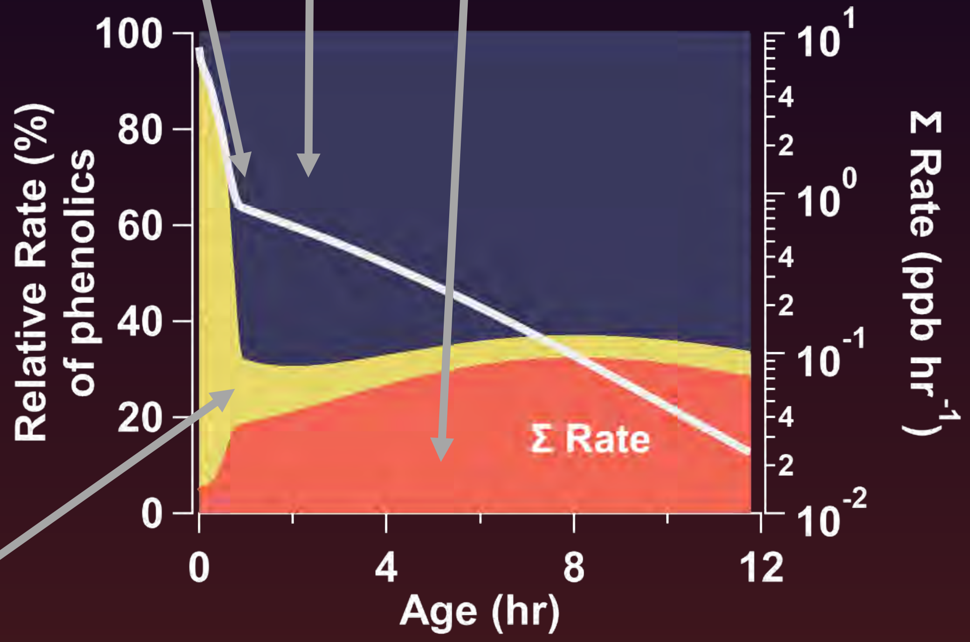

OH dominates phenolic oxidation early

Decker et al. in prep

# Total Oxidation Rate Drops Rapidly During Sunset

Total rate of phenolic oxidation drops rapidly (~10x) until sunset

$NO_3$ and $O_3$ dominate after sunset




OH dominates phenolic oxidation early

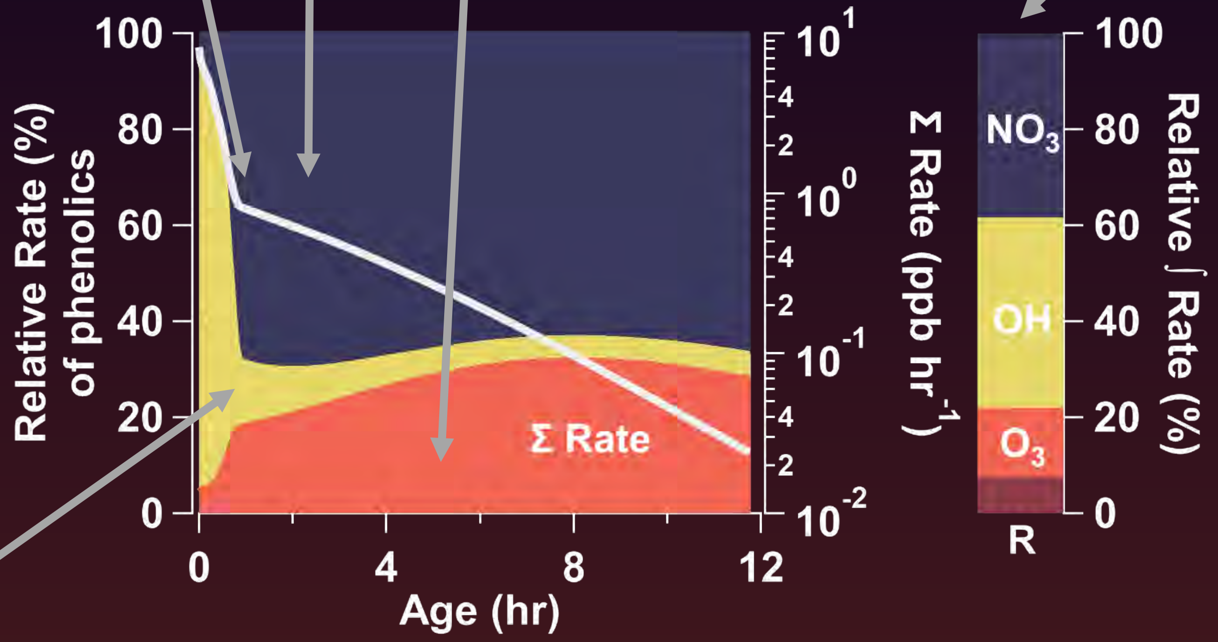
Decker et al. in prep

# Overall $NO_3$ and OH dominate Phenolic Oxidation

Total rate of phenolic oxidation drops rapidly (~10x) until sunset

$NO_3$ and $O_3$ dominate after sunset

From emission to sunrise 38% of emitted phenolics reacted with $NO_3$




OH dominates phenolic oxidation early

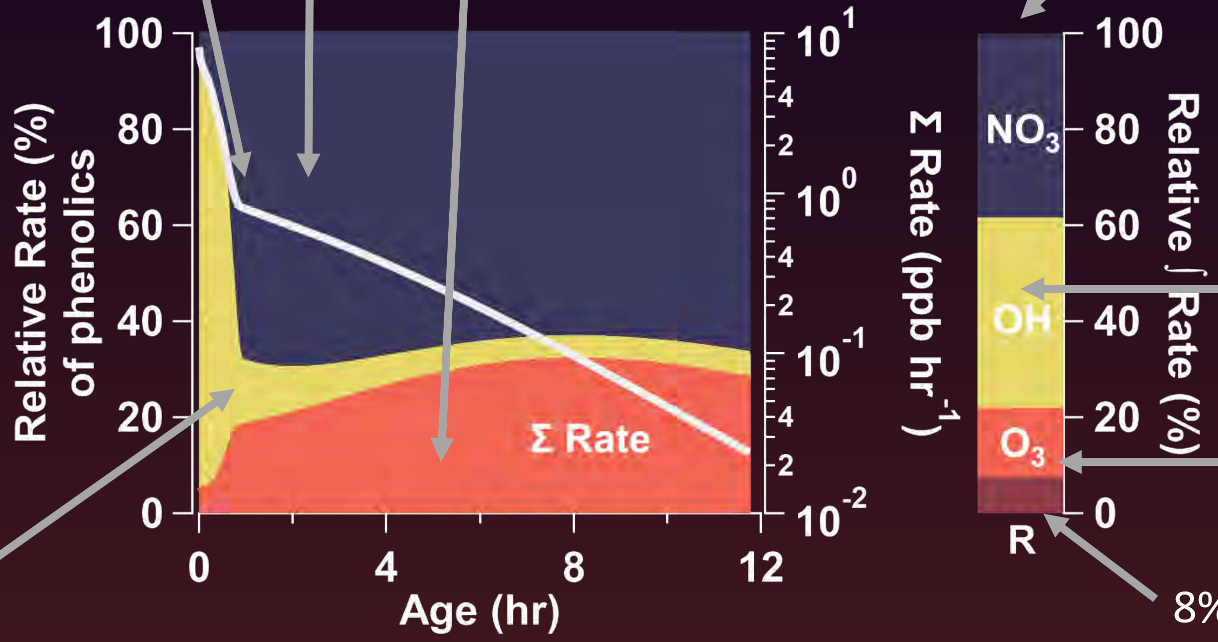
Decker et al. in prep

# About 8% of Phenolics Remain Unreacted by Sunrise

Total rate of phenolic oxidation drops rapidly (~10x) until sunset

$NO_3$ and $O_3$ dominate after sunset

From emission to sunrise 38% of emitted phenolics reacted with $NO_3$




40% reacted with OH

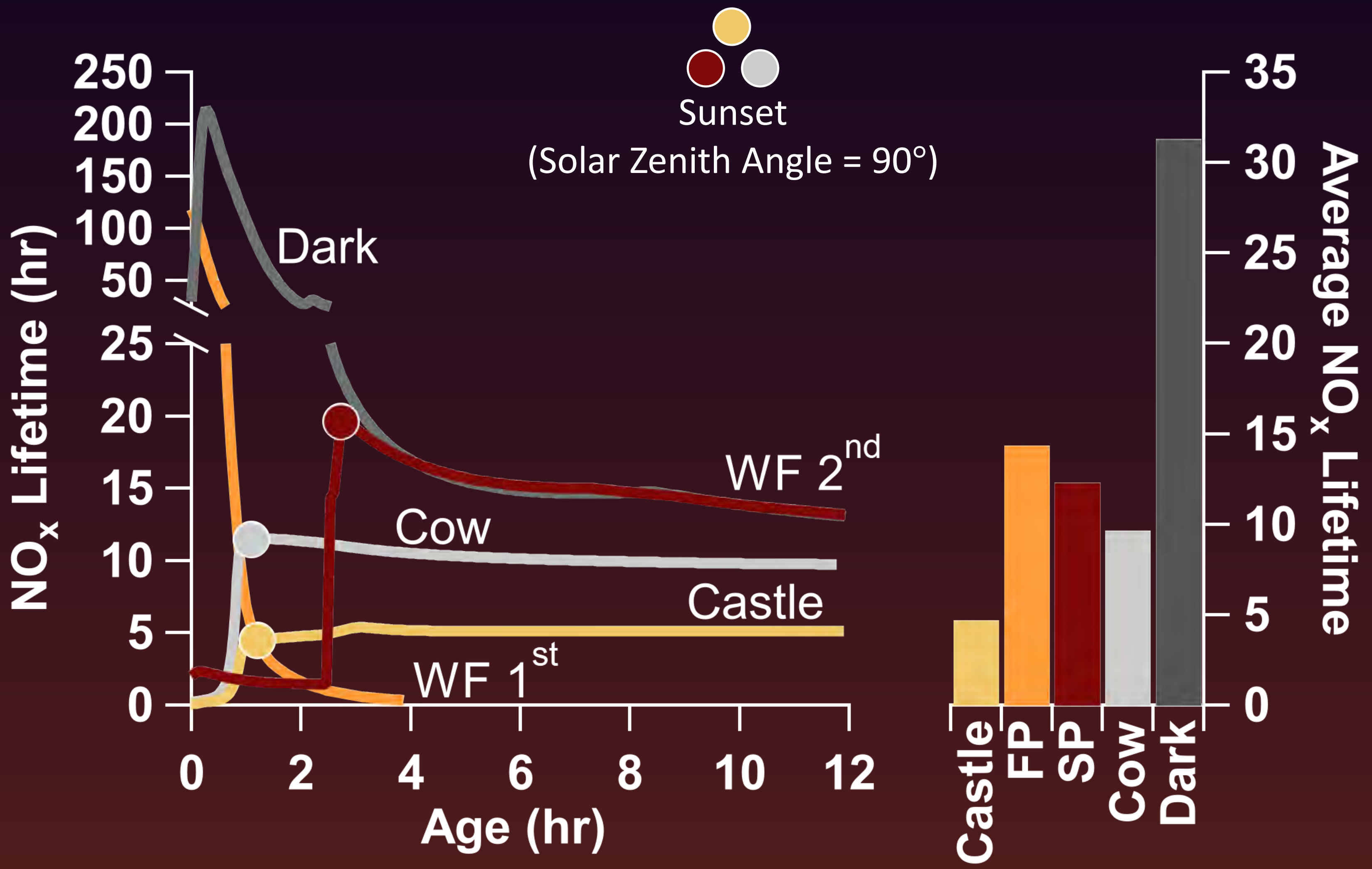
14% reacted with $O_3$

8% remain at sunrise

OH dominates phenolic oxidation early

Decker et al. in prep

# After Sunset $NO_x$ Lifetime Increases Substantially

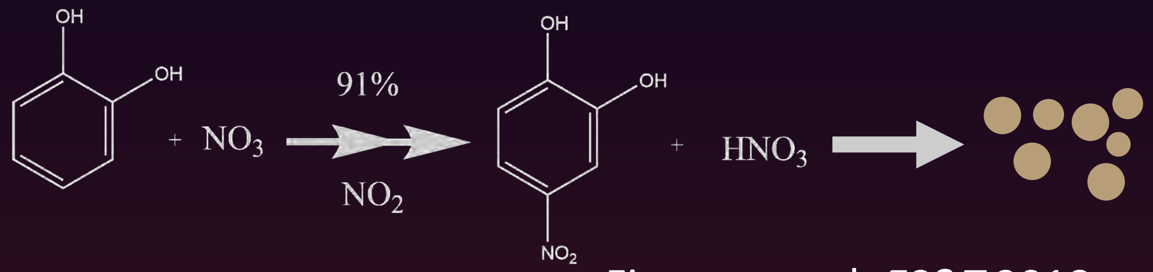



$NO_x$ lifetime is 1-2 hr pre-sunset and ~10 hr post-sunset

Decker et al. in prep

# What Does This Tell Us About Potential BrC Formation?

Catechol reactions can form many products including nitrocatechol, which forms BrC.




Finewax et al. *ES&T* 2018

Decker et al. in prep

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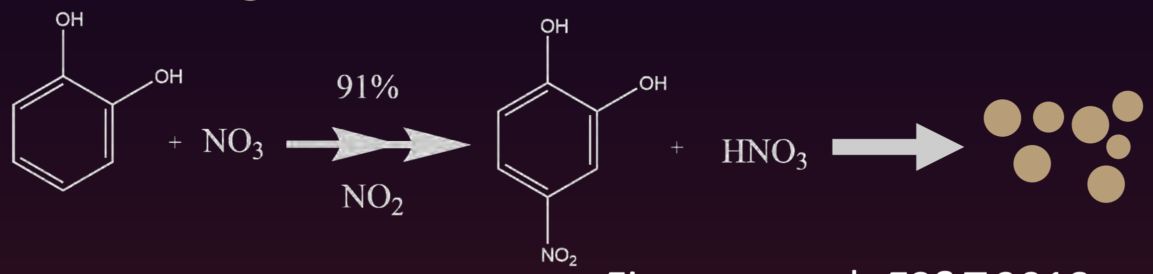
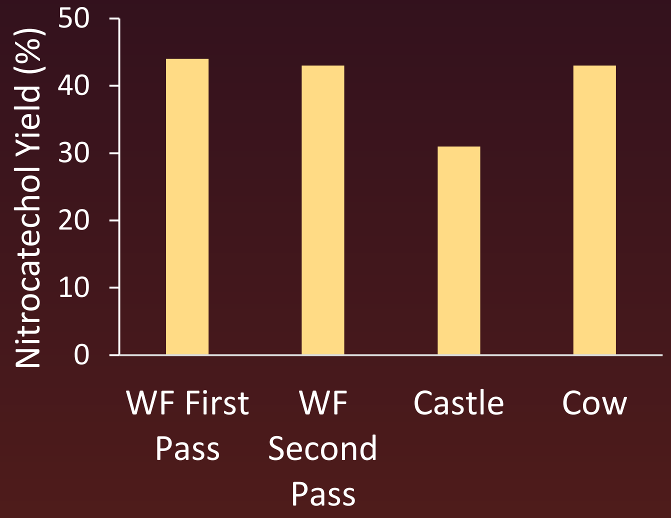



Finewax et al. *ES&T* 2018

Nitrocatechol yield




High $O_3$ and low $NO_x$ in the Castle fire reduce the nitrocatechol yield

Decker et al. in prep

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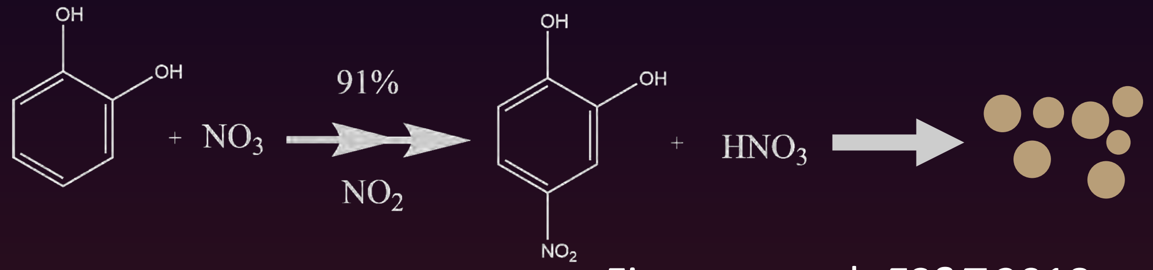
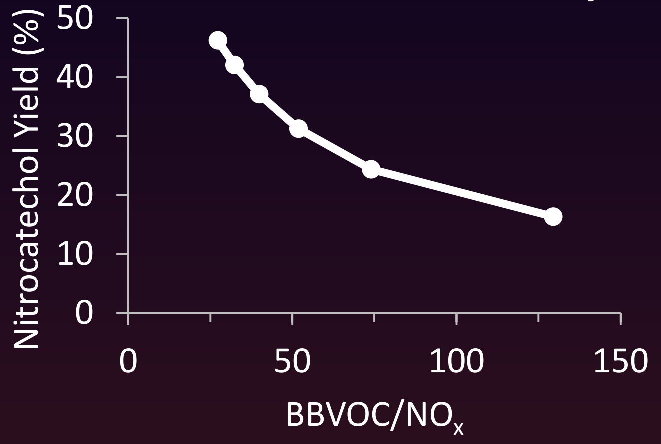


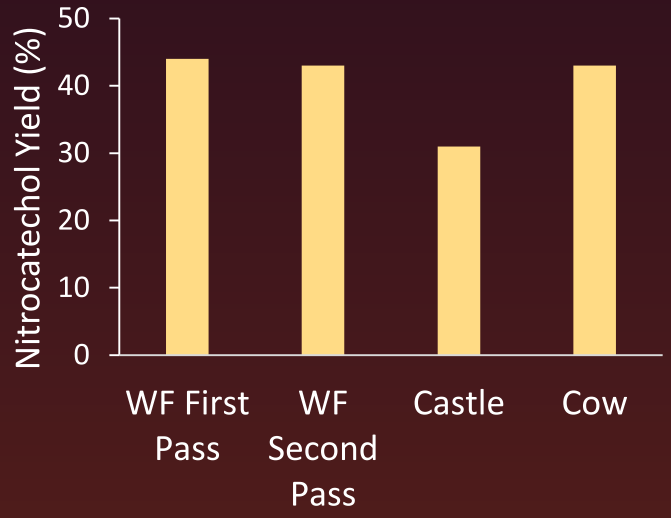

Finewax et al. *ES&T* 2018

Nitrocatechol yield and VOC/$NO_x$




Nitrocatechol yield increases with decreasing VOC/$NO_x$ ratio.

Nitrocatechol yield

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Decker et al. in prep

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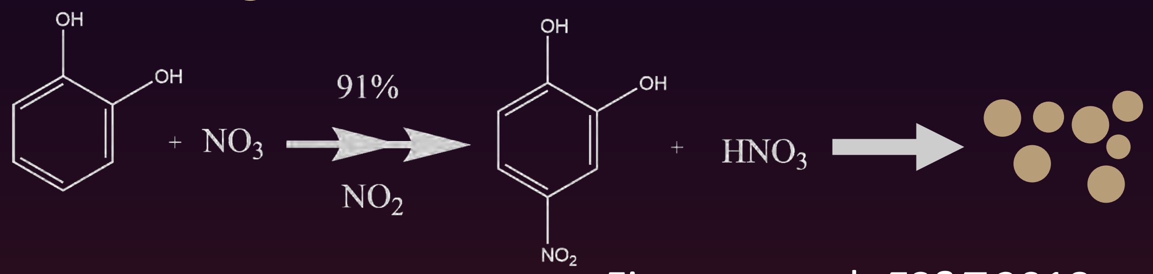
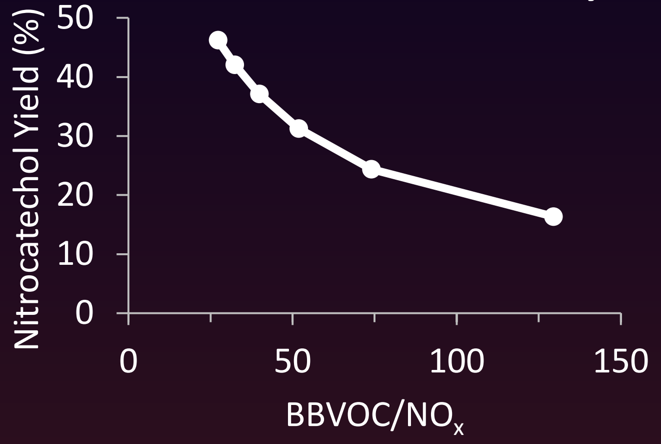



Finewax et al. *ES&T* 2018

## Nitrocatechol yield and VOC/$NO_x$

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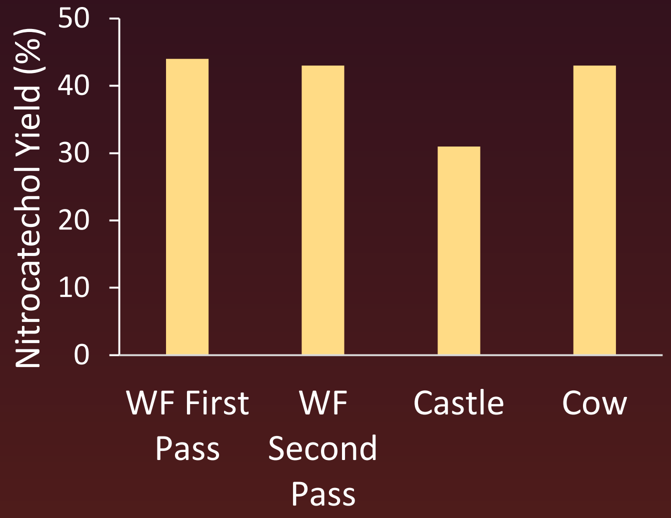
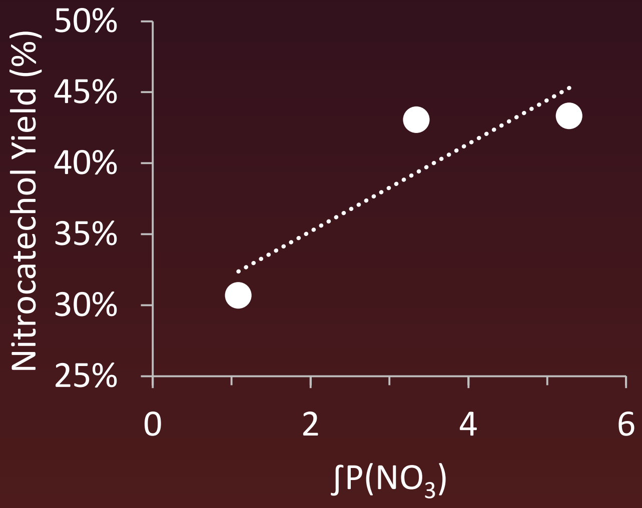
## Nitrocatechol yield




High $O_3$ and low $NO_x$ in the Castle fire reduce the nitrocatechol yield

## Nitrocatechol yield and ∫ P($NO_3$)

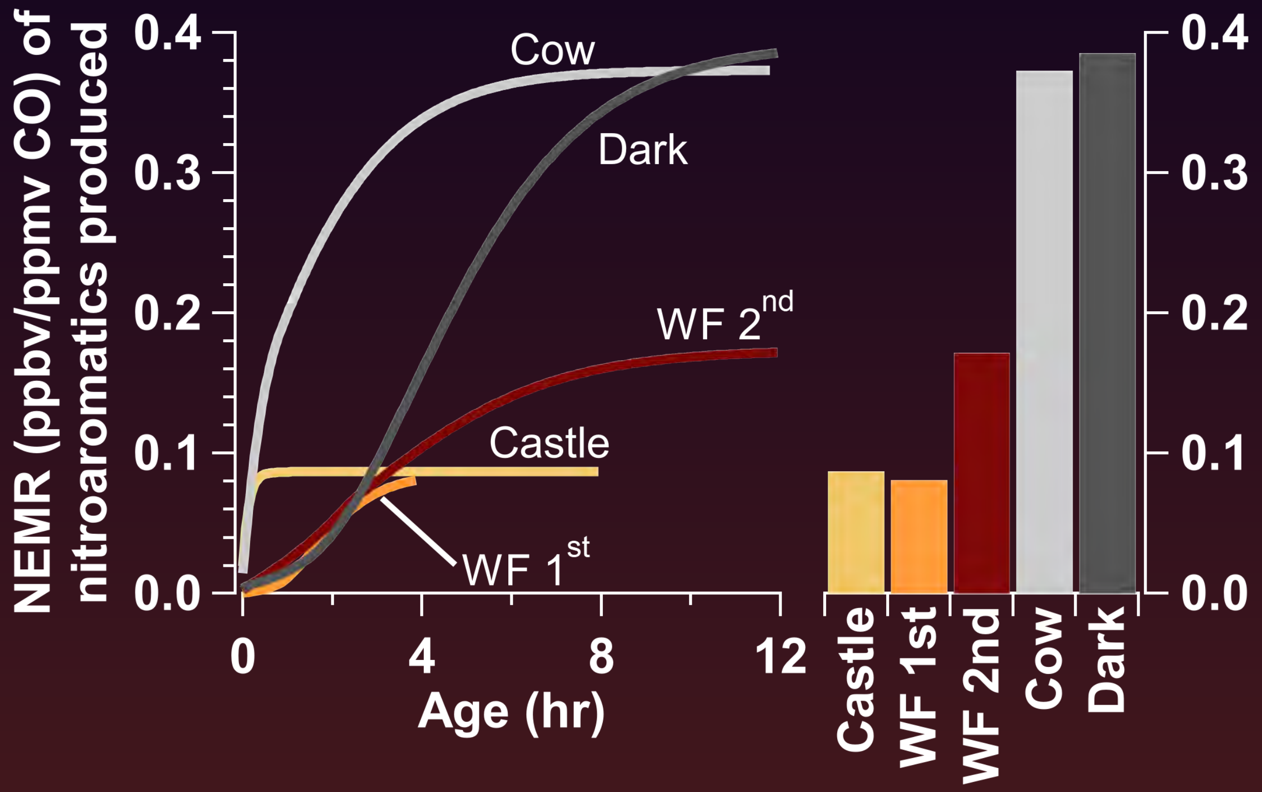



Only a few points, but a good correlation exists ($R^2$=0.8)

$NO_3$ is responsible for 71-83% of nitrocatechol production

Decker et al. in prep

# What Does This Tell Us About Potential BrC Formation?

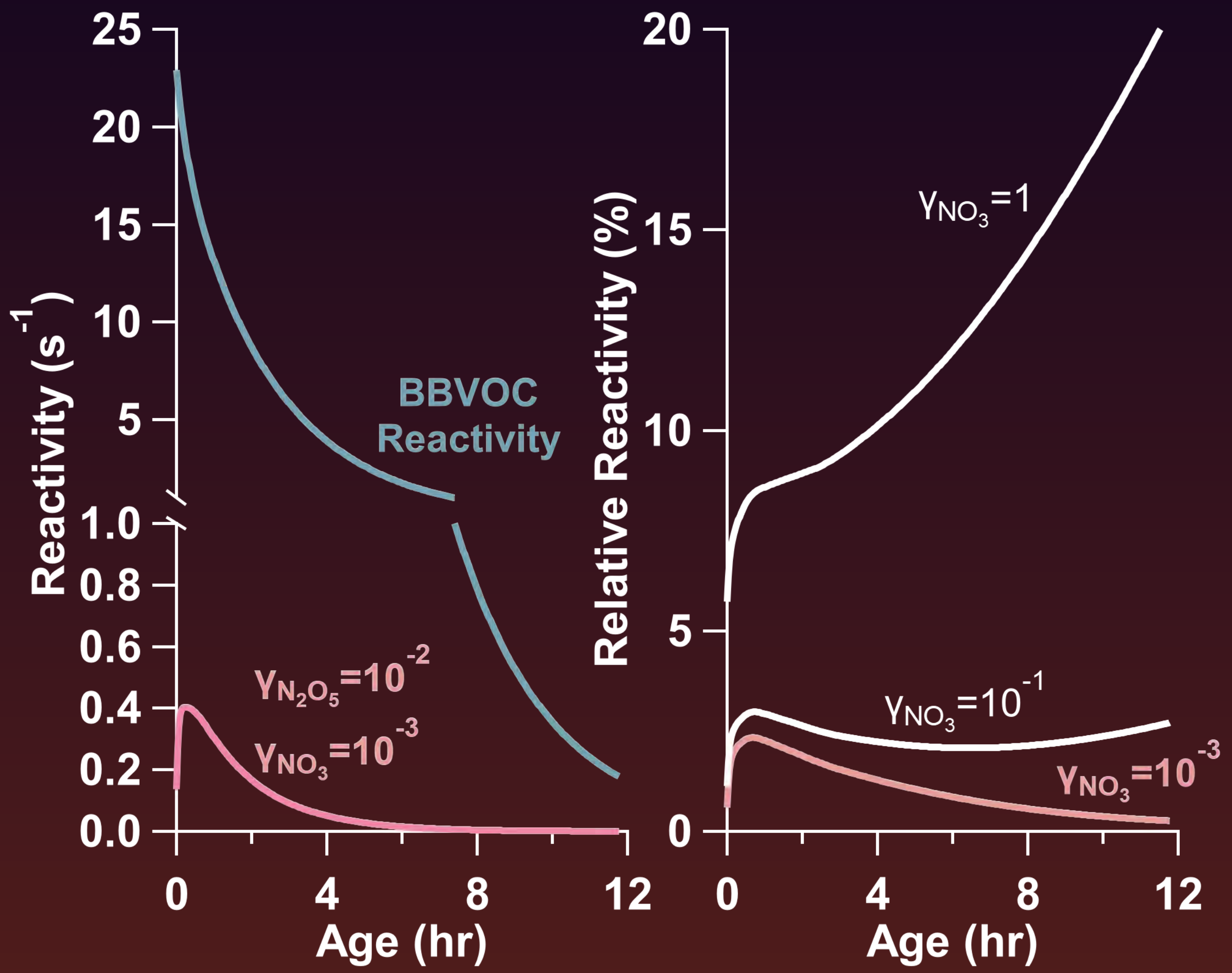



- Nitroaromatics form quickly in the Castle and Cow models
  - $O_3$ is abundant
- But slowly in the Williams Flats models.
  - Large emissions of NO depletes $O_3$

Nitroaromatic formation is dependent on how much $O_3$ is depleted at emission and how quickly it is regenerated.

Decker et al. in prep

# $NO_3$ Heterogeneous Chemistry is Negligible




$$k_{NO_3 \text{ or } N_2O_5} = \frac{\gamma \bar{c} SA}{4}$$

$$\gamma_{N_2O_5} = 10^{-2}\ (*)$$

$$\gamma_{NO_3} = 10^{-3} - 10^{0}$$

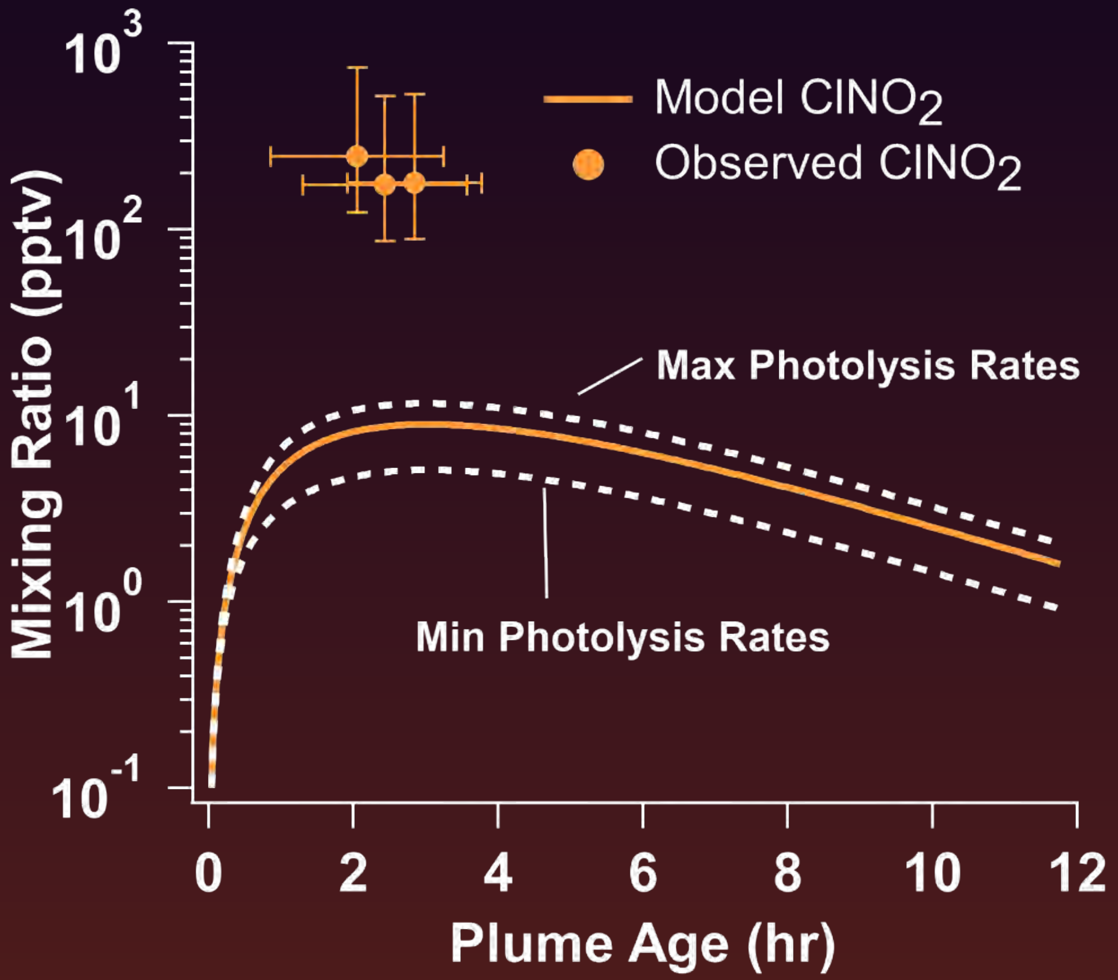
(*) McDuffie et al. 2018 JGR
Decker et al. in prep

# Models Suggest an Unknown Source of $ClNO_2$

$NO_2 + O_3 \rightarrow NO_3$
$NO_2 + NO_3 \rightarrow N_2O_5$
$N_2O_5 + pCl \rightarrow ClNO_2$

Decker et al. in prep

# Models Suggest an Unknown Source of $ClNO_2$




$NO_2 + O_3 \rightarrow NO_3$
$NO_2 + NO_3 \rightarrow N_2O_5$
$N_2O_5 + pCl \rightarrow ClNO_2$

- Model and Observations differ by ~20x

- No pCl or $ClNO_2$ outside of the plume
- AMS Shows elevated pCl (~2 $\mu g/m^3$)
  - But not greater than other flights
- No Structures burned
- No Chloride containing flame retardants

- Changes in $\gamma_{N_2O_5}$ ($N_2O_5$ uptake) are tiny
- $ClNO_2$ calibration error shown here is 2x
  - Reported is 30%, confident this isn't the cause.

Decker et al. in prep

# Conclusions

- We use a detailed chemical box model and observations to study plume chemistry overnight
  - Using the Master Chemical Mechanism and an updated NOAA BB Mechanism
- OH dominates phenolic and furan oxidation within the first hour of emission.
  - $NO_3$ and $O_3$ take over oxidation as the sun sets.
  - Integrated oxidation of phenolics is split almost equally between $NO_3$ and OH.
- Reactivity of OH is spread across many BBVOC groups, while $NO_3$ is mostly phenolics and $O_3$ is mostly alkenes
  - Alkenes dominate OH and $O_3$ reactivity
  - Total OH reactivity reaches at least 400 $s^{-1}$ in the Willams Flats model.
  - $NO_3$ reactivity reaches 80 $s^{-1}$
- $NO_x$ lifetime is 1-2 hrs pre-sunset and ~10 post-sunset
- Modeled nitrocatechol yields are ~40% or lower depending on the available $NO_x$ and $O_3$
  - Nitrocatechol yield decreases with increasing $NO_x$ / BBVOC ratio
  - Nitrocatechol yield is well correlated with $NO_3$ production rate (only 3 points)
  - $NO_3$ is responsible for 71-83% of produced nitrocatechol
- Aerosol reactivity is negligible in comparison to BBVOC reactivity
- Models suggest an unknown source of $ClNO_2$


## Contact

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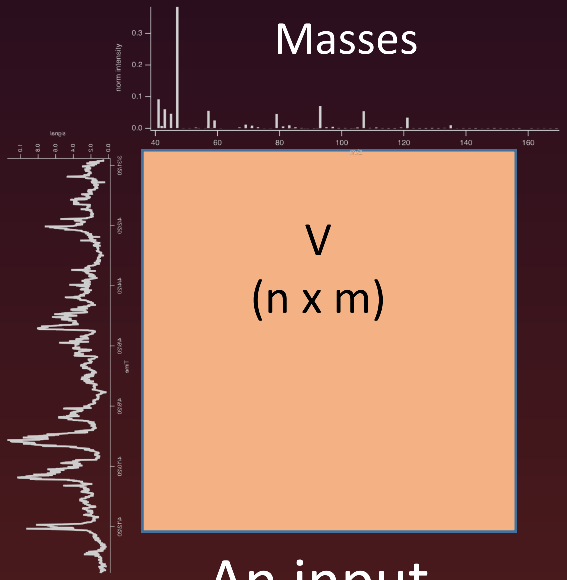
# Can we find trends in BBVOC evolution?

## Positive Matrix Factorization (PMF) is the right tool

Use ~150 I- CIMS raw mass signals from FIREX-AQ Observations

Masses

Time series



V
(n x m)

An input matrix

=

PMF calculates W and H

W
(n x p)

A matrix of trends

•

H
(p x m)

A matrix of weights for each trend

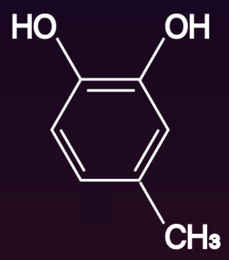
PMF outputs "Factors" or groups of compounds that correlate in time

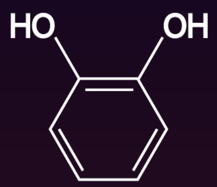
1. Ranked "tracers" for each factor
2. Factor time series

# We Find at Least Three Stages

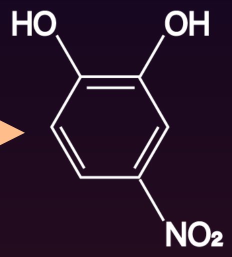
**Fastest Chemistry**

HONO




**Slower Chemistry**




HONO

Primary Emissions

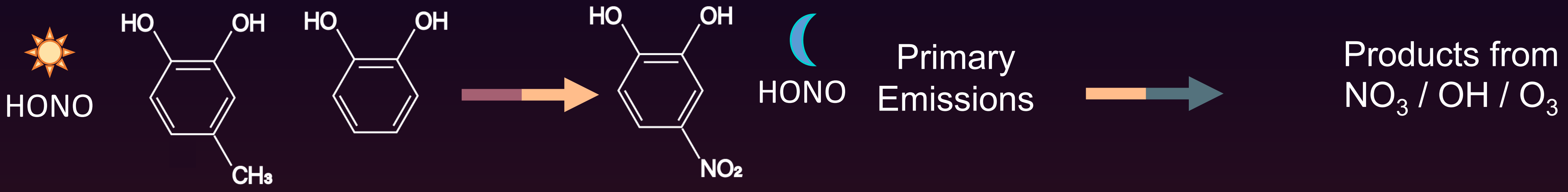
**Oxidation Products**

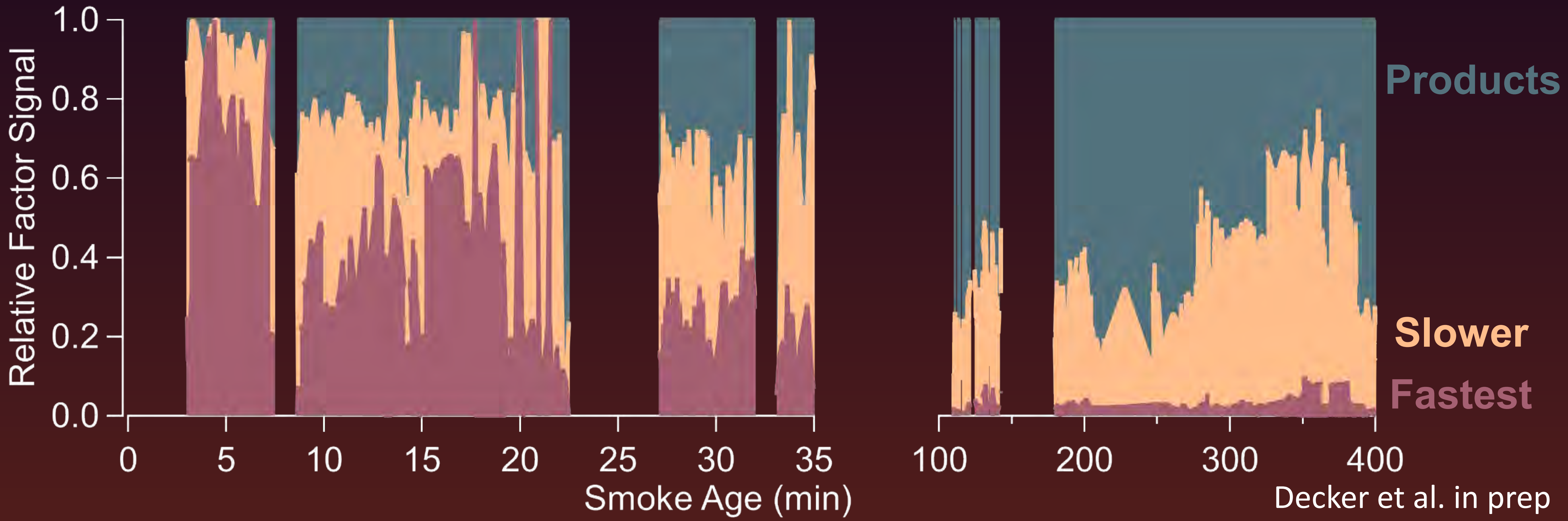
Products from $NO_3$ / OH / $O_3$

Decker et al. in prep

# We Find at Least Three Stages

**Fastest Chemistry** **Slower Chemistry** **Oxidation Products**



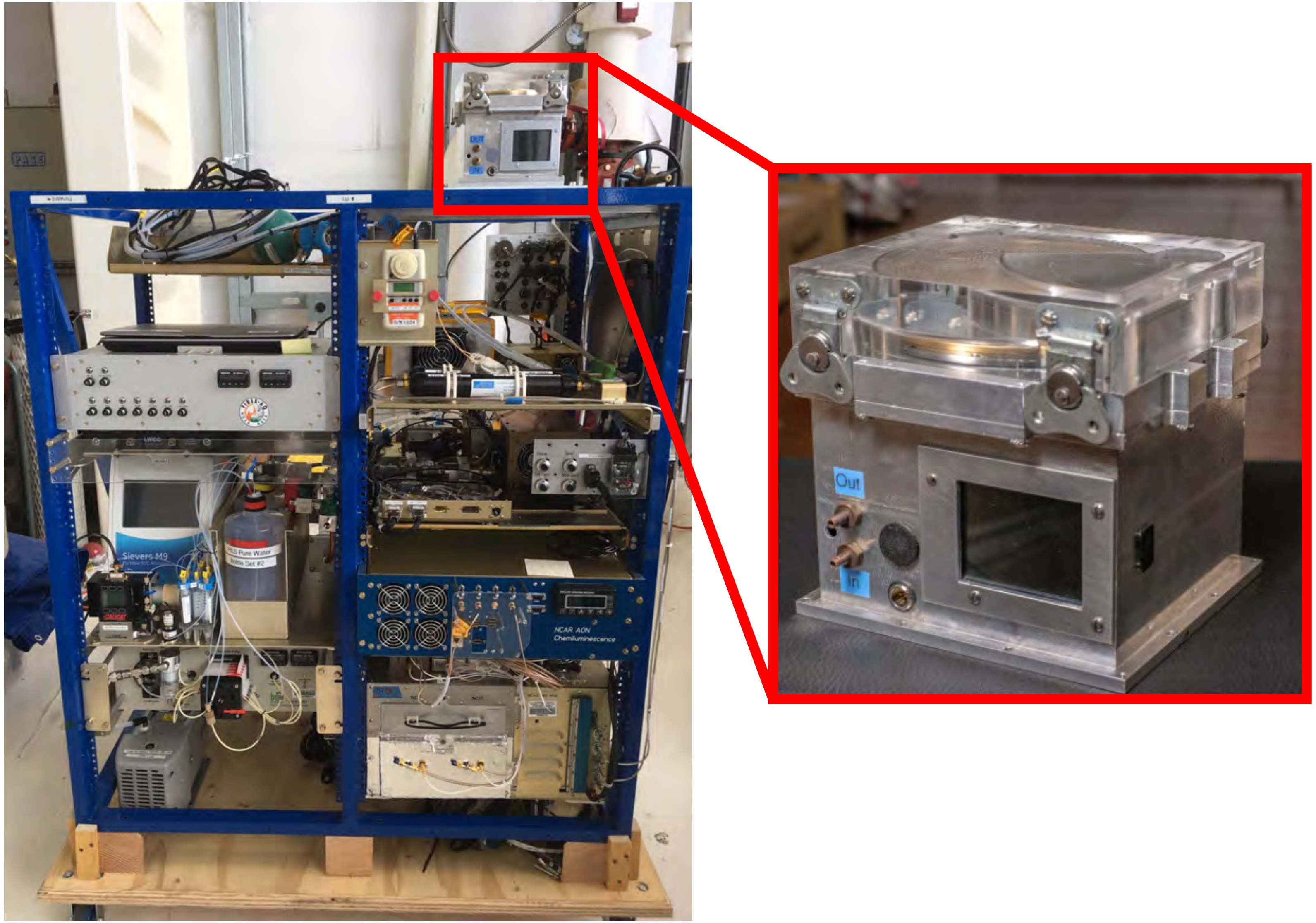

Decker et al. in prep

# Chemical Imaging of Biomass Burning Aerosols

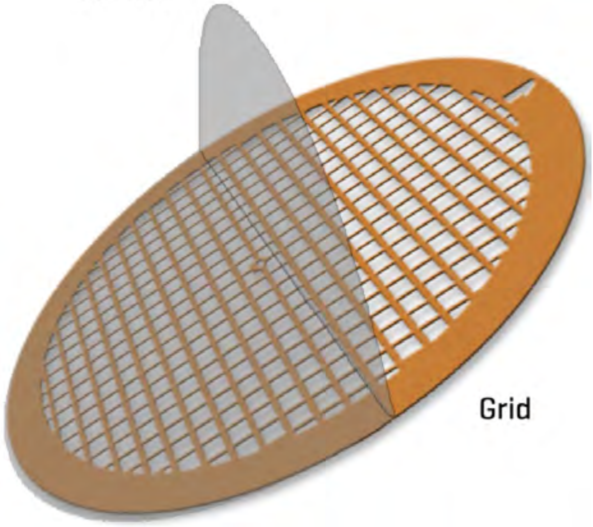
Felipe Rivera-Adorno[1] , Jay Tomlin[1] , Kevin Jankowski[1] , Rebecca Washenfelder[2] , Ann M. Middlebrook[2] , Swarup China[3] , Ryan Moffet[4] , Lisa Azzarello[5] , Alessandro Franchin[6] , Jian Wang[7] , Alexander Laskin[1]

[1]Purdue University-Department of Chemistry, [2]National Oceanic and Atmospheric Administration-Chemical Sciences Division, [3]Pacific Northwest National Laboratory-Environmental Molecular Sciences Laboratory, [4]Sonoma Technology, [5]York University-Department of Chemistry, [6]National Center for Atmospheric Research, [7]Canadian Light Source

# Time-resolved Aerosol Collector (TRAC)




Top-view of metal disc

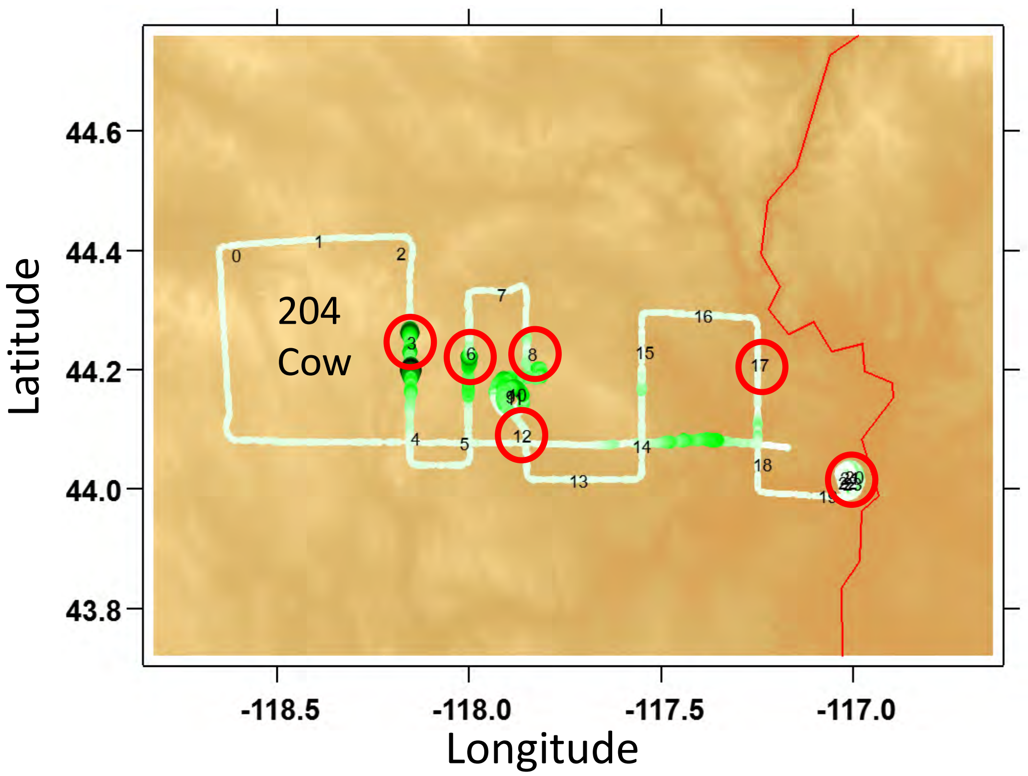



https://www.chem.purdue.edu/jafci/projects/trac.html

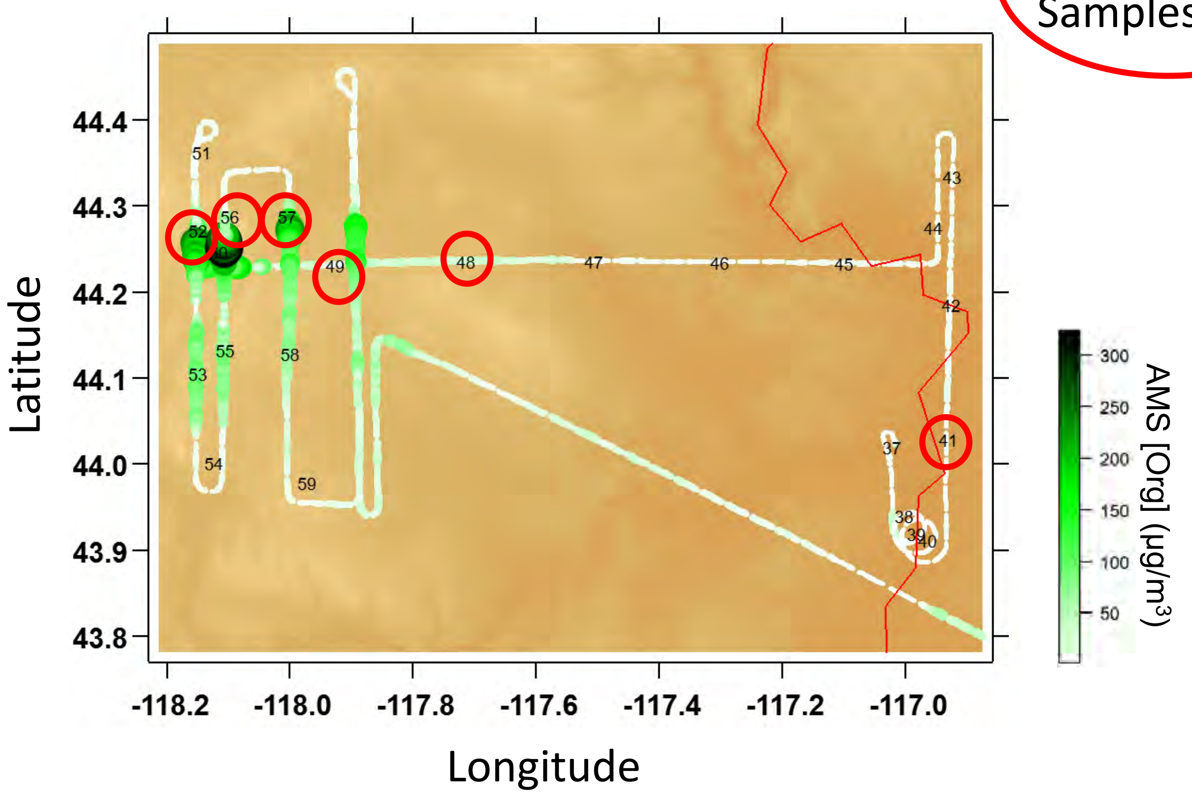
https://emresolutions.com/product/carbon-film-on-nickel-300-mesh-50/

# Particle Collection and Sample Selection for Analysis:08/28 Flights

## Daytime (L2)



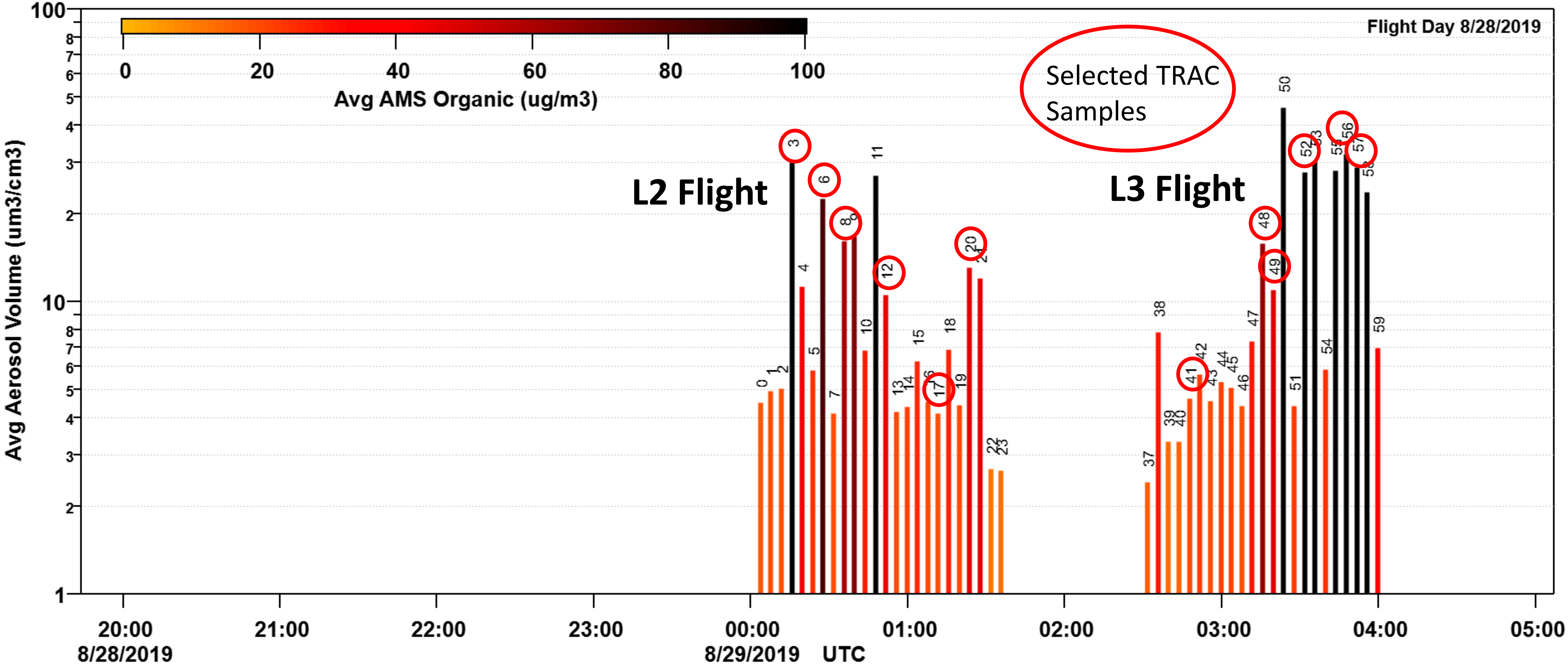

## Nighttime (L3)




Selected TRAC Samples

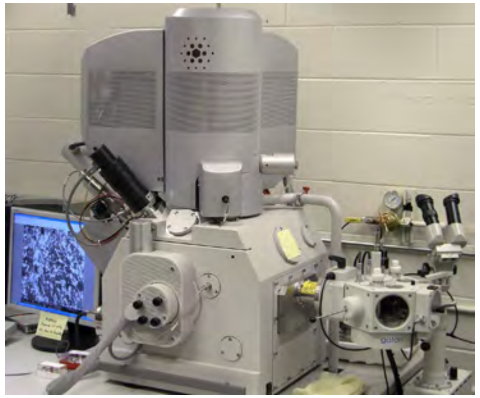
*Data provided by R. Washenfelder (NOAA)

# Particle Collection and Sample Selection



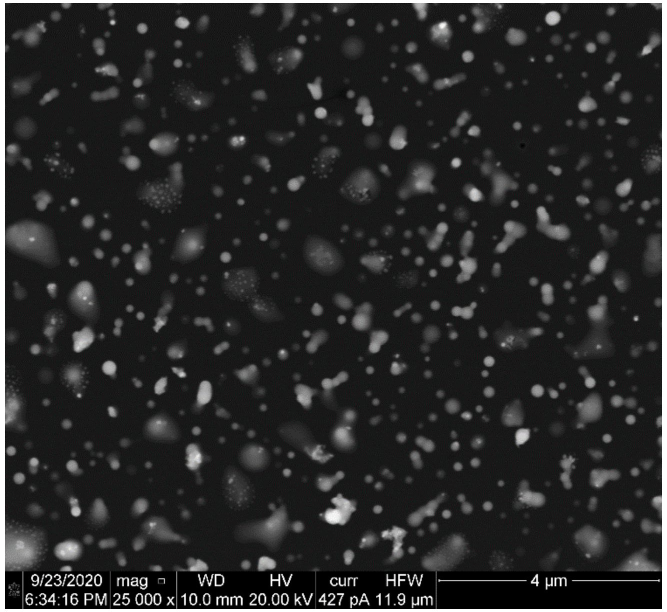

*Data provided by R. Washenfelder (NOAA)

# Particle-type Population and External Mixing

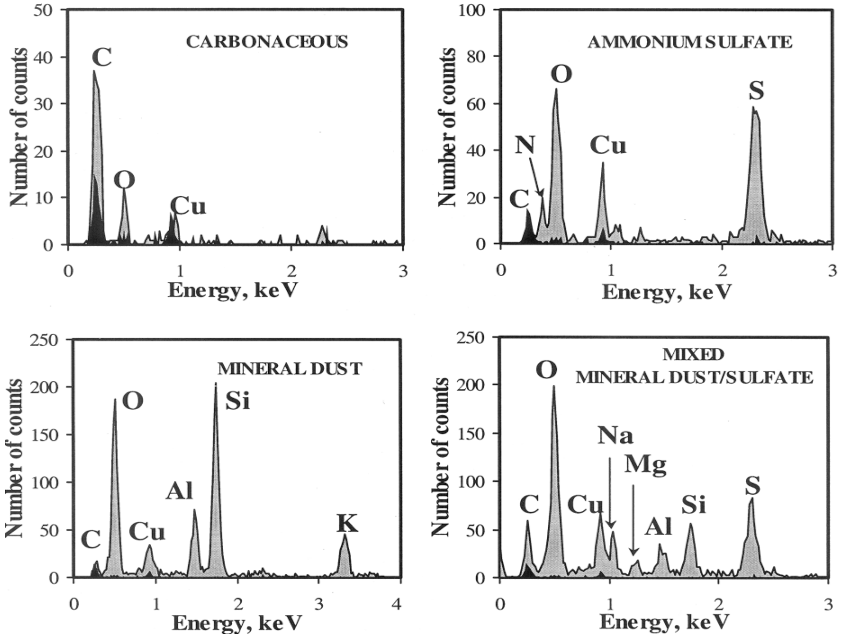


Pacific Northwest
NATIONAL LABORATORY

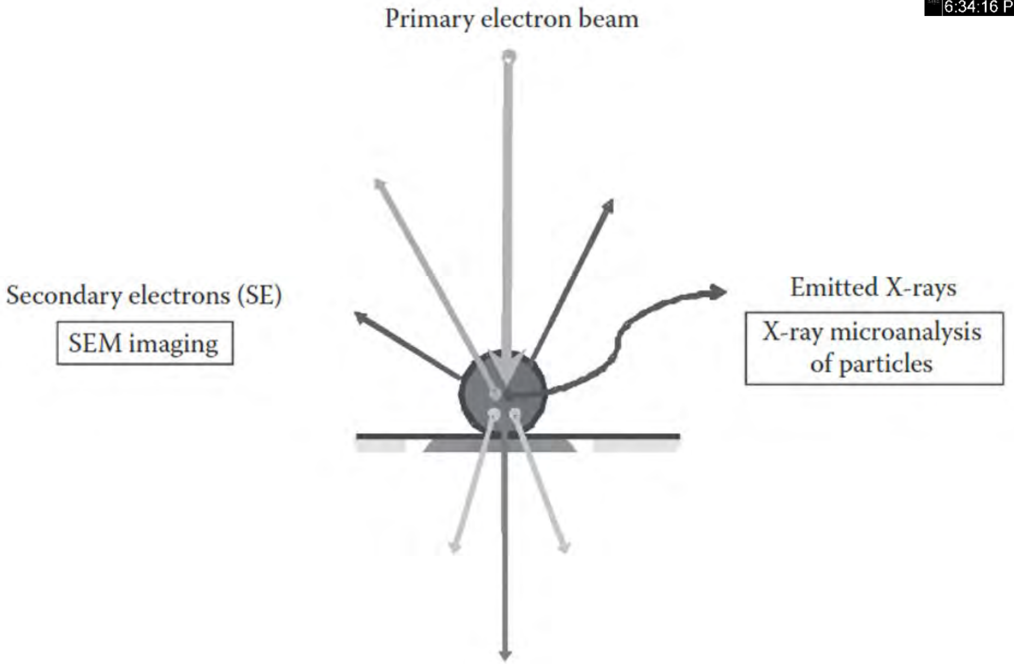
EMSL

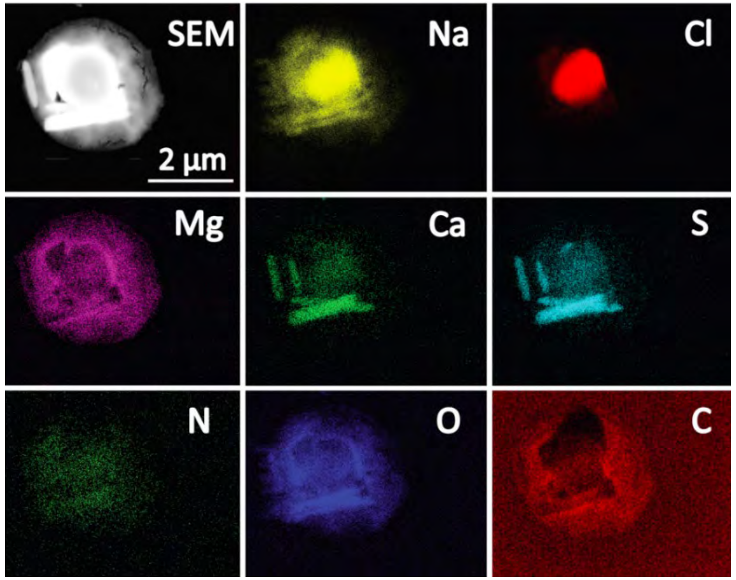



FIREX-AQ Sample



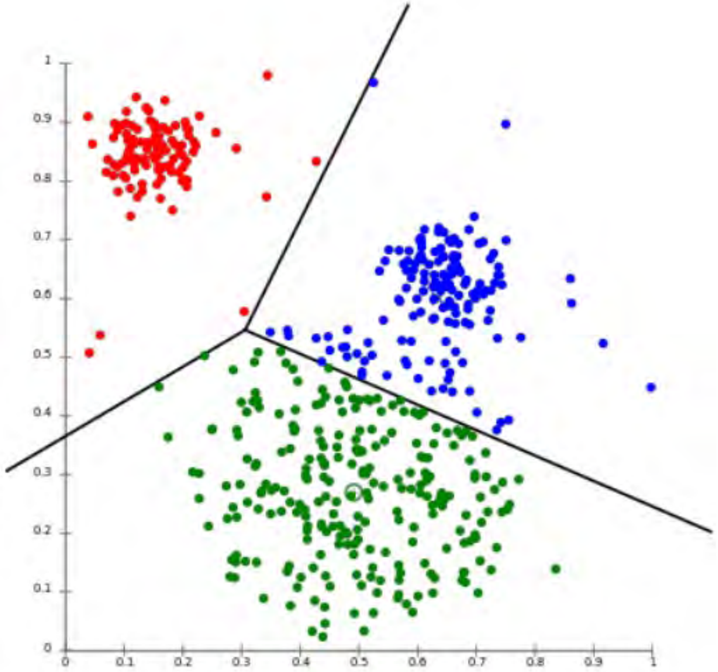

Laskin et al, *AST* , *37,* 246–260. © 2003, *Taylor and Francis*

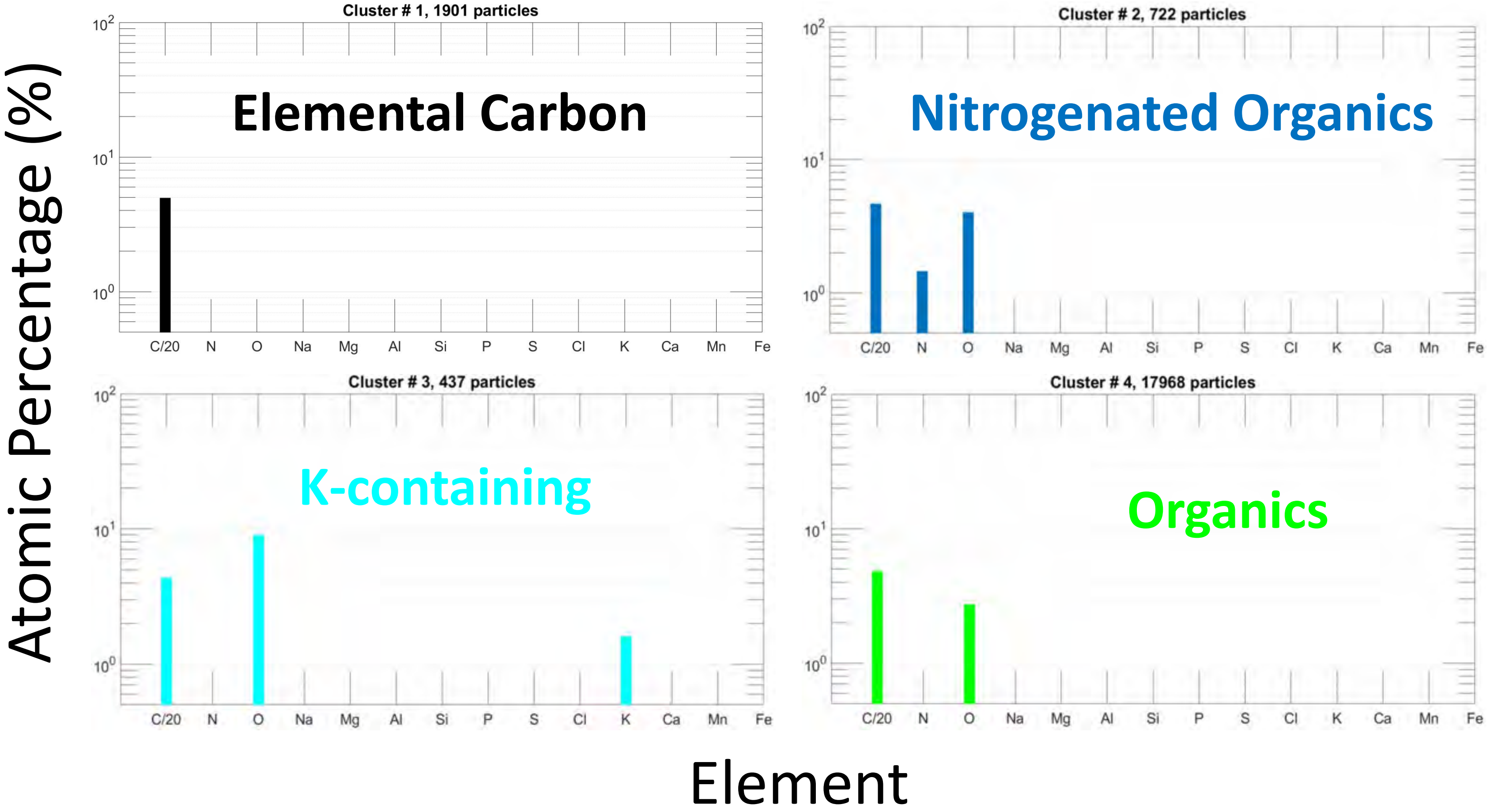



Laskin et al. *JGR,* 117, D15302, © 2012, *AGU*

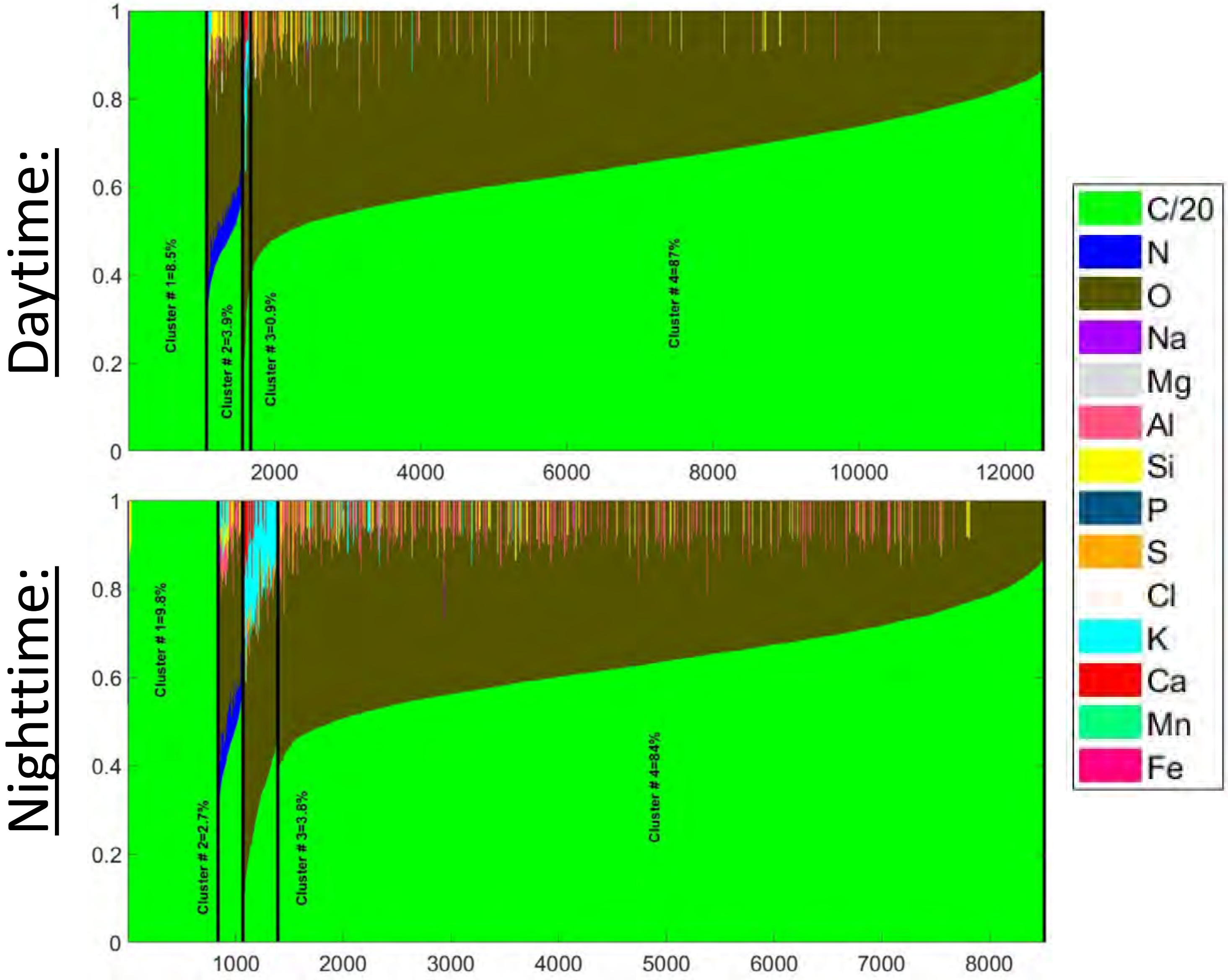
# K-means Cluster Analysis:






https://aws.amazon.com/blogs/machine-learning/k-means-clustering-with-amazon-sagemaker/

# Particle-type Population: Day vs Night

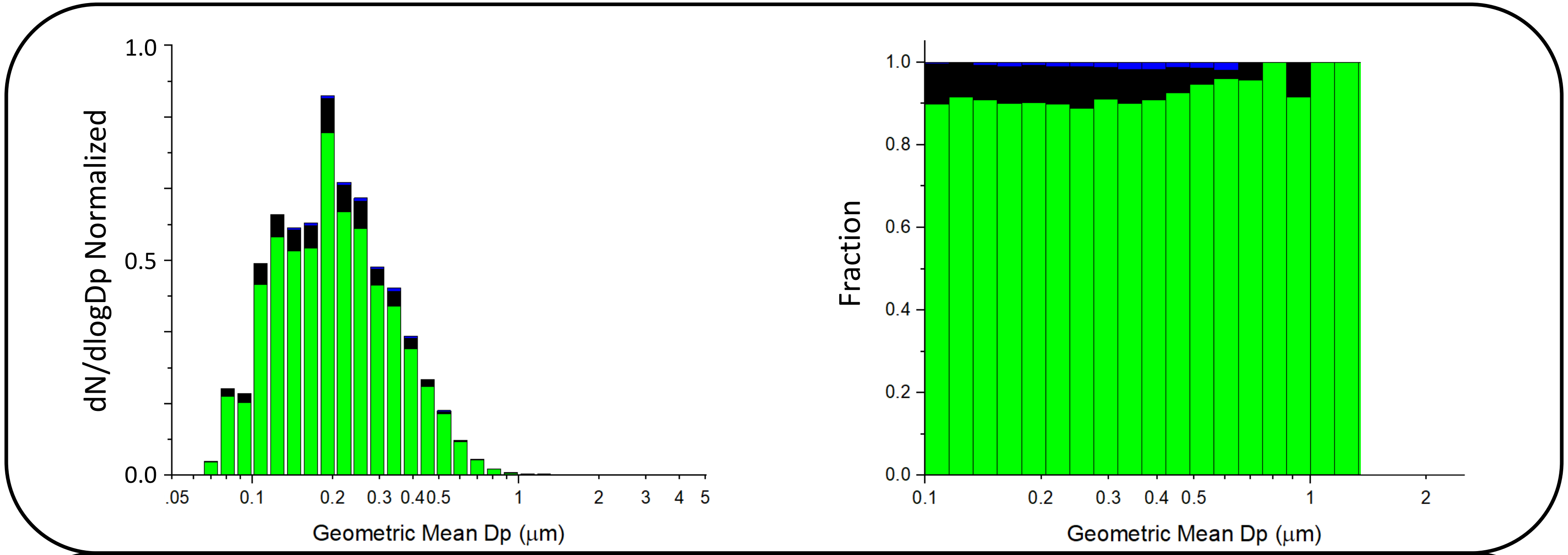



Main Findings:

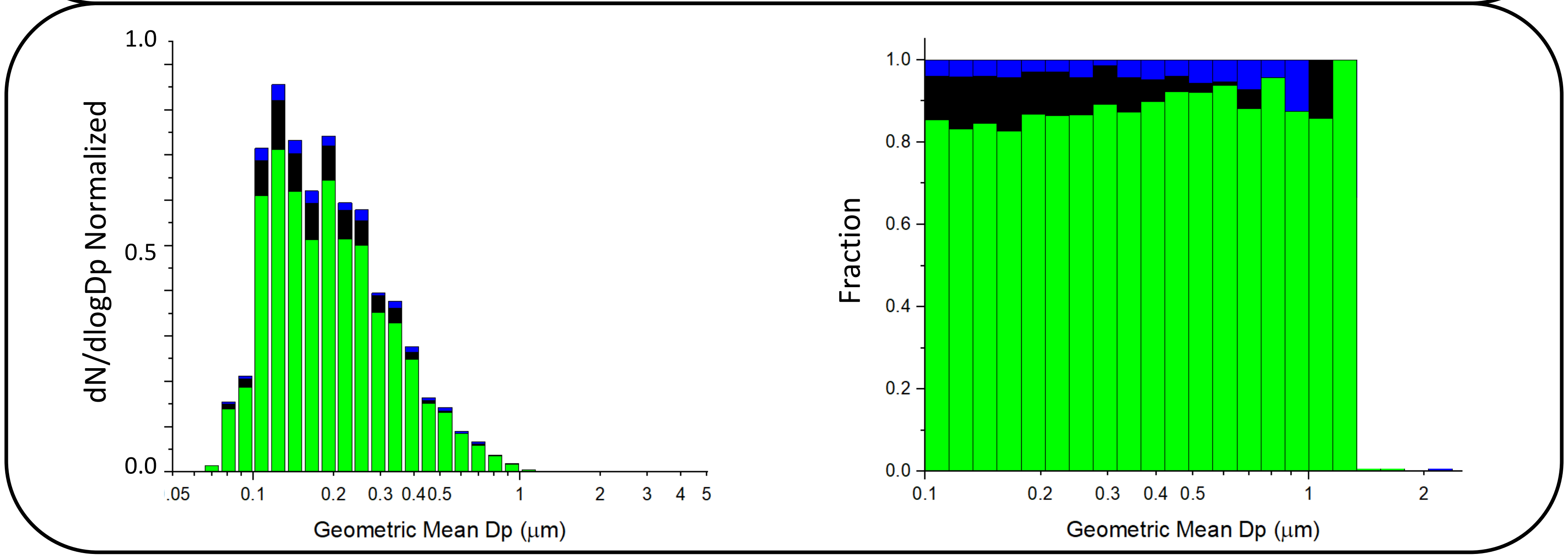
- K-means cluster analysis suggests slightly higher contribution of inorganics in the nighttime sample compared with daytime (3.8% vs 0.9%).
- Overall, daytime and nighttime seem to be very similar in elemental composition.

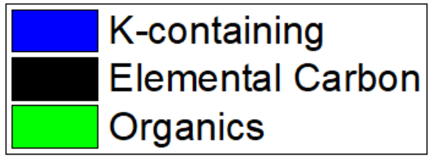
# Particle Size Distribution: External Mixing

Daytime:




Nighttime:

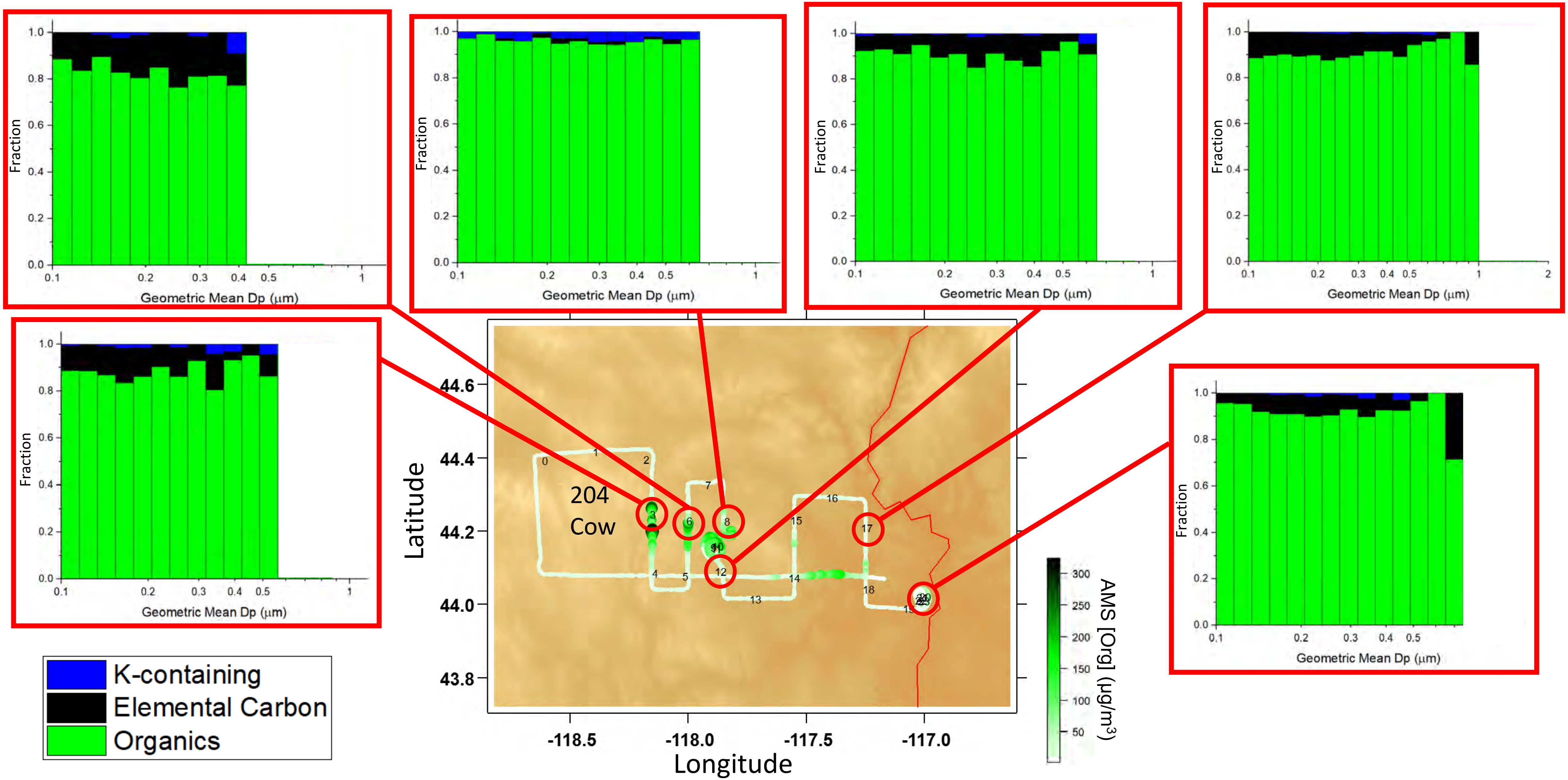


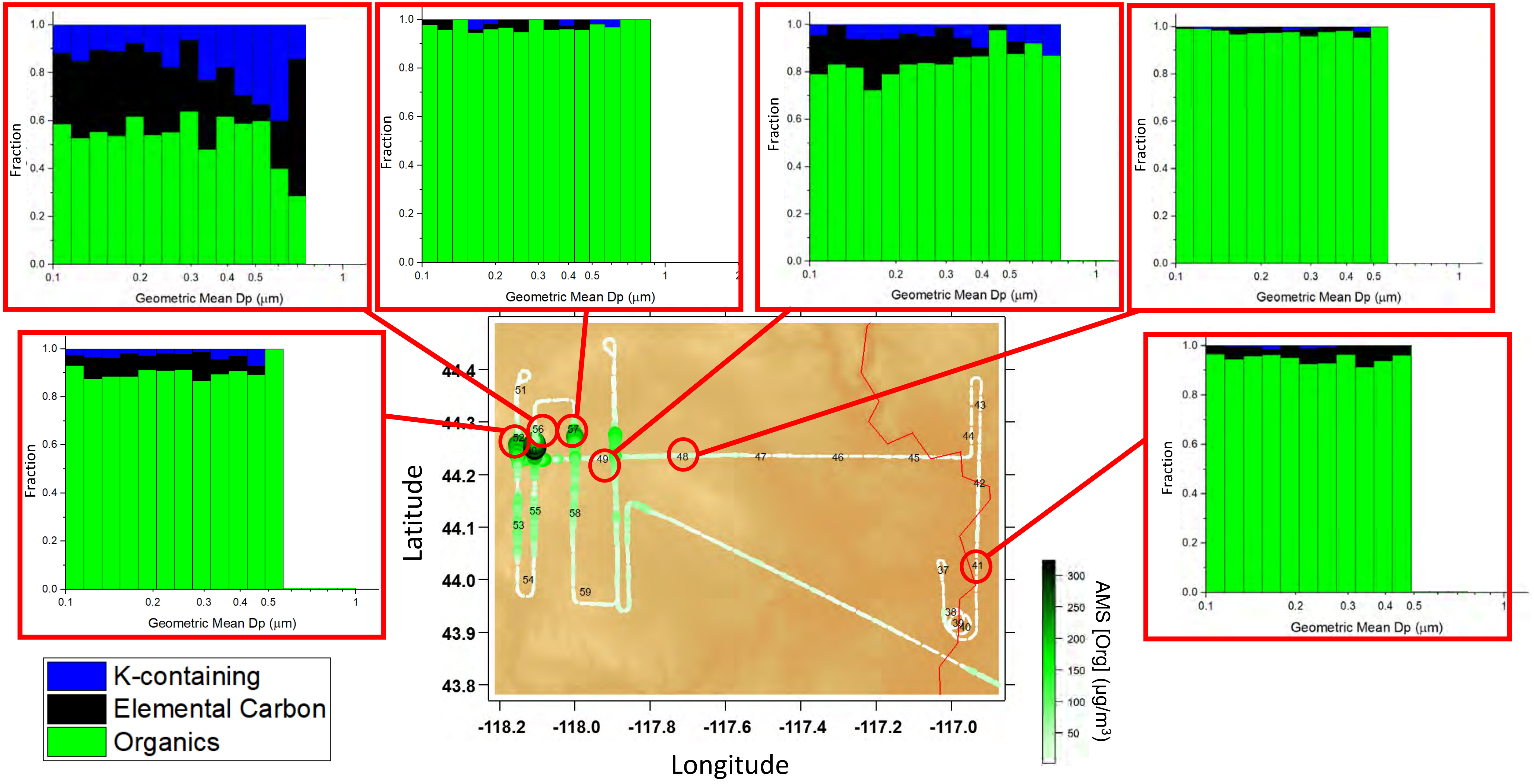

Main Findings:

- Normalized PSD and fractions of clusters show dominance of organic components in both daytime and nighttime.

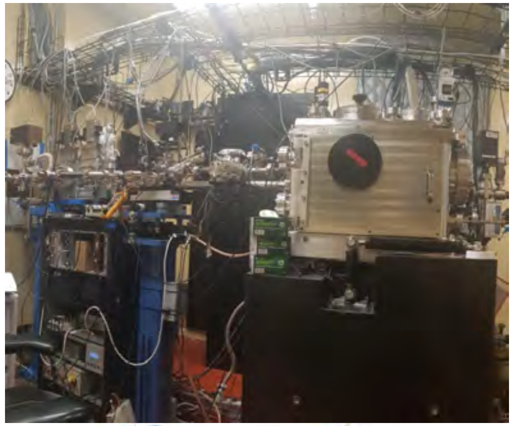
# External Mixing Along the Plume: Day



# External Mixing Along the Plume: Night

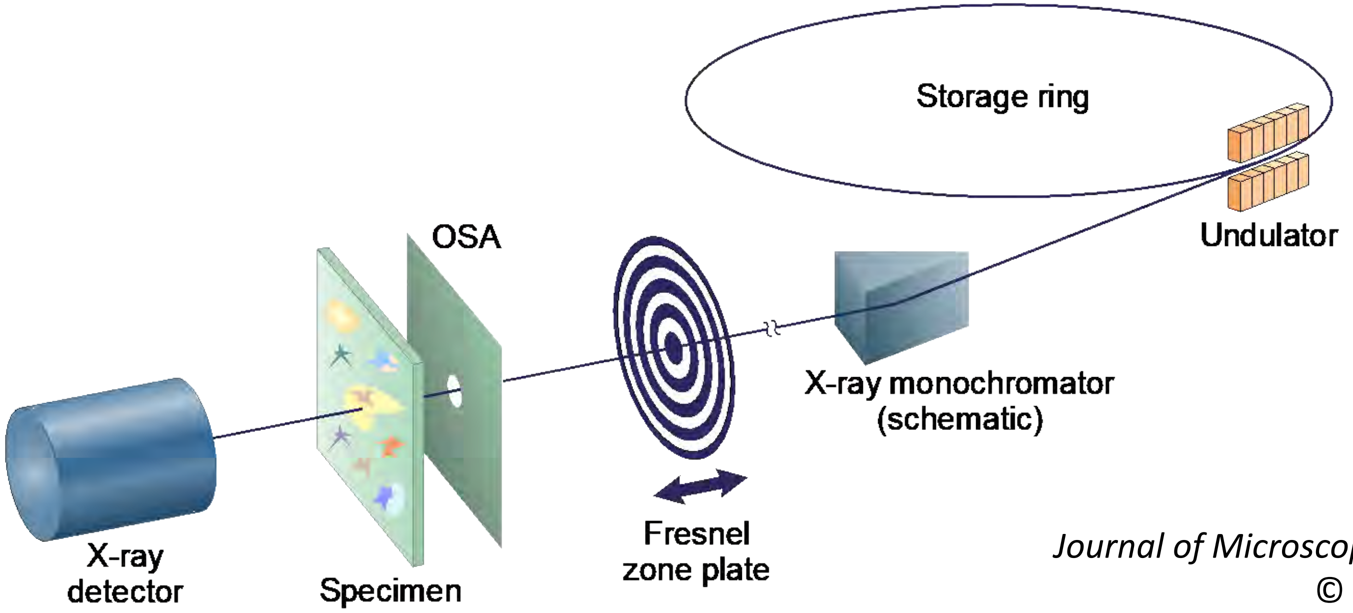


# Particle Chemical Heterogeneity and Internal Mixing

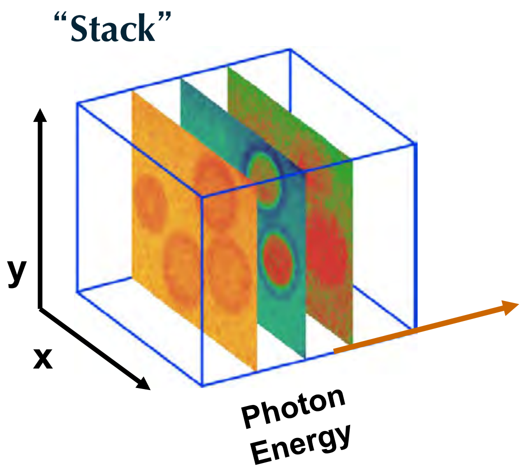


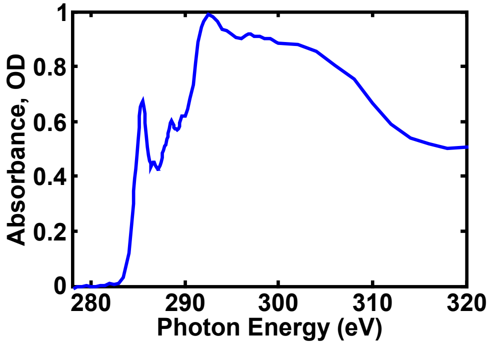
ALS ADVANCED LIGHT SOURCE

Canadian Light Source Centre canadien de rayonnement synchrotron

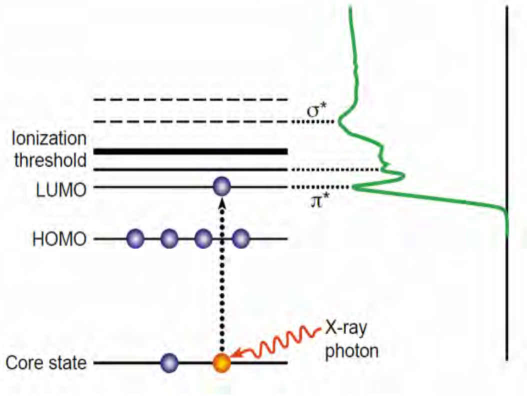



Maser et al. *Journal of Microscopy* 197, 68–79.

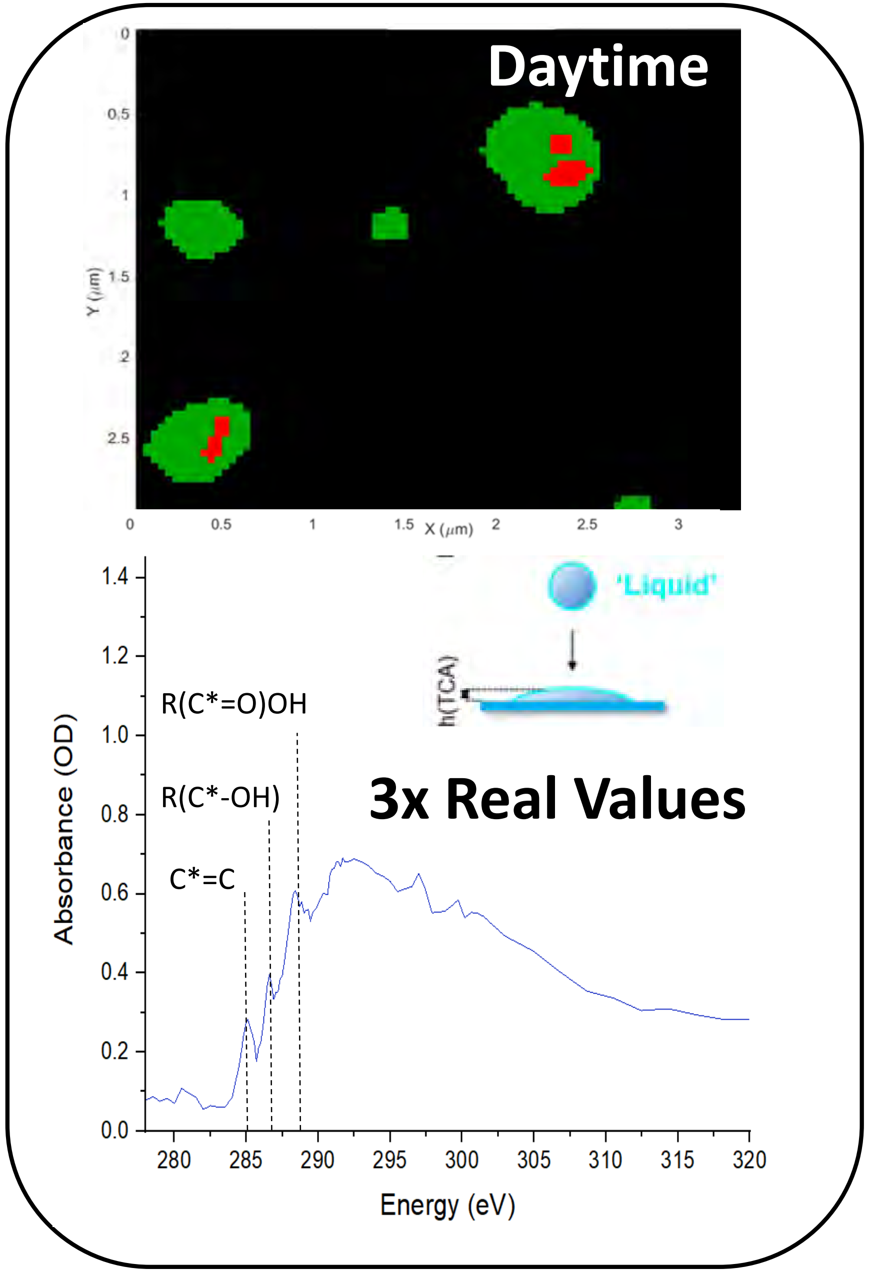



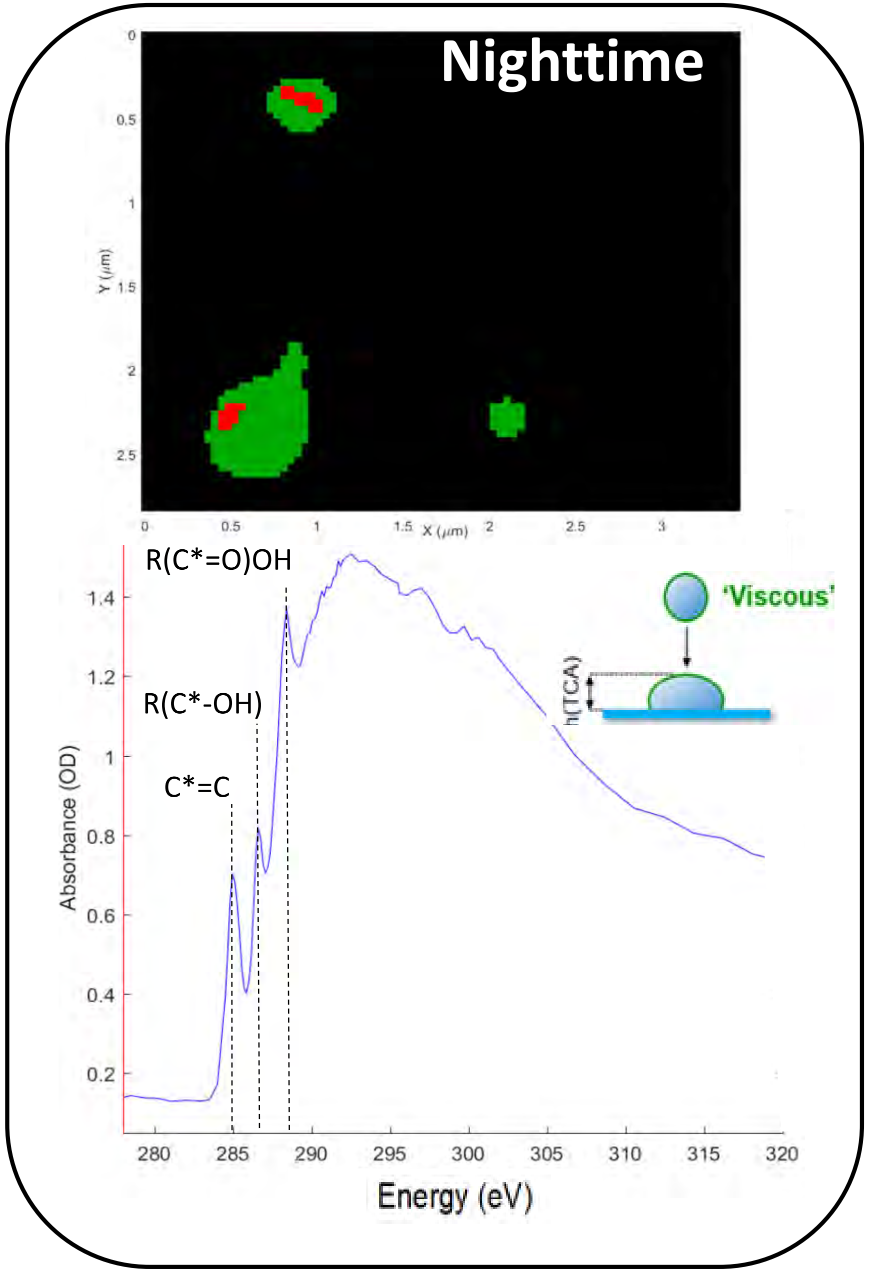

X-ray absorption data collected at each pixel



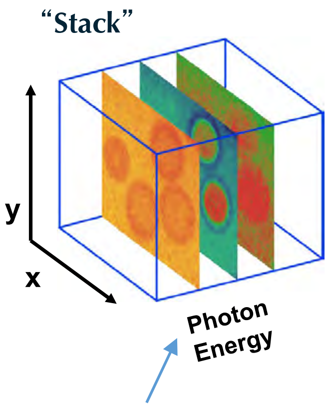

Chemical bonding information

# STXM/NEXAFS: Stacks



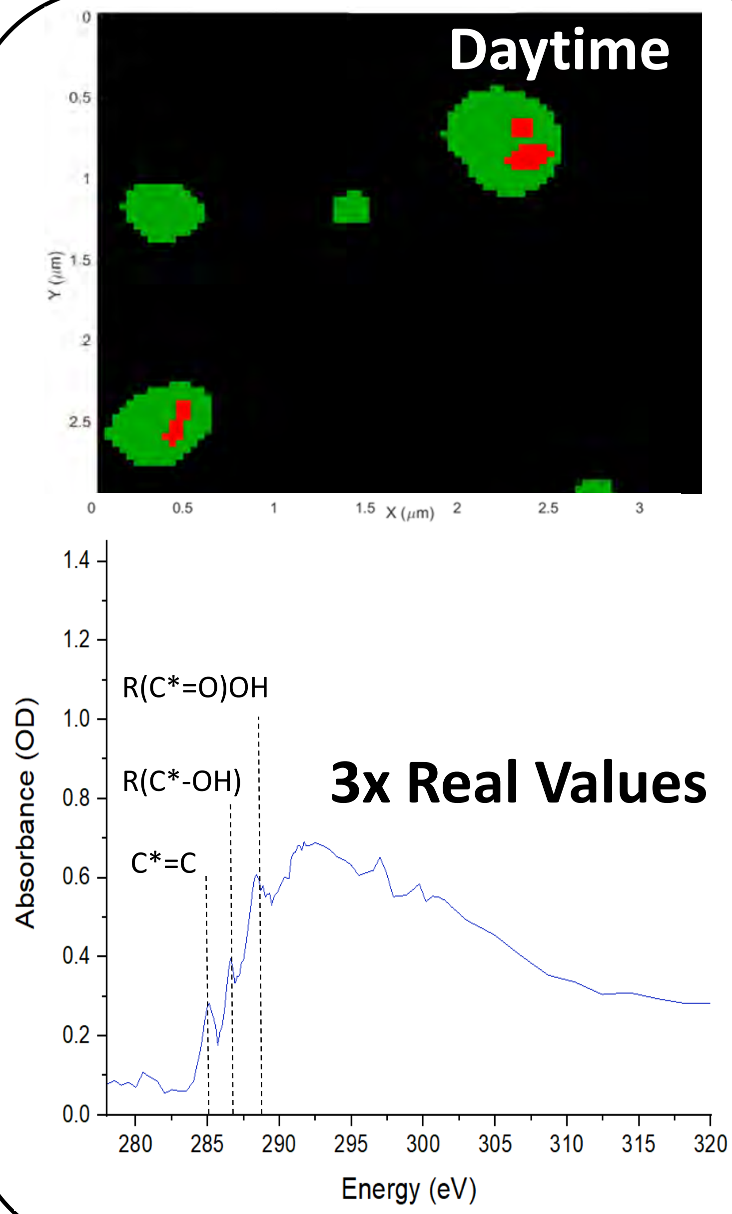



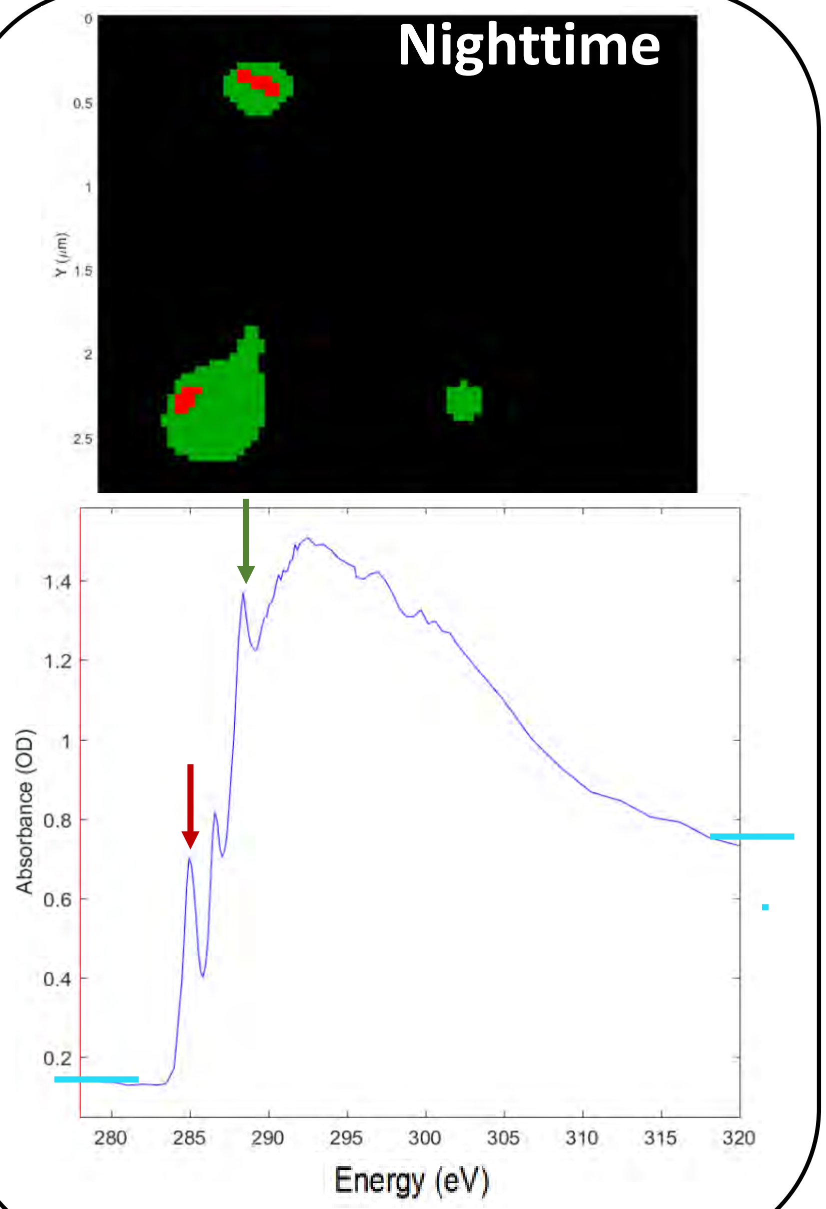

Organic Carbon
Elemental Carbon



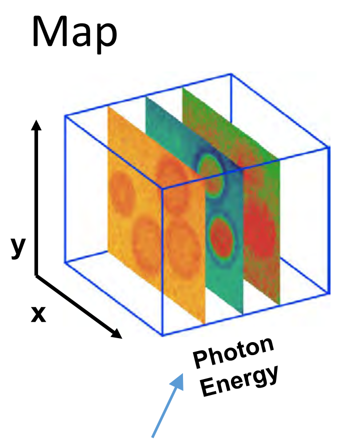

96 energy settings
40-60 min/stack
~5 particles/stack

# STXM/NEXAFS: Stacks



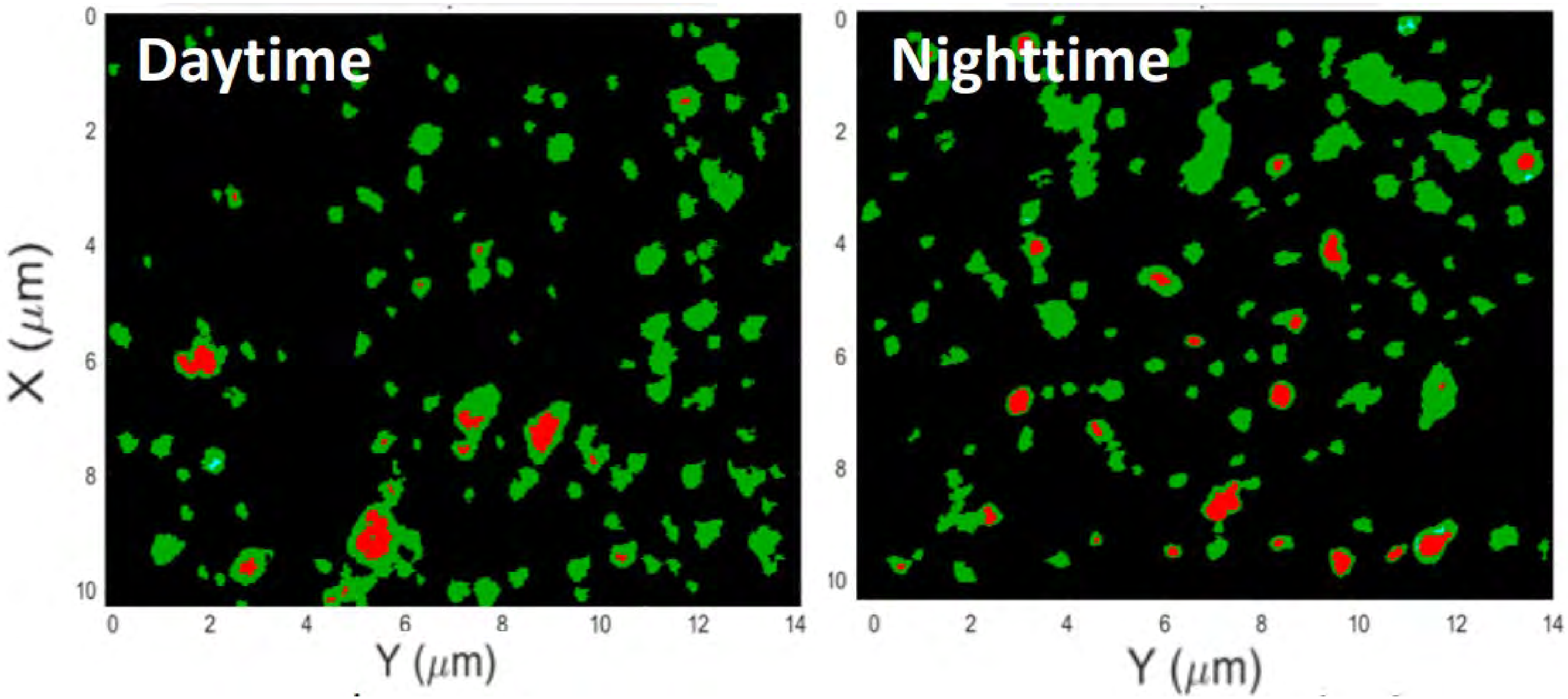




Organic Carbon
Elemental Carbon




4 energy settings
10-15 min/stack
~50-100 particles/stack

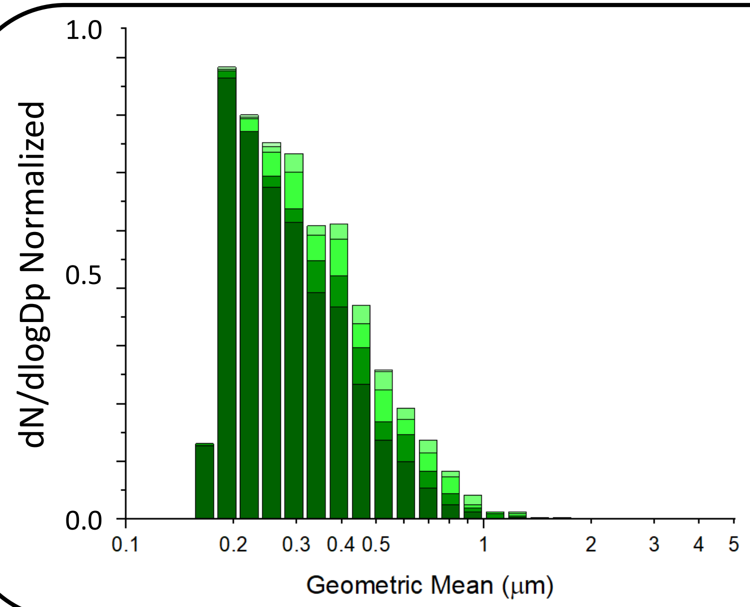
# STXM/NEXAFS: Maps

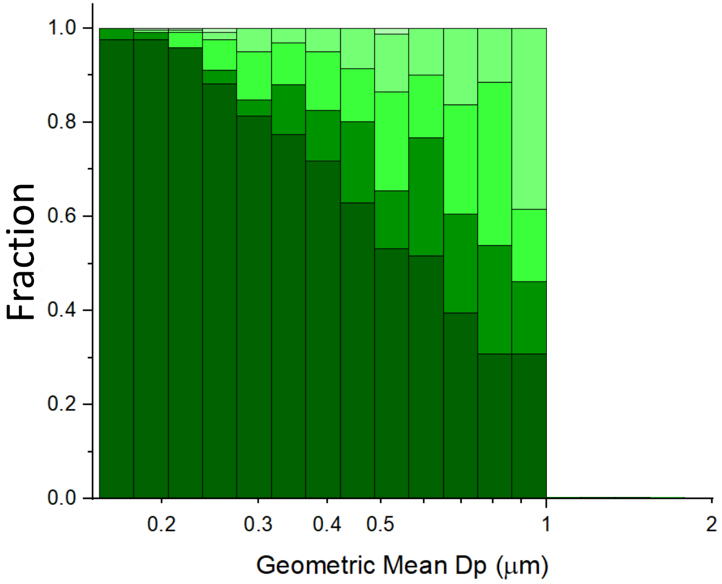


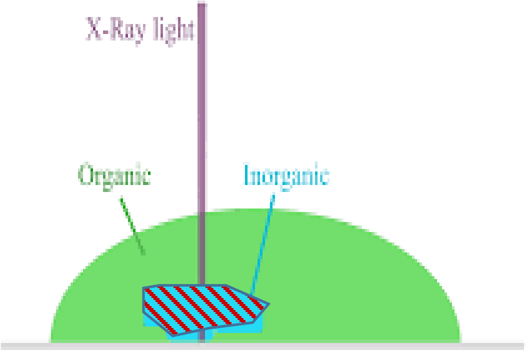

**STXM particle-type grouping based on carbon speciation** illustrates *internal mixing* of individual particles: mixtures of organic carbon (green) and elemental carbon (red) are dominating on both daytime and nighttime samples; there is little inorganic (blue) material

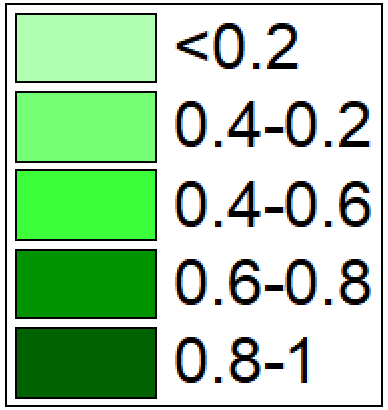
# Organic Volume Fractions

Daytime:

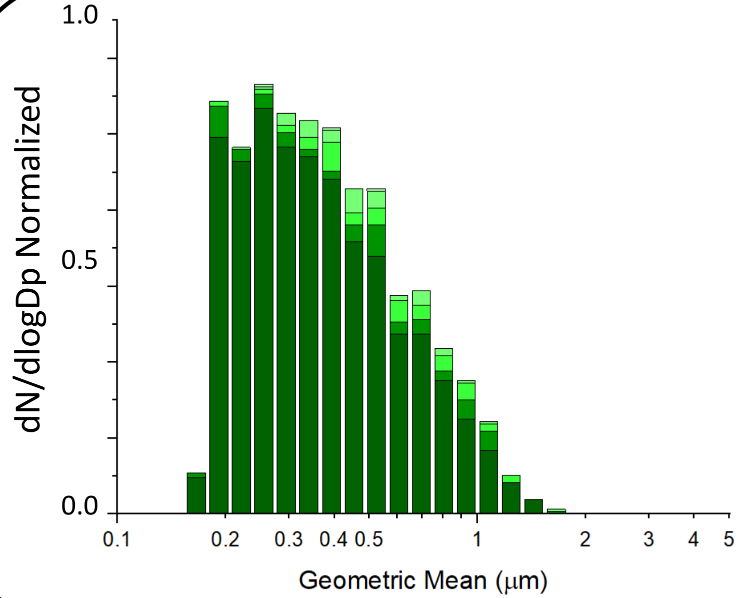


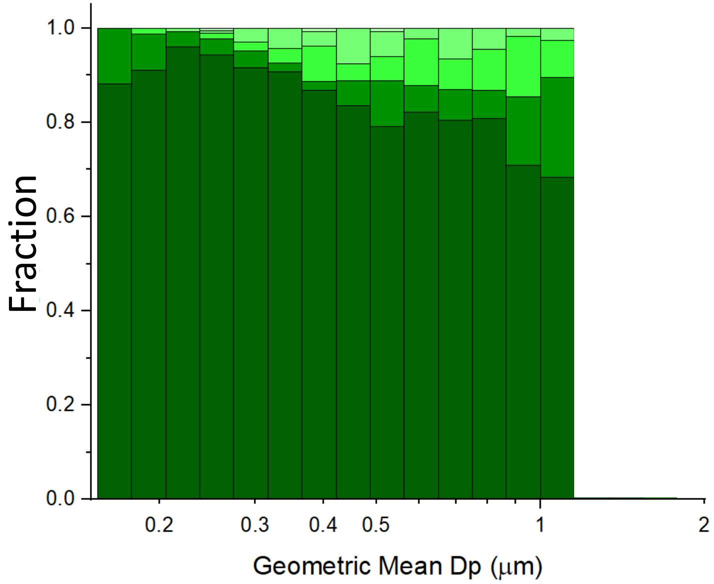



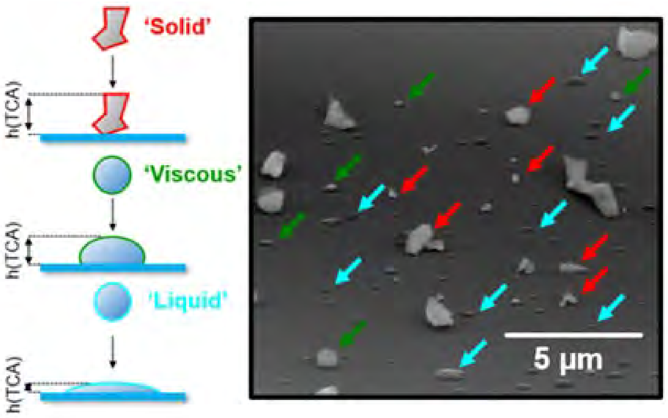



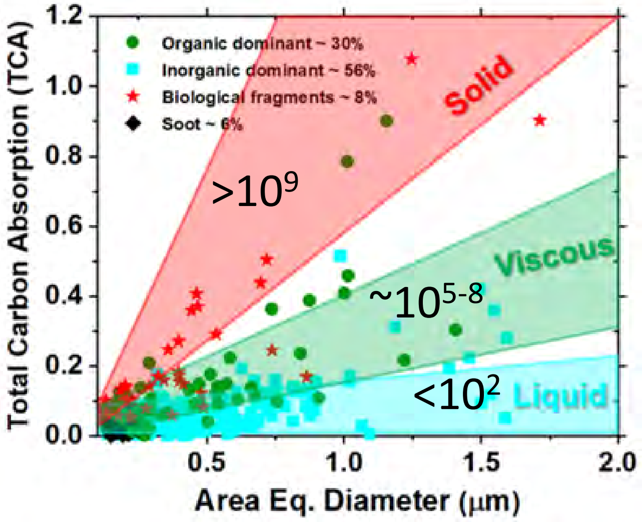

Nighttime:



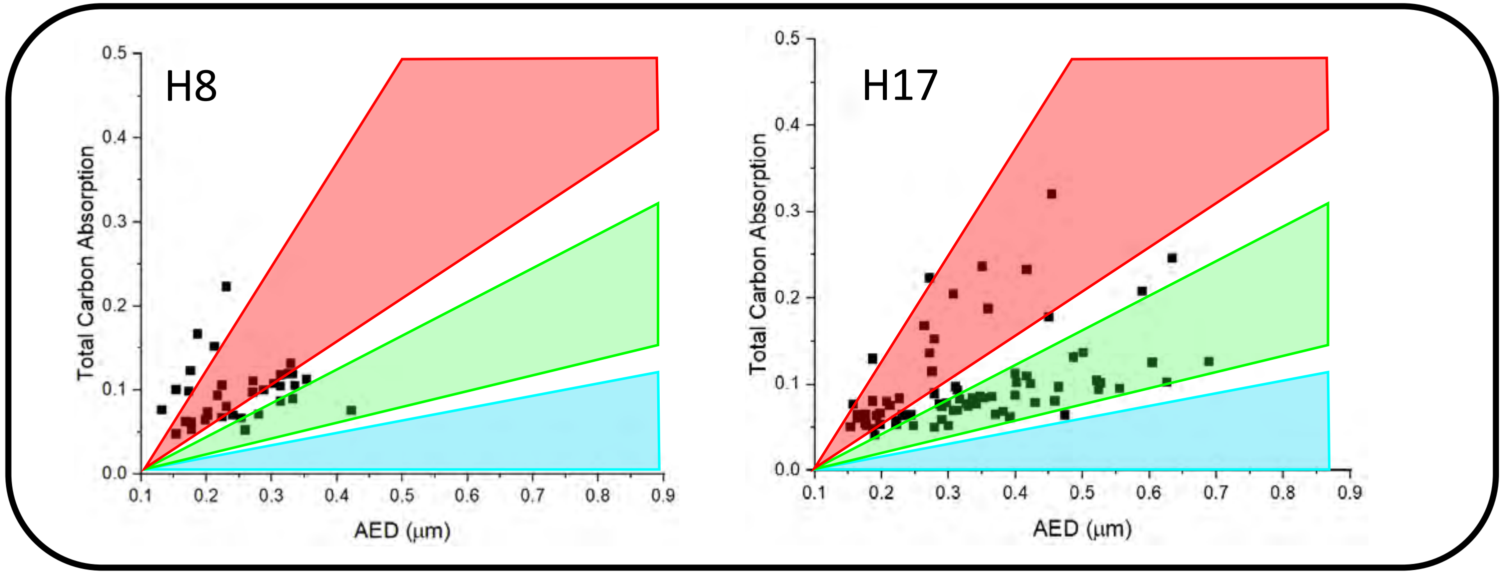



# Total Carbon Absorption: Organic Carbon




Daytime




Nighttime