Using Individual Particle Signatures to Discriminate Between HDV and LDV Emissions (+ recent ATOFMS advances)

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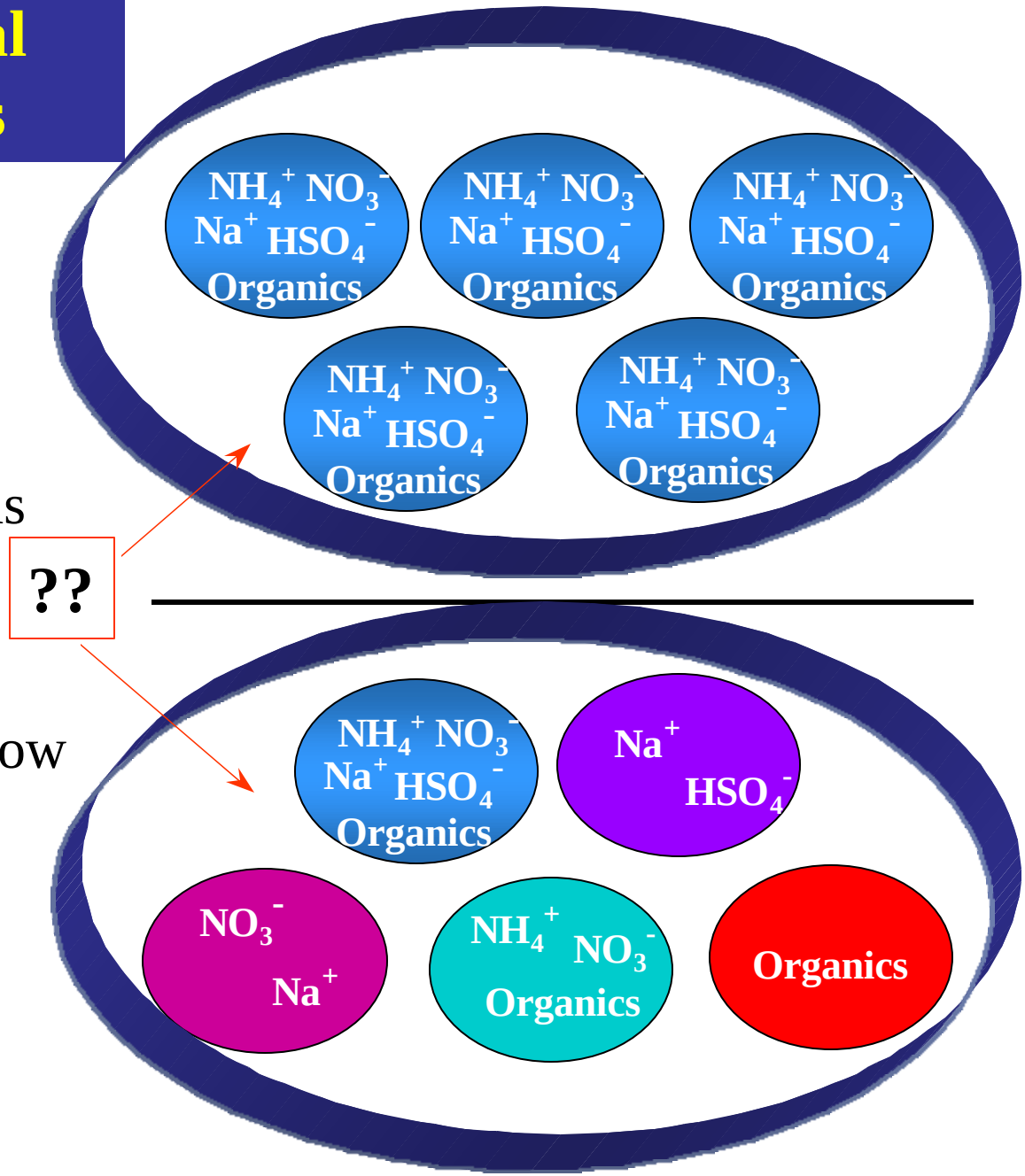
Primary Research Goals

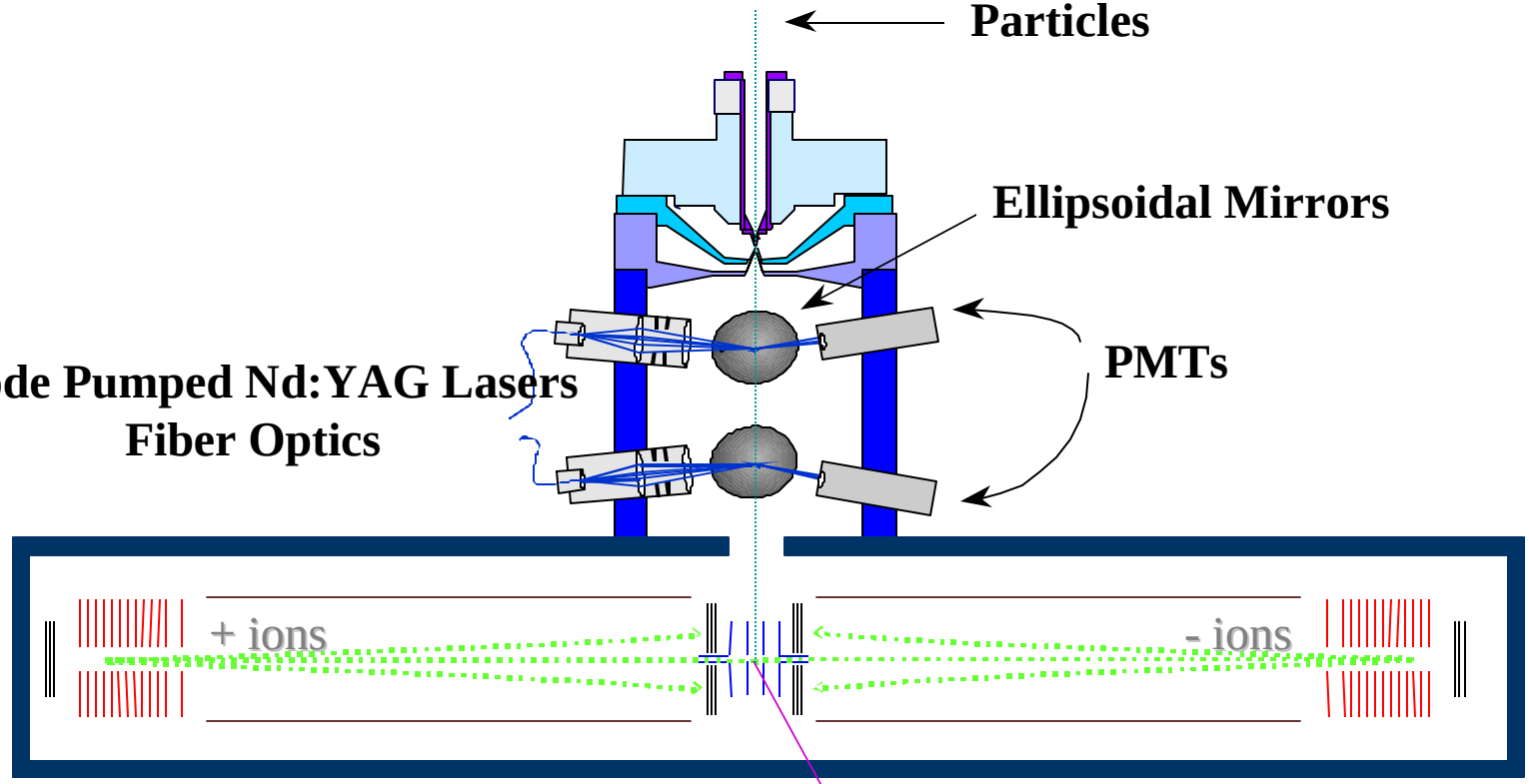
- Aerosol Time-of-Flight Mass Spectrometry (ATOFMS)
  - Characterization of PM at the single particle level (size and composition)
    - Identify different particle types
    - Characterize associations of chemical species within individual particles
    - Correlate particle chemistry with gas phase and met. data
    - Characterize spatial and temporal variability of PM
    - Perform source apportionment at single particle level

Bulk vs. individual particle analysis

- Chemical associations
- Chemical transformations
- Health effects
- Determination of source
- Size and composition allow for scaling raw counts



ATOFMS



$C_nH_m^+$ (organic species)
Metals (Fe, V, Pb)$^+$

Nd:YAG Laser

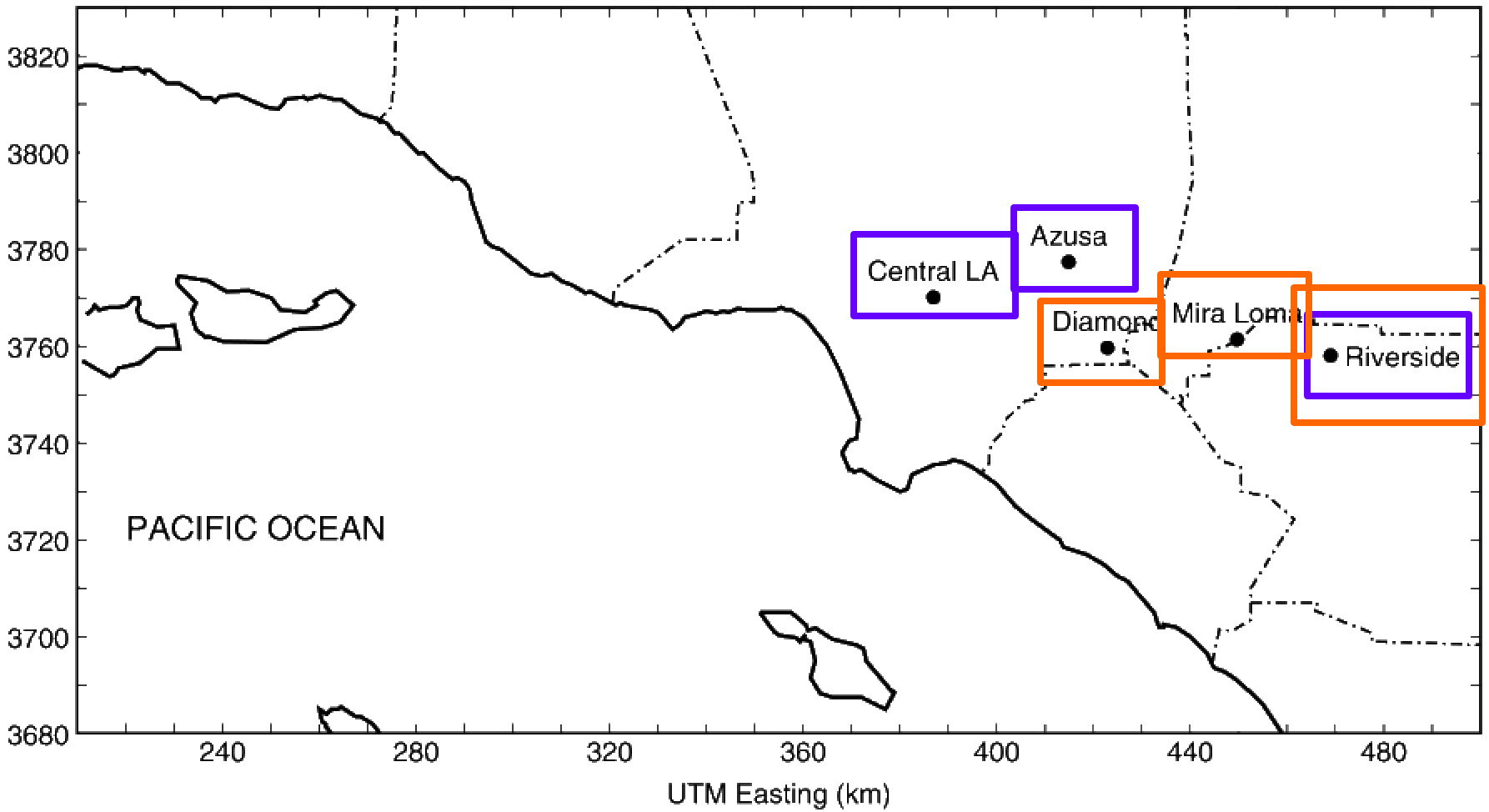
$C_nH_m^-$ (organic species)
Nitrates, sulfates, phosphates, chloride
Metal oxides

Goals of Previous ARB Project

- “REFINEMENT, CALIBRATION, AND FIELD STUDIES INVOLVING TRANSPORTABLE AEROSOL TIME-OF-FLIGHT MASS SPECTROMETERS”

- Refinement and calibration of ATOFMS systems
- Major test—SCOS97
- Examine particle evolution over different trajectories
- Compare with basic source seeds from dyno testing
- Development of data analysis tools (ART-2a, others)
- Quantitation (mass, ammonium, nitrate, multivariate)

SCOS-97 Locations



- Trajectory 1: Central LA-Azusa-Riverside (vehicle)
- Trajectory 2: Diamond Bar-Mira Loma-Riverside (NH4/NO3)

SCOS-97 Dates

Date	Sampling Location	ATOFMS instrument
mid-June – mid-October	Riverside Pierce Hall UCR	lab-based (BST)
late June – early July	Riverside CE-CERT	transportable (JKE)
late June – early July	Mt. Wilson	transportable (ELD)
August	Central Los Angeles	transportable (JKE)
August	Azusa	transportable (ELD)
September	Diamond Bar	transportable (JKE)
September	Mira Loma	transportable (ELD)

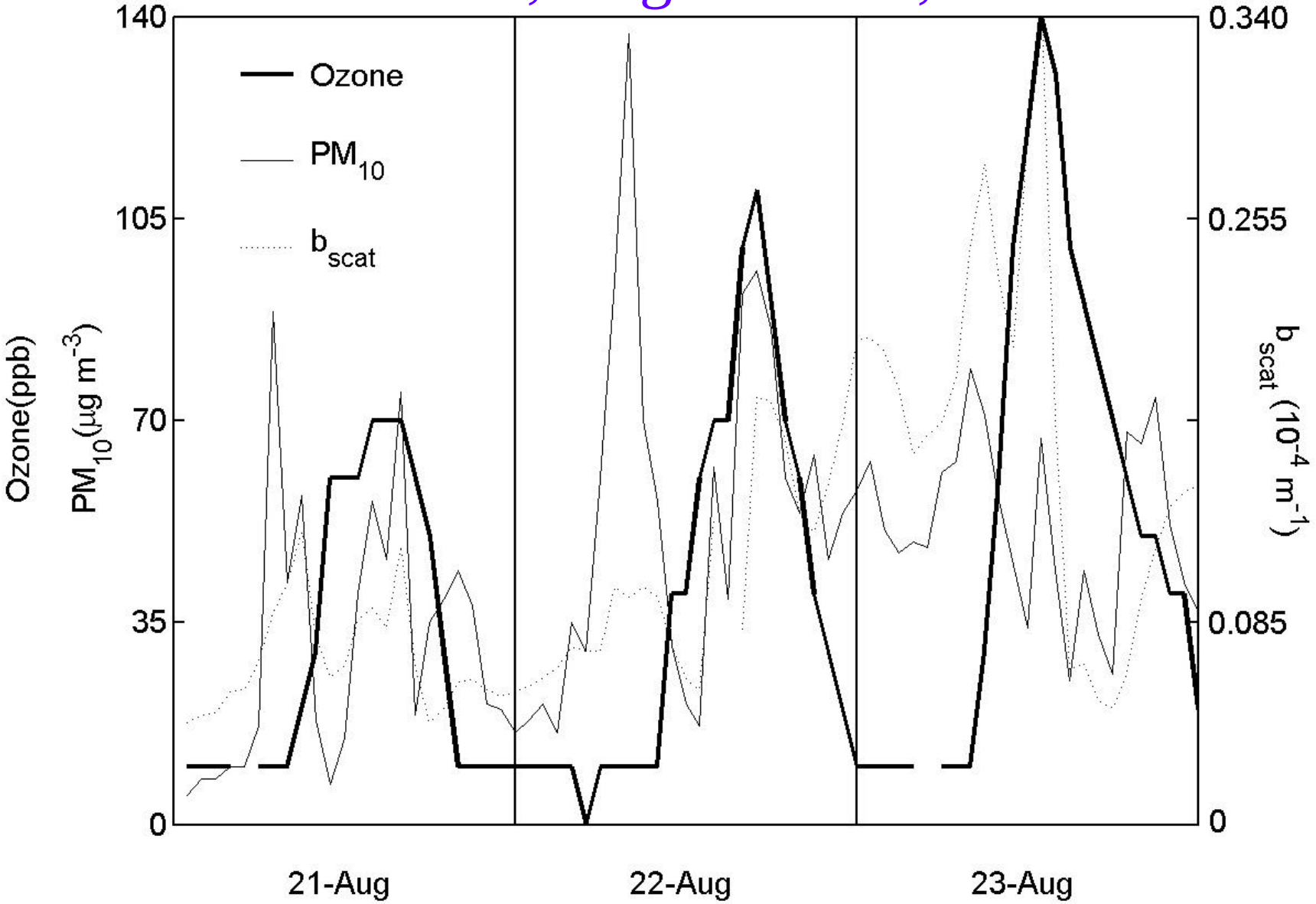
Measurements

- ATOFMS - Single Particle Size and Composition

- Scanning Mobility Particle Sizer (SMPS)
  - Aerosol Size Distribution (0.02 - 0.7 µm)
- Optical Particle Counter (OPC)
  - Aerosol Size Distribution (0.1 - 2.0 µm)
- Aerodynamic Particle Sizer (APS)
  - Aerosol Size Distribution (0.5 - 20 µm)
- Filter based methods (MOUDI), semi-continuous methods (nitrate, carbon, PM2.5)

- Meteorological Conditions - Wind Speed, Wind Direction, Temperature, Relative Humidity

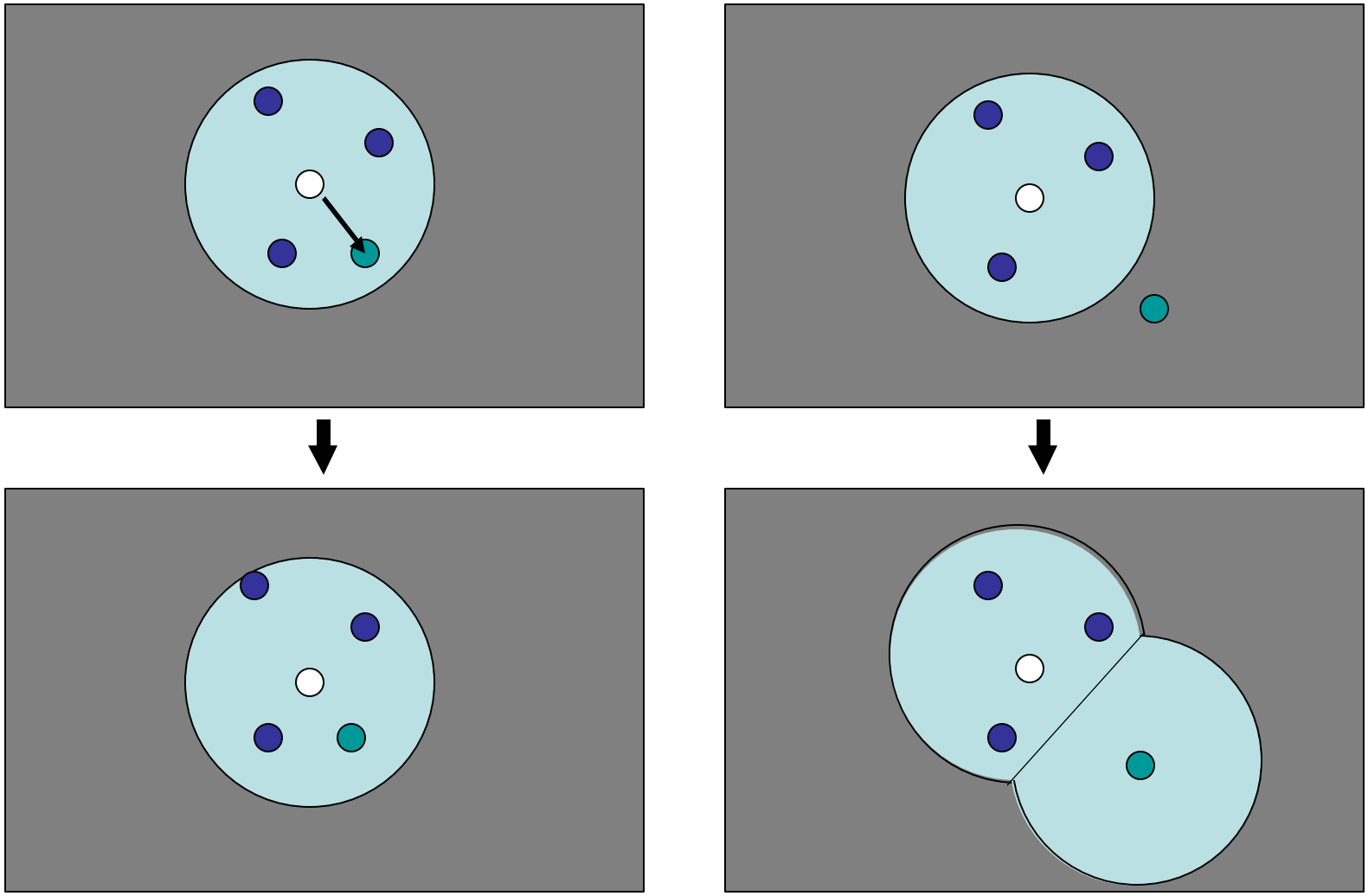
Ozone and PM10 Variations
Riverside, August 21-23, 1997



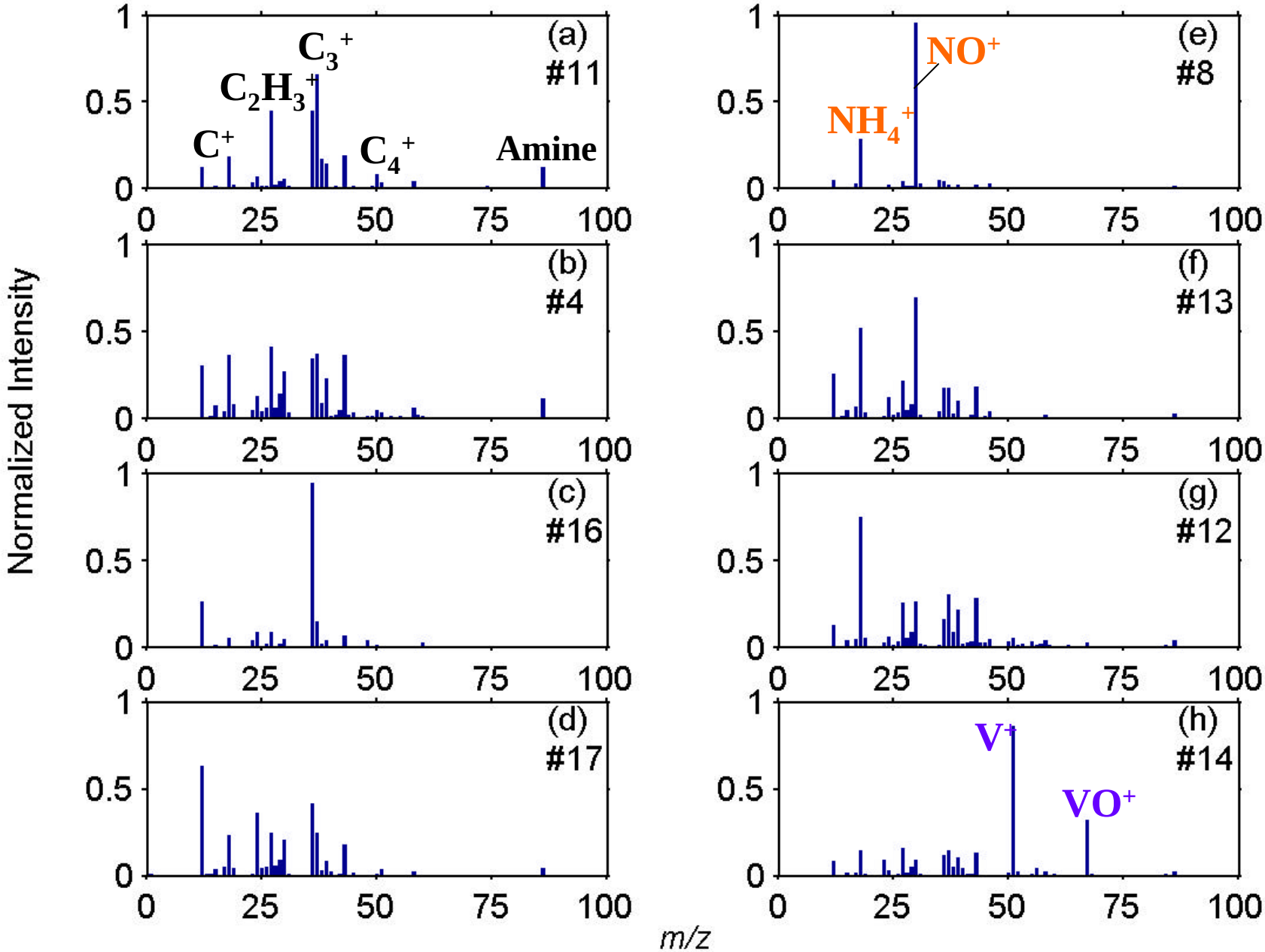
Data Analysis
ART-2a

- Adaptive Resonance Theory neural network.
- An analysis procedure for finding clusters
  - Clusters have a maximum size (vigilance factor)
  - The number of clusters will be modified as required to classify all particles.

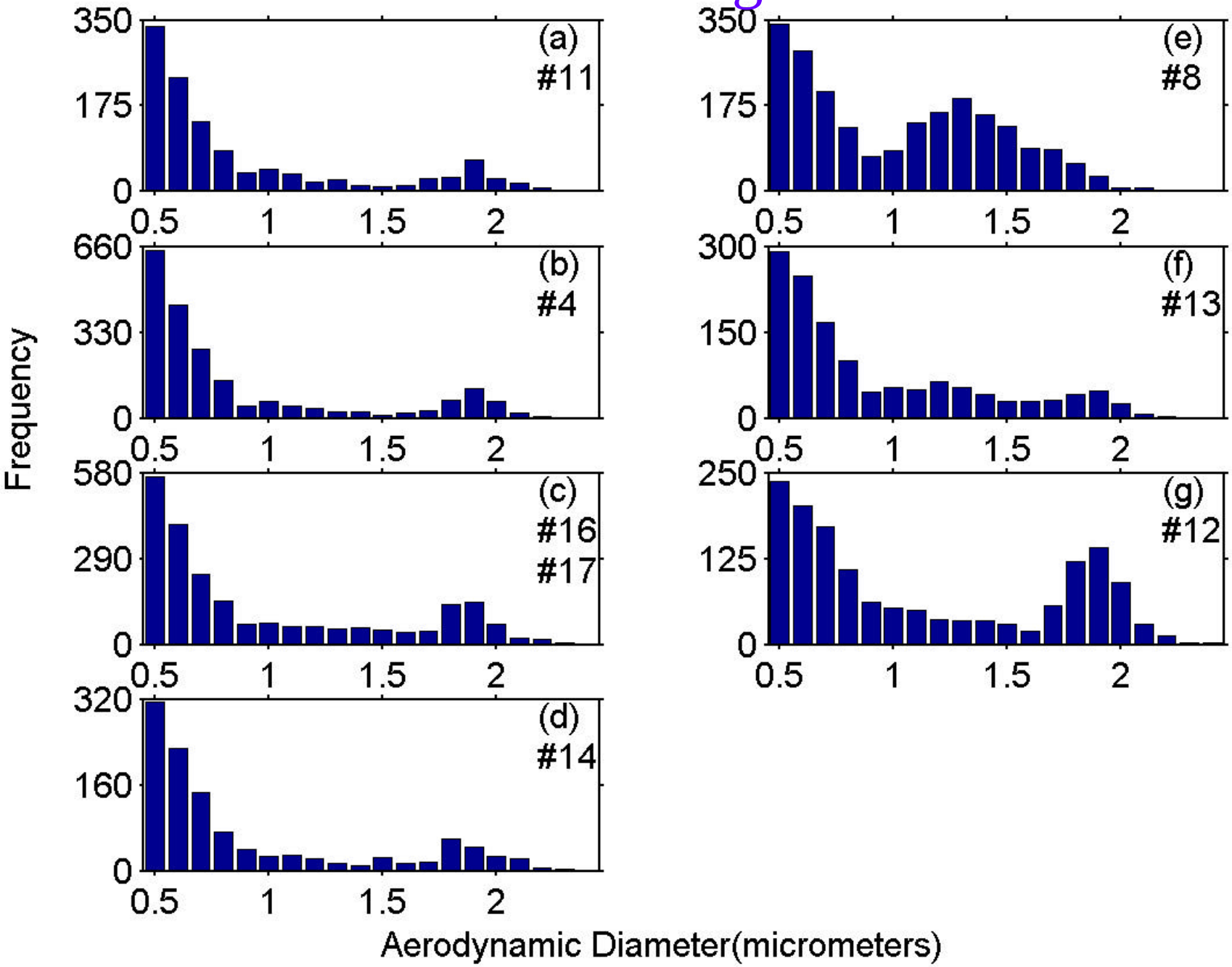
Neurons and Particles



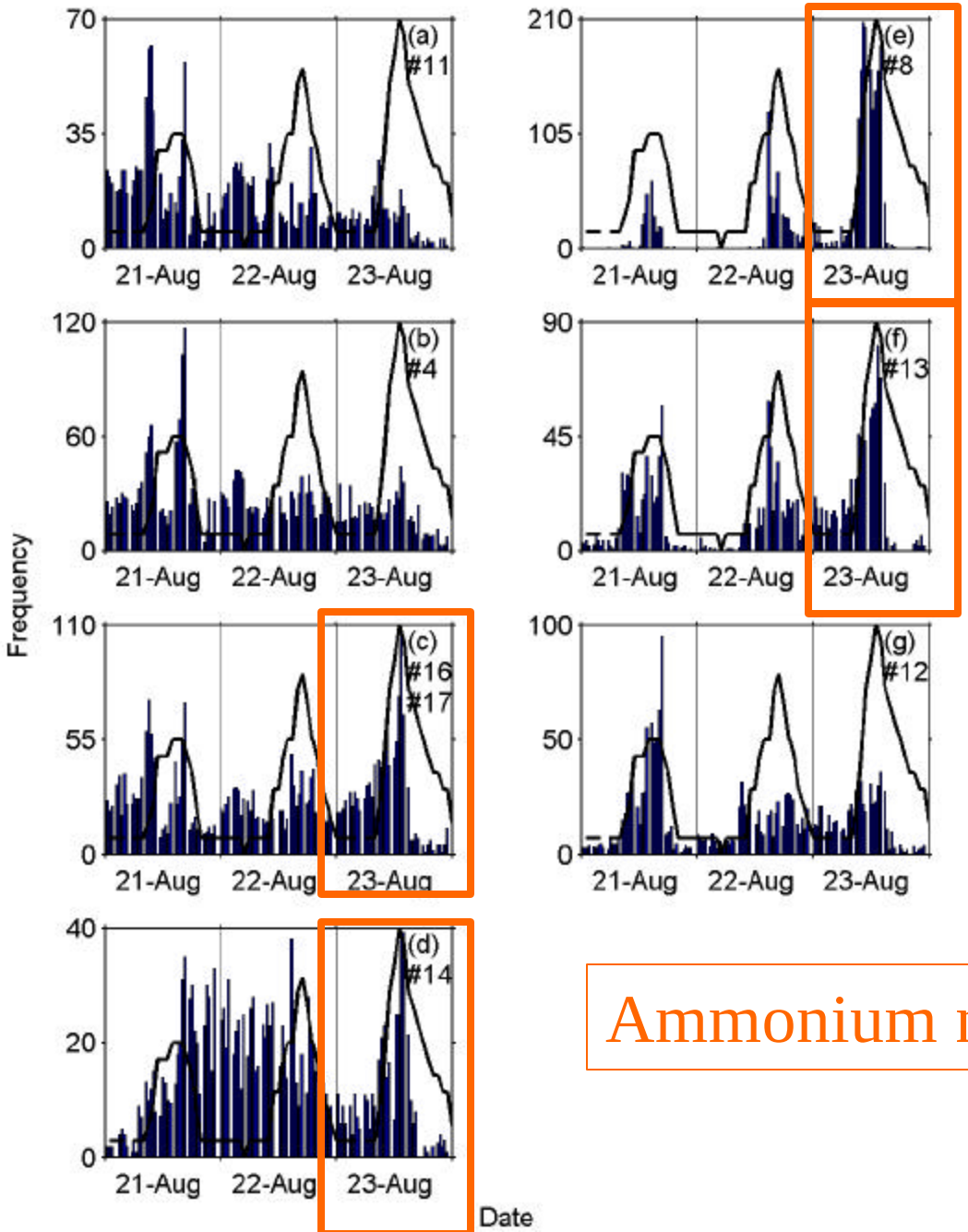
Riverside (Organic WM)



Sizes of Organics

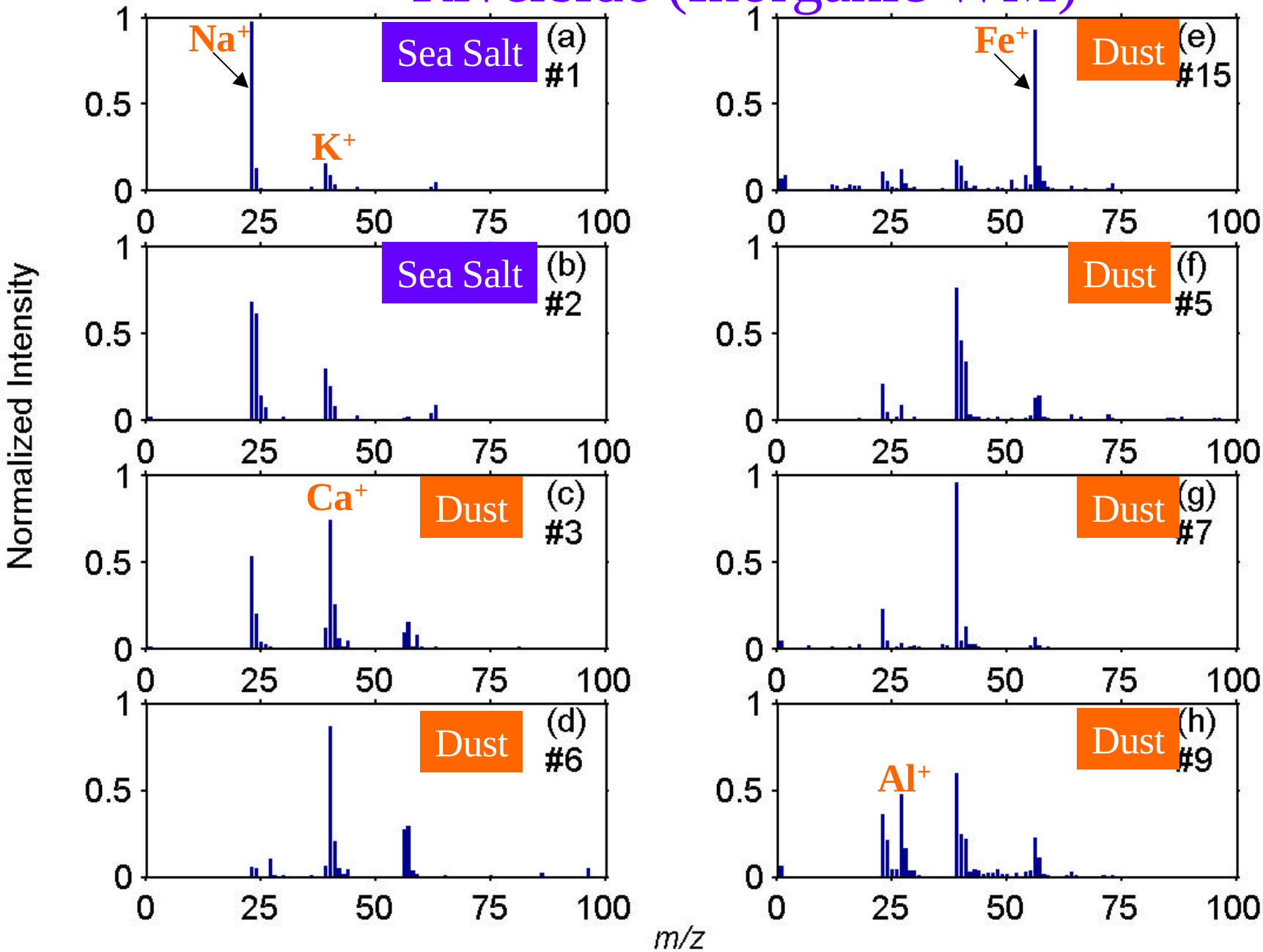


Evolution of Organic Types vs. Ozone (and bscat)

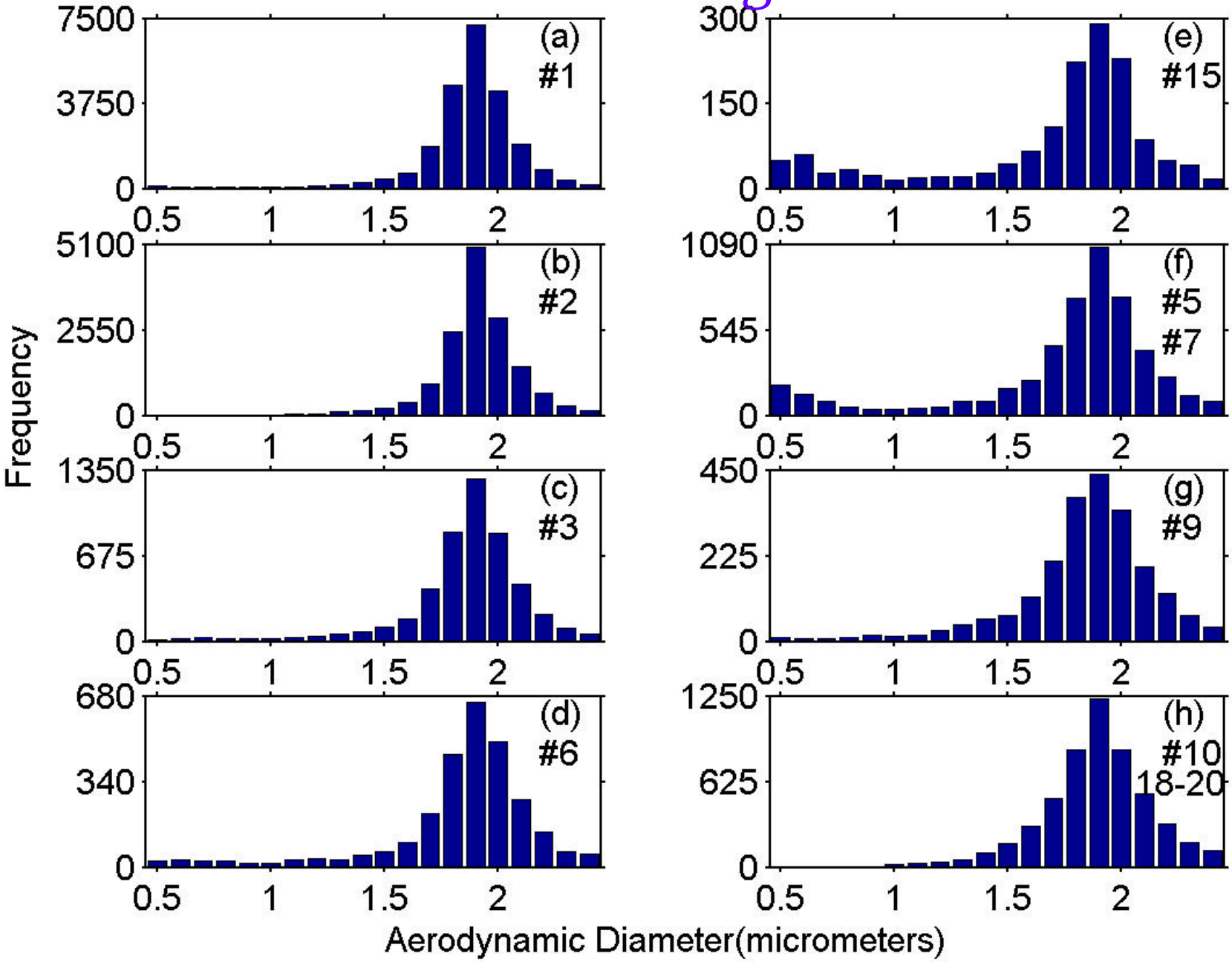


Ammonium nitrate rich

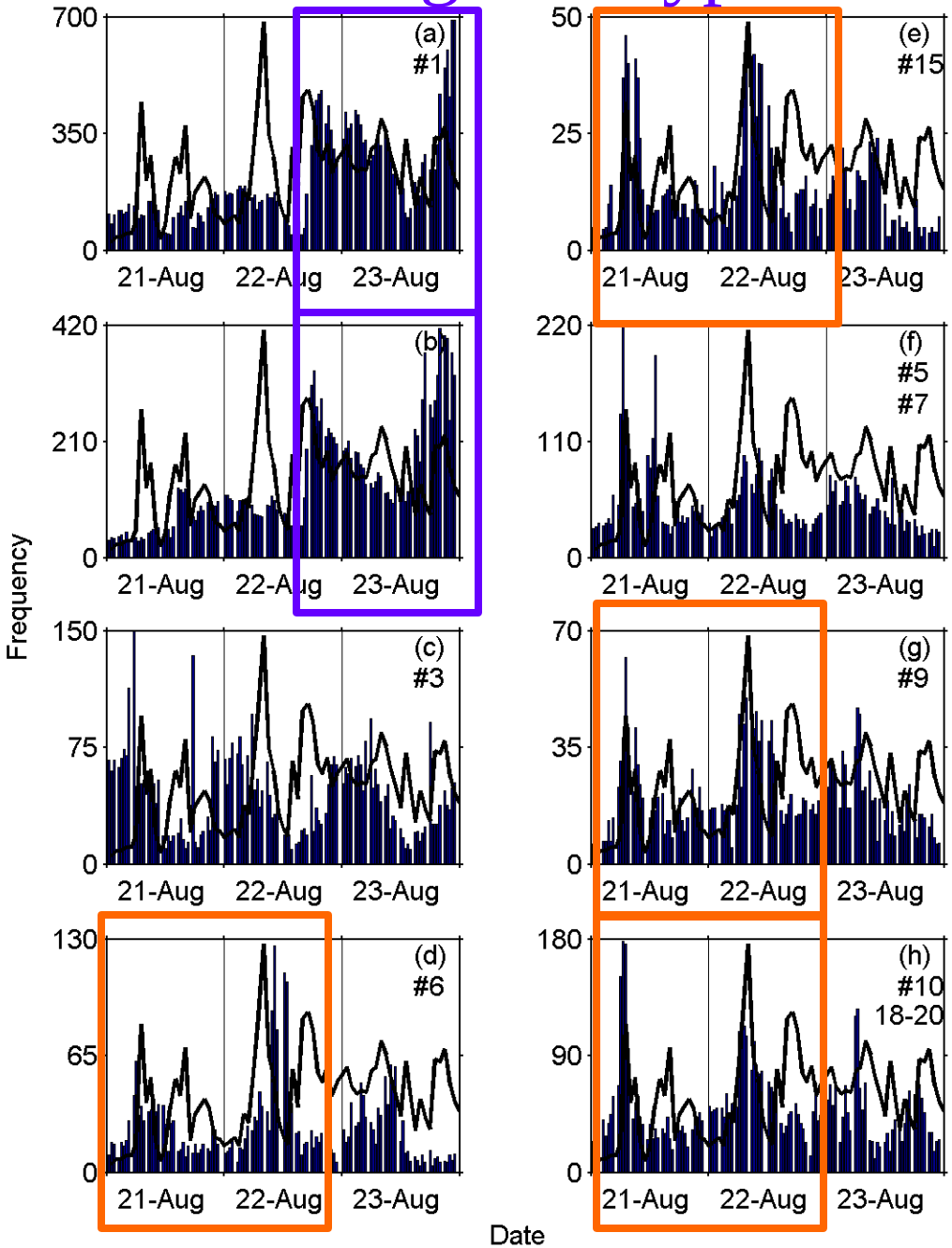
Riverside (Inorganic WM)



Sizes of Inorganics



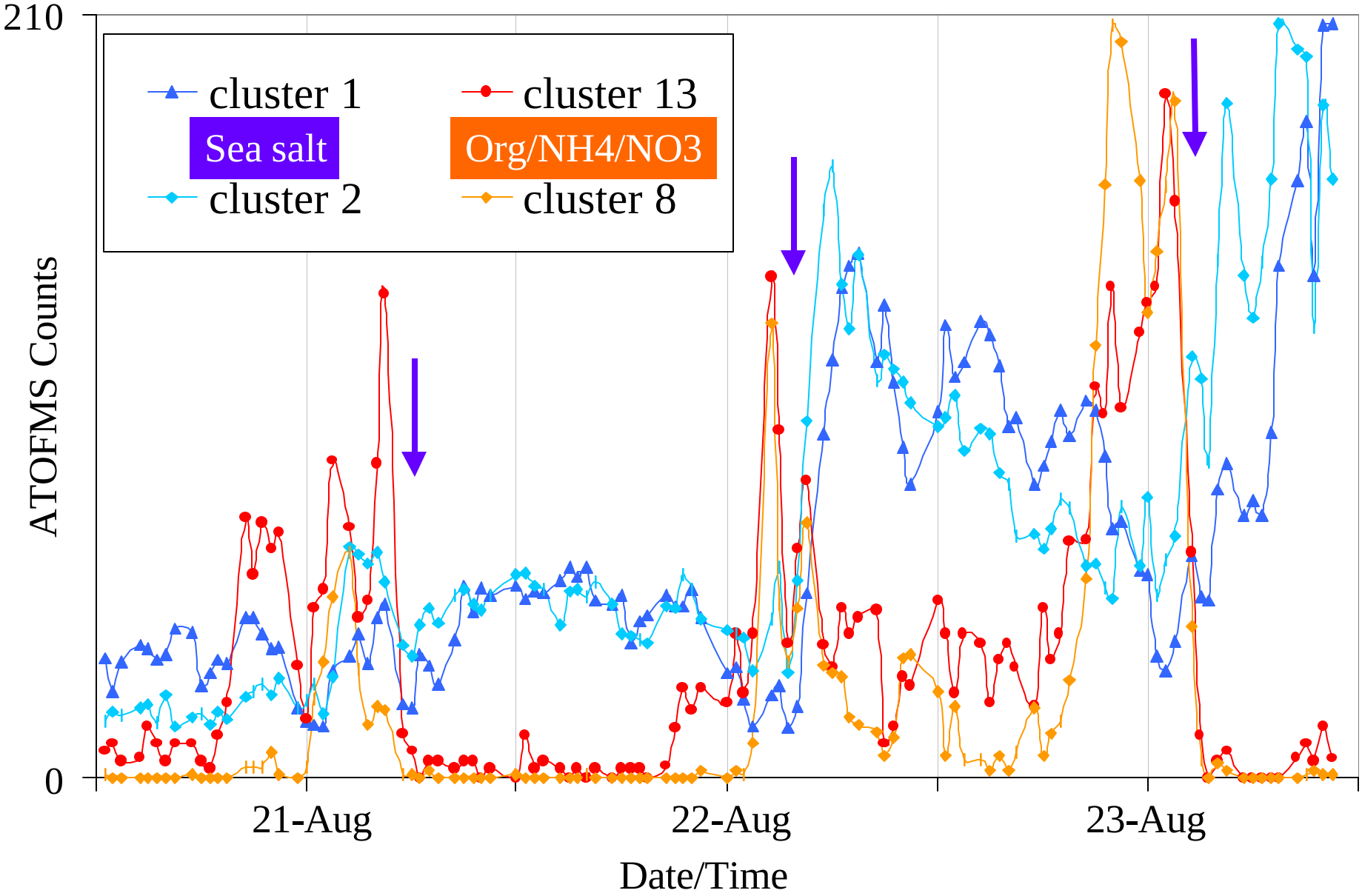
Evolution of Inorganic Types vs. PM10



Dust

Sea Salt

Temporal Evolution of Major Types
Riverside, August 21-23, 1997



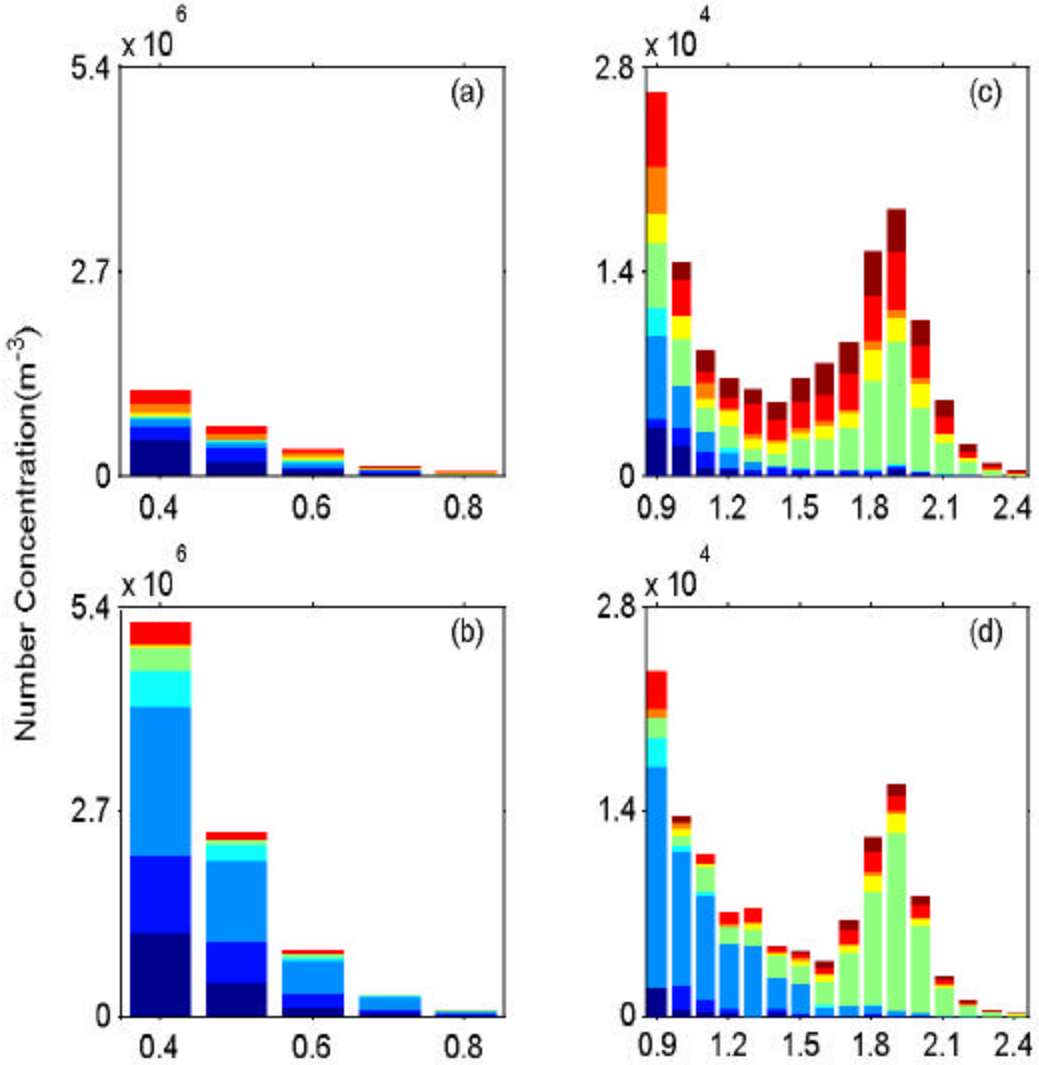
Scaled ATOFMS Particle Types (Riverside, CA)

High PM, Low Ozone

- Organic Carbon with Amines
- Elemental Carbon
- Organic Carbon with Ammonium Nitrate
- Vanadium-rich
- Sea Salt
- Calcium-rich
- Iron-rich
- Potassium-rich
- Soil Dust

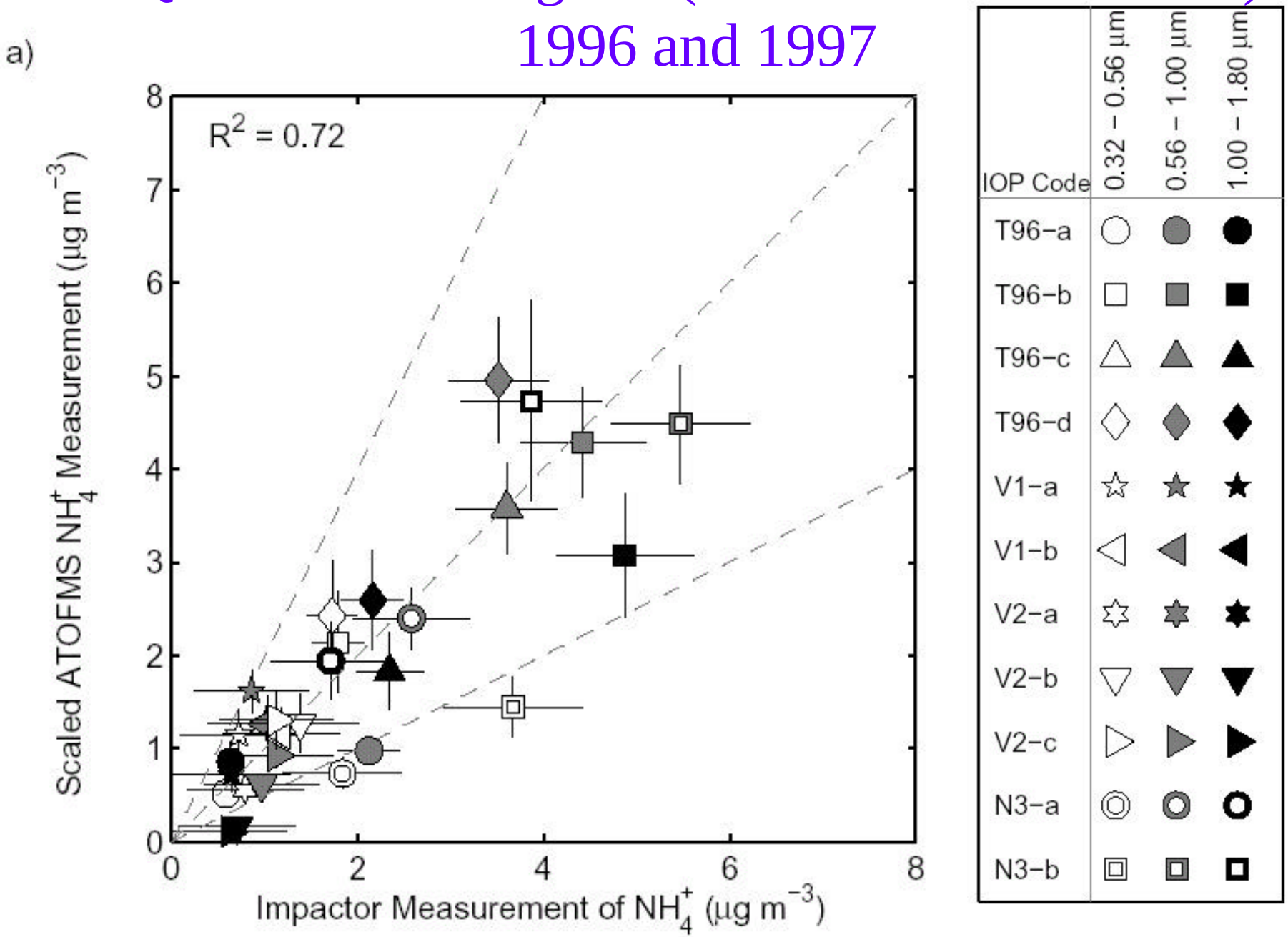
High PM, High Ozone

Number Concentration

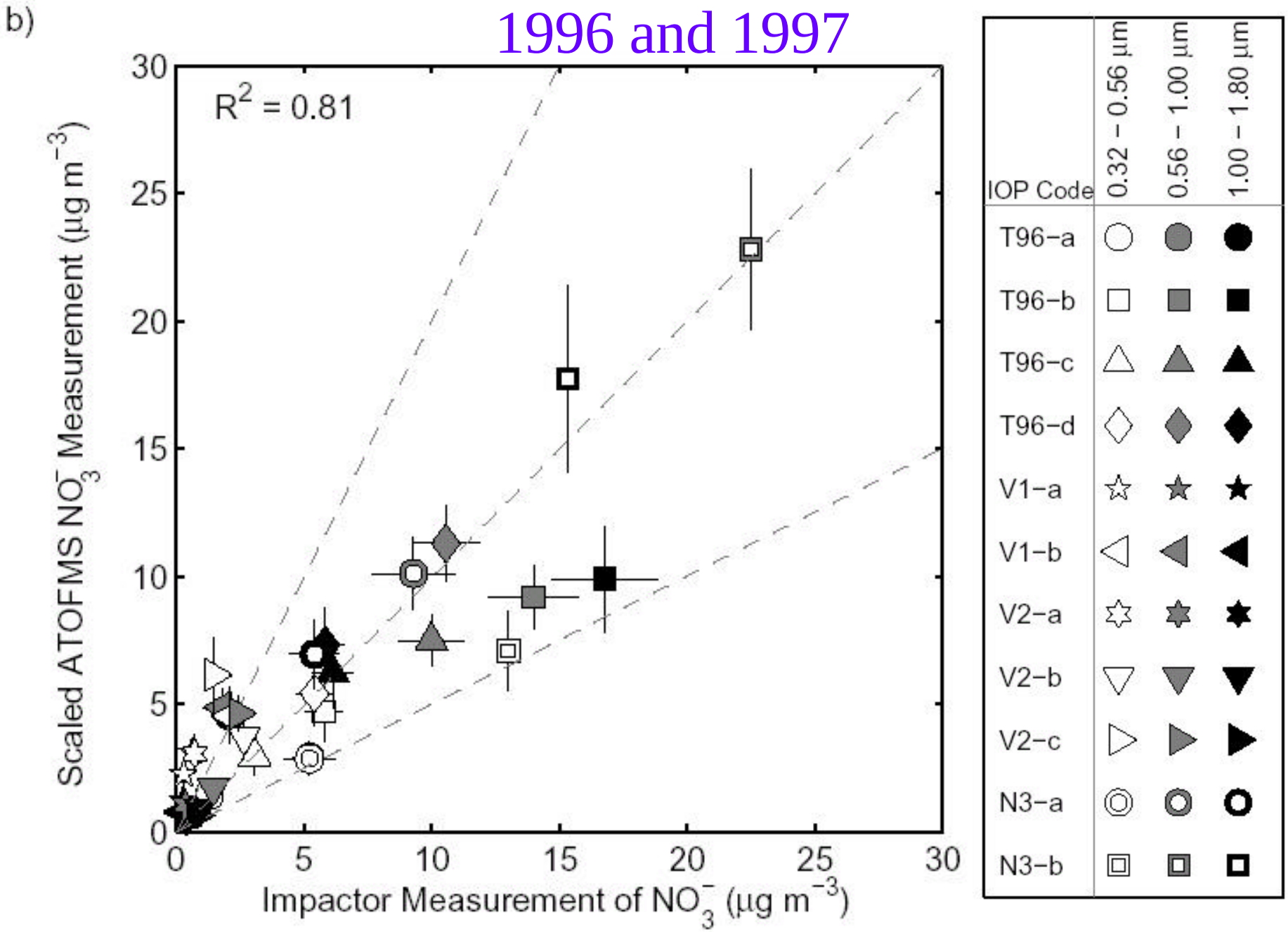


Aerodynamic Diameter (μm)

Quantitation Progress (Univariate Calibration) 1996 and 1997



Quantitation Progress (Univariate Calibration) 1996 and 1997



Quantitation Progress (Multivariate Calibration)
44 species simultaneously

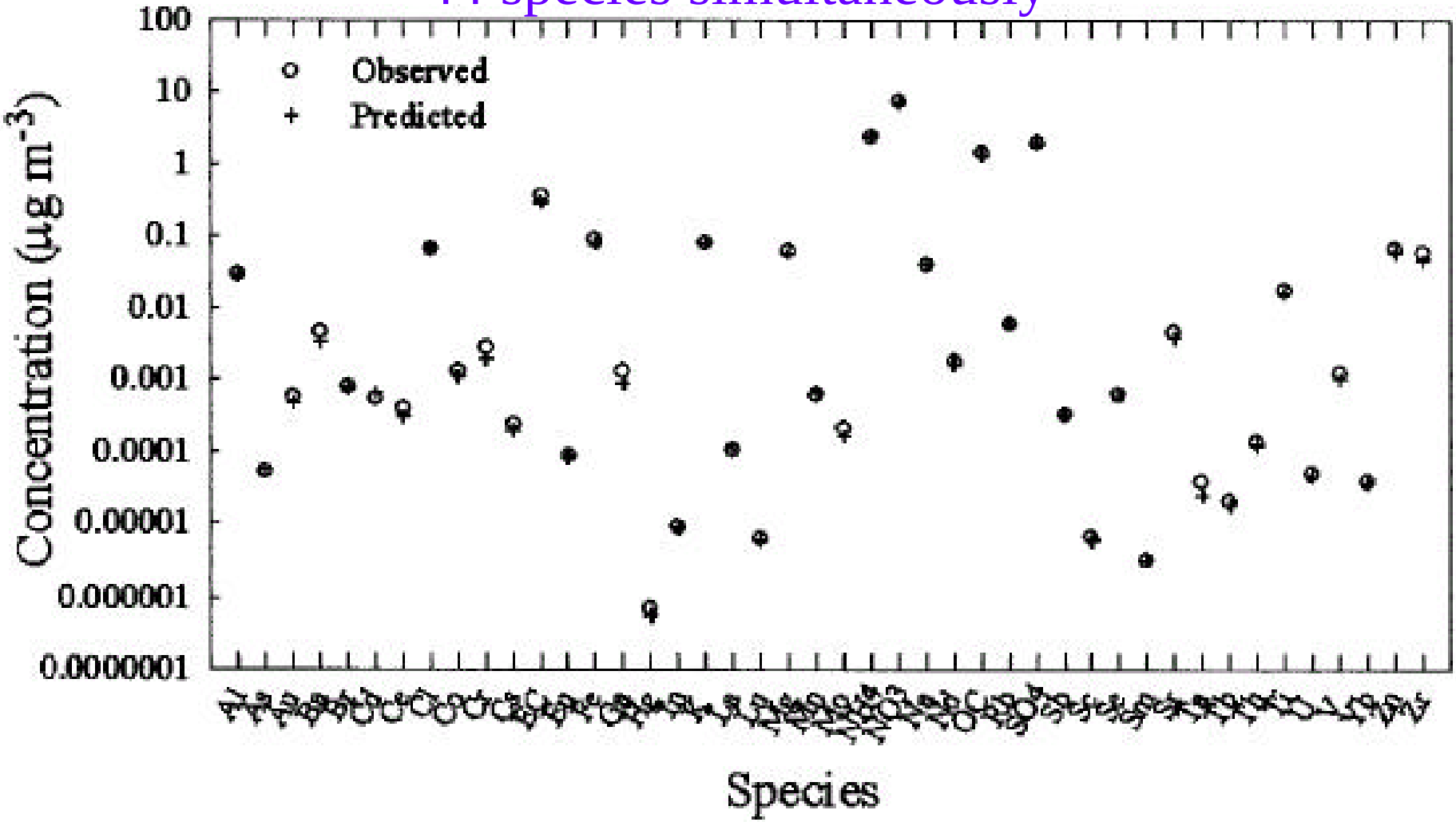
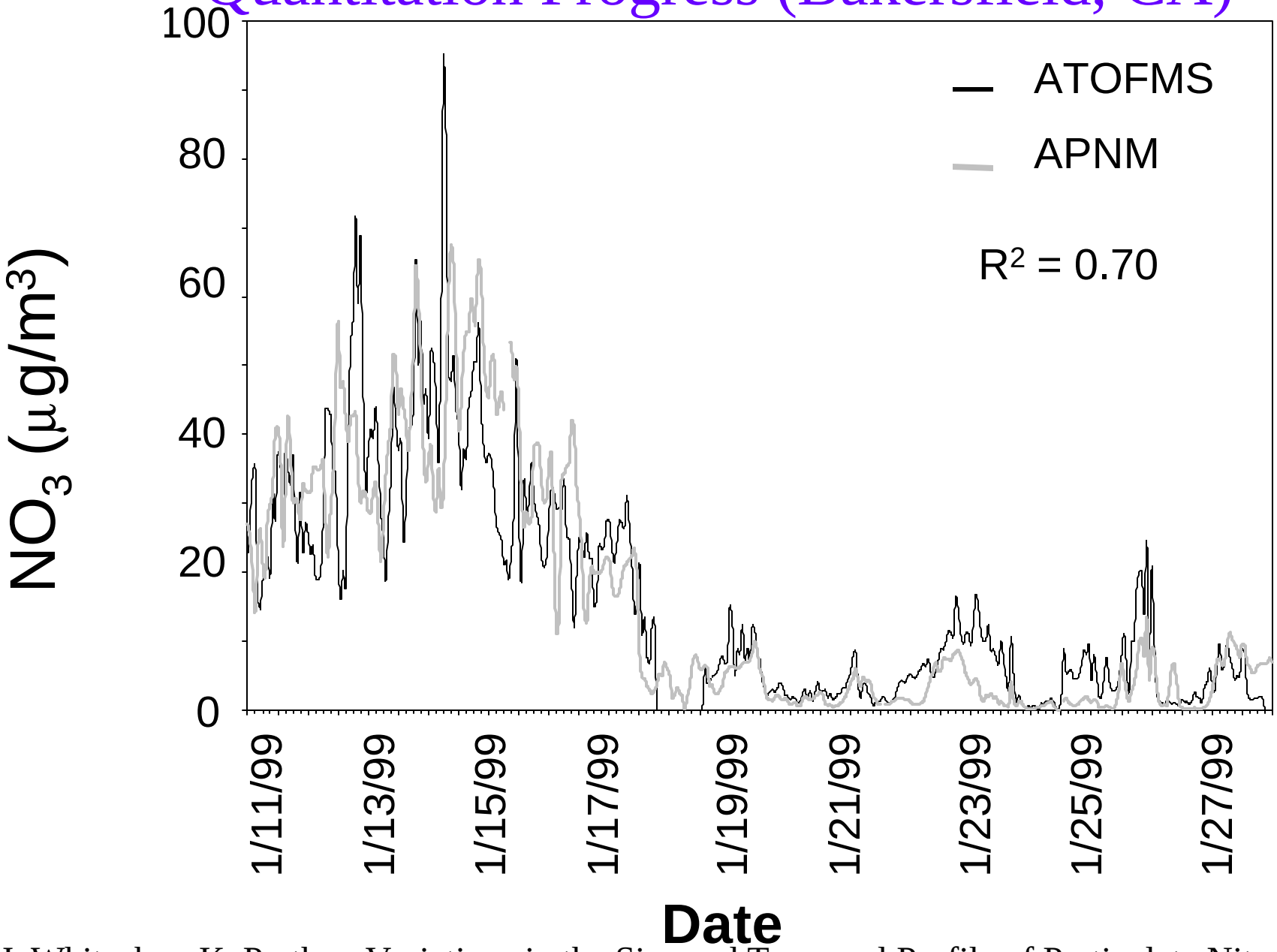


Figure 1. Predicted concentration vs the observed concentration for each species, averaged over the 12 samples.

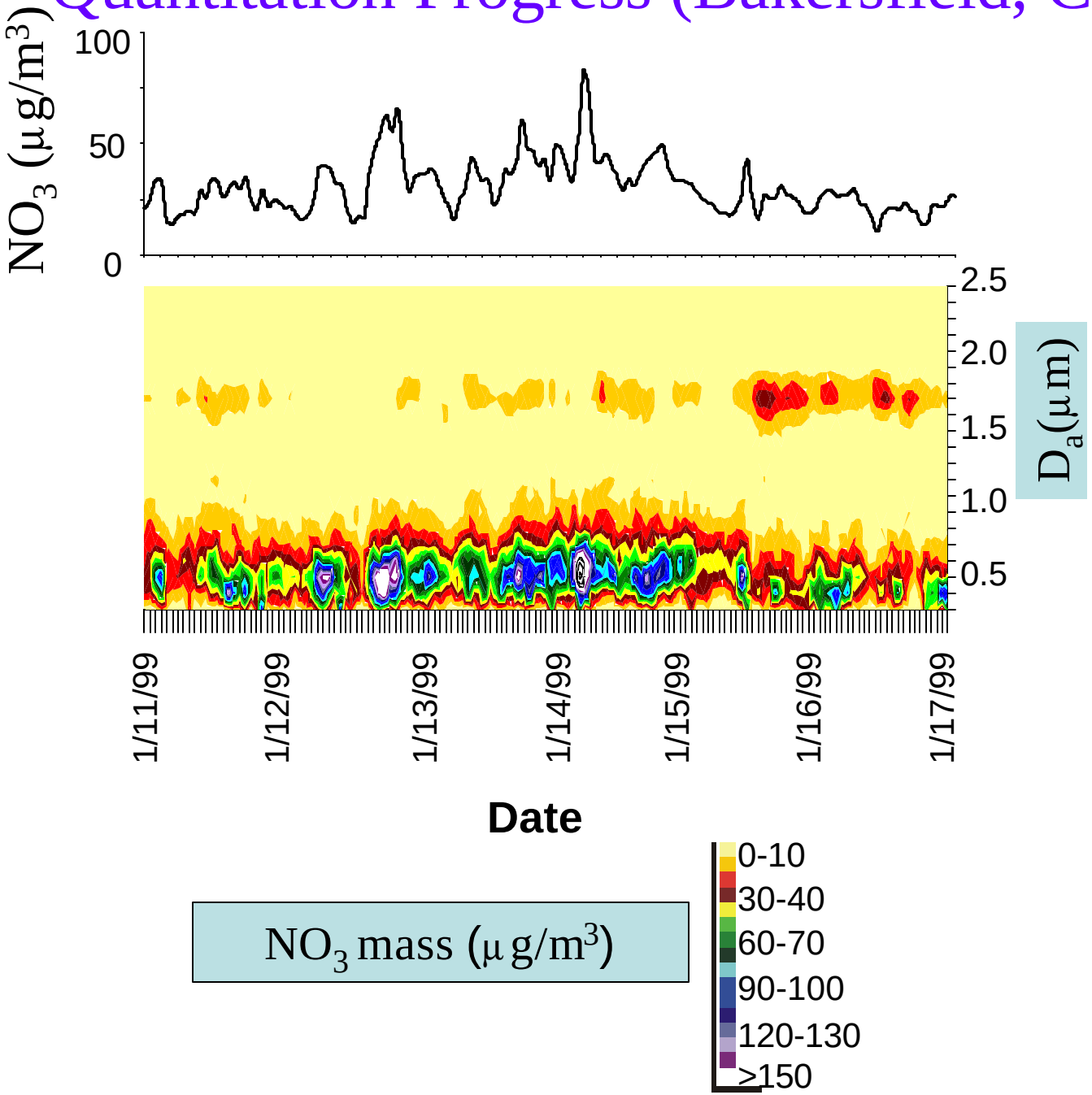
David P. Fergenson, Xin-Hua Song, Ziad Ramadan, Jonathan O. Allen, Lara Hughes, Glen R. Cass, and Philip K. Hopke, Kimberly A. Prather, "Quantitation of ATOFMS Data Using Multivariate Methods", *Anal. Chem.* **73**, 3535-3541 (2001).

Quantitation Progress (Bakersfield, CA)

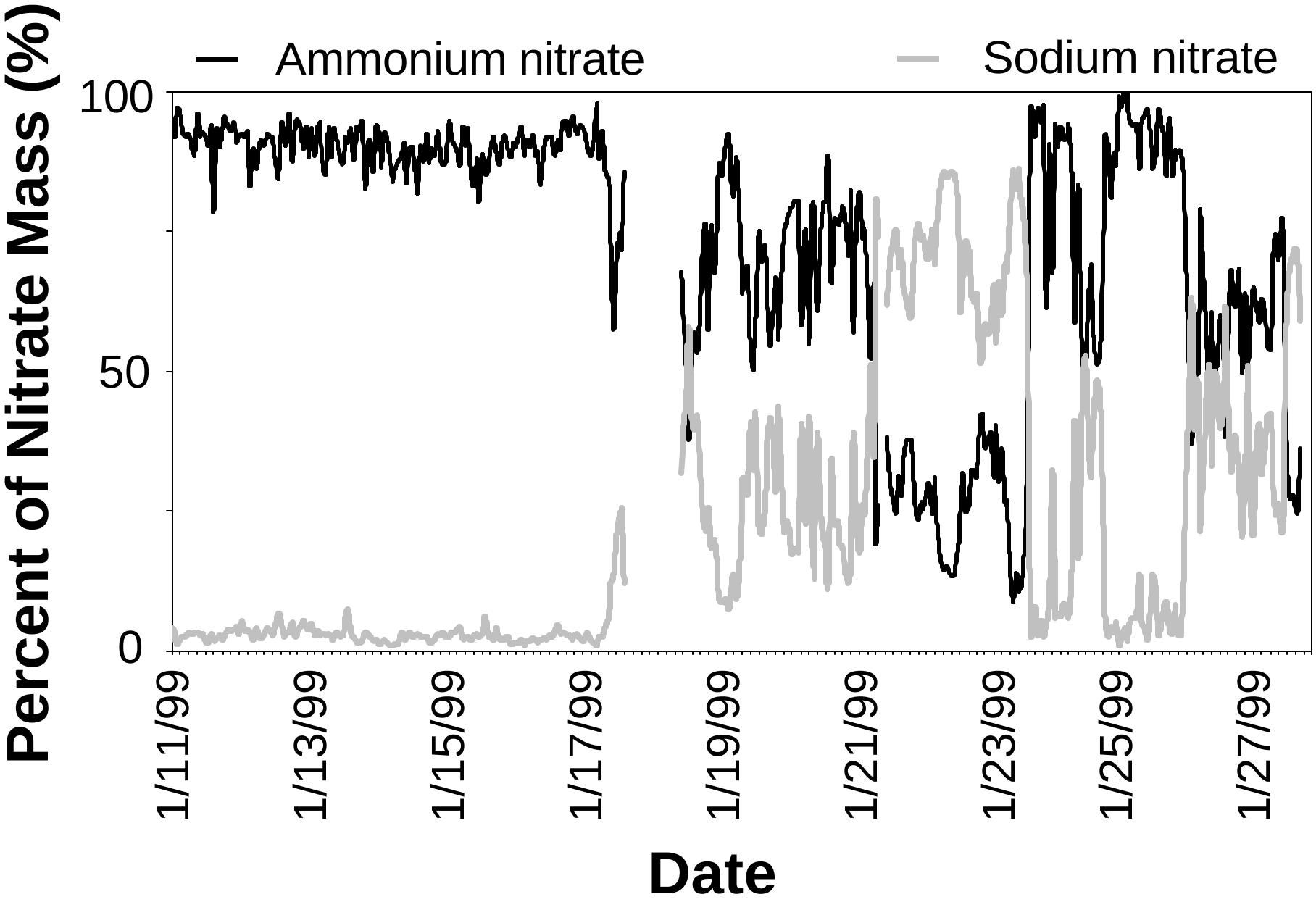


J. Whiteaker, K. Prather, Variations in the Size and Temporal Profile of Particulate Nitrate, submitted Atmos. Environ. 2002

Quantitation Progress (Bakersfield, CA)



Quantitation Progress (Bakersfield, CA)



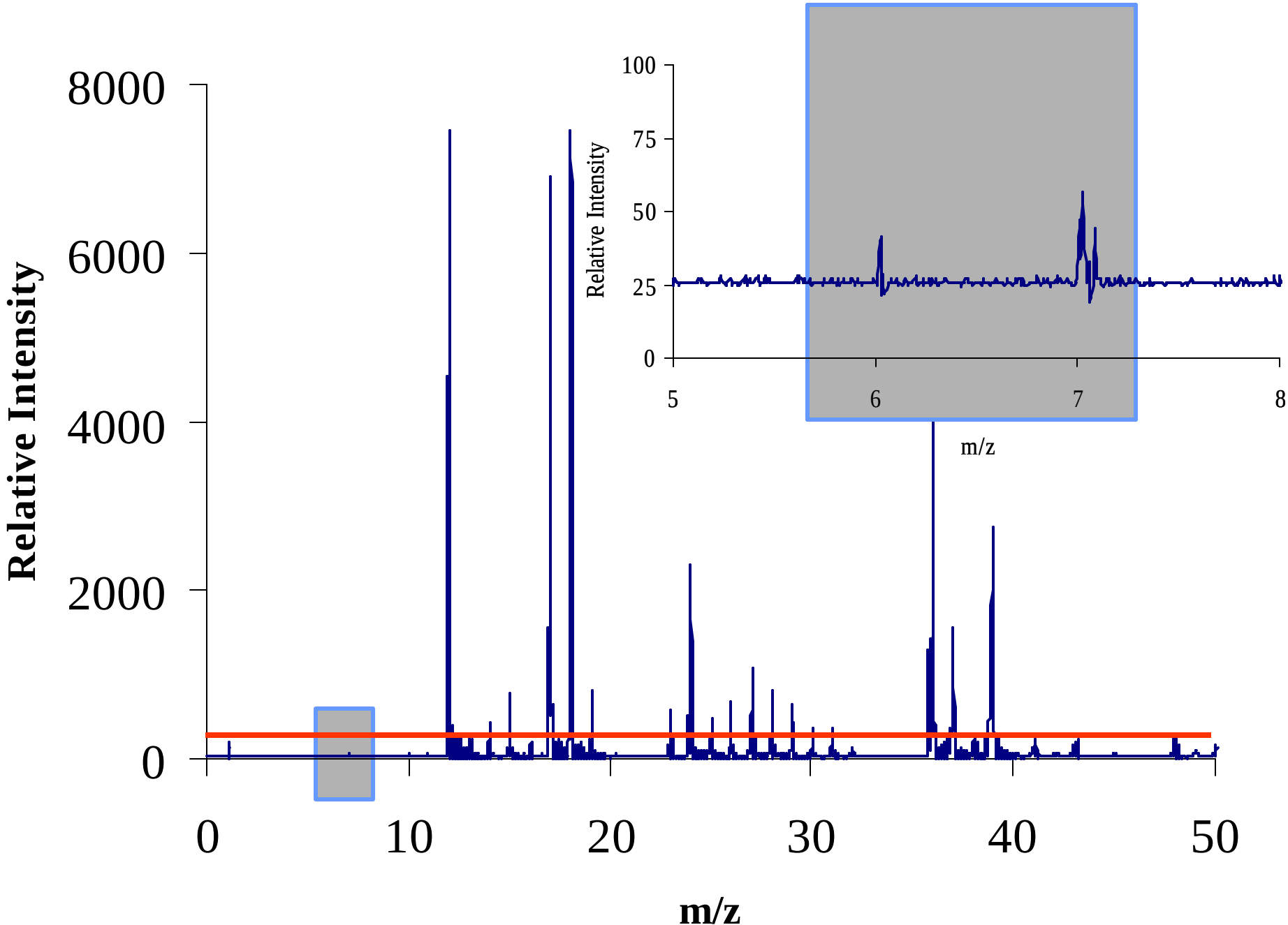
Summary (SCOS-97)

- Calibration of instruments for mass, NH_4^+, NO_3^-, concentrations
- Established single particle differences in various regions in southern California
- Correlations between single particle size and composition and meteorology, gas phase concentrations (ozone), PM10
- Developed data analysis and quantitation procedures
- Learned lessons in field, leading to more stable instruments

Current Research Goals
Where next…..

- Extend dynamic range for quantitation
- Characterize origin (and transformation) of particles
  - Develop better source signatures (HDV, LDV…)
- Test instrument calibration factors at more locations and over longer periods of time
- Compare with other instrumentation (i.e. # concentrations)
- Further develop data analysis and quant. tools
- Detect smaller particles (UF; <100 nm)

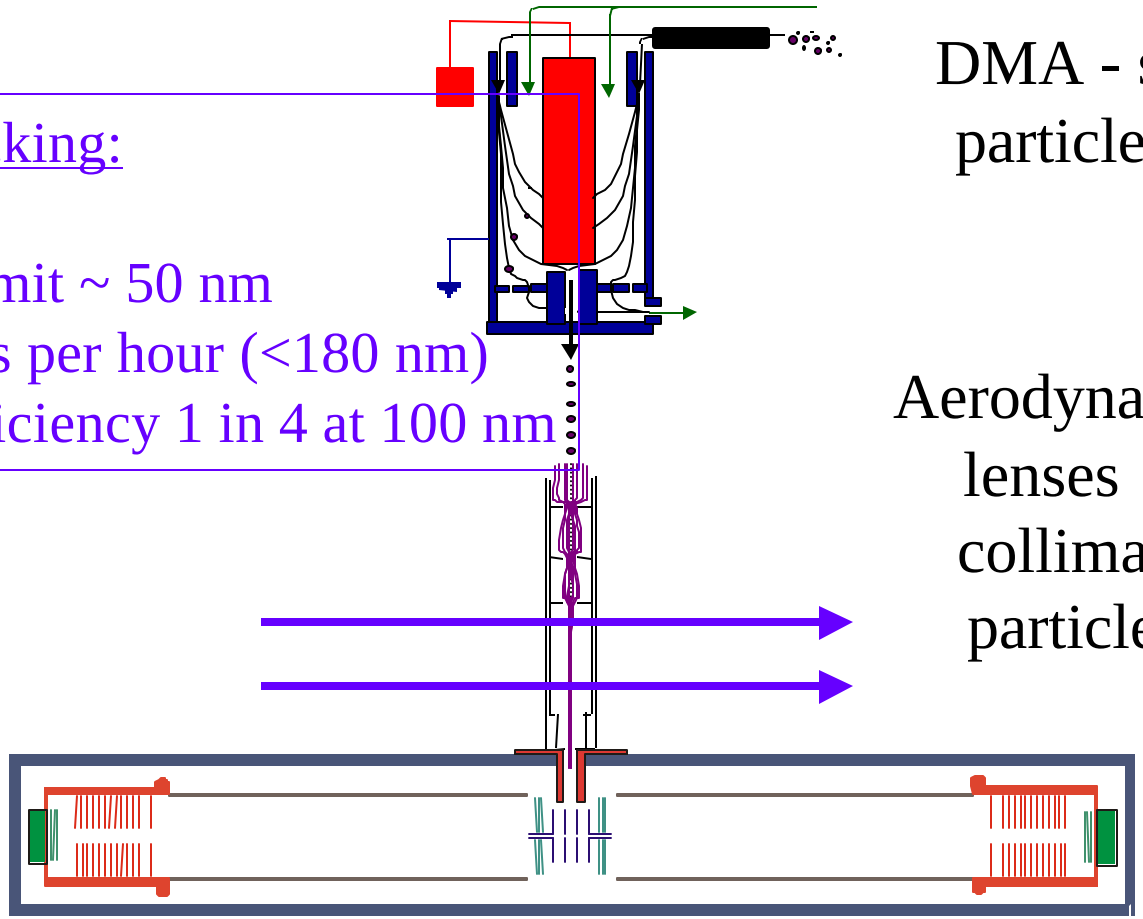
WDR Acquisition Mode



Ultrafine (<100 nm) Analysis
Original Design (detect down to 30 nm)

<u>With optical tracking:</u>

- Lower size limit ~ 50 nm
- 2000 particles per hour (<180 nm)
- Detection efficiency 1 in 4 at 100 nm

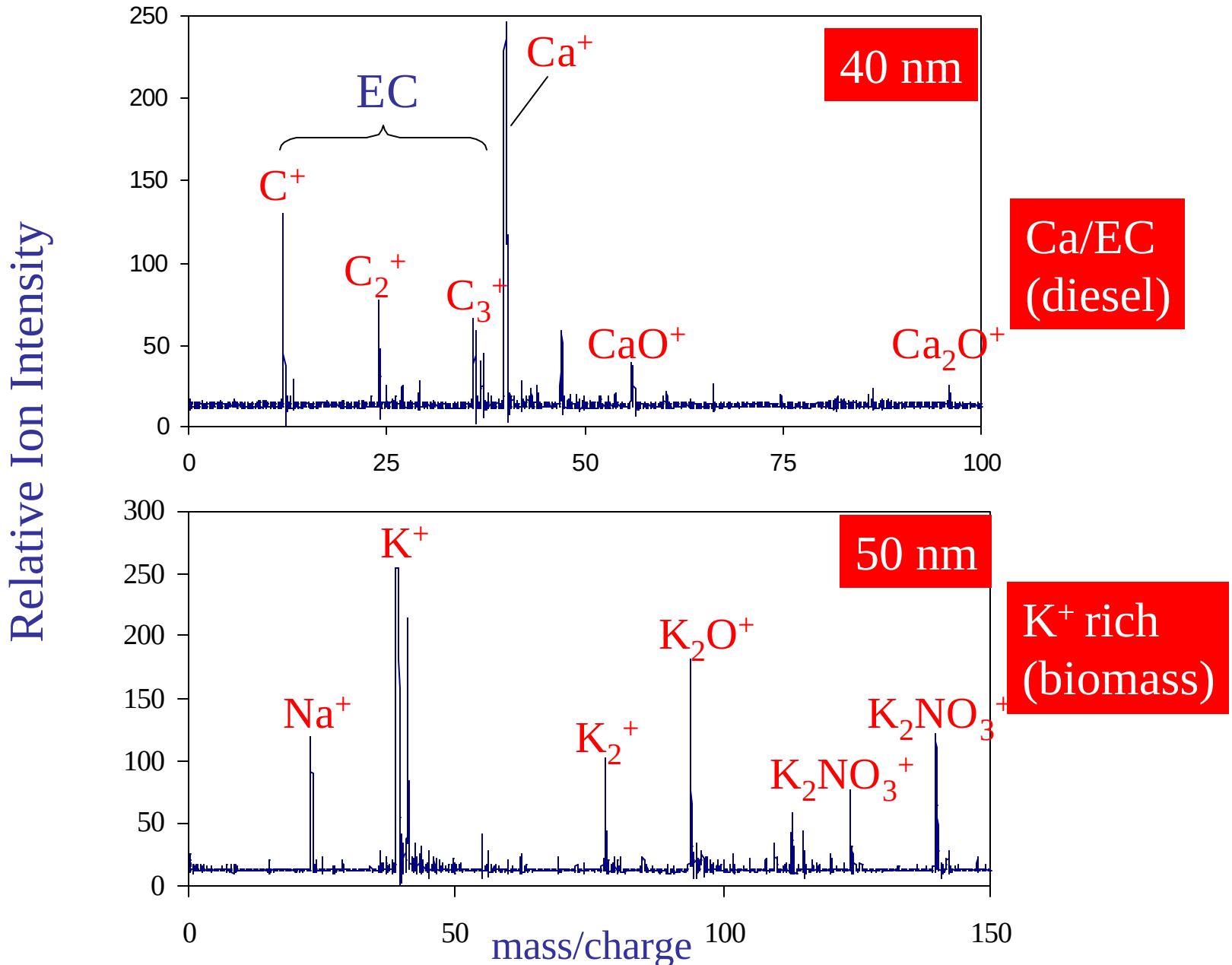


DMA - select particle size

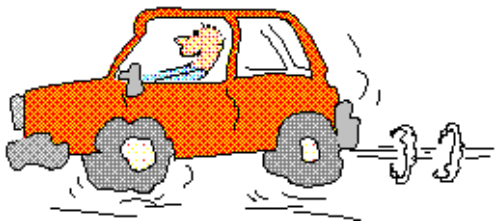
Aerodynamic lenses - collimate particles

TOFMS - analyze particle composition

Ultrafine Ambient Single Particles (Riverside; 04/10/01)



Source Characterization

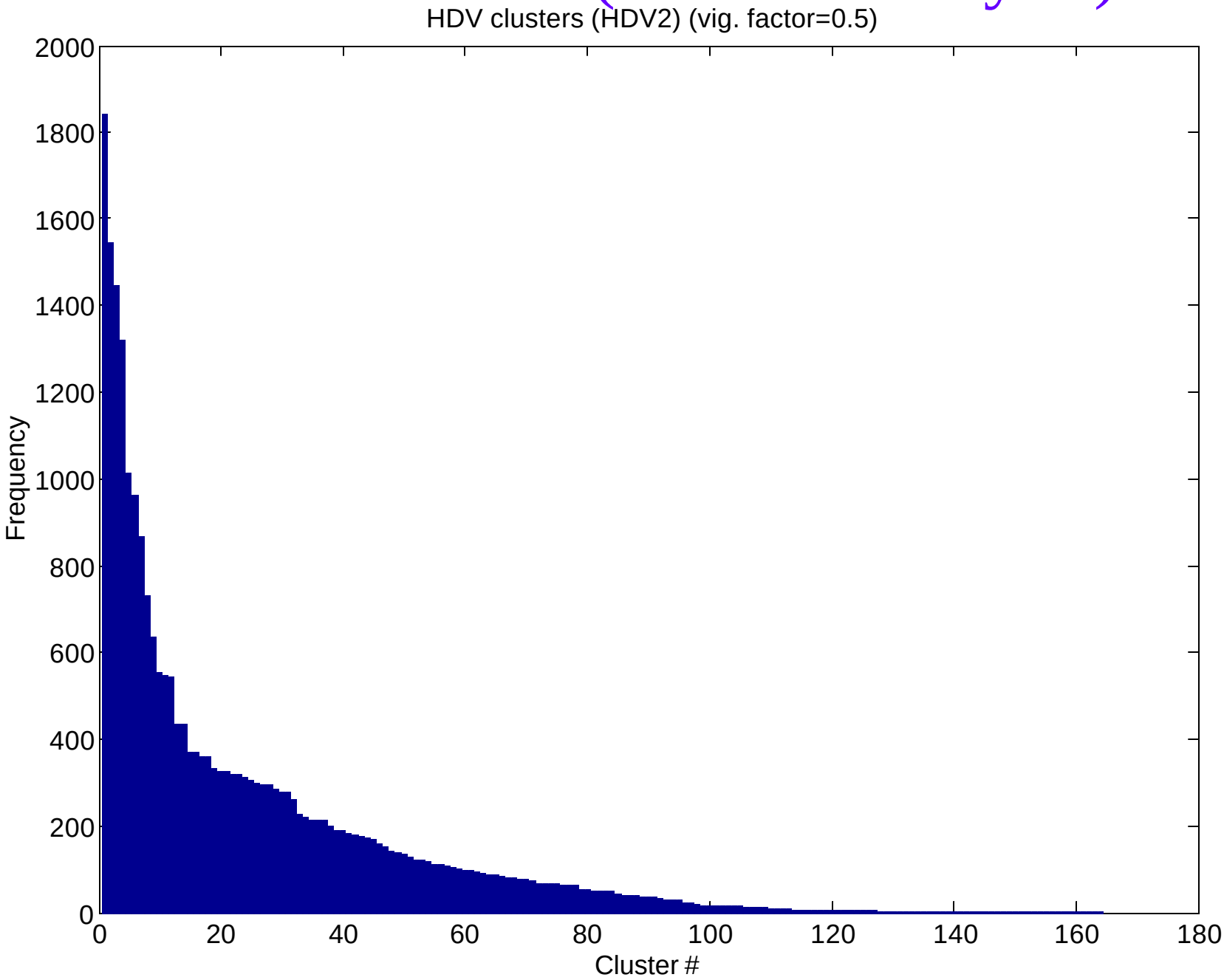


- Source characterization
  - Determine unique fingerprints
    - Cars (LDV) and trucks (HDV)
    - Meat cooking
    - Biomass burning
    - Soil chemistry
    - Sea salt chemistry
    - Indoor aerosols
    - Coal
    - Ship tracks
    - Reactions…

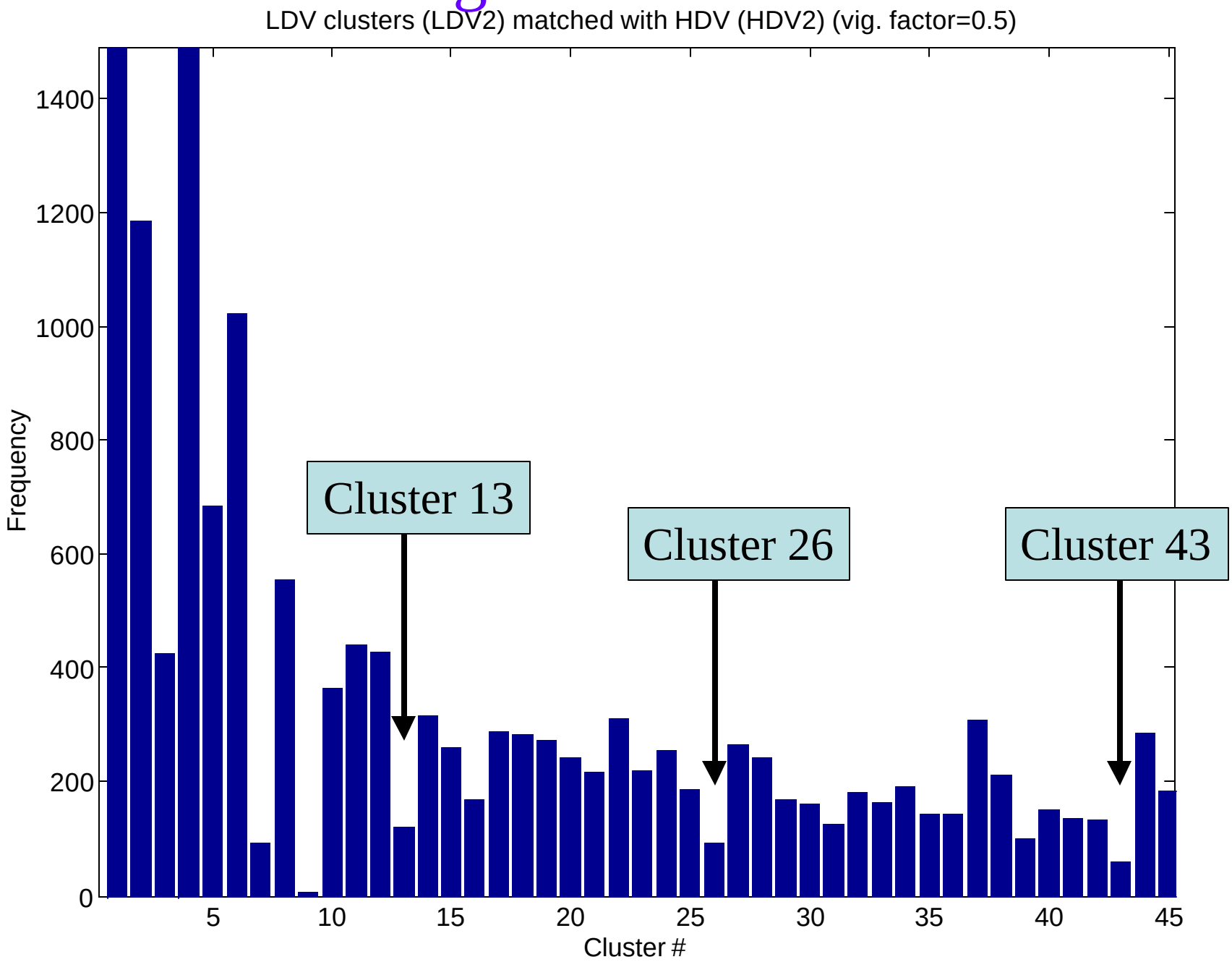
ATOFMS Vehicle Studies

- Caldecott 1997
- Freeway study 1998
- LDV and HDV dynamometer study (El Monte)
- Caldecott 2000
- HDV dyno study; Fall, 2001 (Riverside; w/CRC)

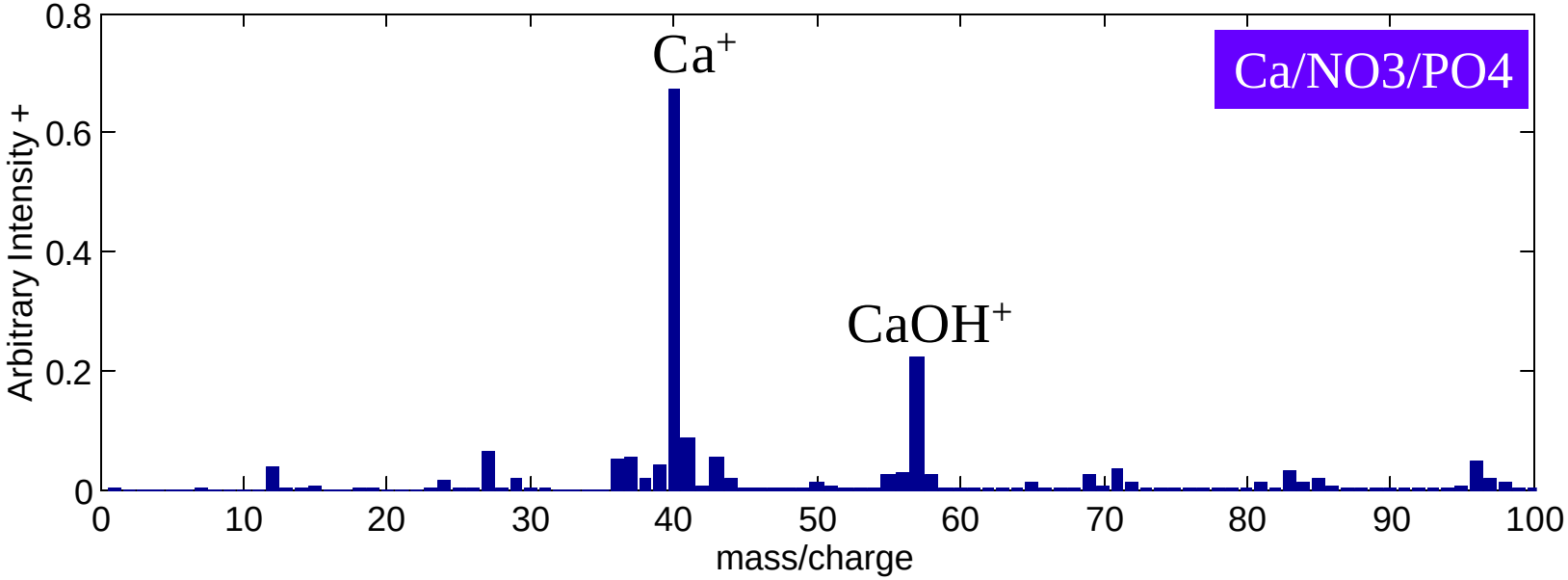
Caldecott 2000 (ART-2a analysis)

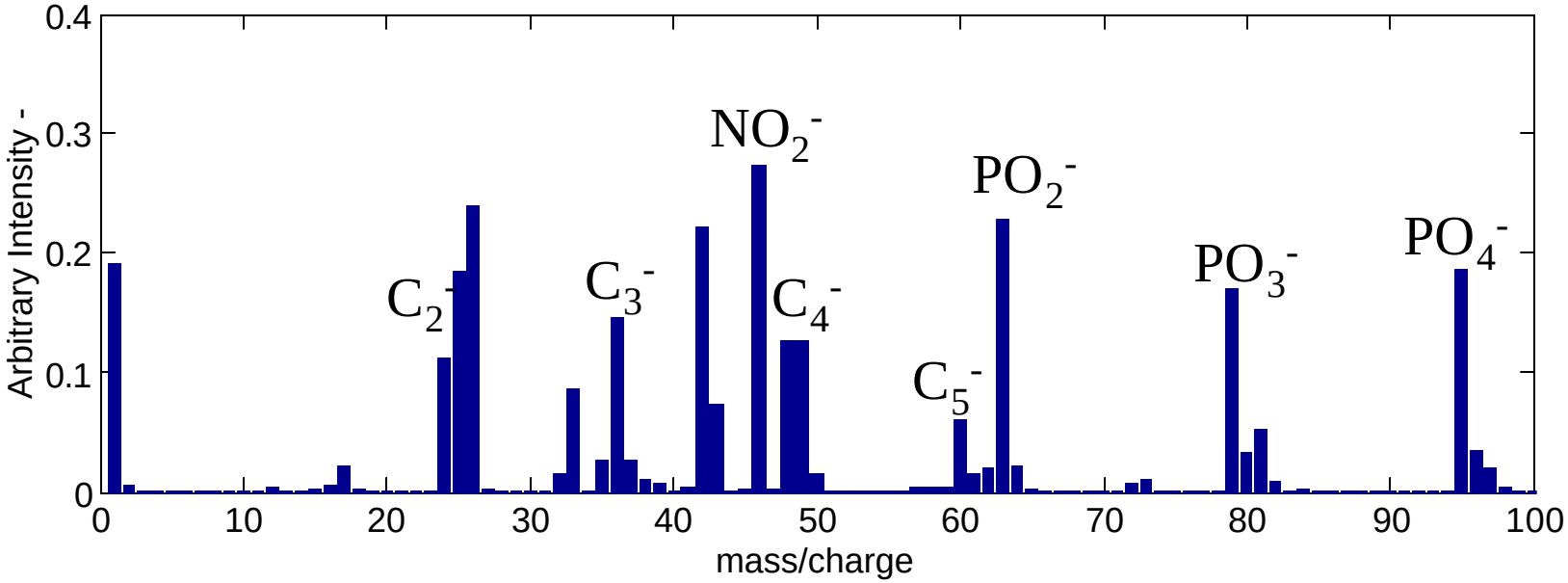


Matching LDV with HDV

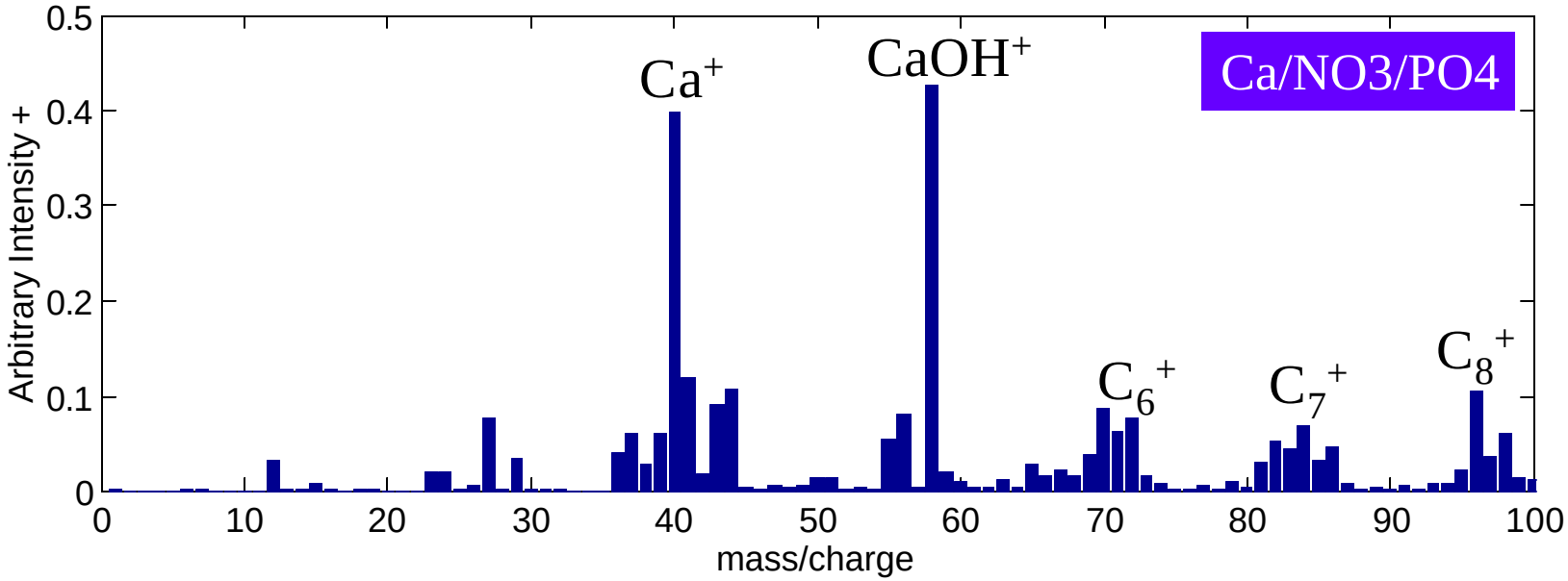


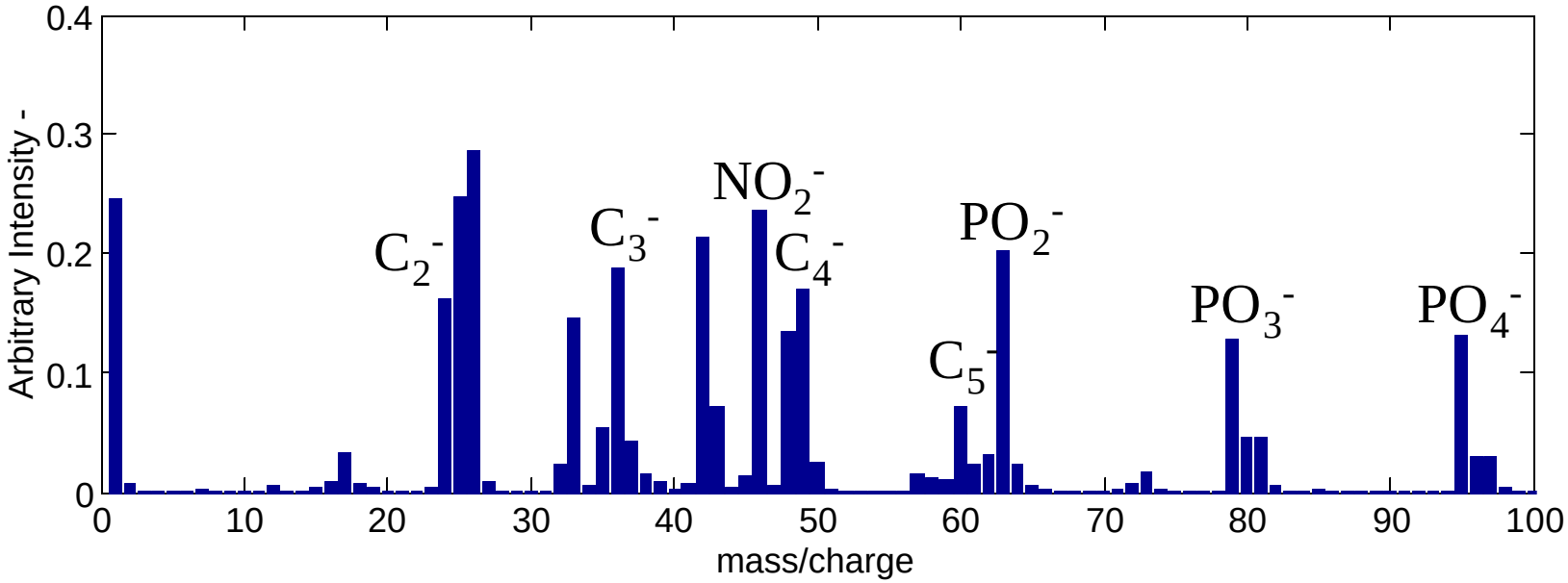
Cluster 13 (Caldecott 2000)





Cluster 26 (Caldecott 2000)





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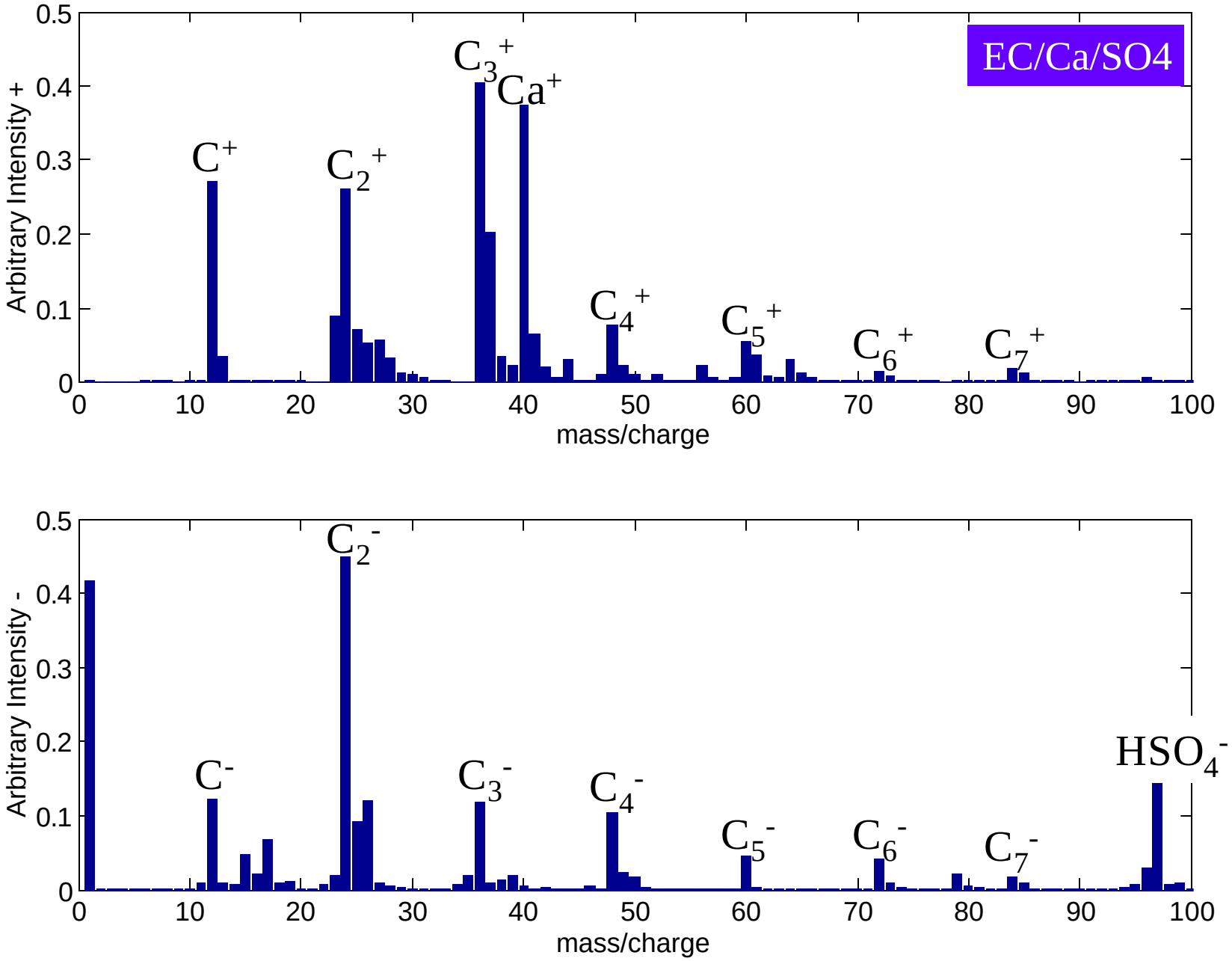
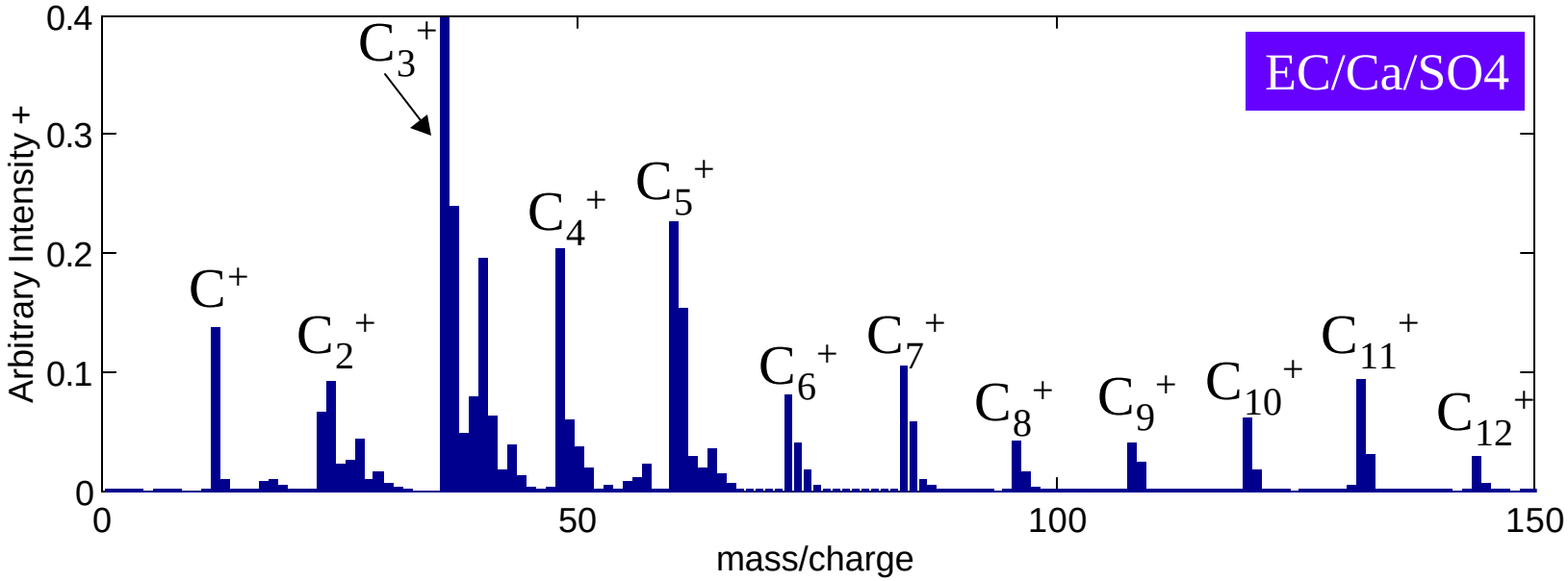
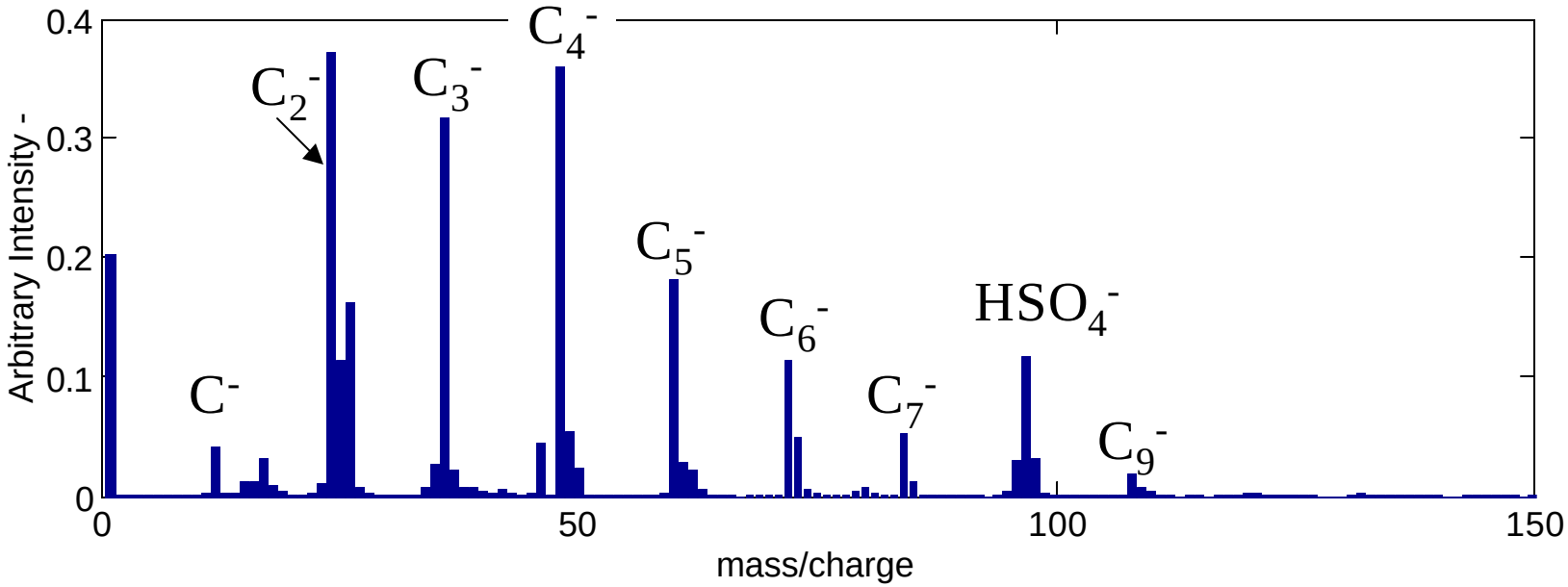
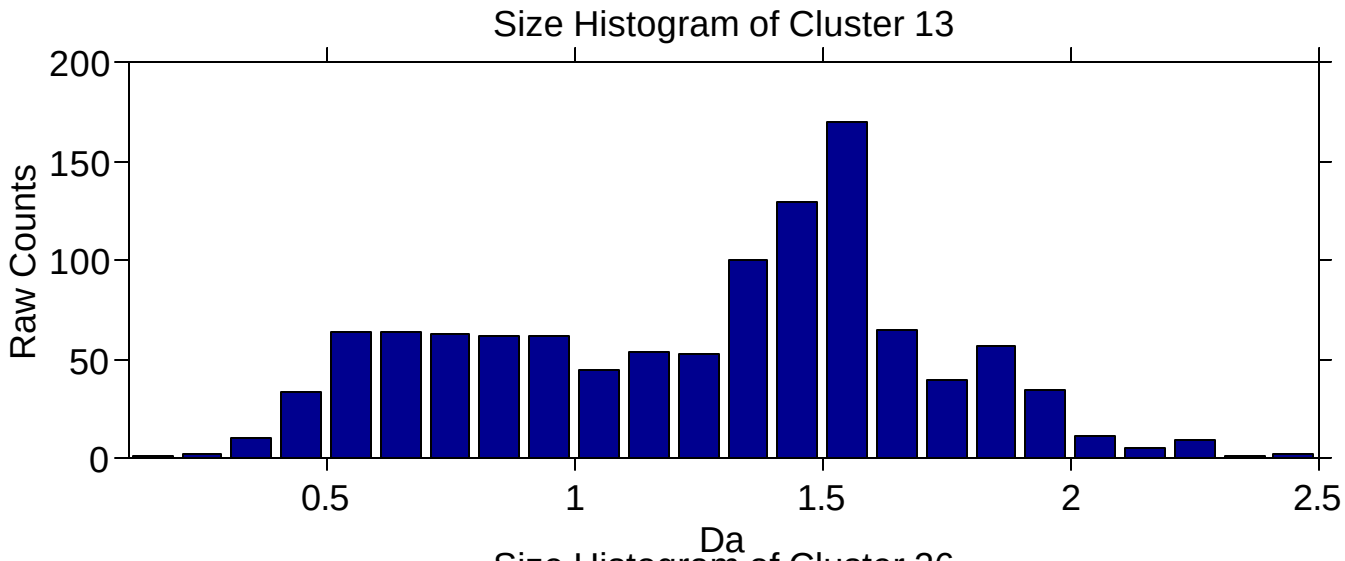


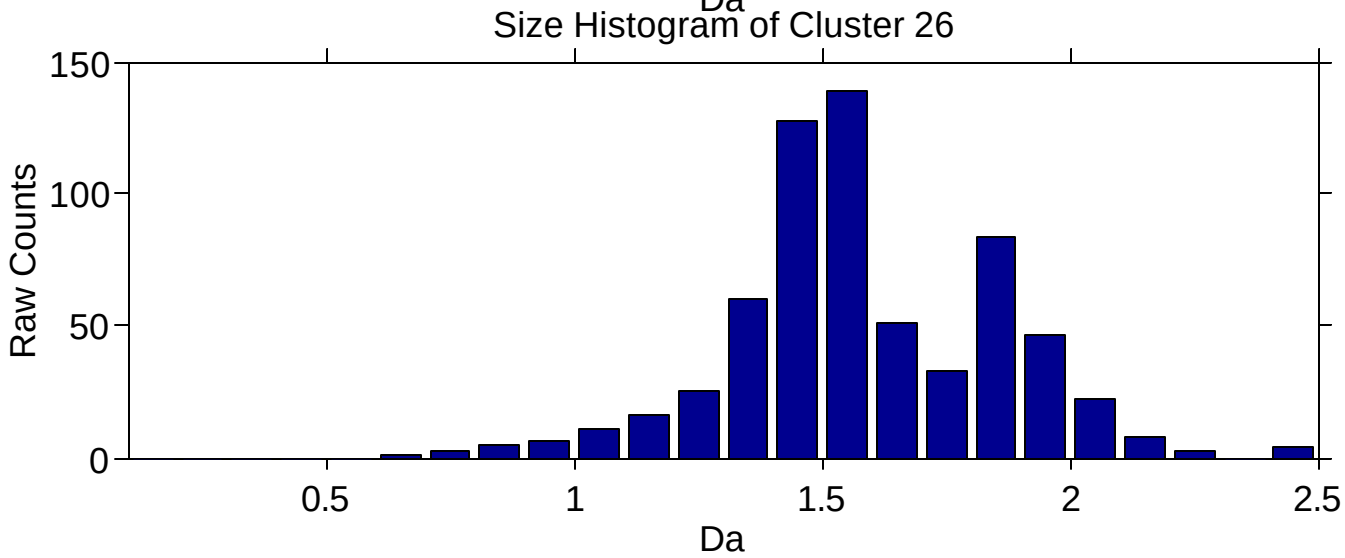
Cluster 55 (Caldecott 2000)



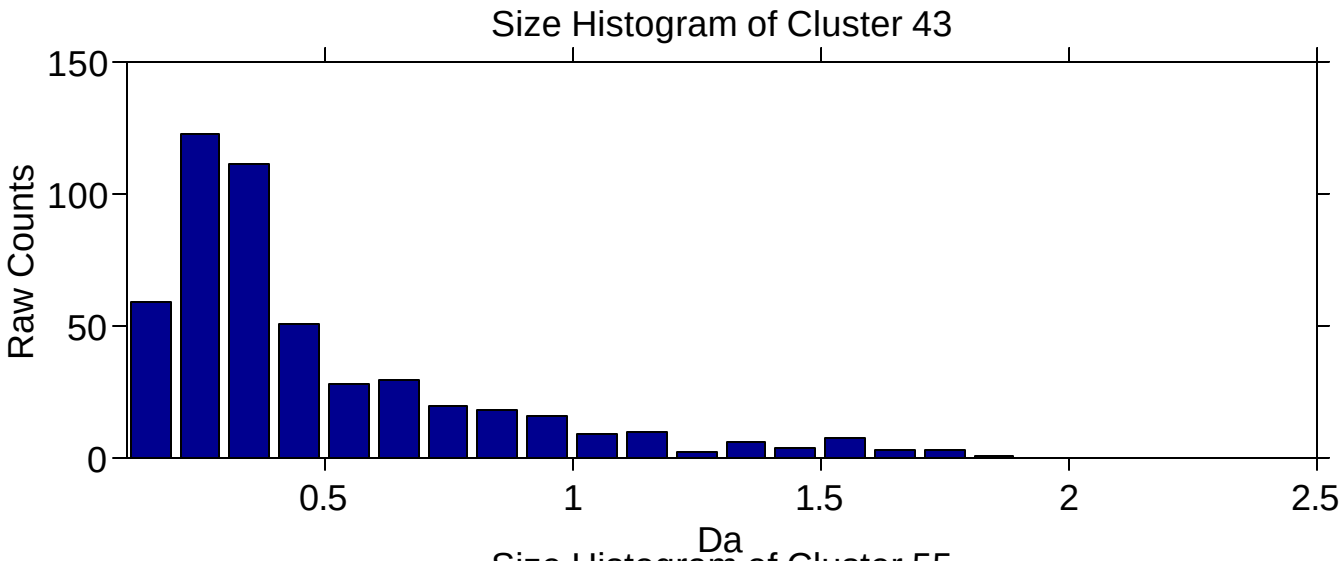


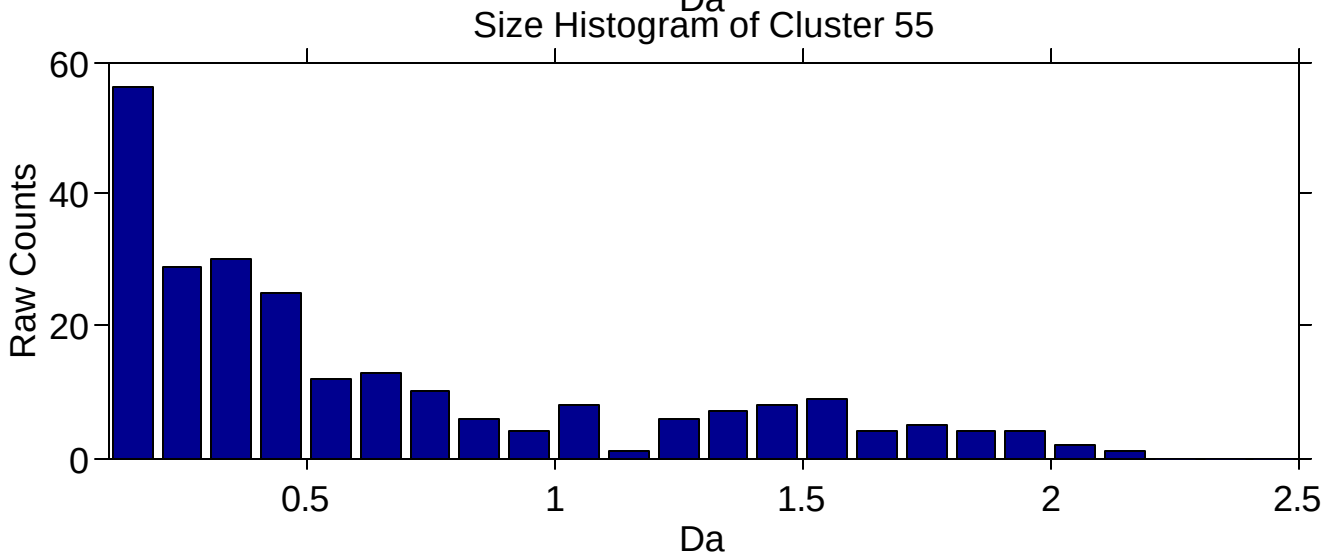
Ca Types (Sizes)



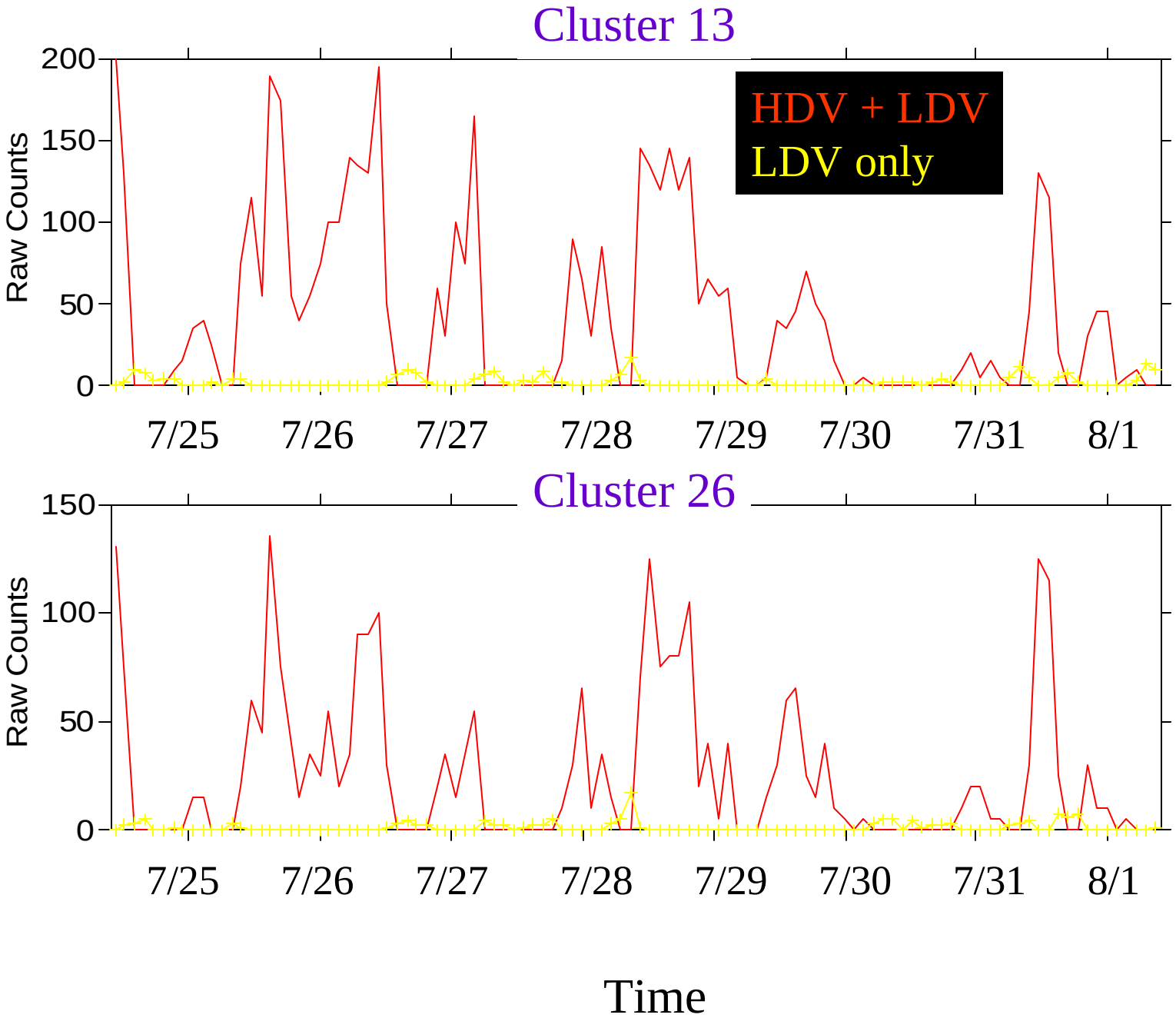


EC Types (Sizes)

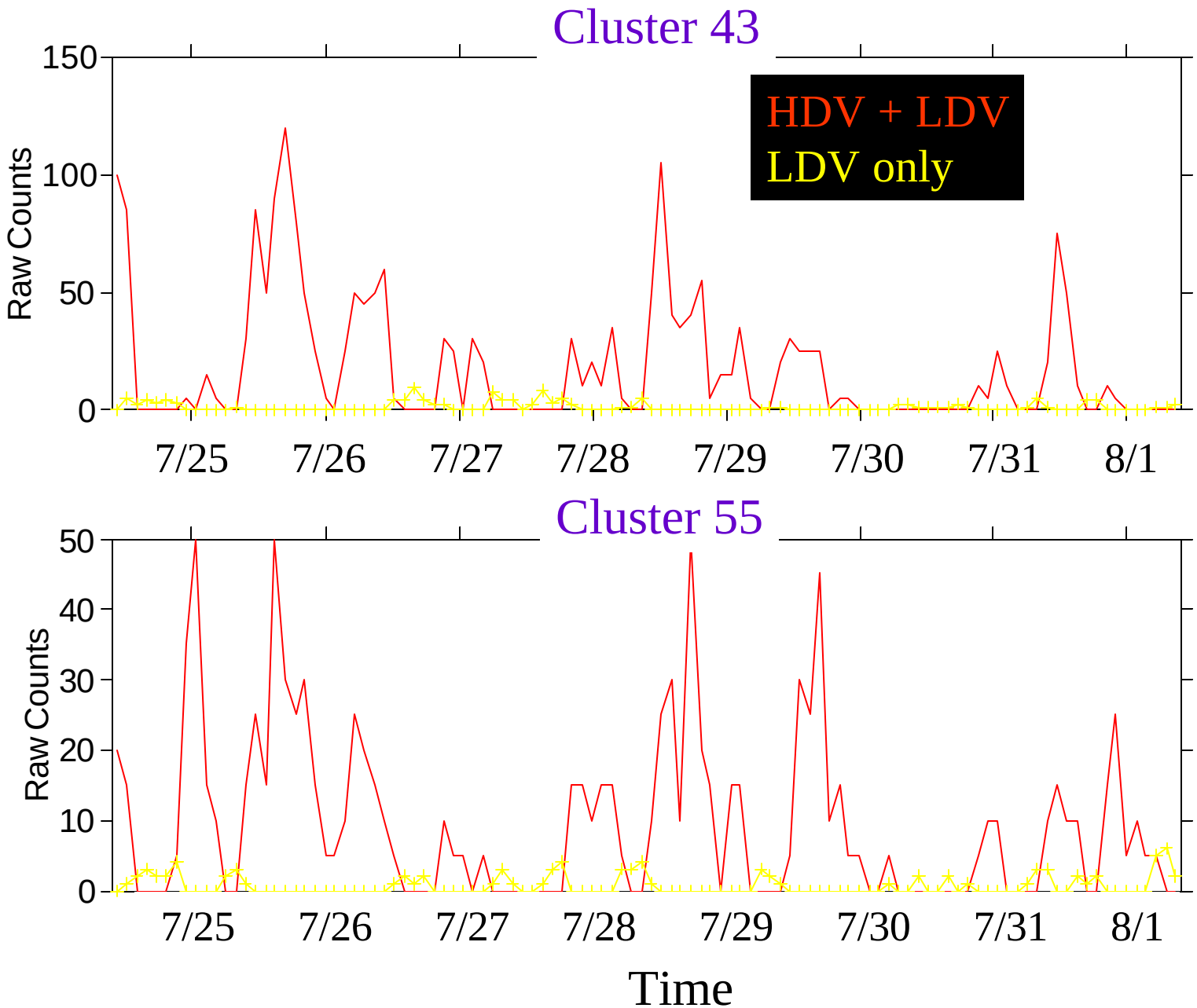




Temporal Variations (Caldecott 2000)



Temporal Variations (Caldecott 2000)



HDV Dyno Study (Fall, 2001)

Table 1. Truck Descriptions

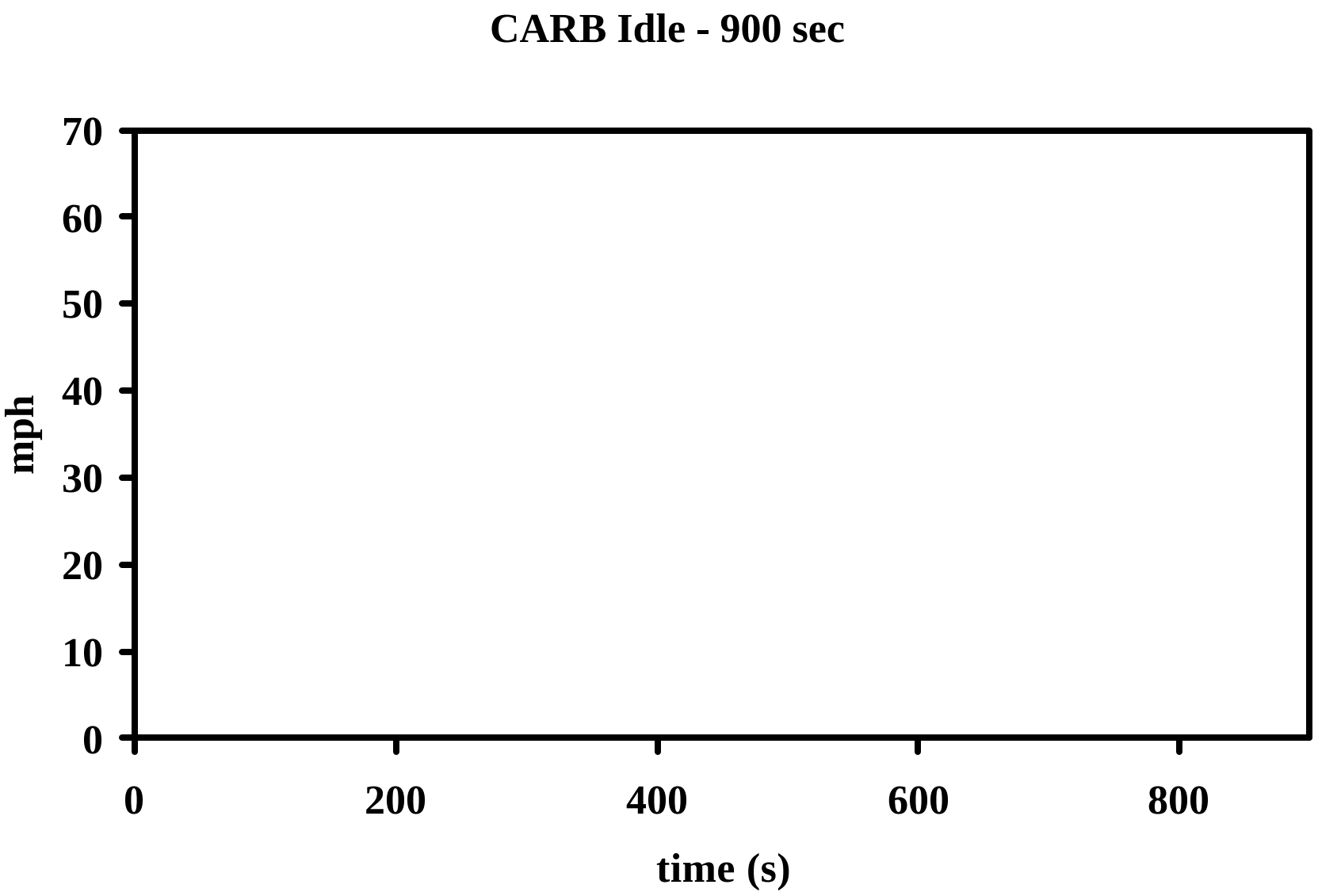
#	Year	Type	Make	GVW (lbs)	Miles
1	1985	HDD Tractor	International	32000	501,586
2	1990	HDD Tractor	Peterbuilt	50000	399,224
3	1994	HDD Tractor	Freightliner	52000	639,105
4	1995	HDD Tractor	Freightliner	50000	241,843
5	1995	HDD Tanker	Freightliner	45000	689,536
6	1996	HDD Tractor	Kenworth	32000	507855
7	1998	HDD Tractor	Peterbuilt	48000	607,968
8	2000	HDD Tractor	Navistar International	52000	92,362
9	2000	HDD Tractor	Freightliner	52000	166981
10	2000	HDD Tractor	Freightliner	35000	17048

Major goals: Test effects of dilution conditions, vehicle, dyno cycles

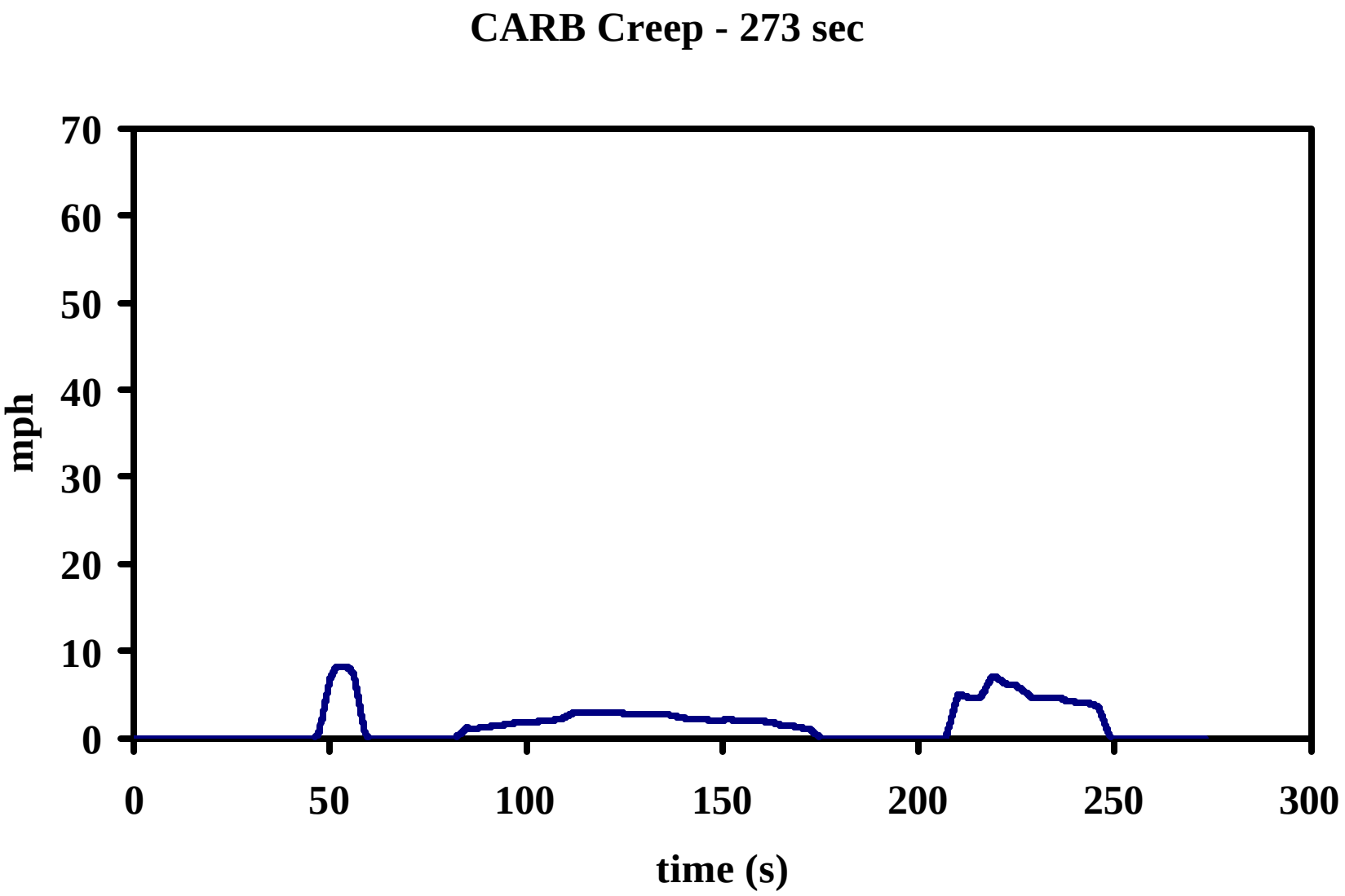
*Also, refuse truck, MDD truck, 2 city buses

**With WDR capabilities

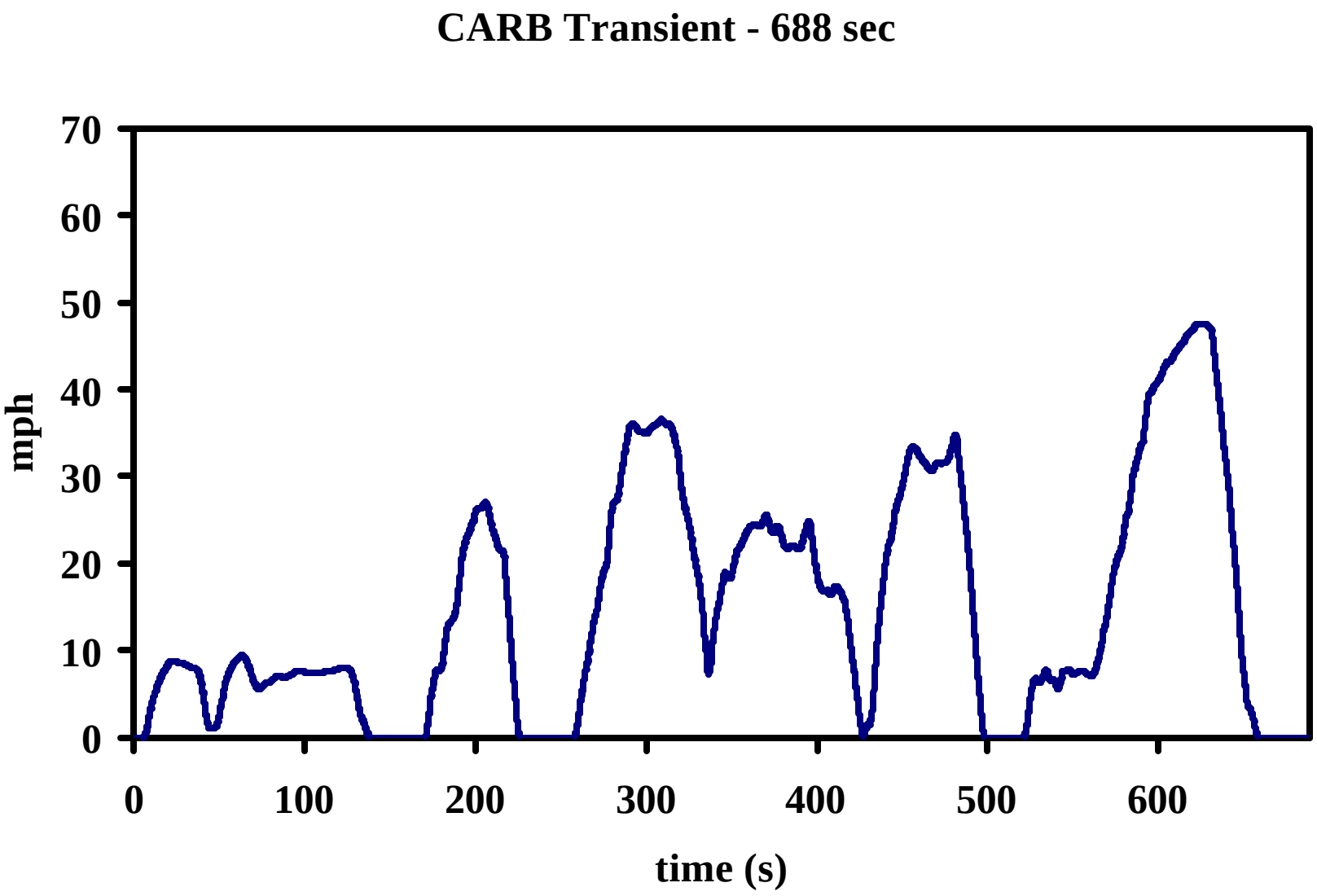
Dyno Cycles (I)



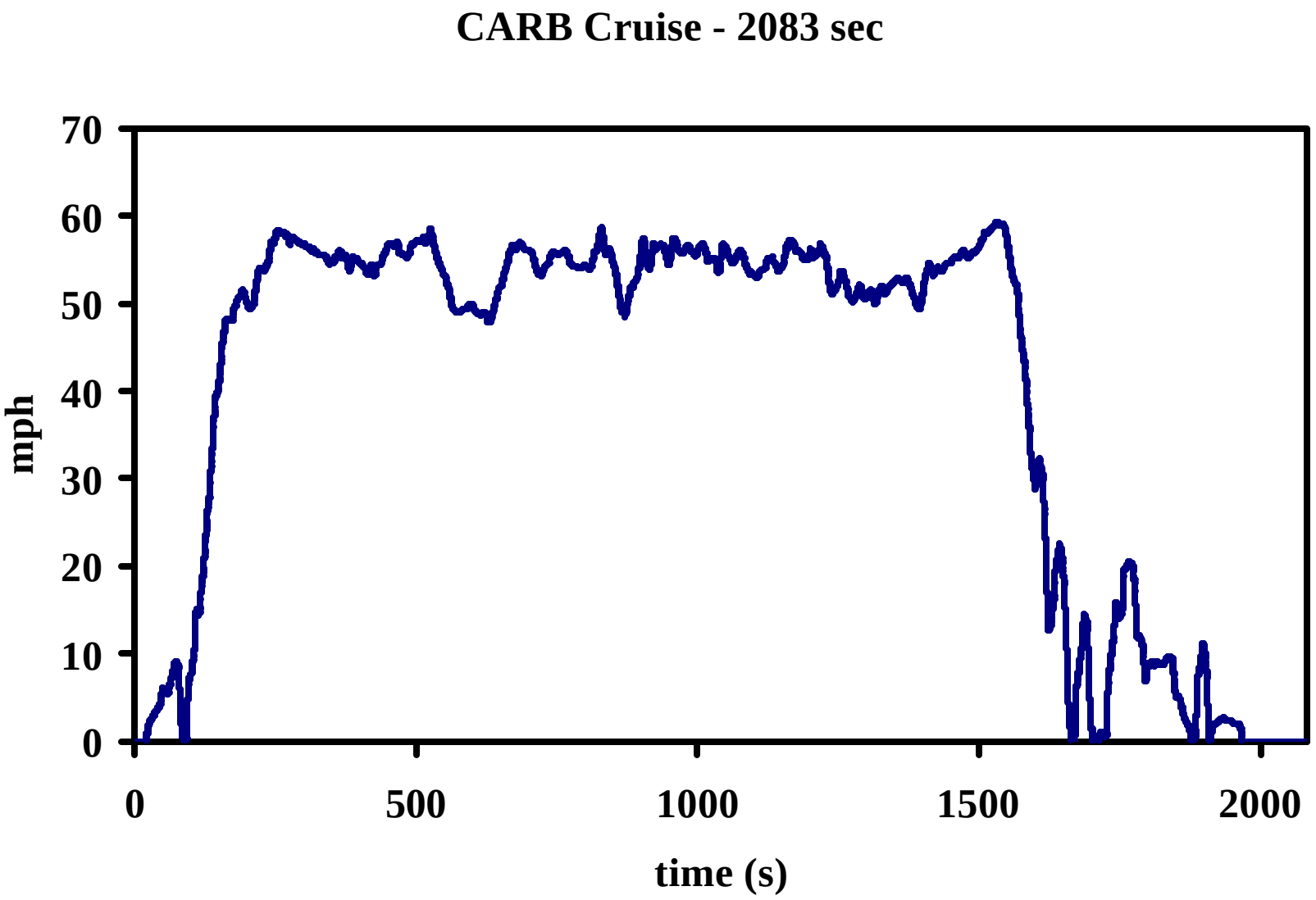
Dyno Cycles (II)



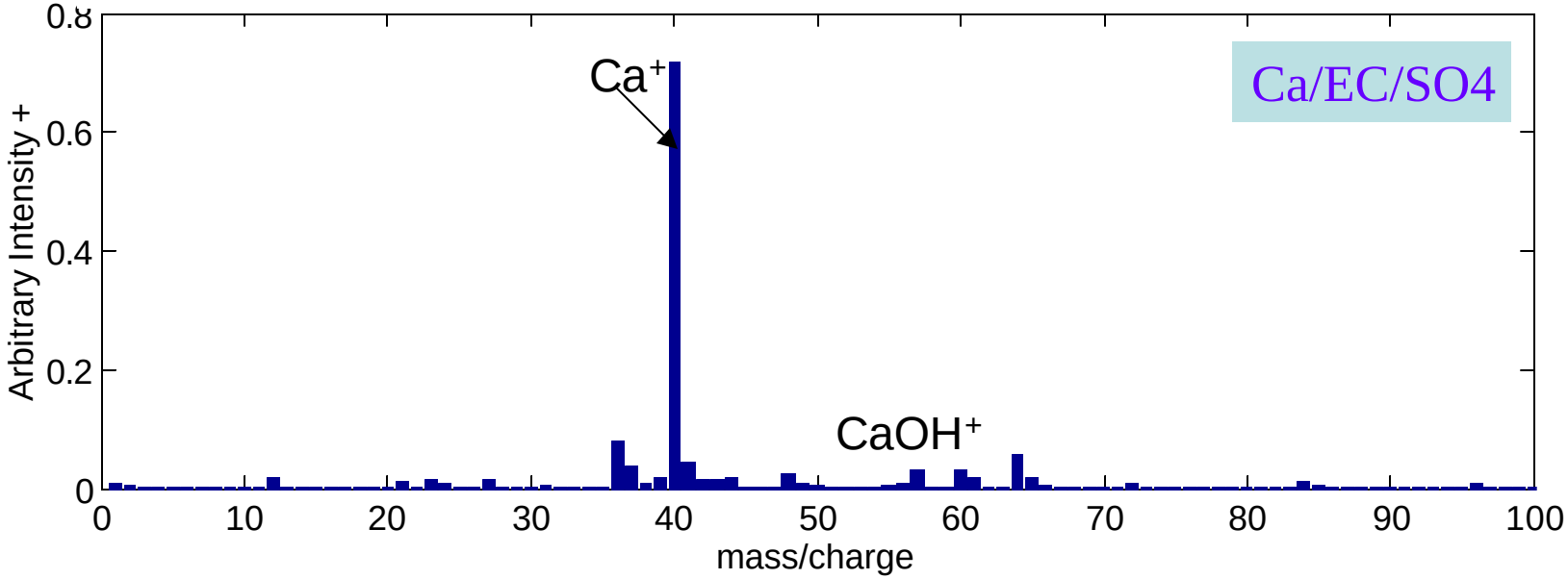
Dyno Cycles (III)

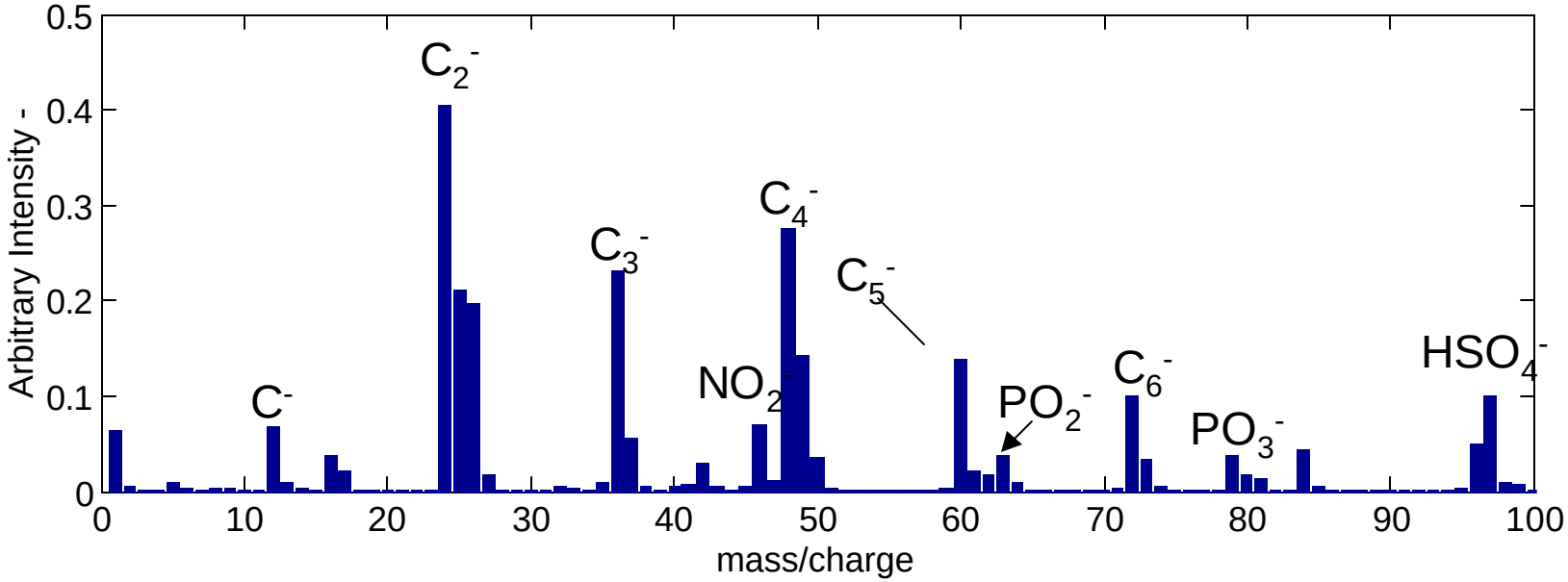


Dyno Cycles (IV)

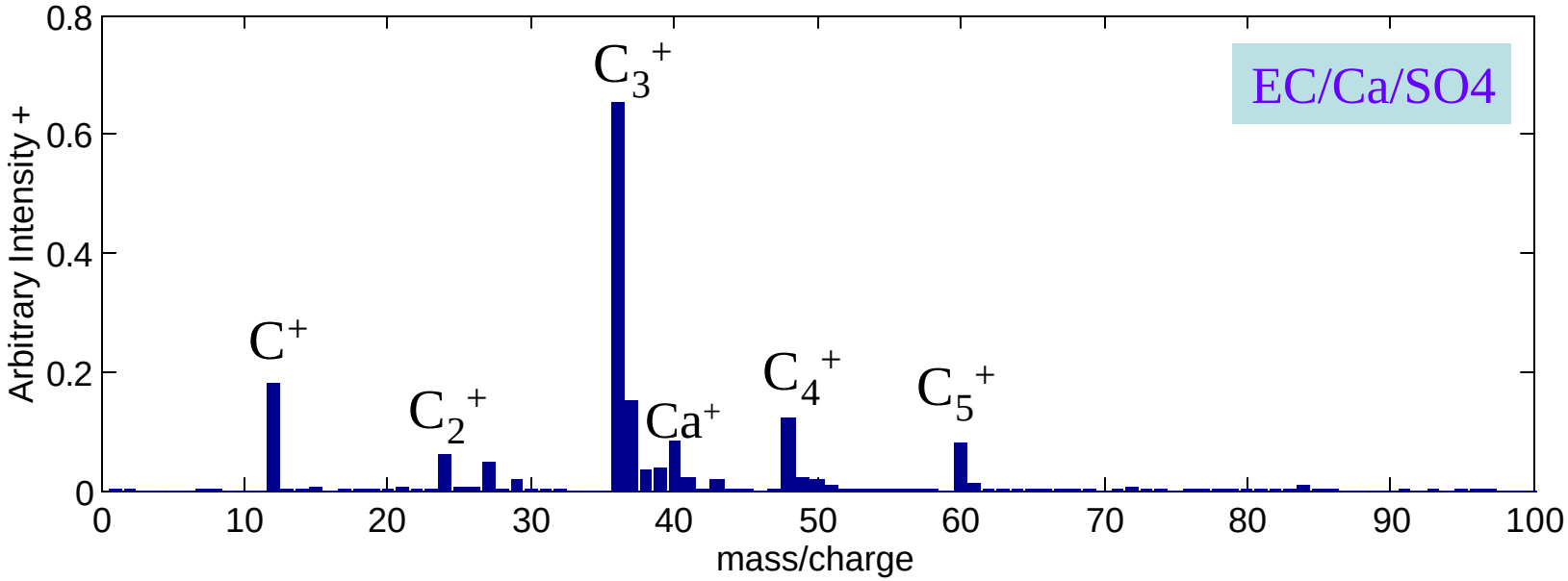


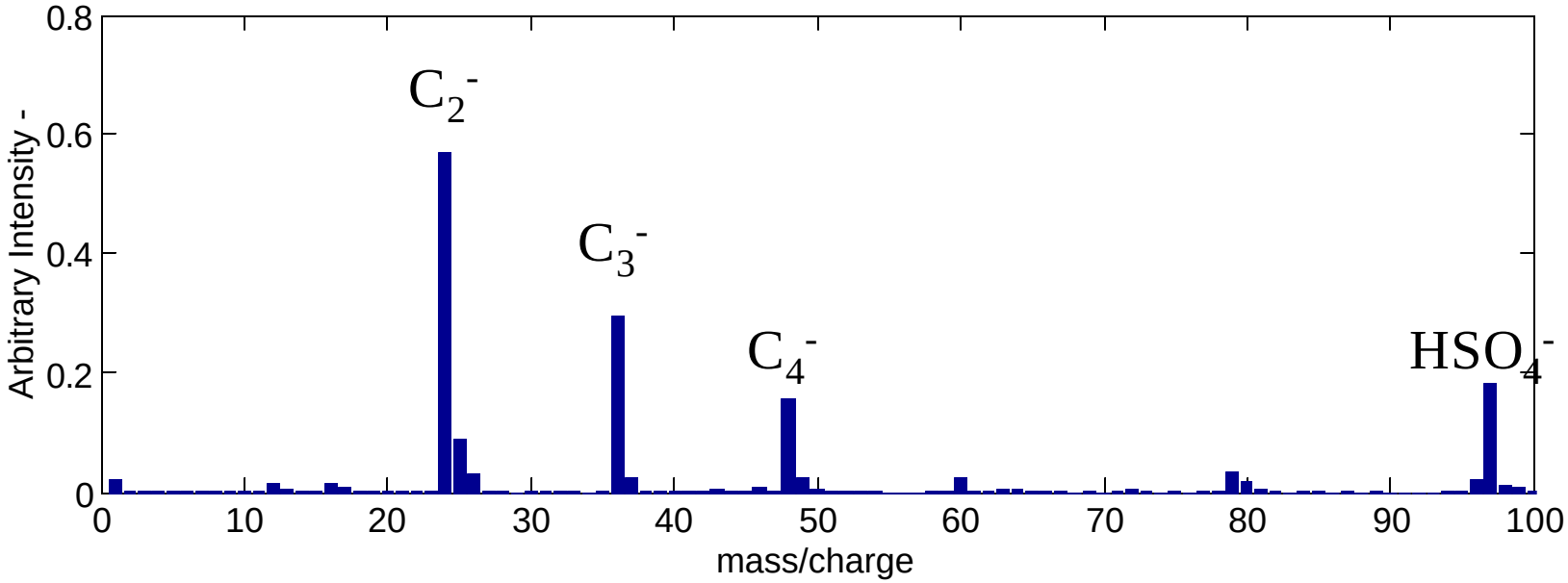
Cluster 1 (Diesel Dyno 2001)



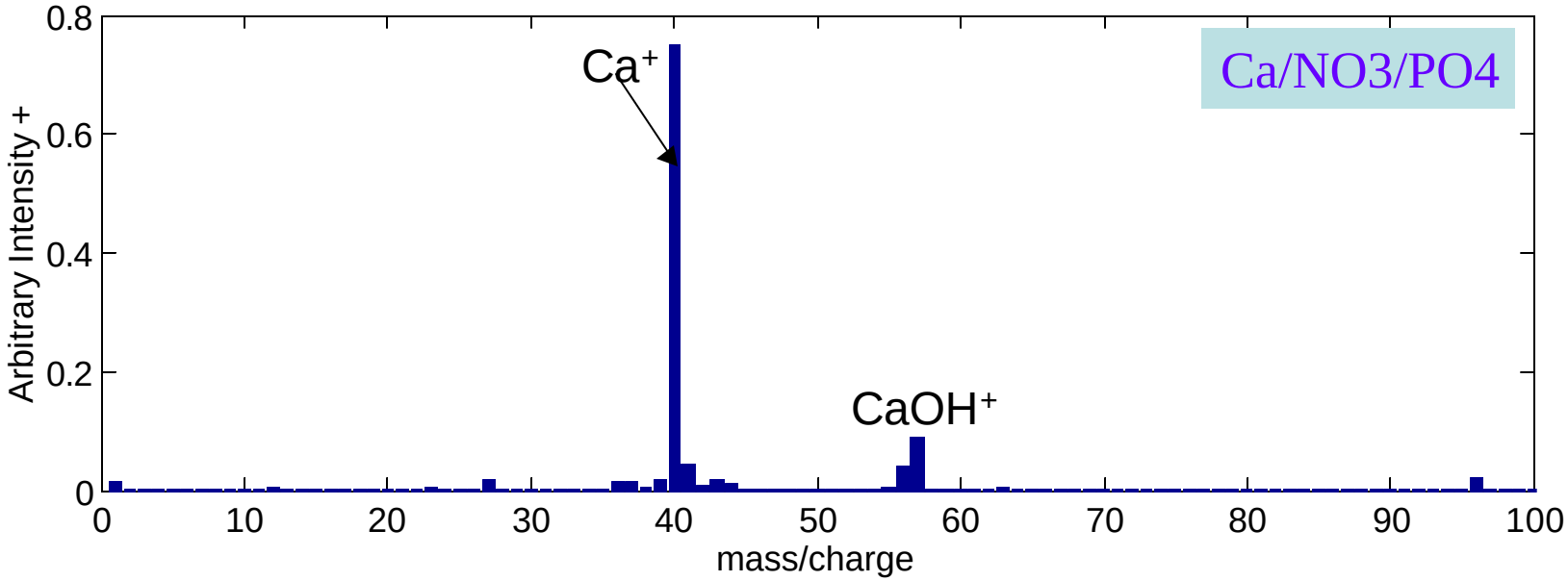


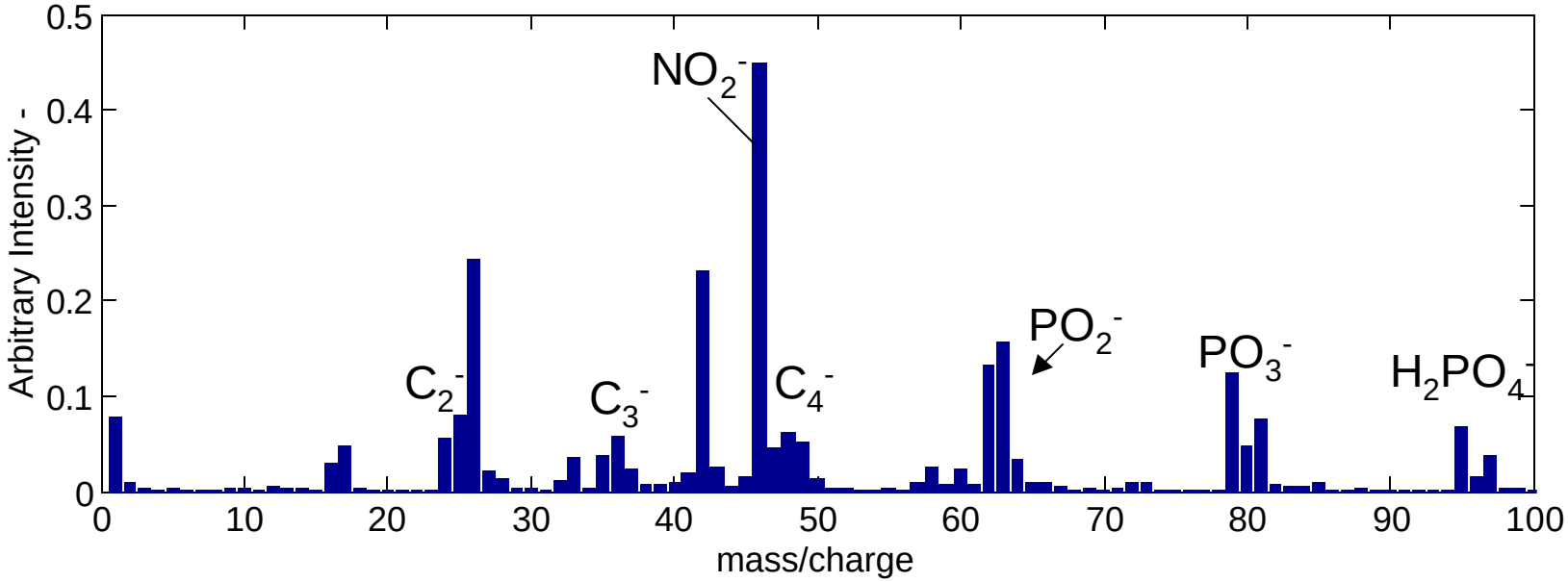
Cluster 2 (Diesel Dyno 2001)



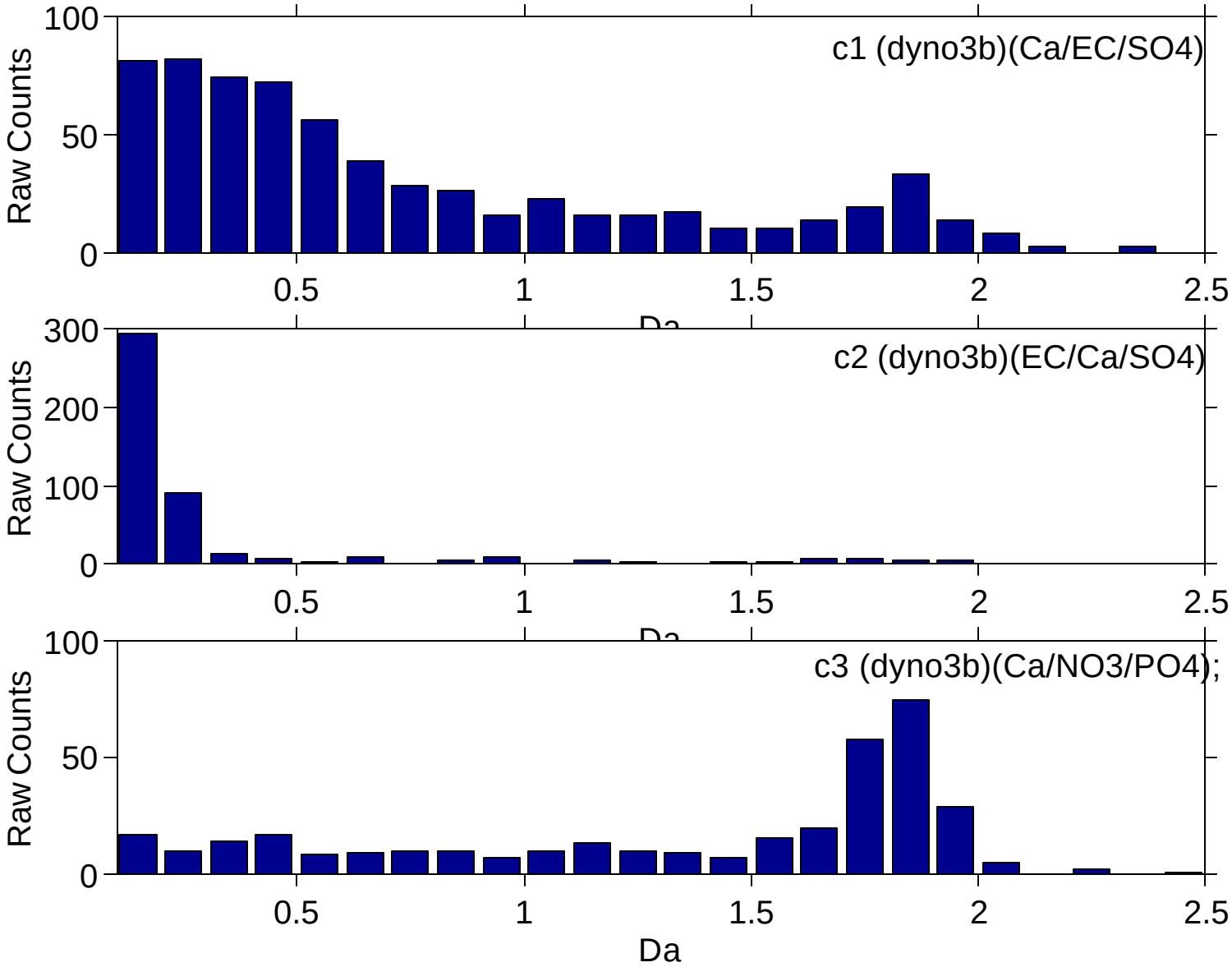


Cluster 3 (Diesel Dyno 2001)

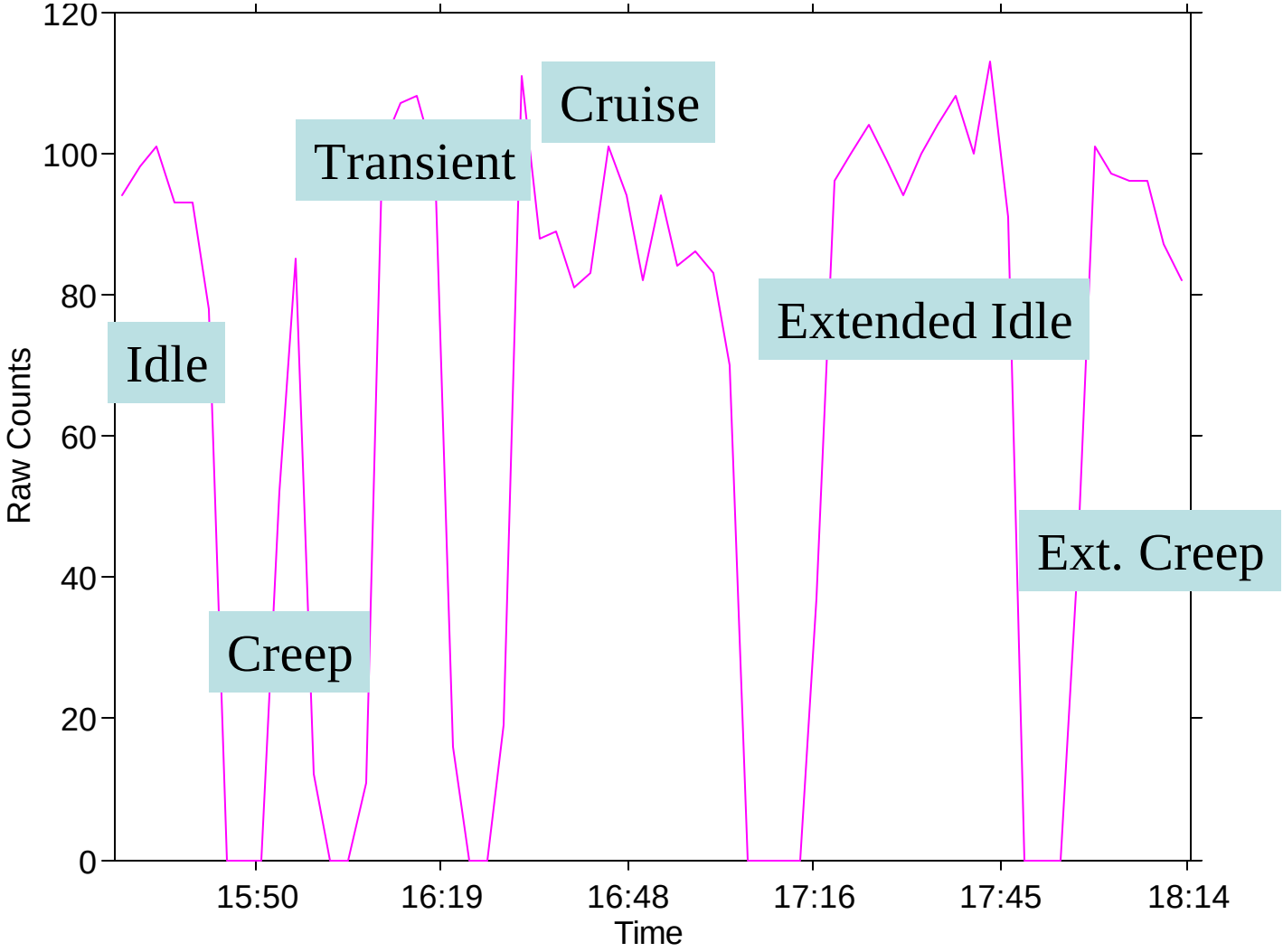




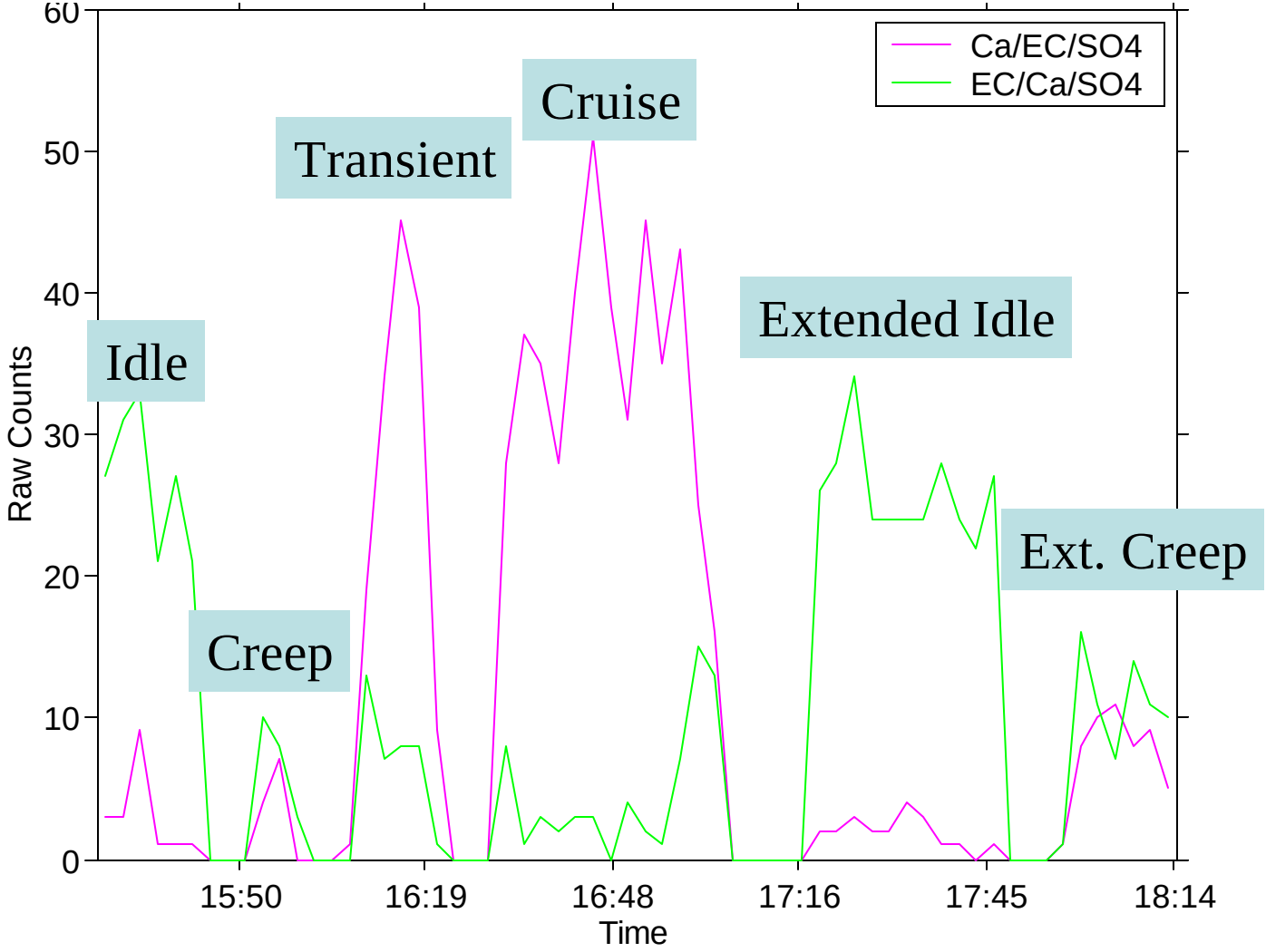
Particle Sizes (Diesel Dyno 2001)



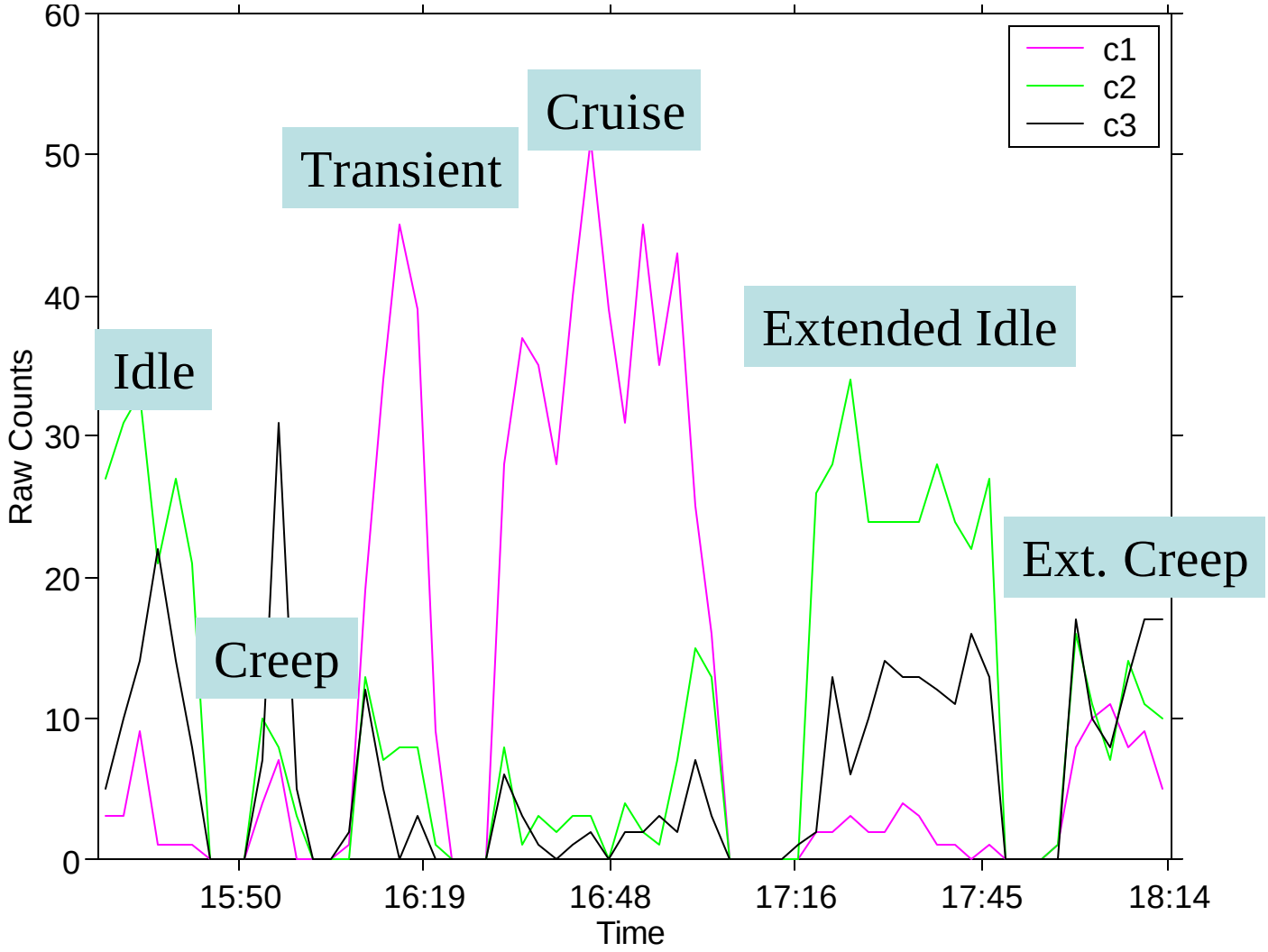
Temporal Histogram
Total ATOFMS Hits



Temporal Histogram of c1 and c2

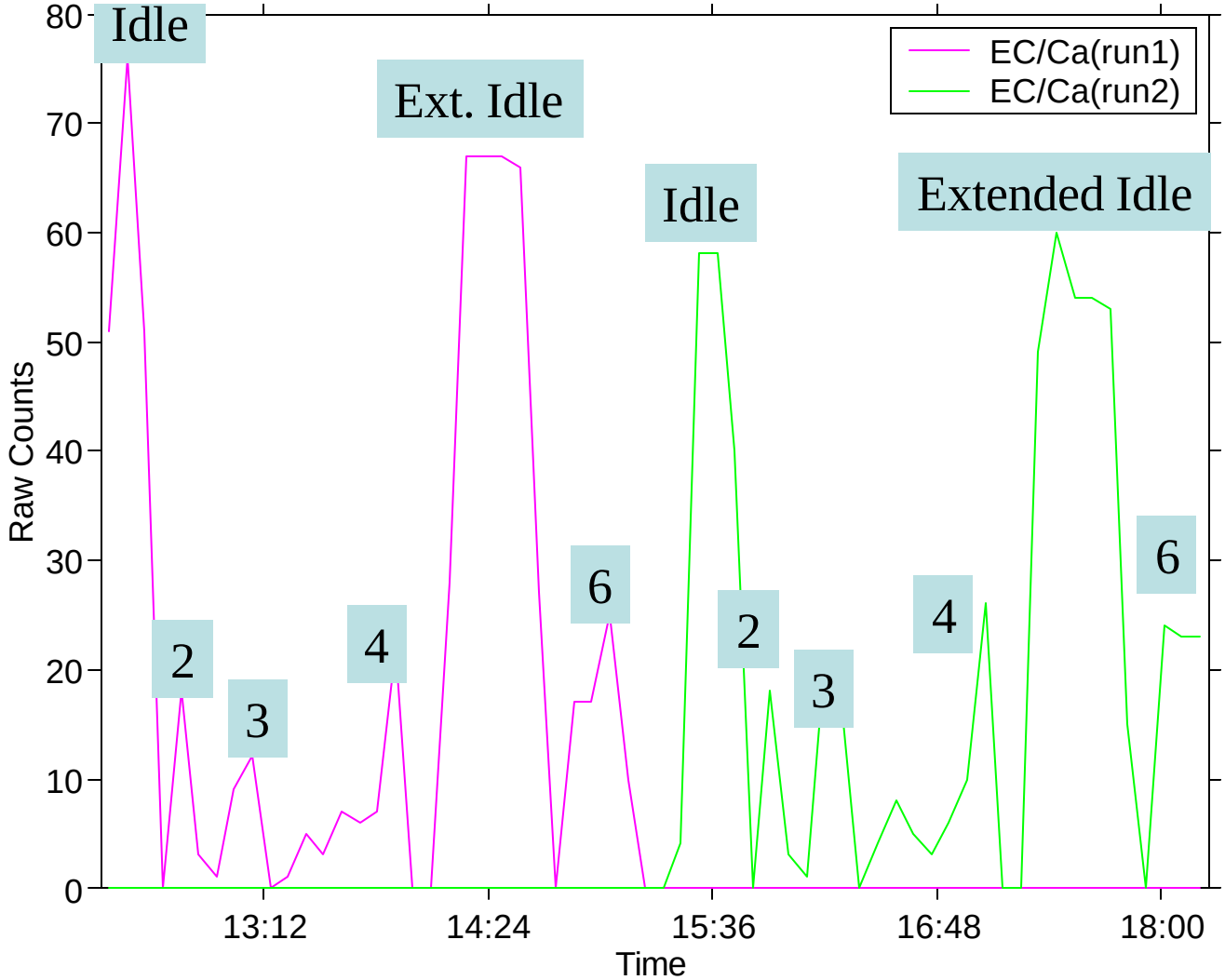


Temporal Histogram of c1, c2, and c3

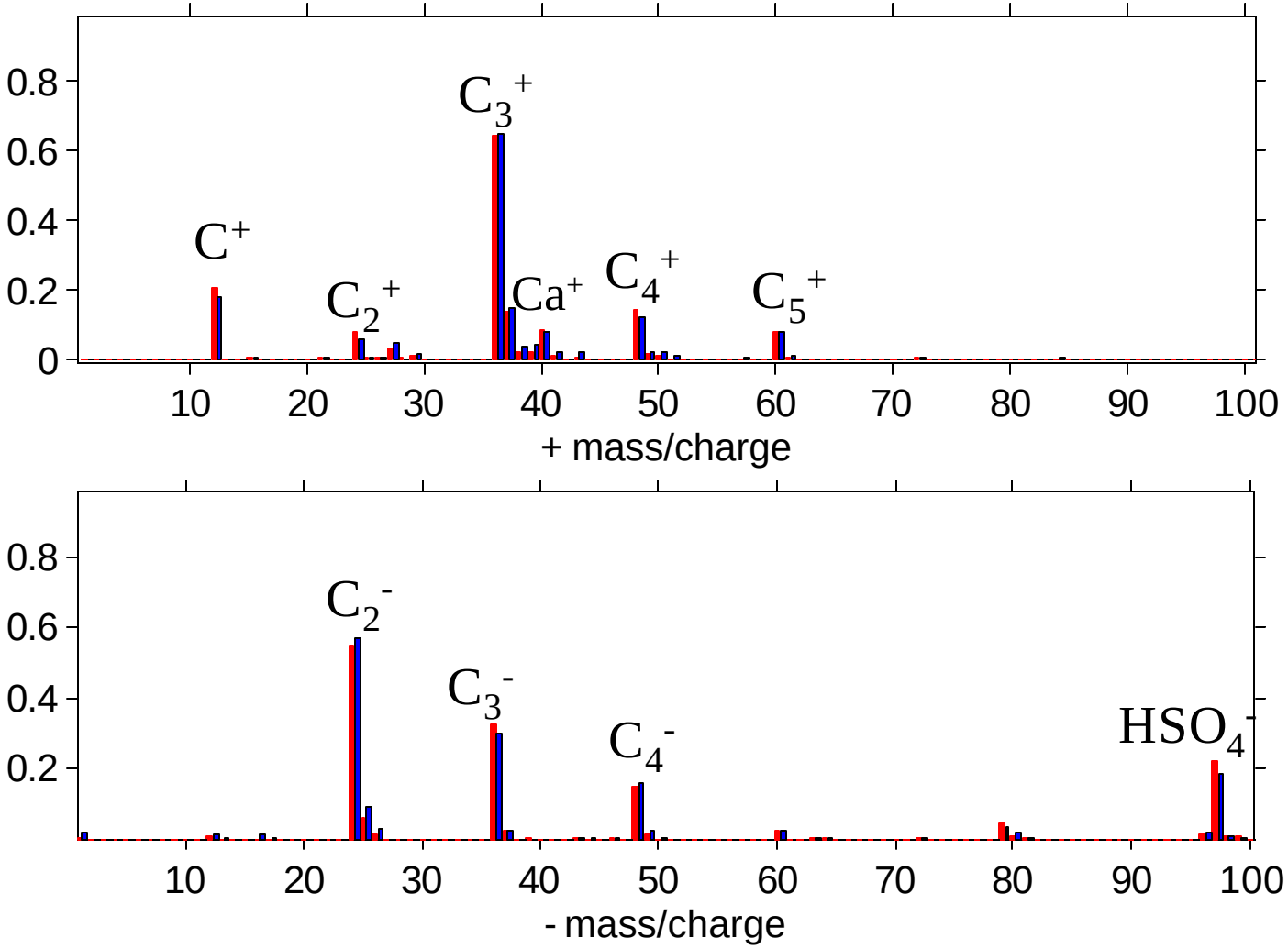


Temporal Histogram of c2 (EC/Ca)
Back-to-back dyno runs (same HDV)

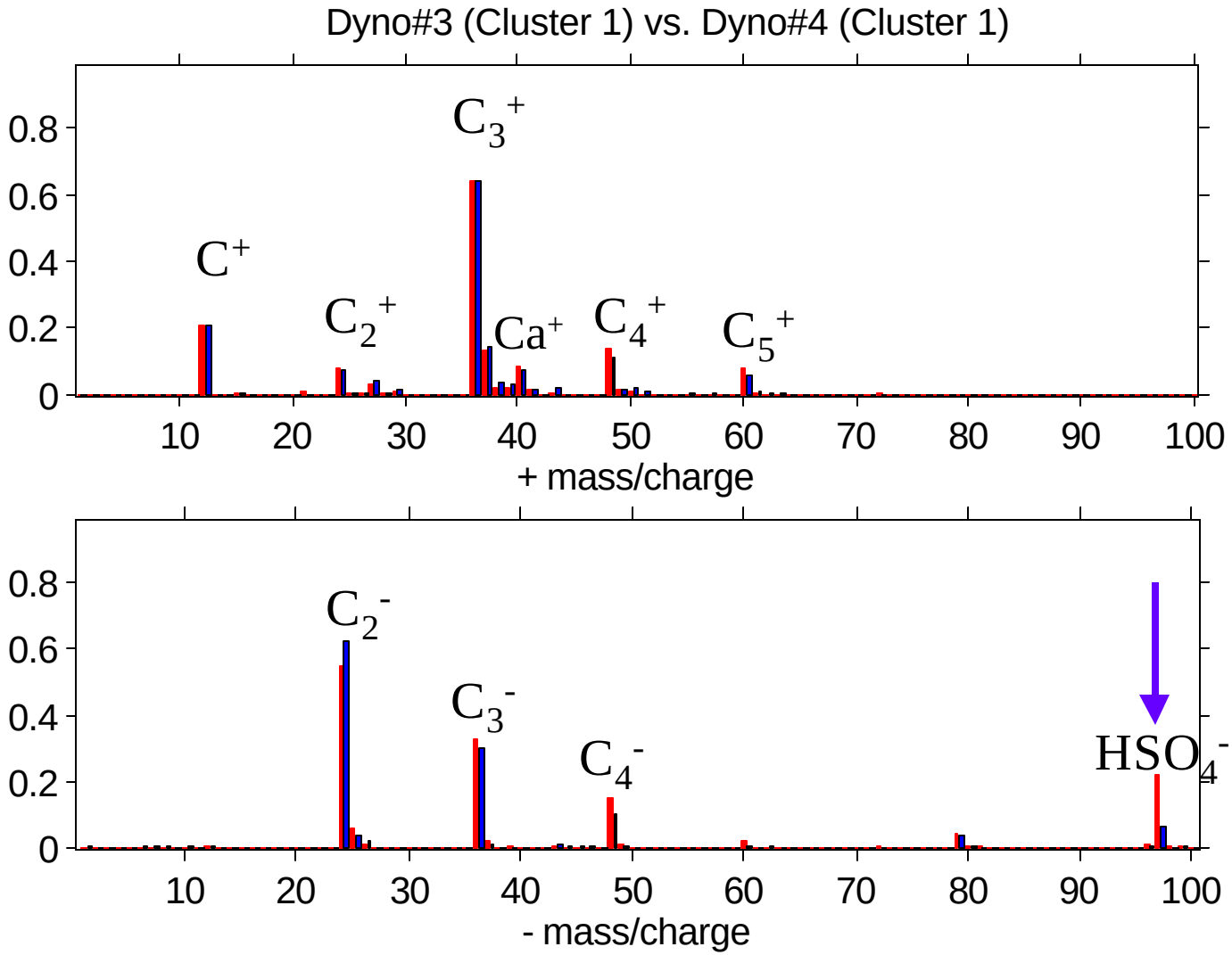
- Idle
- Creep
- Transient
- Cruise
- Ext. Idle
- Ext. Creep



Chemical Reproducibility (c2; EC/Ca)
Dyno Run-Dyno Run



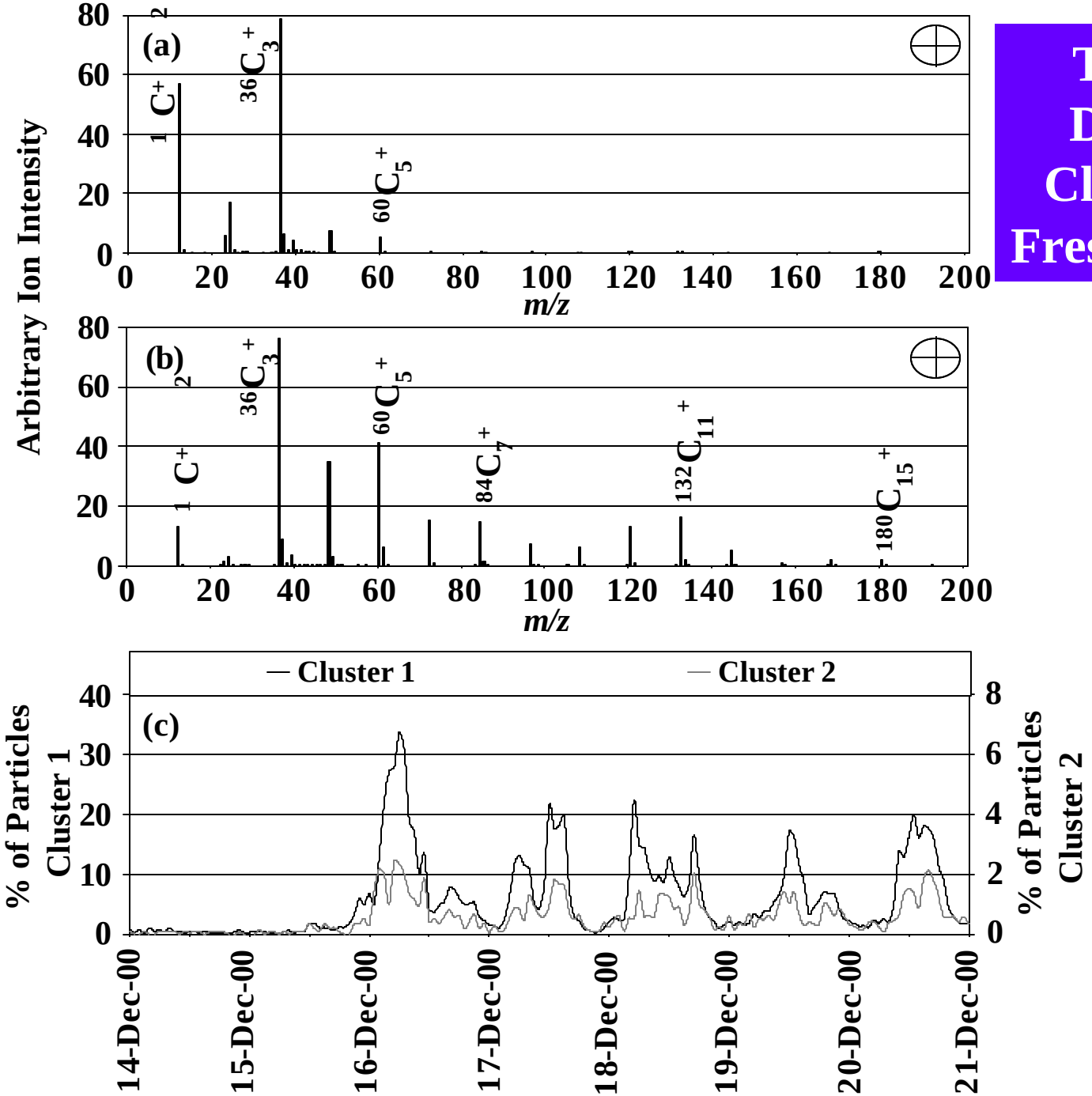
Chemical Variability
HDV-HDV Variations



Can we see these dyno signatures in ambient ATOFMS data?

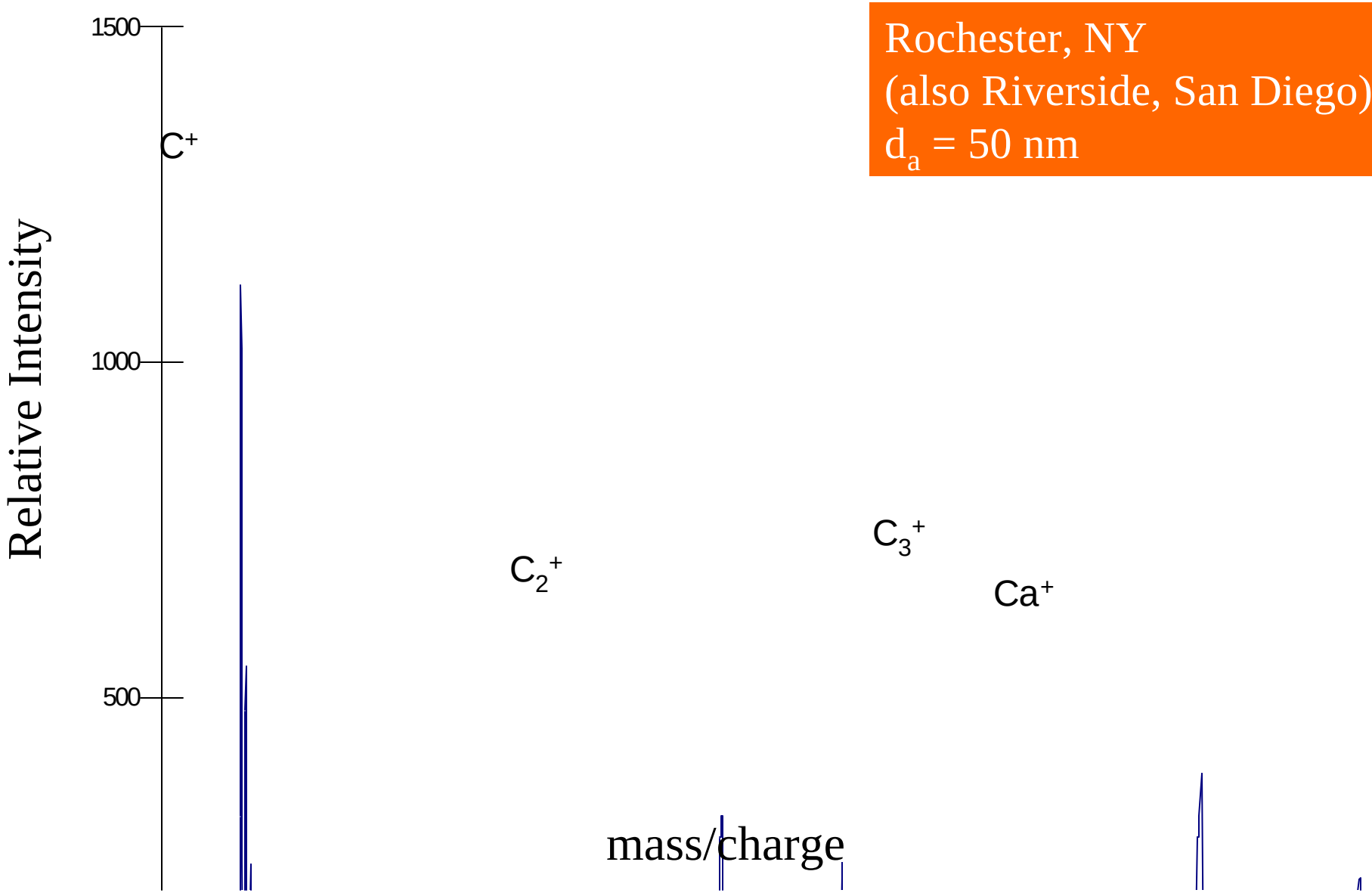
Yes, in Caldecott…..other places??

Top 2 Diesel Clusters Fresno, CA



Ultrafine Ambient Particles

Rochester, NY
(also Riverside, San Diego)
d_a = 50 nm



Summary—Dyno study and ambient comparisons

Can we see these dyno signatures in ambient ATOFMS data?

Yes, in Caldecott…..other places??

Detect “fresh” emissions

Better dyno-dyno than dyno-ambient correlations

????

•Fast aging/transformations

<u>and/or</u>

•Dyno not simulating ambient conditions

Summary (studies to date)

- Development of stable ATOFMS systems
- Multiple field studies
- Development of quant. and data analysis tools
- UF instrument
  - Detection efficiency increased from 1 in 10^6 at 200 nm to 1 in 4 at 100 nm
  - Detection of particles 50-500 nm
- Single particle perspective of southern and central CA aerosols
- Establishing database of source seeds for future source apportionment of single particles

Future plans

- LDV testing (summer 2002)
- Caldecott Tunnel (summer 2003)
- Upwind/downwind freeway study for single particle source apportionment of HDV/LDV
- Further source testing….
- Further refinement of data analysis and quant. tools

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Entire Cass Group

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Source studies

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Data Analysis and Quant.

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