

# **Development of Event Trigger data analysis approach for single particle characterization**

**(Event trigger data from SP-AMS)**

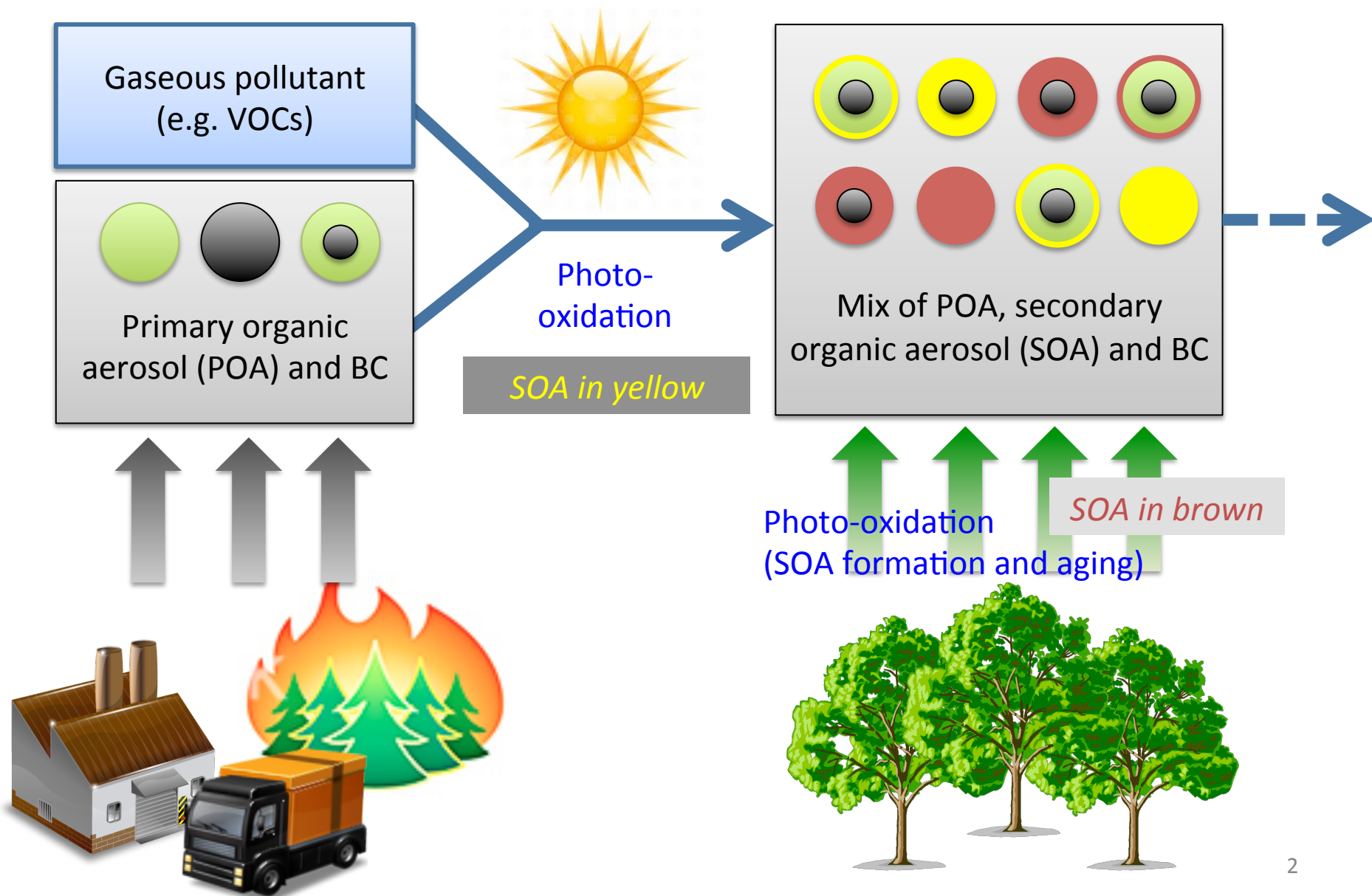
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<sup>2</sup>Department of Chemistry, University of Toronto, Canada

**17<sup>th</sup> AMS users meeting, Oct 23, 2016**

# Formation of organic coating on BC particles



# Sampling period and location – Fontana, CA

July 4-28, 2015

~ 80 km east of Los Angeles

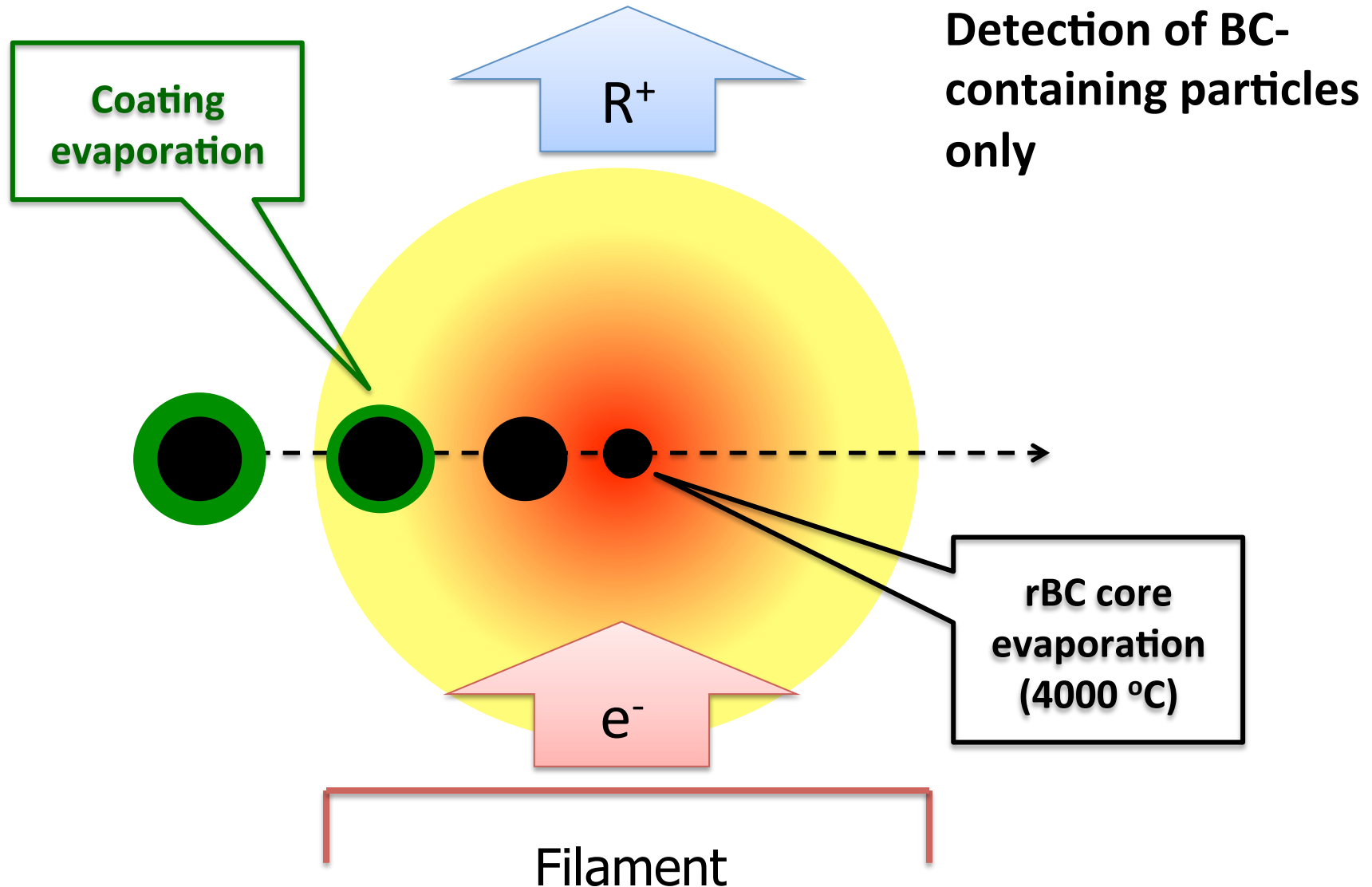


*Lynn Russell, UCSD*



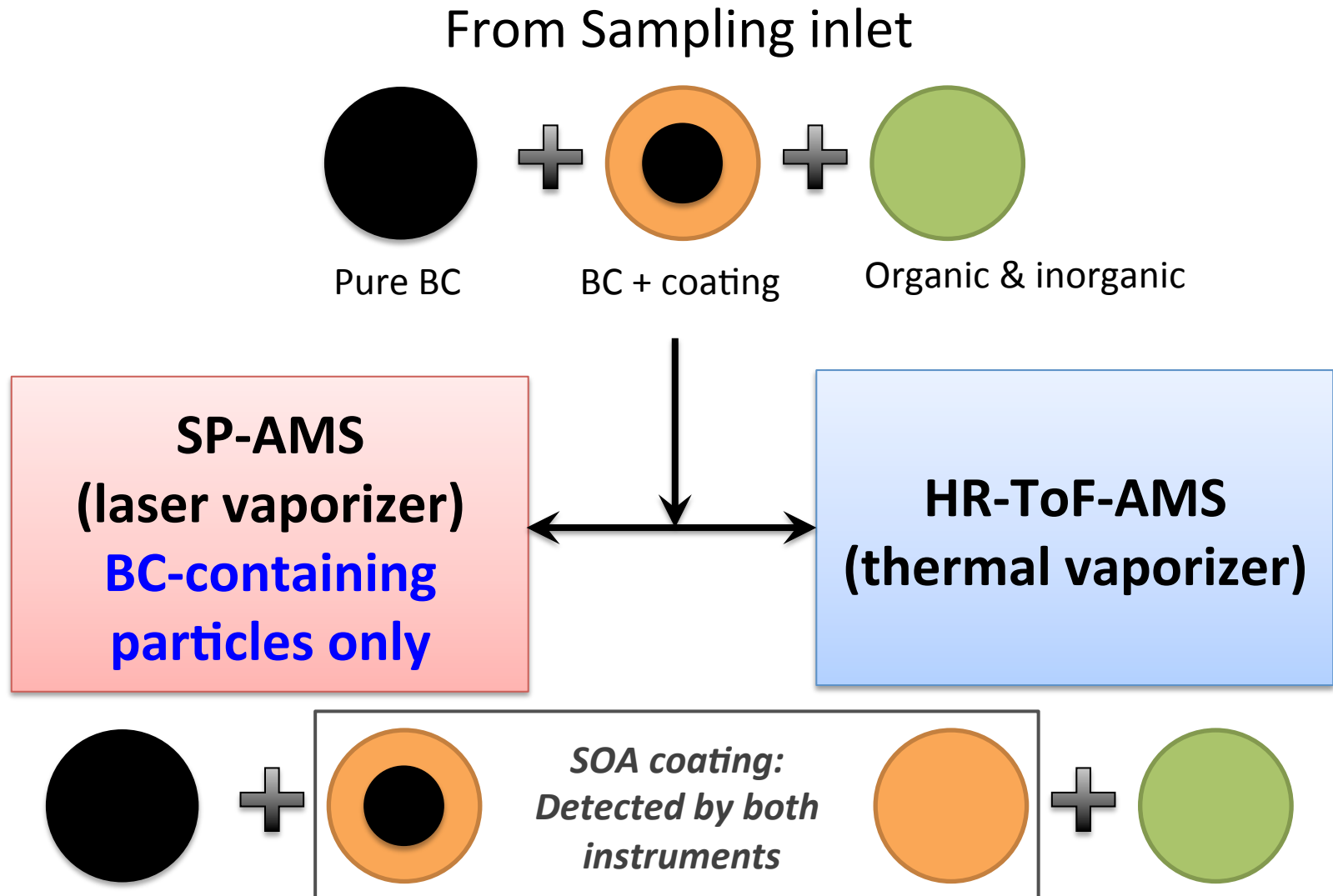
***South Coast Air Quality Management District-managed site (Fontana Fire Department at 14360 Arrow Highway)***

# SP-AMS (Thermal vaporizer removed)



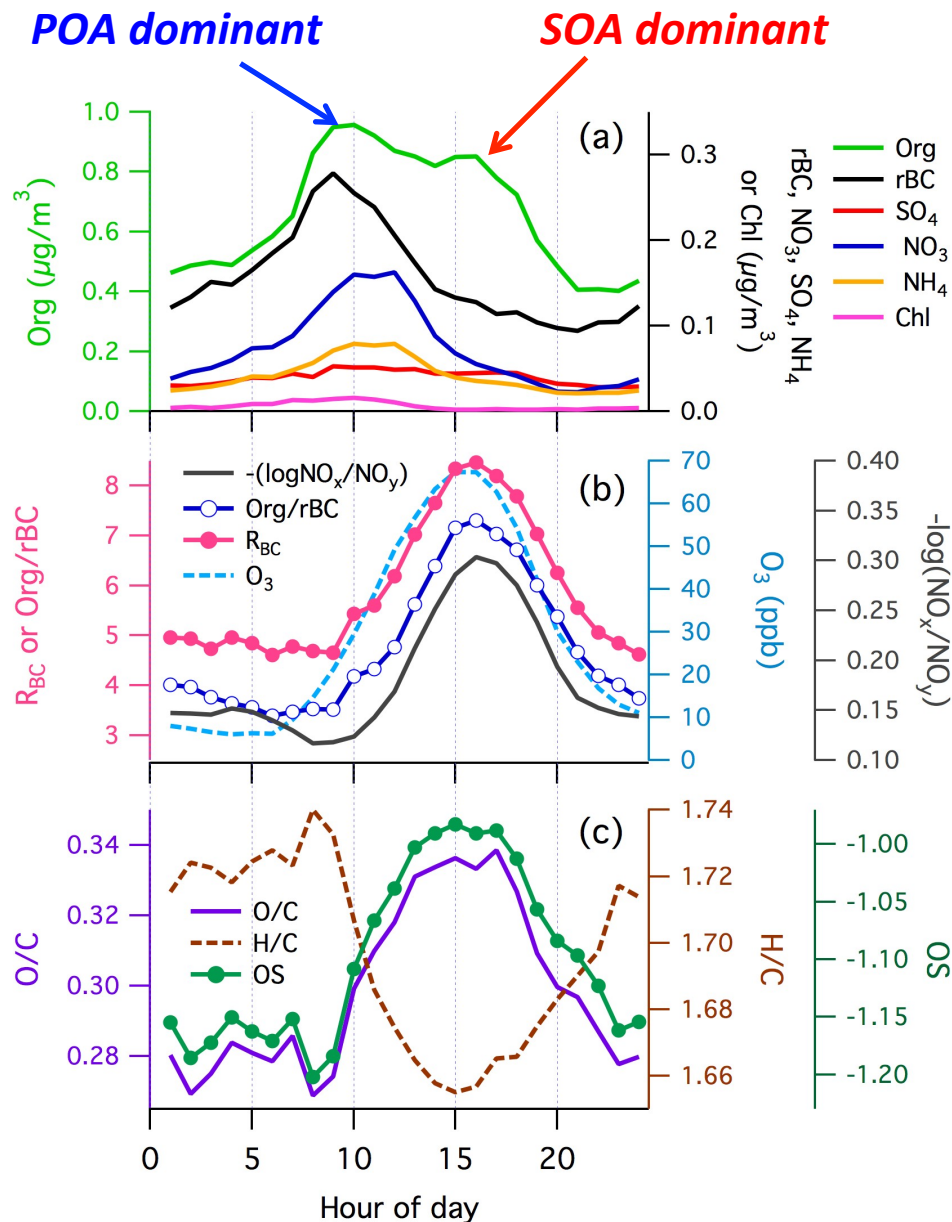


# Soot particle aerosol mass spectrometer (SP-AMS) vs. HR-ToF-AMS



# Formation of SOA coating on BC surface

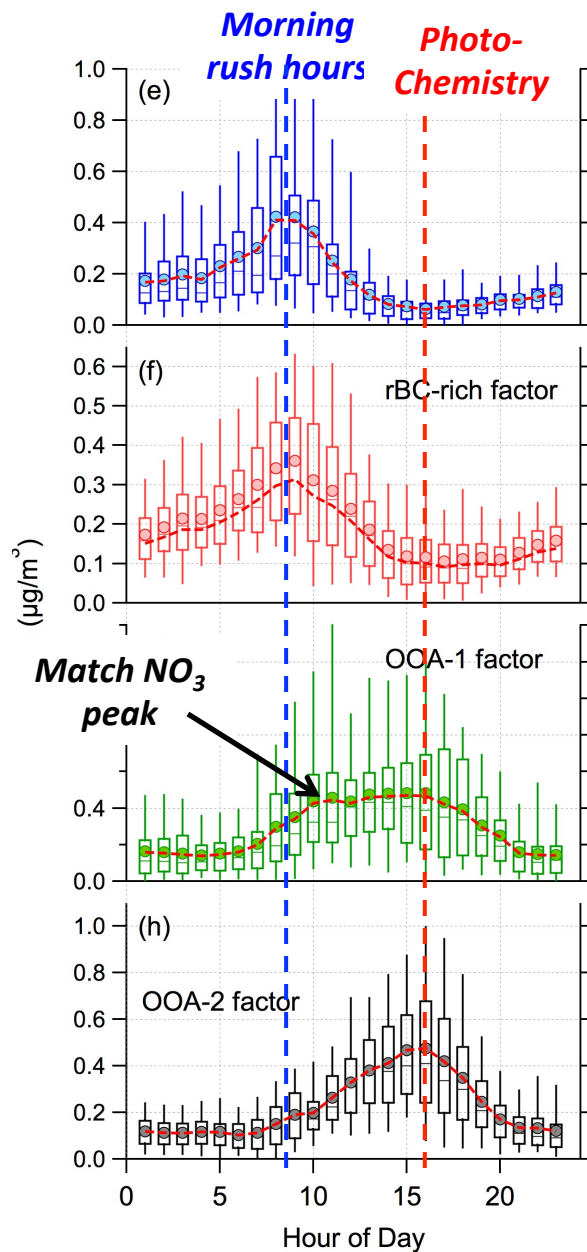
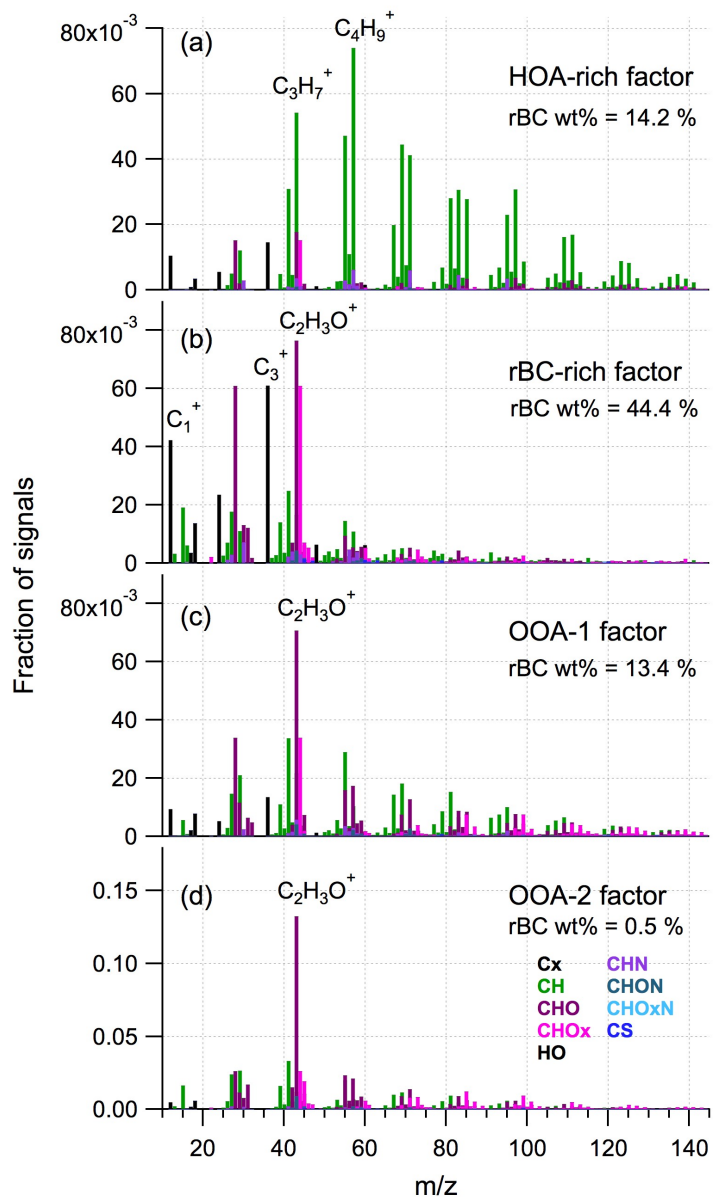
**Coating thickness**  
 $R_{BC} = NR-PM/rBC$   
 or  $Org/rBC$



**Photochemical clock**  
 $-\log(NO_x/NO_y) \propto$   
 exposure time to  $[OH]$

**Higher O/C and oxidation state (OS) for SOA**

# PMF analysis: 4-factors solution



**Hydrocarbon-like OA (HOA)-rich factor**



**rBC-rich factor**  
(with the support of single particle characterizations)

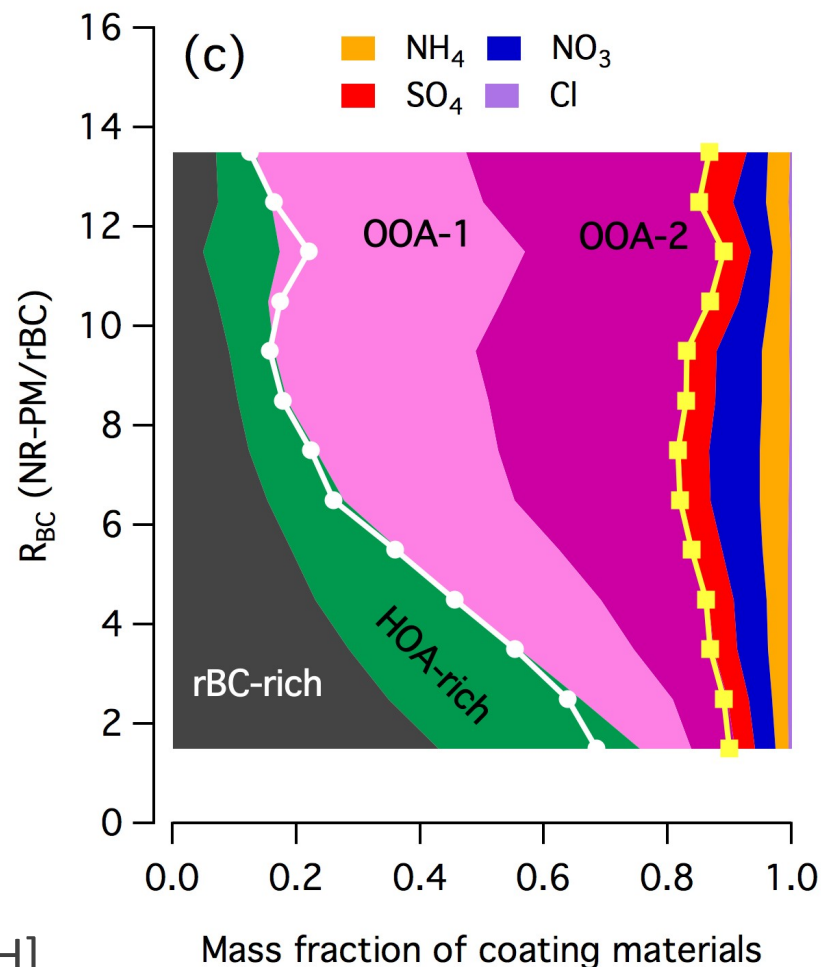
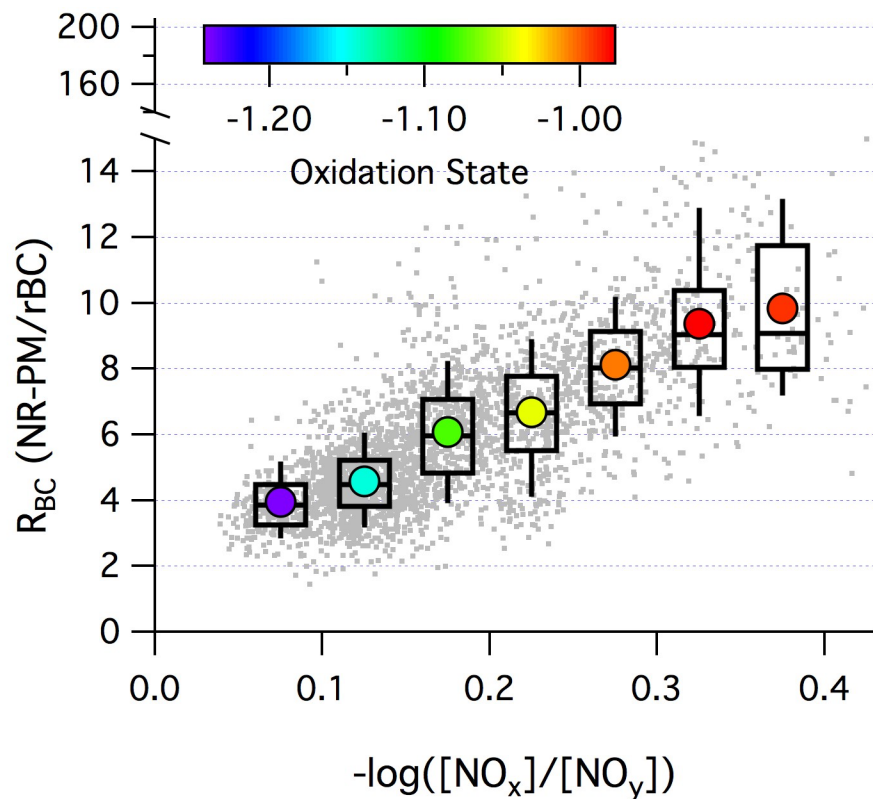
**Oxygenated OA OOA-1 factor**



**OOA-2 factor**

# Photochemical age: Fresh or aged SOA?

*OOA-1 & OOA-2 → Fresh SOA*



$$\text{Photochemical age} = -\log([NO_x]/[NO_y])/k_{rxn}[OH]$$

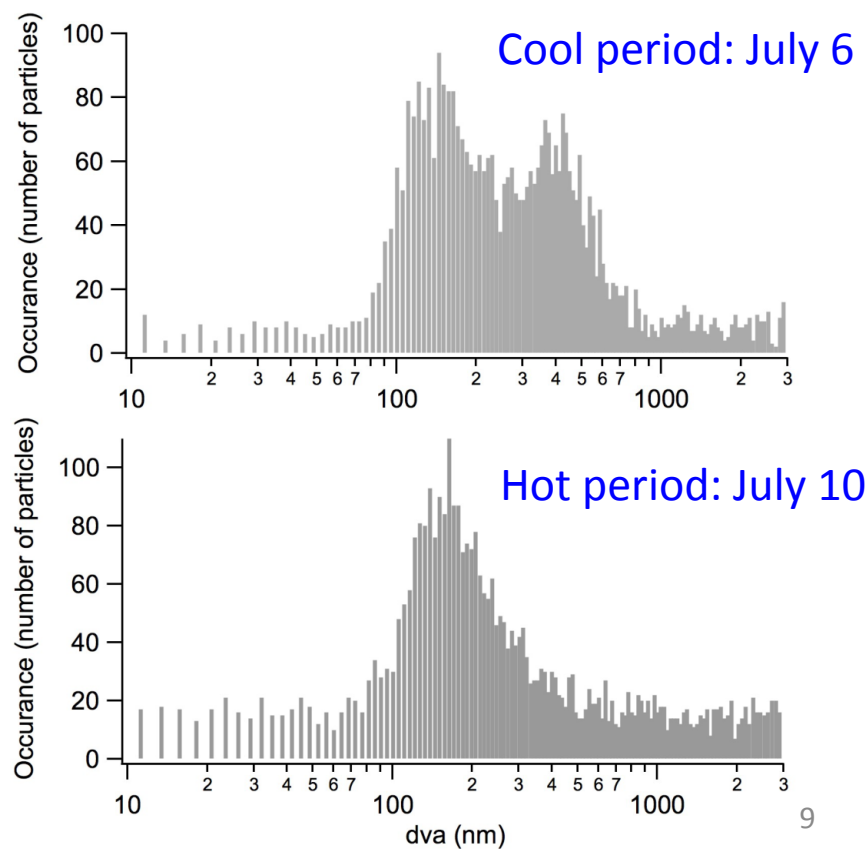
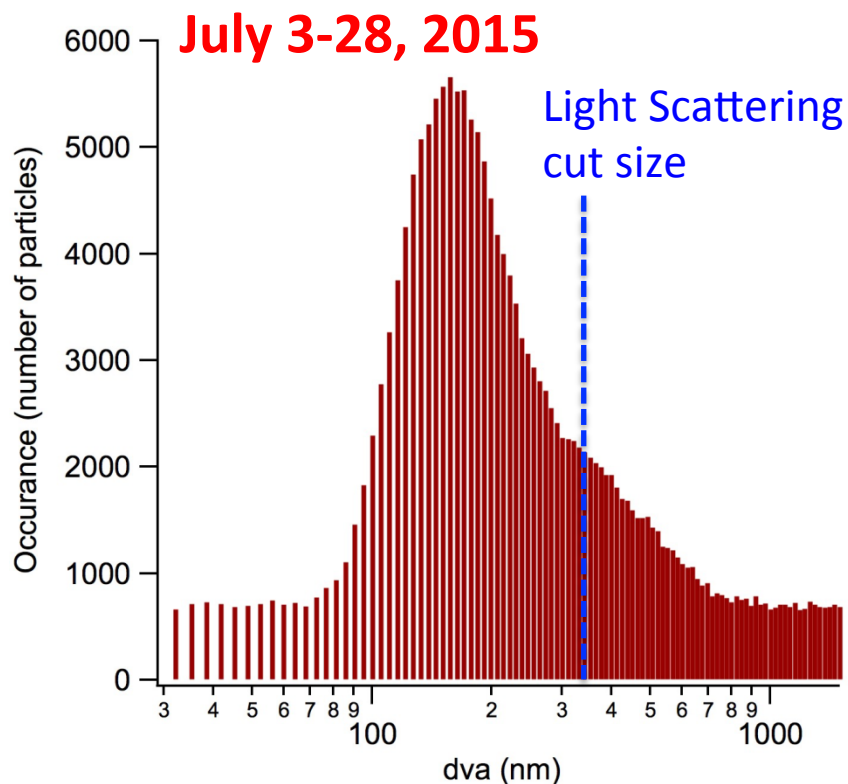
$$k_{rxn} = 7.9 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}, [OH] = 4 \times 10^6 \text{ molecules cm}^{-3}$$



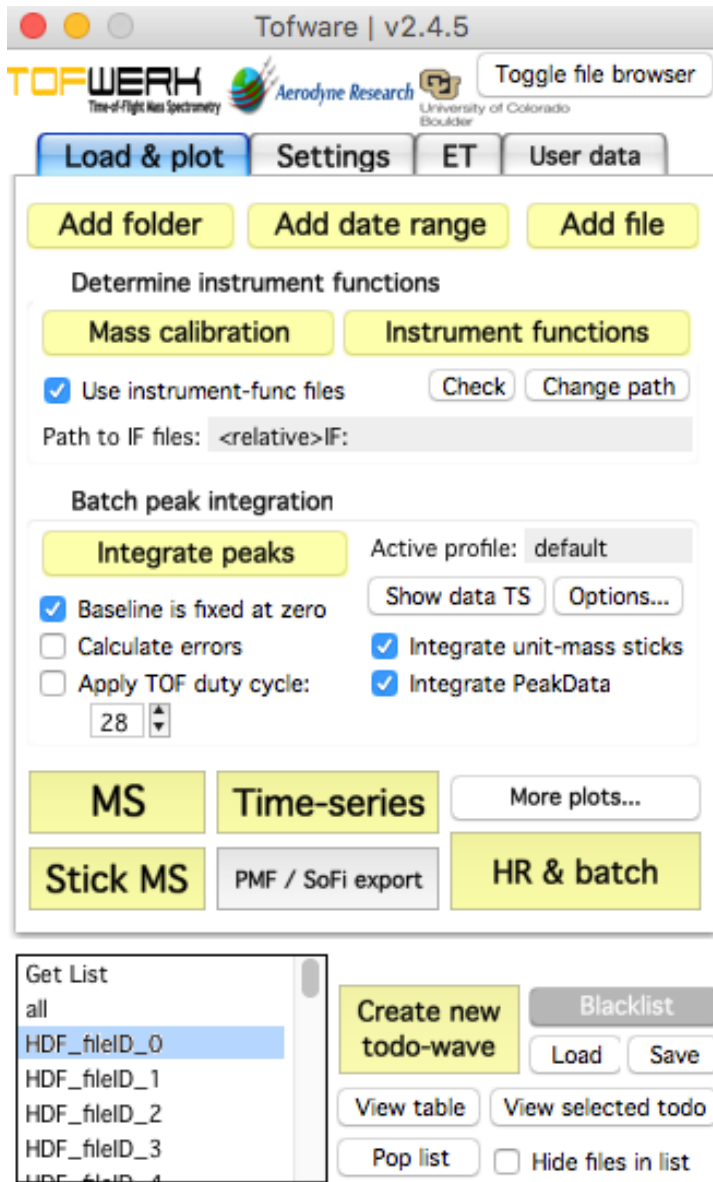
# Single particle detection: Event trigger (ET)

**SP-AMS menu setting** (2 min per 10 min cycle)

- ROI1:  $m/z$  45-150 (Org) – 5 ions → **Nitrate**, **sulfate**, **organic**
- Or ROI2:  $m/z$  43 (Org) – 4 ions → **Organic**
- Or ROI3:  $m/z$  36 (BC) – 3 ions → **Black carbon**
- **Number of particles:** 410,100 (~10,000 using LS in Toronto)

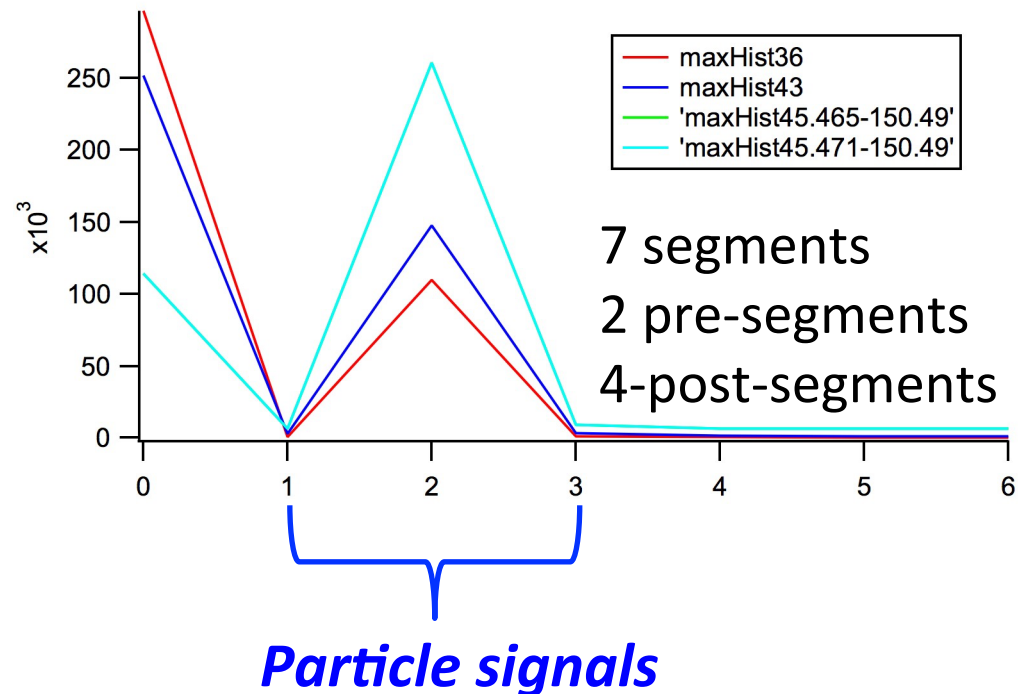


# Tofware (v2.4.5) – Data pre-processing



## From Tofware:

- ChopTimes (pToF data)
- MSSft\_all (MS matrix)
- t\_start\_wr (time)



# Clustering Input Preparation Panel (CIPP)

CIPP\_Panel

**Clustering Input Preparation Panel v.2.1ET**  
Developed by Alex Lee and Megan Willis (U. of Toronto)

**Settings** Frag table Run

**Mass Spectrum Setting**

m/z for air fragments: 14,18,28,32,40

m/z to be removed for clustering: 15,16,17,23

Initial m/z (Check from ensemble data): 3

**Ion Threshold Calculation**

Particle region (dva, nm): Start 50 End 1100

Background 1 (dva, nm): Start 10 End 40

Background 2 (dva, nm): Start 2000 End 4000

☒ Exclude background ion: < 1 > 20

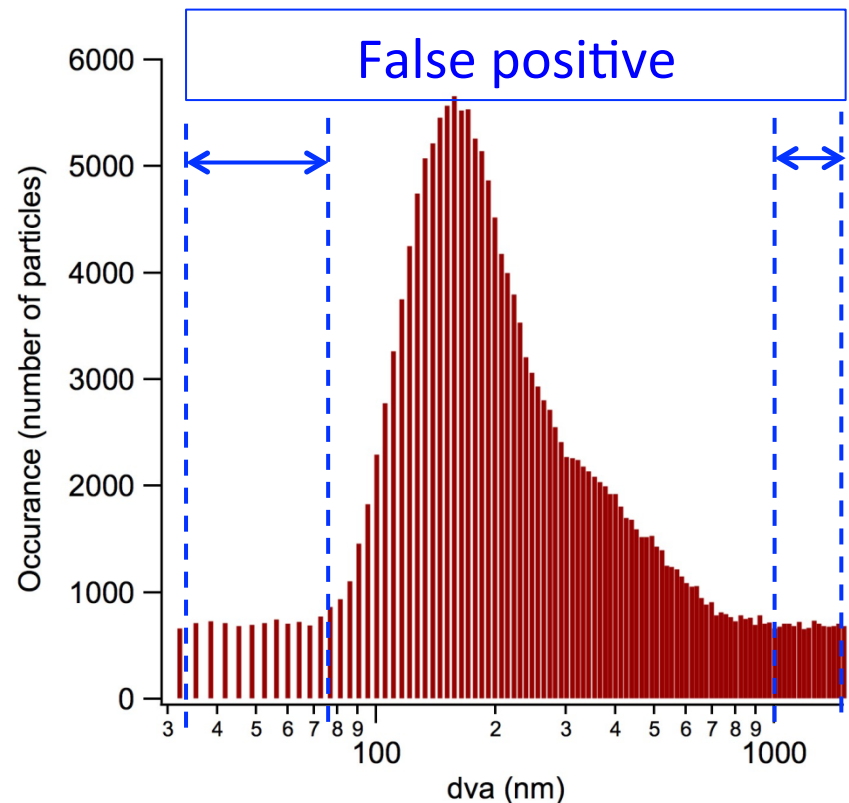
**PToF Parameters**

vl 41.56 vg 329.2! Dx 52.85! b 0.7431

Chamber length (m): 0.295

## Main Functions:

1. Remove false positive (or identify real particles)
2. Prepare waves and matrix for cluster analysis



# Remove false positive (or identify real particles)

The screenshot shows the 'CIPP\_Panel' window with the title 'Clustering Input Preparation Panel v.2.1ET' and 'Developed by Alex Lee and Megan Willis (U. of Toronto)'. It has three tabs: 'Settings' (selected), 'Frag table', and 'Run'. The 'Mass Spectrum Setting' section is highlighted with a red dashed box and contains three input fields: 'm/z for air fragments' with the value '14,18,28,32,40', 'm/z to be removed for clustering' with the value '15,16,17,23', and 'Initial m/z (Check from ensemble data)' with the value '3'. Below this is the 'Ion Threshold Calculation' section with fields for 'Particle region (dva, nm): Start 50 End 1100', 'Background 1 (dva, nm): Start 10 End 40', 'Background 2 (dva, nm): Start 2000 End 4000', and a checked checkbox for 'Exclude background ion:' with values '< 1' and '> 20'. The 'PToF Parameters' section at the bottom includes fields for 'v1 41.56', 'vg 329.2', 'Dx 52.85', 'b 0.7431', and 'Chamber length (m) 0.295'.

**Step 1:** Calculate total ion signals of individual event

Remove air fragment from the matrix for total ion calculation and cluster analysis

Remove m/z from the matrix for cluster analysis

The first m/z of MS



# Remove false positive (or identify real particles)

CIPP\_Panel

Clustering Input Preparation Panel v.2.1ET  
Developed by Alex Lee and Megan Willis (U. of Toronto)

Settings Frag table Run

Air (UMR, Diff, Filter period)

air[29]/air[28]	0.0069329	air[30]/air[28]	9.88486e-01
air[44]/air[28]	0.0010231	air[16]/air[14]	0.392589

H<sub>2</sub>O (UMR, Open)

H <sub>2</sub> O[16]/H <sub>2</sub> O[18]	0.0157	H <sub>2</sub> O[17]/H <sub>2</sub> O[18]	0.2519
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Aerosol components (HR/UMR, Diff)

SO <sub>4</sub> [32]/SO <sub>4</sub> [48]	0.21	SO <sub>4</sub> [81]/SO <sub>4</sub> [98]	2.1211
SO <sub>4</sub> [32]/SO <sub>4</sub> [80]	0.068	NH <sub>4</sub> [15]/NH <sub>4</sub> [16]	0.064
SO <sub>4</sub> [65]/SO <sub>4</sub> [64]	0.19385	NO <sub>3</sub> [14]/NO <sub>3</sub> [46]	0.04

☒ SP-AMS BC detection:

BC[12]/BC[36]	0.478
BC[24]/BC[36]	0.37975
BC[48]/BC[36]	0.098266
BC[60]/BC[36]	0.10477

☒ K detection:

K[41]/K[39]	0.0722
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## Simplified fragmentation table

- Parameters are determined from UMR and HR ensemble data or default fragmentation table in squirrel

“BC” option for SP-AMS data

“K” option for data with strong BBOA signal

# Remove false positive (or identify real particles)

**Step 2:** Calculate ion threshold for real particle events

**Threshold = Mean + 3\*std deviation**

CIPP\_Panel

Clustering Input Preparation Panel v.2.1ET  
Developed by Alex Lee and Megan Willis (U. of Toronto)

Settings Frag table Run

Mass Spectrum Setting

m/z for air fragments 14,18,28,32,40

m/z to be removed for clustering 15,16,17,23

Initial m/z (Check from ensemble data) 3

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Particle region (dva, nm): Start 50 End 1100

Background 1 (dva, nm): Start 10 End 40

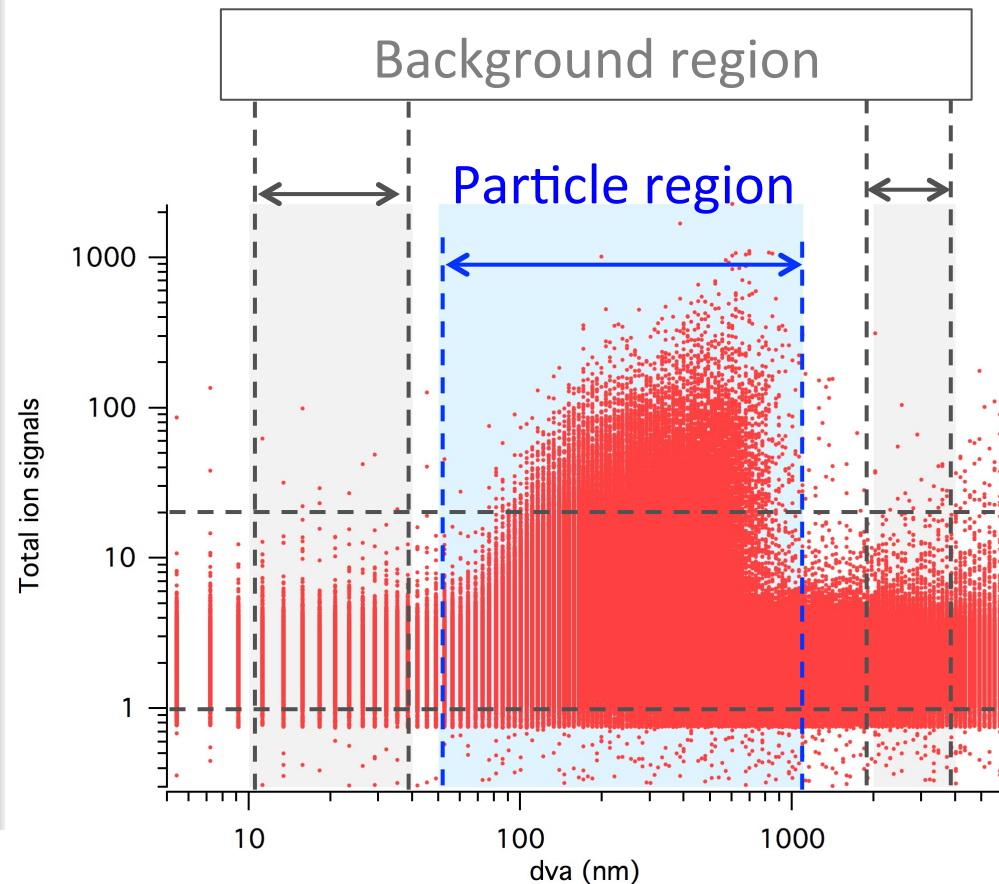
Background 2 (dva, nm): Start 2000 End 4000

☒ Exclude background ion: < 1 > 20

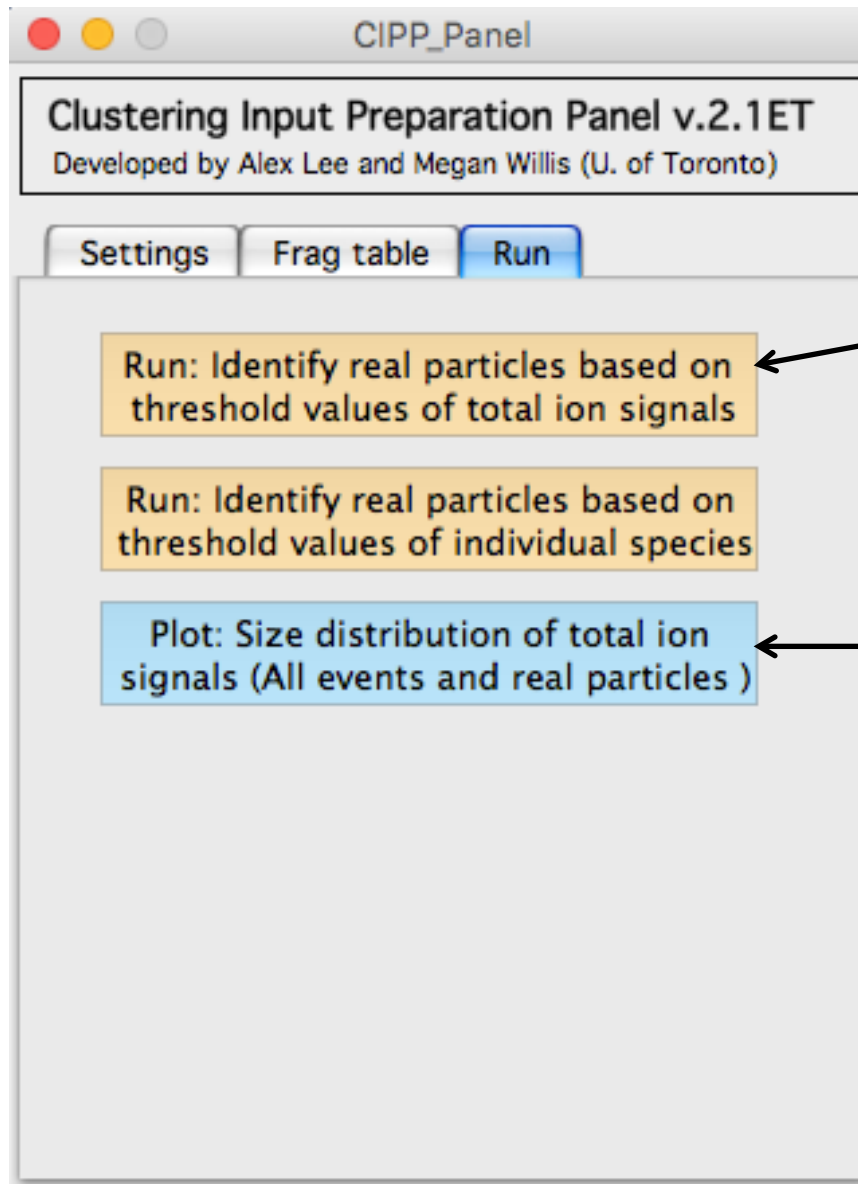
PTOF Parameters

vl 41.56 vg 329.2! Dx 52.85! b 0.7431

Chamber length (m) 0.295



# Clustering Input Preparation Panel



Run the ion threshold calculation (total ions)

Plot the results

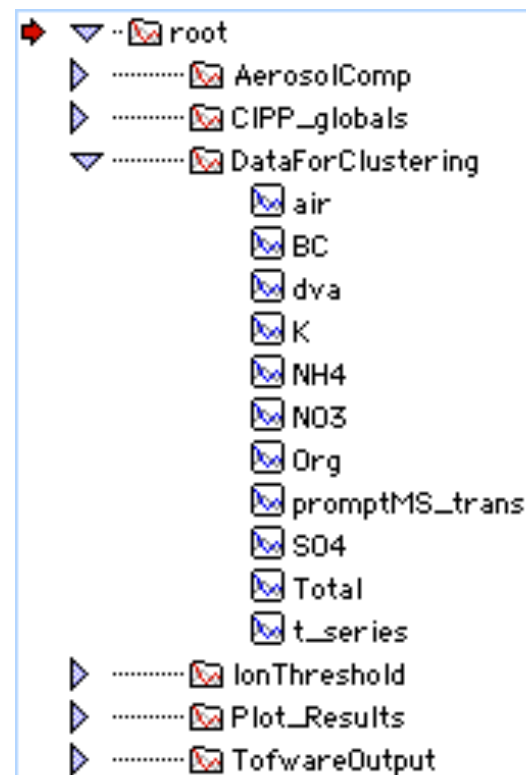
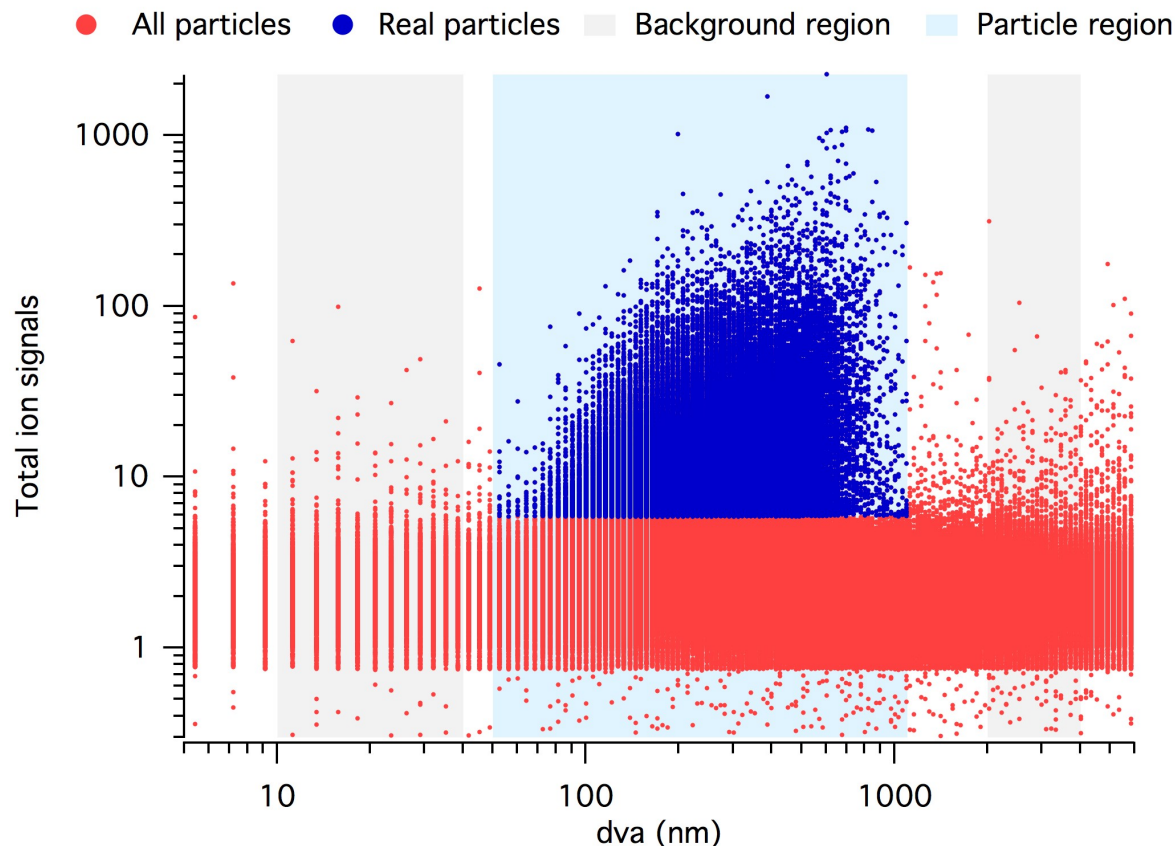
# Results from CIPP

Background average = 2.2932

Standard derivation = 1.1892

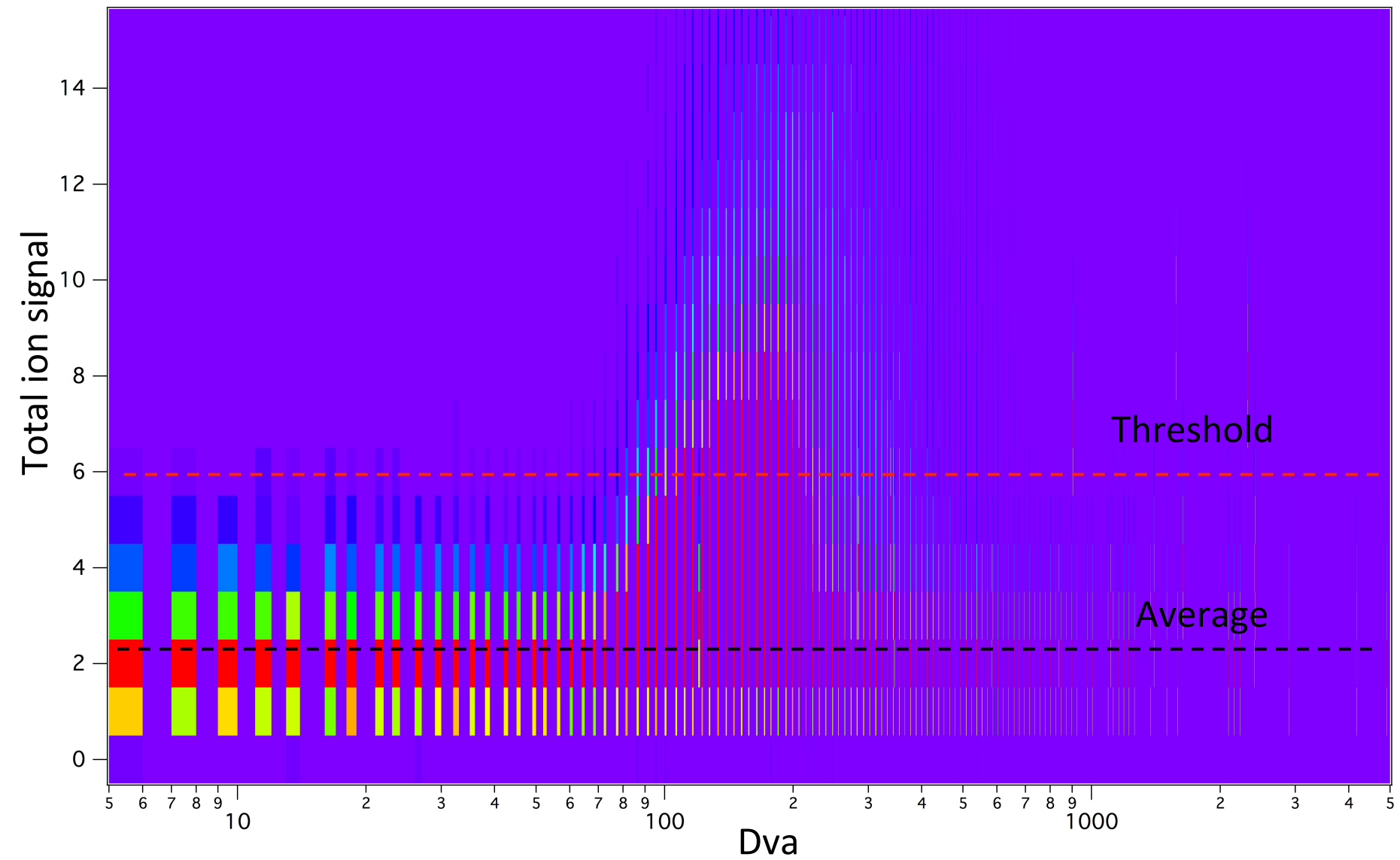
Total ion threshold = 5.8609

Particle # = 70695 of 4.101e+05 (17.238%)

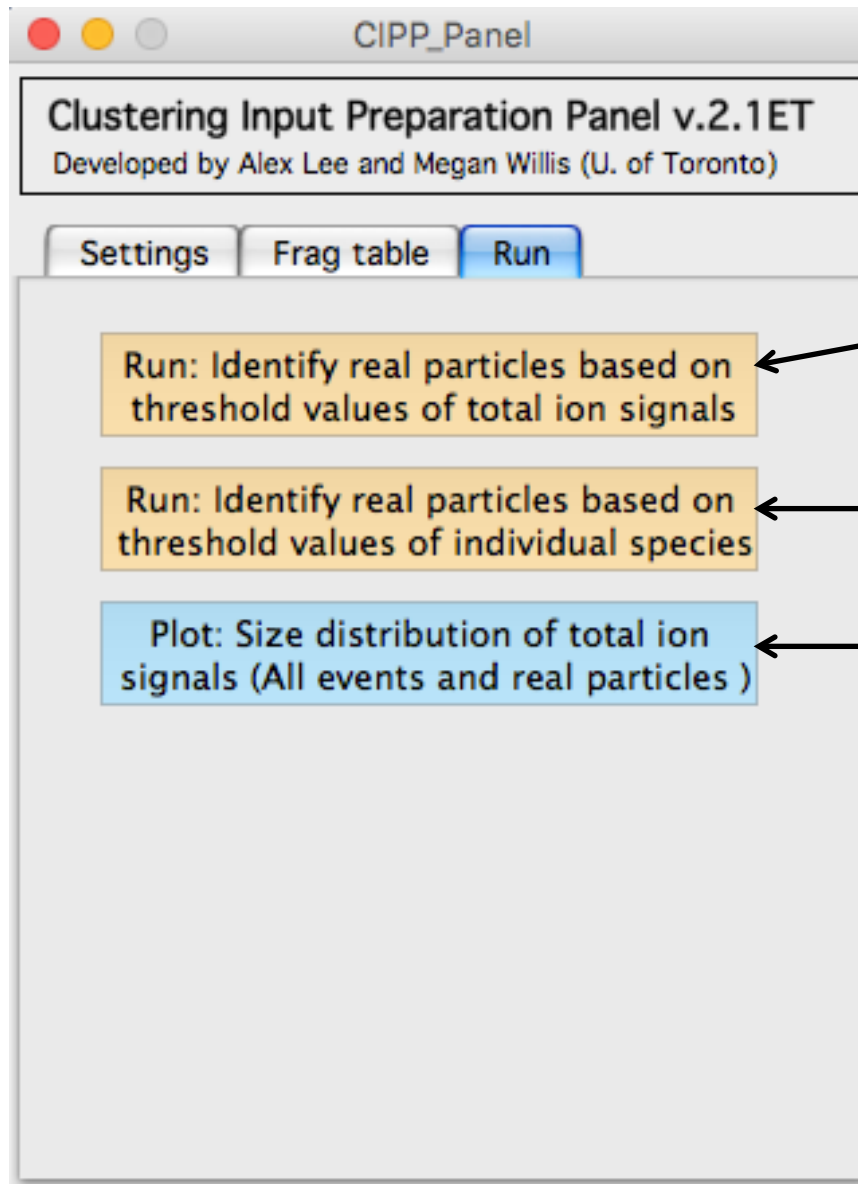




# Setting the threshold too high?



# Clustering Input Preparation Panel

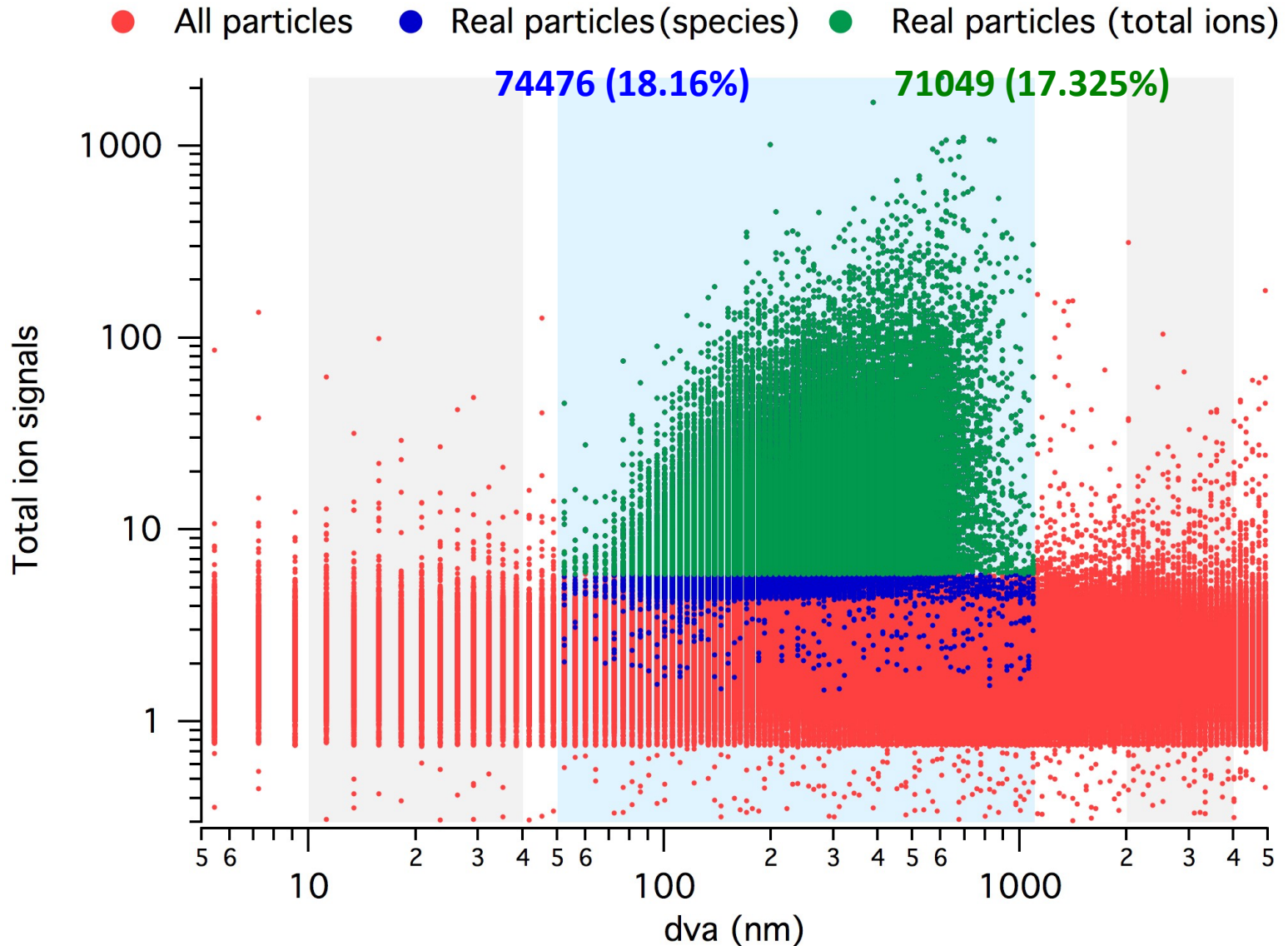


Run the ion threshold calculation (total ions)

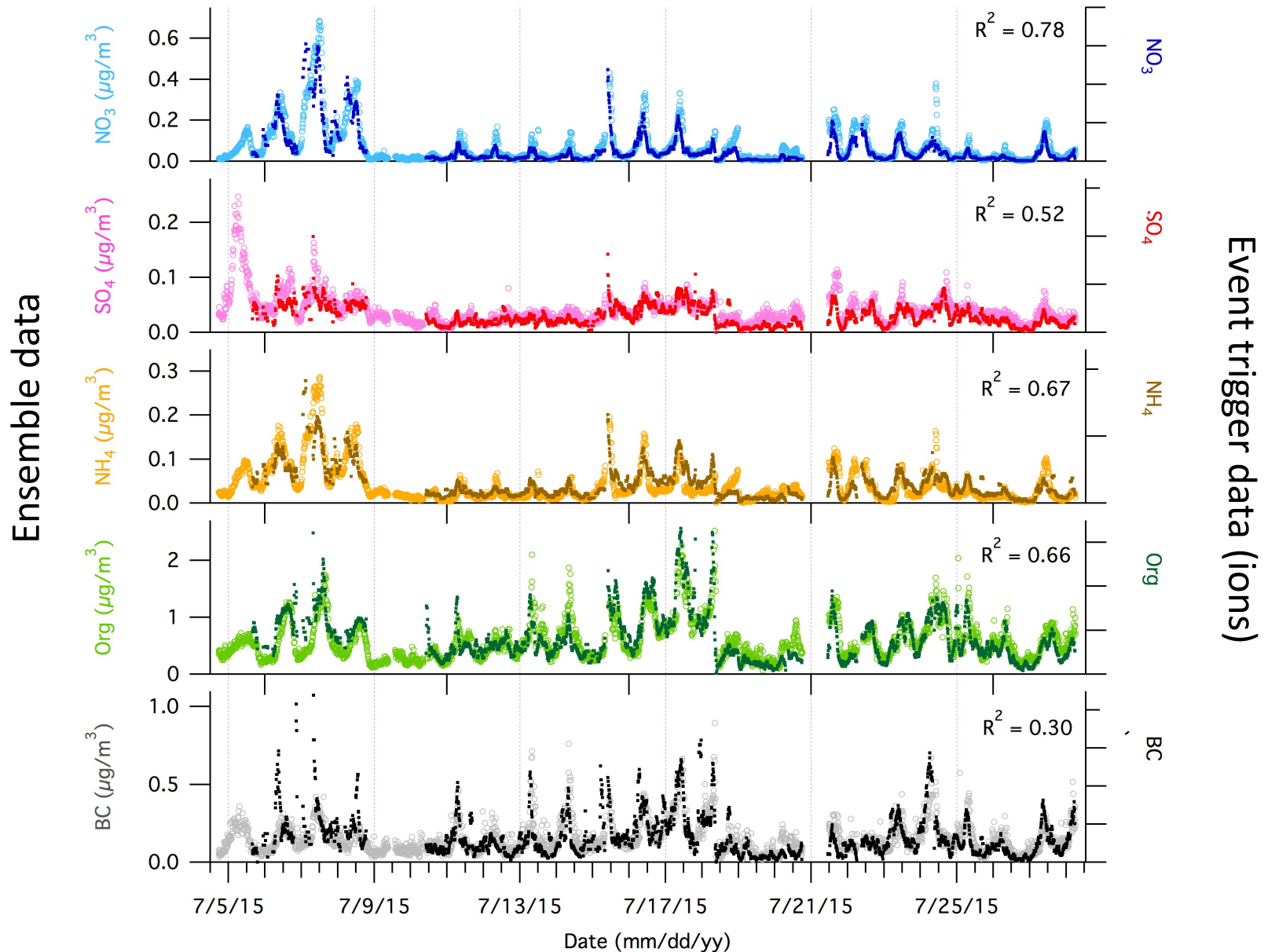
Run the ion threshold calculation (species, testing)

Plot the results

# Results from CIPP

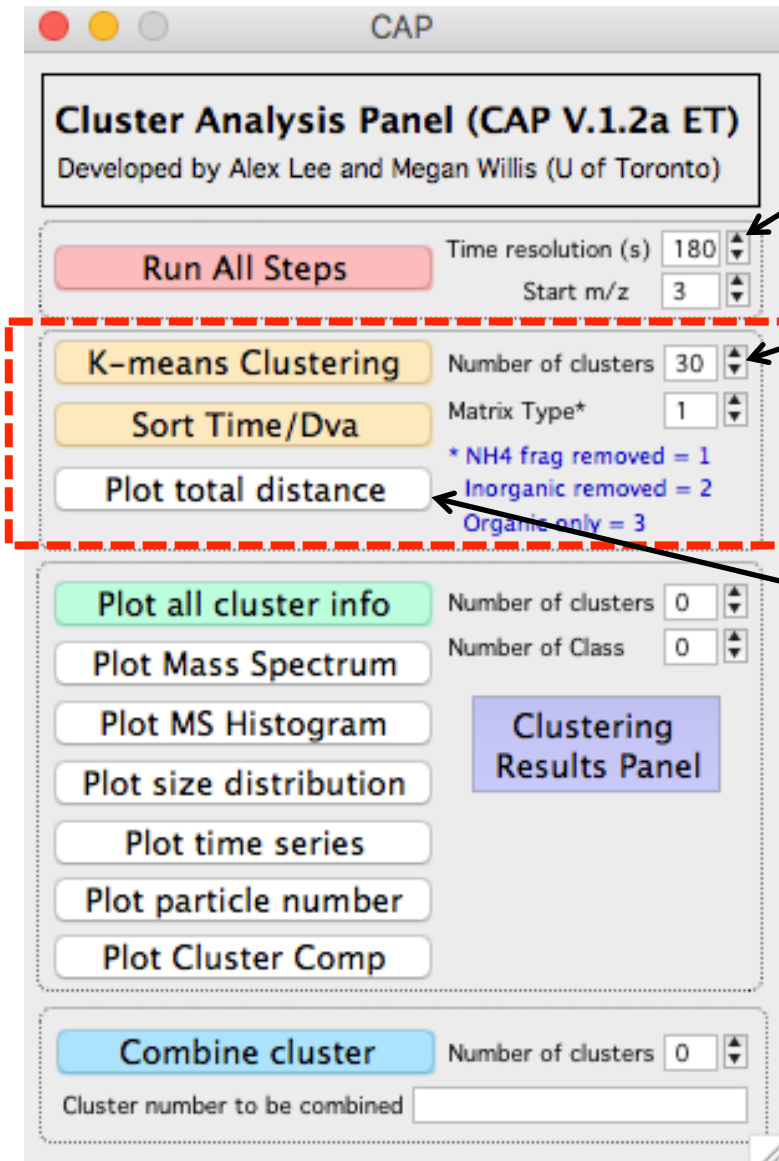


# Ensemble vs. Event trigger data (smoothed)



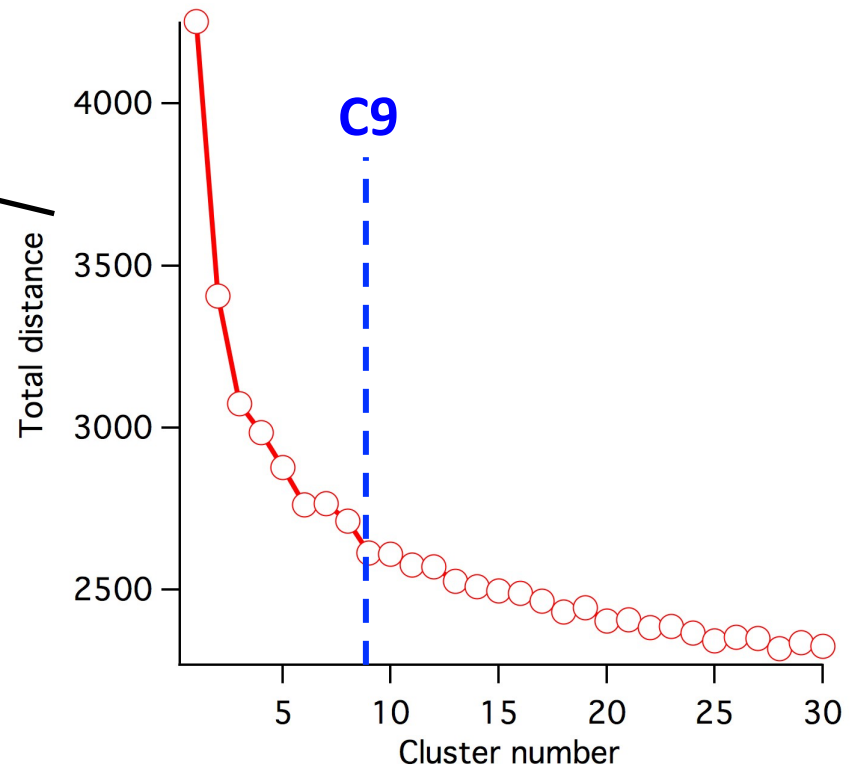


# Cluster analysis Panel (CAP)



Time resolution (for plotting time series of event trigger data)

Number of cluster (Max = 30, built in k-means clustering from IGOR Pro)



# Cluster analysis Panel (CAP)

**Cluster Analysis Panel (CAP V.1.2a ET)**  
Developed by Alex Lee and Megan Willis (U of Toronto)

**Run All Steps** Time resolution (s) 180 Start m/z 3

**K-means Clustering** Number of clusters 30 Matrix Type\* 1

**Sort Time/Dva**

**Plot total distance**

\* NH4 frag removed = 1  
Inorganic removed = 2  
Organic only = 3

**Plot all cluster info** Number of clusters 0 Number of Class 0

**Plot Mass Spectrum**

**Plot MS Histogram**

**Plot size distribution**

**Plot time series**

**Plot particle number**

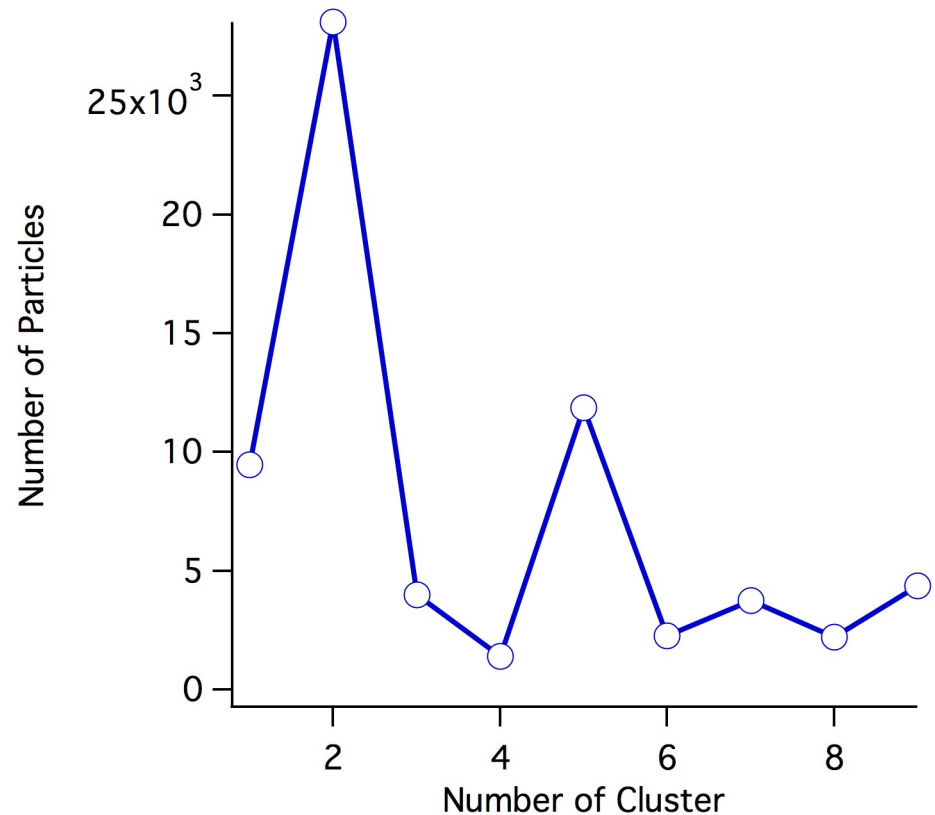
**Plot Cluster Comp**

**Clustering Results Panel**

**Combine cluster** Number of clusters 0

Cluster number to be combined

Particle number in each cluster



# Cluster analysis Panel (CAP)

**Cluster Analysis Panel (CAP V.1.2a ET)**  
Developed by Alex Lee and Megan Willis (U of Toronto)

**Run All Steps** Time resolution (s) 180 Start m/z 3

**K-means Clustering** Number of clusters 30 Matrix Type\* 1

**Sort Time/Dva**

**Plot total distance**

\* NH4 frag removed = 1  
Inorganic removed = 2  
Organic only = 3

**Plot all cluster info** Number of clusters 0

**Plot Mass Spectrum** Number of Class 0

**Plot MS Histogram**

**Plot size distribution**

**Plot time series**

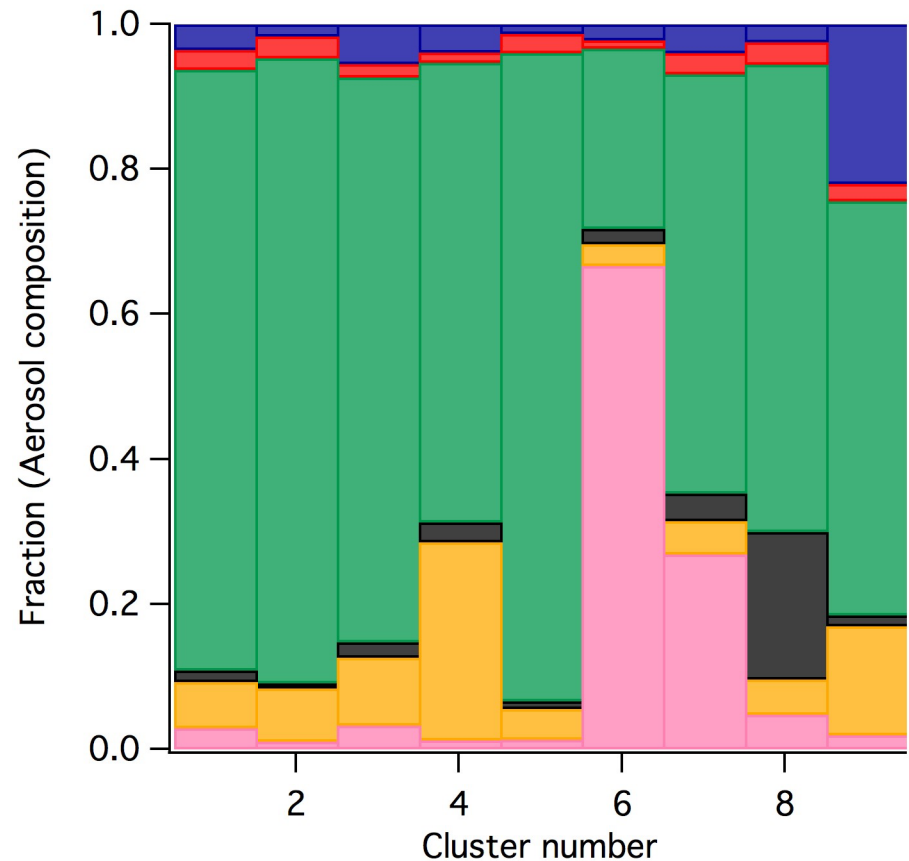
**Plot particle number**

**Plot Cluster Comp**

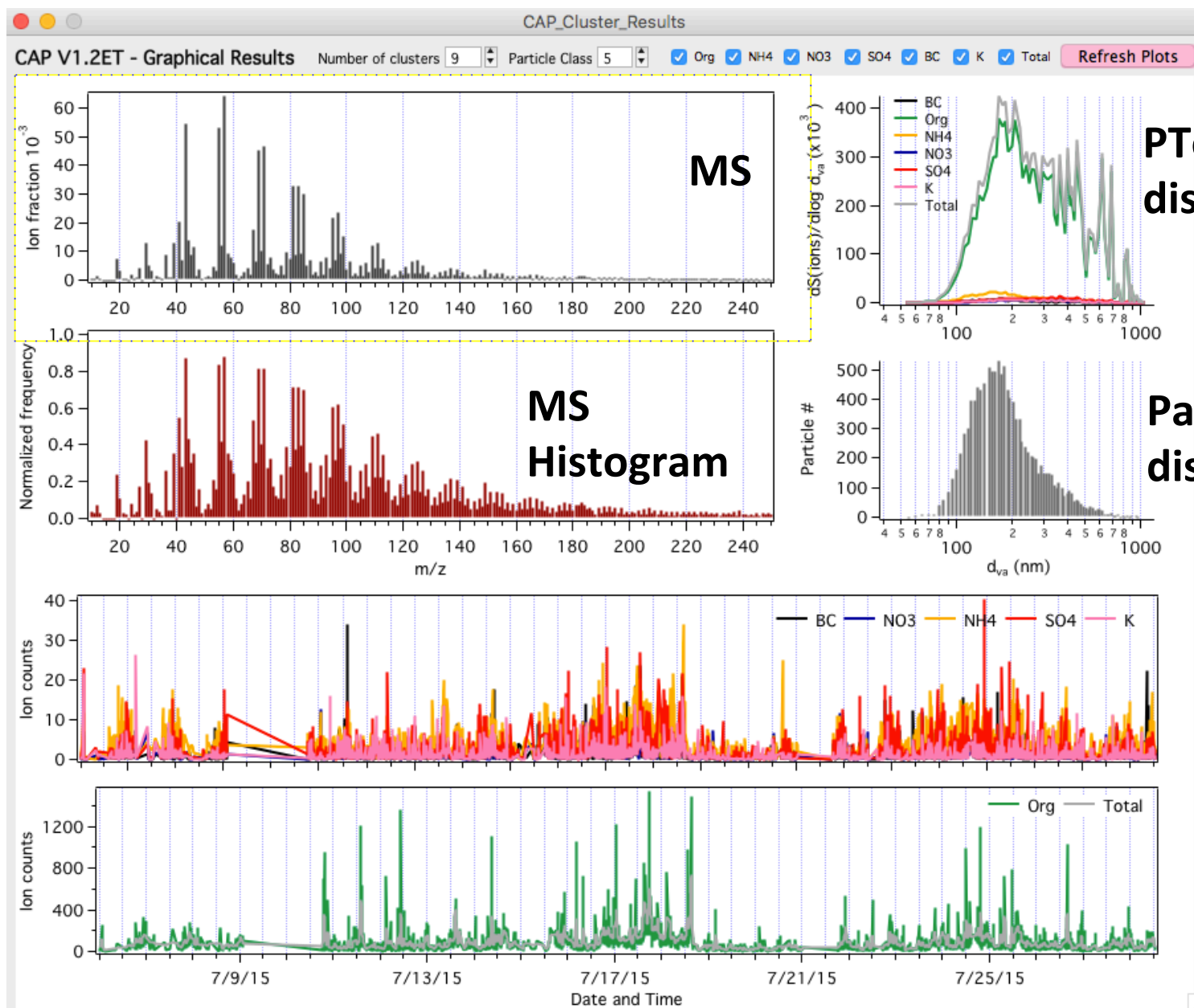
**Combine cluster** Number of clusters 0

Cluster number to be combined

Fraction of ion signal in each cluster



# Graphical Results Panel

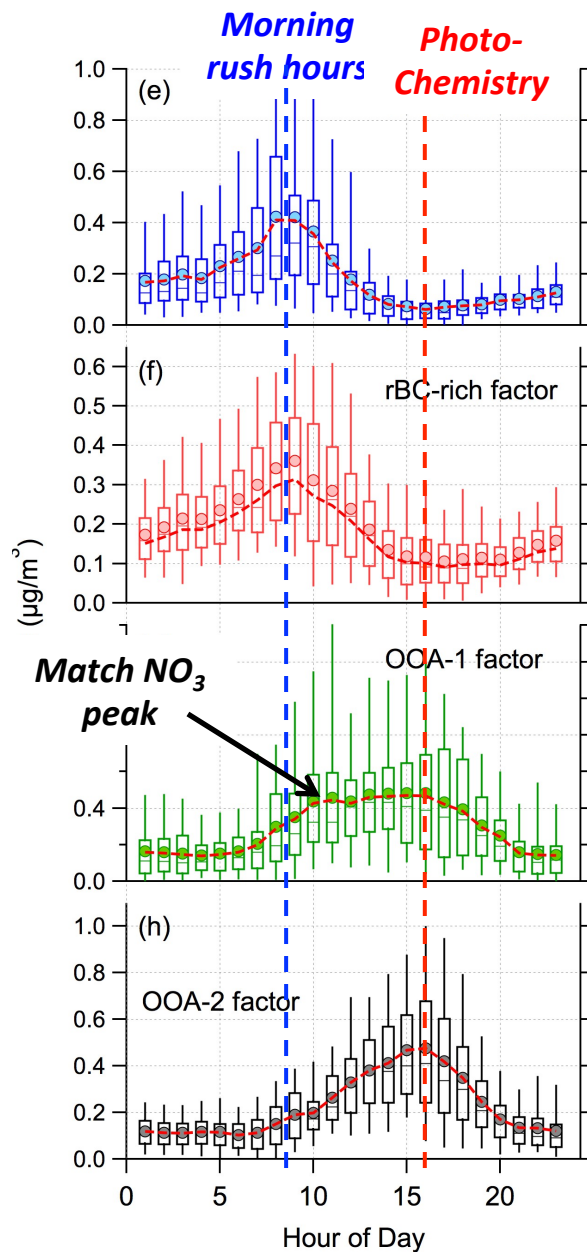
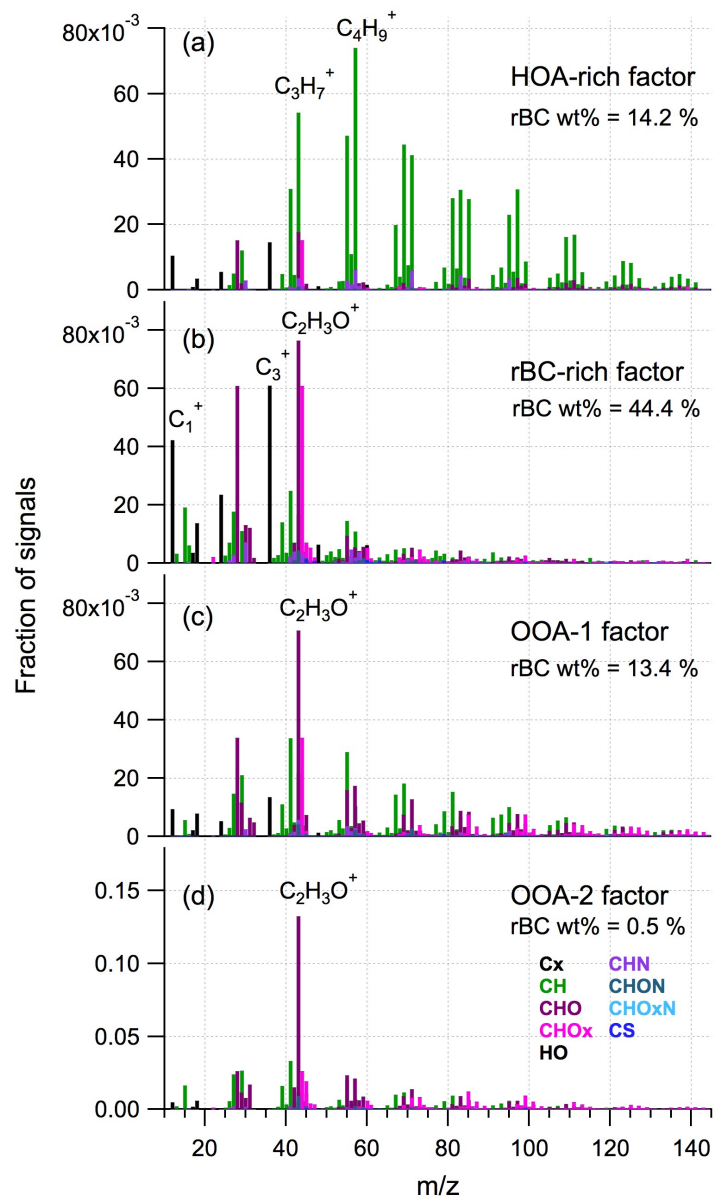


**PToF  
distribution**

**Particle #  
distribution**

**Time  
series**

# PMF analysis: 4-factors solution



**Hydrocarbon-like OA (HOA)-rich factor**



**rBC-rich factor**  
(with the support of single particle characterizations)

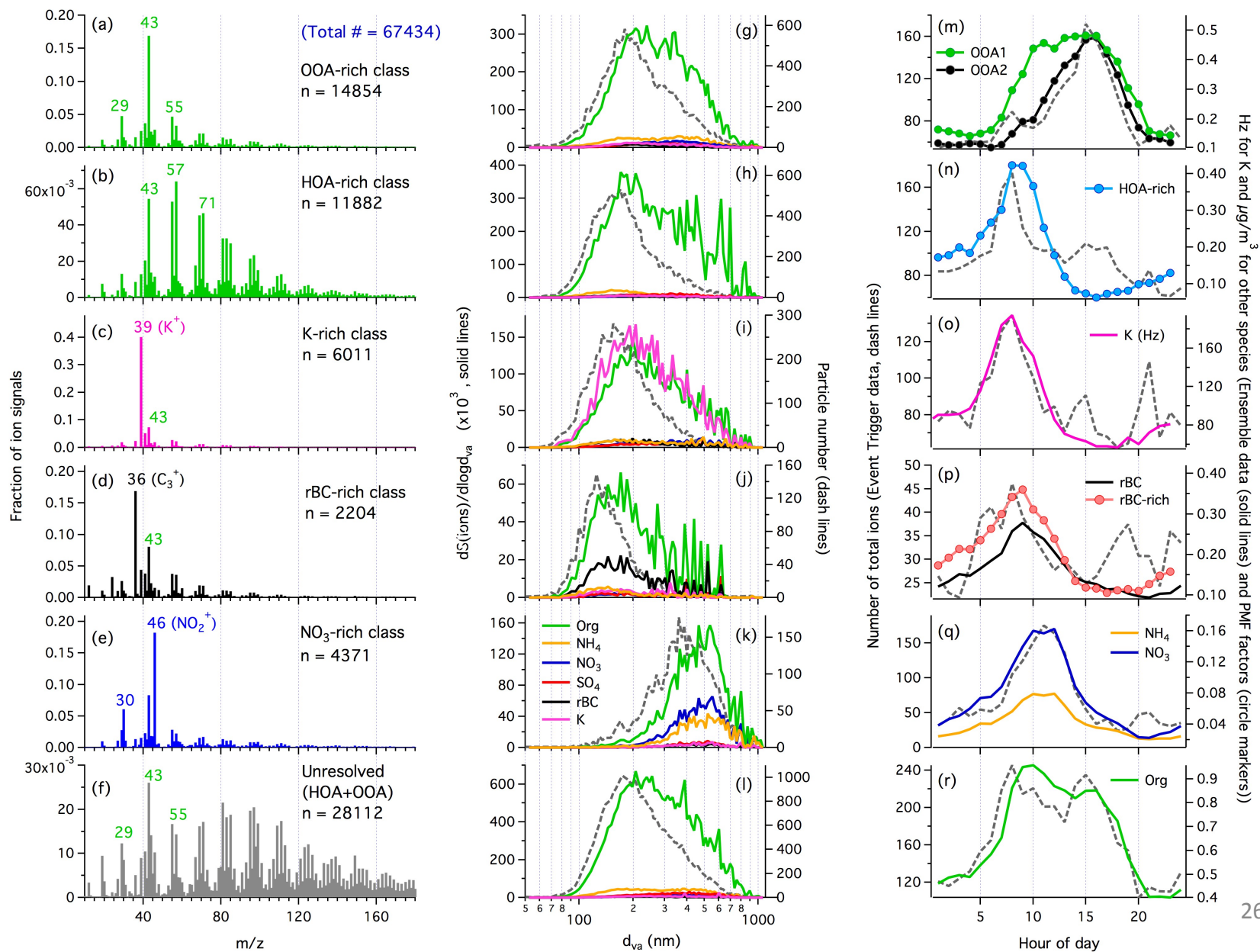
**Oxygenated OA OOA-1 factor**



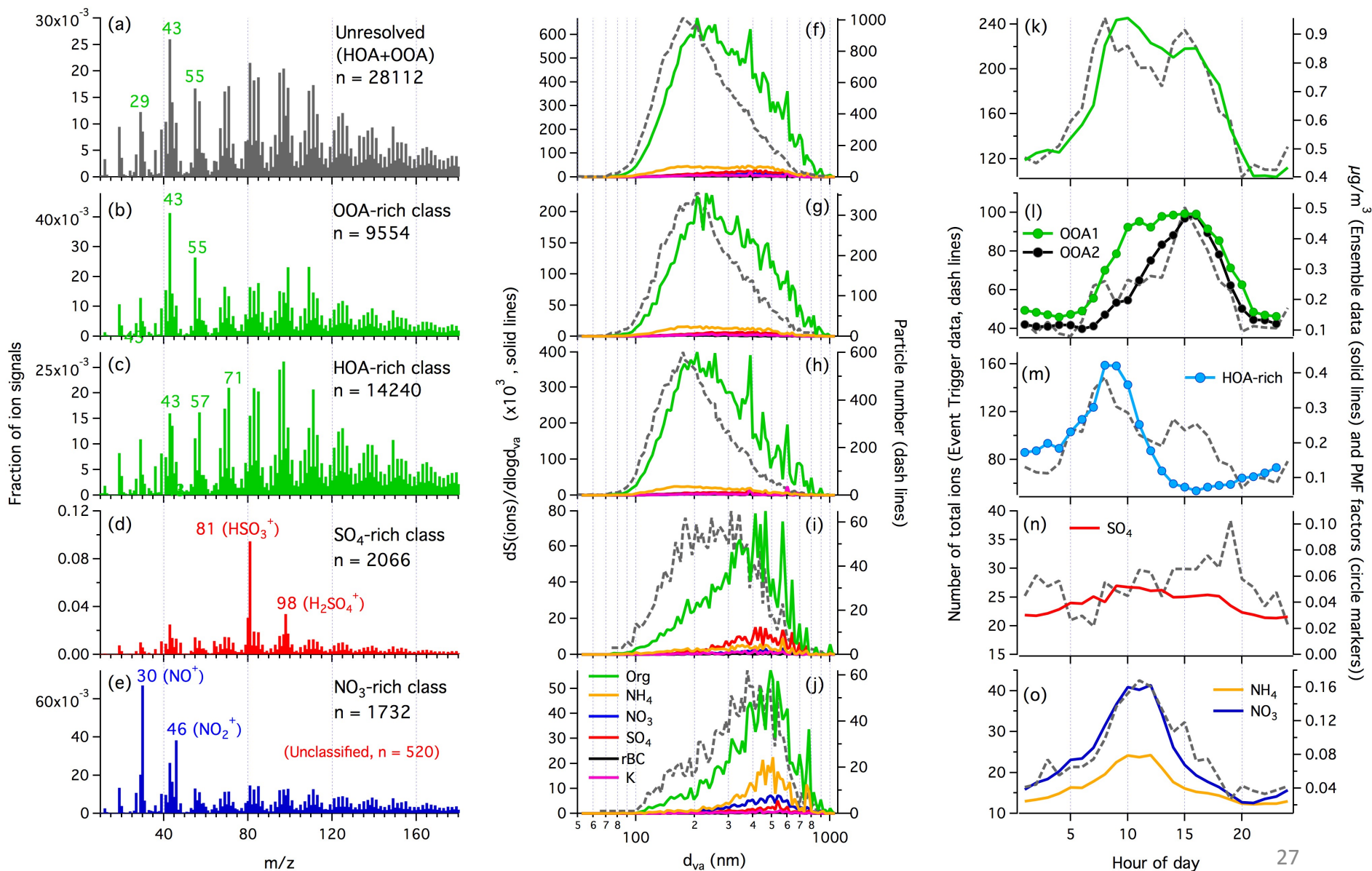
**OOA-2 factor**



# Clustering results: 1<sup>st</sup> run (9-clusters solution)



# Clustering results: 2<sup>nd</sup> run



# Summary

- Remove false positive (improvement?)
- K-means clustering (works! Match PMF results)
- How to determine duty cycle for event trigger?
- Light scattering?