ATOFMS Measurements at Urban and Rural Locations: Comparison of Single Particle Size and Composition

Xueying Qin and Kimberly A. Prather, UCSD
Prakash V. Bhave, U.S. EPA

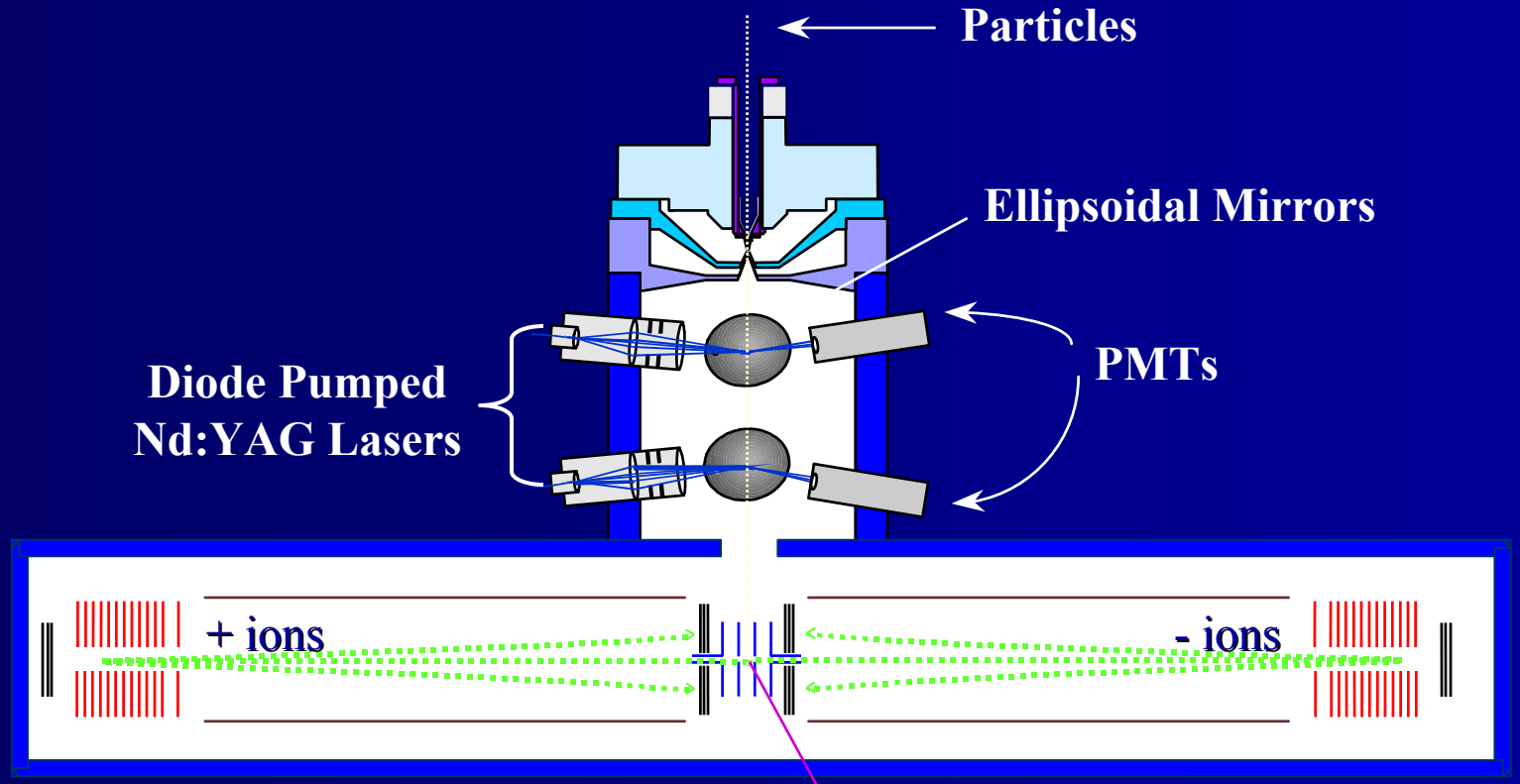
Overview

- Quantification of ATOFMS measurement
- Application of quantification method to field measurements

Field Campaign

- Participated in CRPAQS winter program
- Ambient sampling in Fresno and Angiola
  - Fresno: urban site, total of 1,861,319 particles
  - Angiola: rural site, total of 2,099,788 particles
  - different chemical matrices due to aging effect
- Goal: quantitatively compare ambient particle size and chemical composition in urban and rural locations

Aerosol Time-of-Flight Mass Spectrometer (ATOFMS)



$C_nH_m^+$, $(Fe, V, Pb)^+$

$C_nH_m^-$, Nitrates, sulfates, phosphates, chloride

Nd:YAG Laser

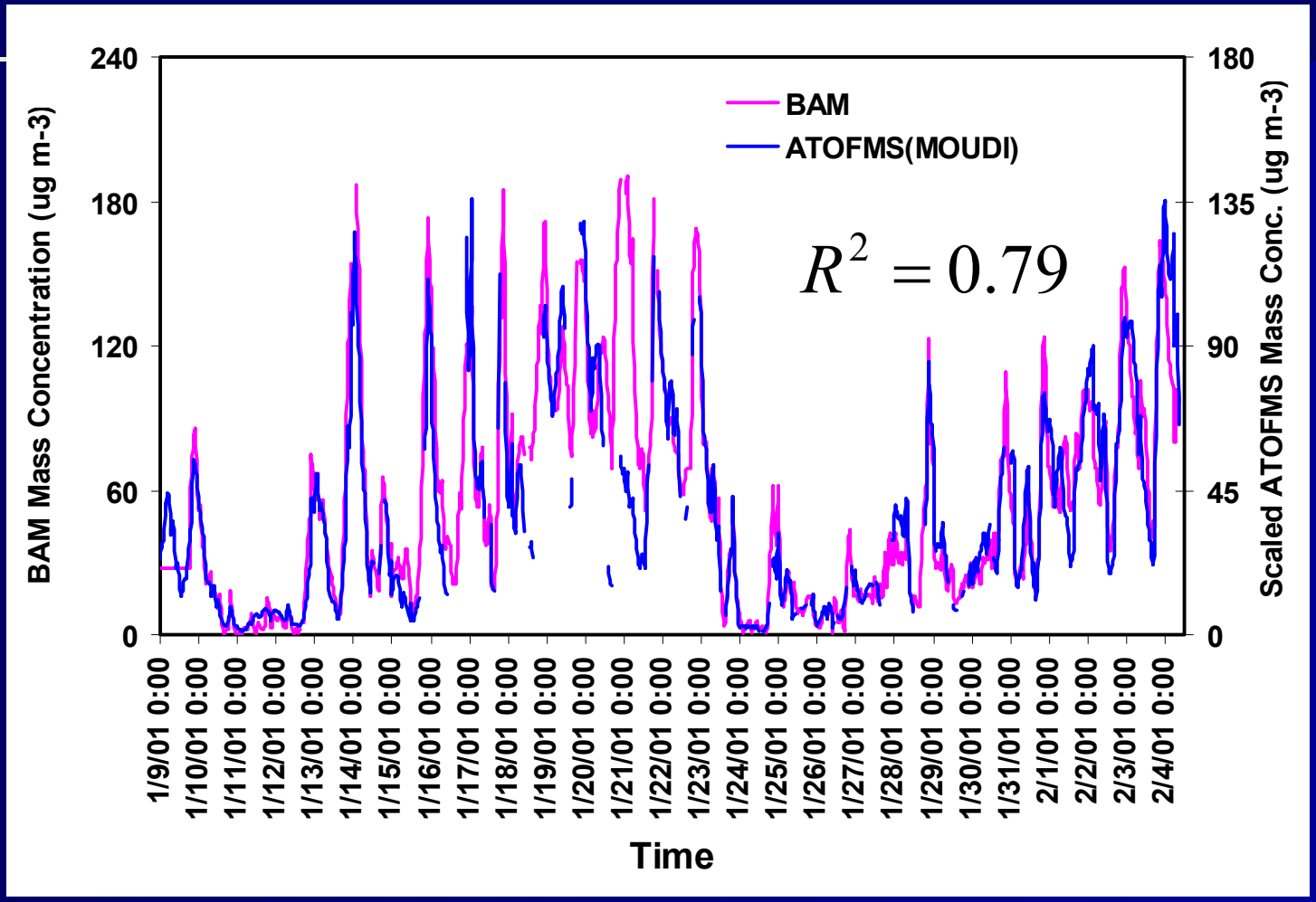
Can ATOFMS Provide Quantitative Information?

- **ATOFMS unscaled counts capture ambient particle concentration information**
- **Scale ATOFMS unscaled particle counts with reference measurements**
  - **Mass: scale with MOUDI**

    scale with micro-orifice uniform deposit impactor (ATOF-M)
  - **Number: scale with APS**

    scale with aerodynamic particle sizer (ATOF-N)

ATOF-M vs. BAM

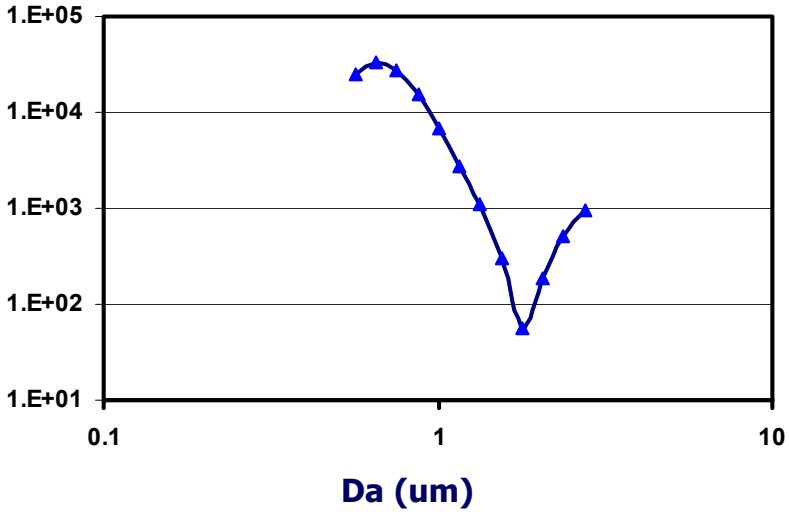


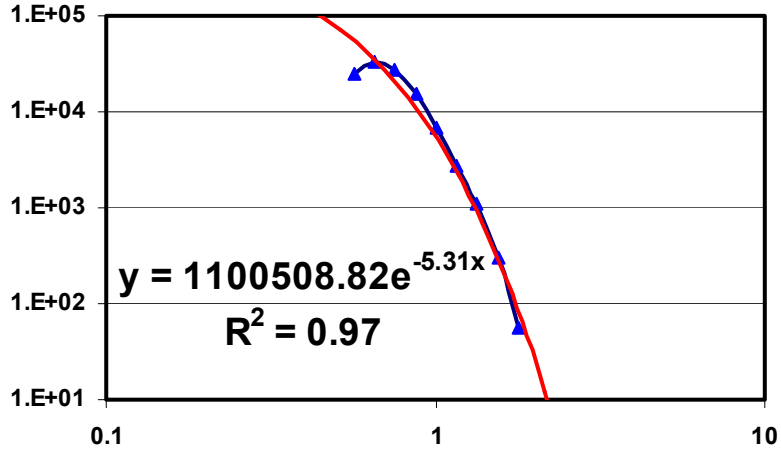
Allen et al.,Environ. Sci. Technol. 2000,34,211-217; Bhave et al., Environ. Sci. Technol. 2002,36,4868-4879

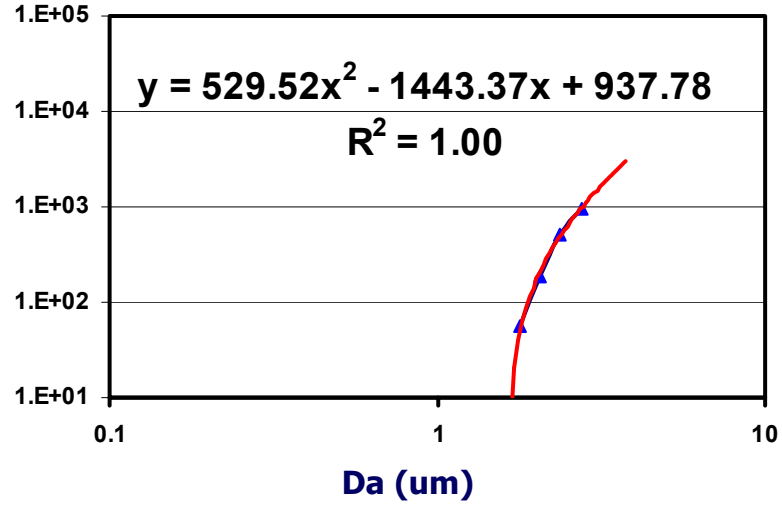
Scale with APS

- Compare ATOFMS counts with APS # concentrations (size range 0.5-2.5 μm)
- Scaling factor (f):
  - f = APS Counts / ATOFMS Counts
  - exponential regression and polynomial regression
  - when Da < 1.783 um: $\varphi = C_1 \cdot e^{(D_a \cdot C_2)}$
  - when Da ≥ 1.783 um: $\varphi = C_3 \cdot D_a^{\ 2} - C_4 \cdot D_a + C_5$

f (APS) vs. Da


1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
0.1
1
10
Da (um)


1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
y = 1100508.82e^-5.31x
R^2 = 0.97
0.1
1
10

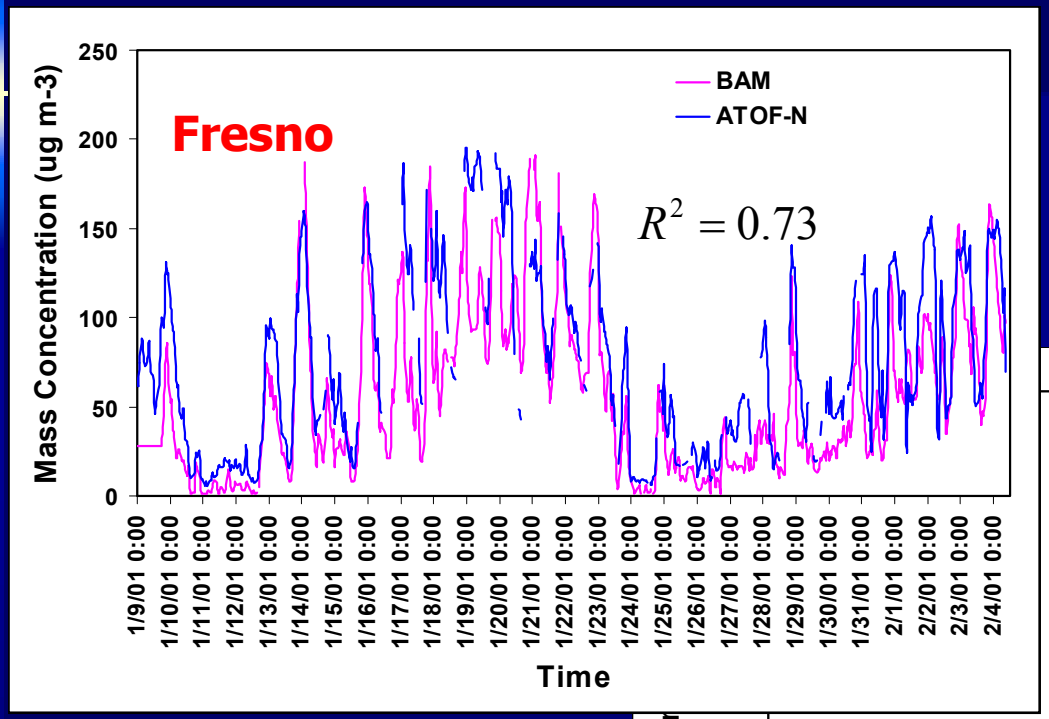

1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
y = 529.52x^2 - 1443.37x + 937.78
R^2 = 1.00
0.1
1
10
Da (um)

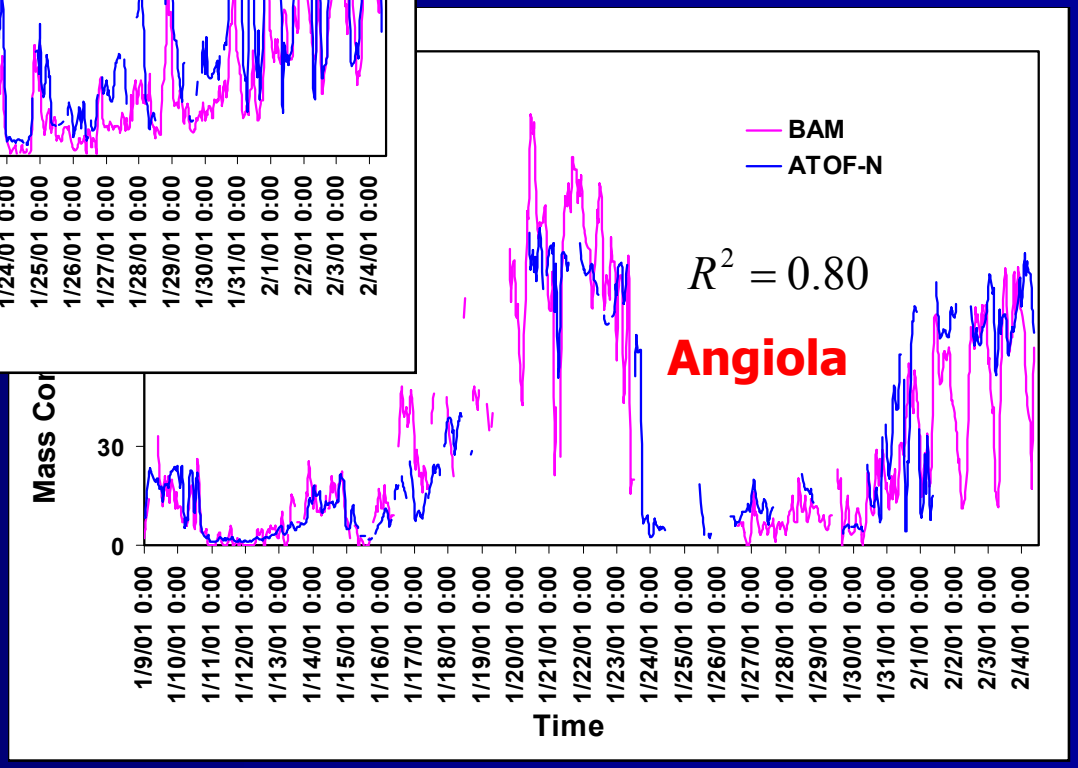
Scaled Mass Concentration

- Convert ATOFMS counts into mass conc.
  - assume all particles are spherical
  - assume uniform density of 1.3 g·cm-3
- Calculate scaling factor for individual particle
- Scaled ATOFMS mass concentration – ATOF-N:

$$m_{scaled_ATOFMS} = \sum_i \varphi_{Da,i} \cdot m_i$$

ATOF-N vs. BAM


Fresno
BAM
ATOF-N
$R^2 = 0.73$
Mass Concentration (ug m-3)
250
200
150
100
50
0
1/9/01 0:00
1/10/01 0:00
1/11/01 0:00
1/12/01 0:00
1/13/01 0:00
1/14/01 0:00
1/15/01 0:00
1/16/01 0:00
1/17/01 0:00
1/18/01 0:00
1/19/01 0:00
1/20/01 0:00
1/21/01 0:00
1/22/01 0:00
1/23/01 0:00
1/24/01 0:00
1/25/01 0:00
1/26/01 0:00
1/27/01 0:00
1/28/01 0:00
1/29/01 0:00
1/30/01 0:00
1/31/01 0:00
2/1/01 0:00
2/2/01 0:00
2/3/01 0:00
2/4/01 0:00
Time


BAM
ATOF-N
$R^2 = 0.80$
Angiola
30
0
1/9/01 0:00
1/10/01 0:00
1/11/01 0:00
1/12/01 0:00
1/13/01 0:00
1/14/01 0:00
1/15/01 0:00
1/16/01 0:00
1/17/01 0:00
1/18/01 0:00
1/19/01 0:00
1/20/01 0:00
1/21/01 0:00
1/22/01 0:00
1/23/01 0:00
1/24/01 0:00
1/25/01 0:00
1/26/01 0:00
1/27/01 0:00
1/28/01 0:00
1/29/01 0:00
1/30/01 0:00
1/31/01 0:00
2/1/01 0:00
2/2/01 0:00
2/3/01 0:00
2/4/01 0:00
Time

PM2.5 Measurements

- **Fresno Site**

  Nephelometer (**NEPH**) Aethelometer (**AETH**)

  Beta attenuation monitor (**BAM**)

  Tapered element oscillating microbalance (**TEOM**)

  Dust aerosol monitor (**DAM**)

  ATOFMS mass conc. scaled with APS (**ATOF-N**)

- **Angiola Site**

  NEPH **AETH** **BAM** **ATOF-N**

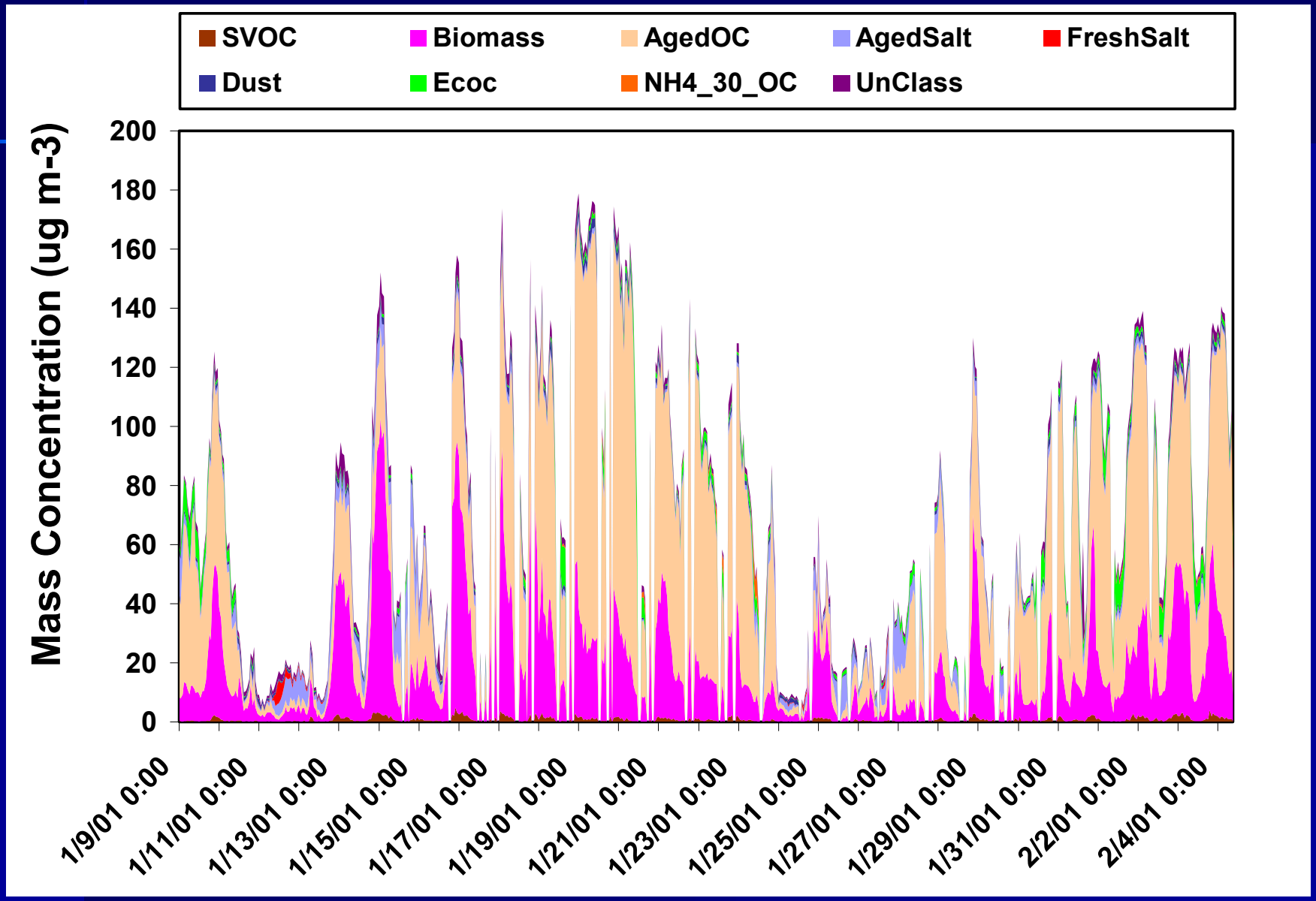
Fresno PM2.5 Measurements Comparison

R2	BAM	TEOM	DAM	NEPH	AETH	ATOF-N
BAM	1.00	0.86	0.93	0.75	0.79	0.73
TEOM	0.86	1.00	0.59	0.60	0.94	0.57
DAM	0.93	0.59	1.00	0.70	0.53	0.73
NEPH	0.75	0.60	0.70	1.00	0.58	0.78
AETH	0.79	0.94	0.53	0.58	1.00	0.59
ATOF-N	0.73	0.57	0.73	0.78	0.59	1.00

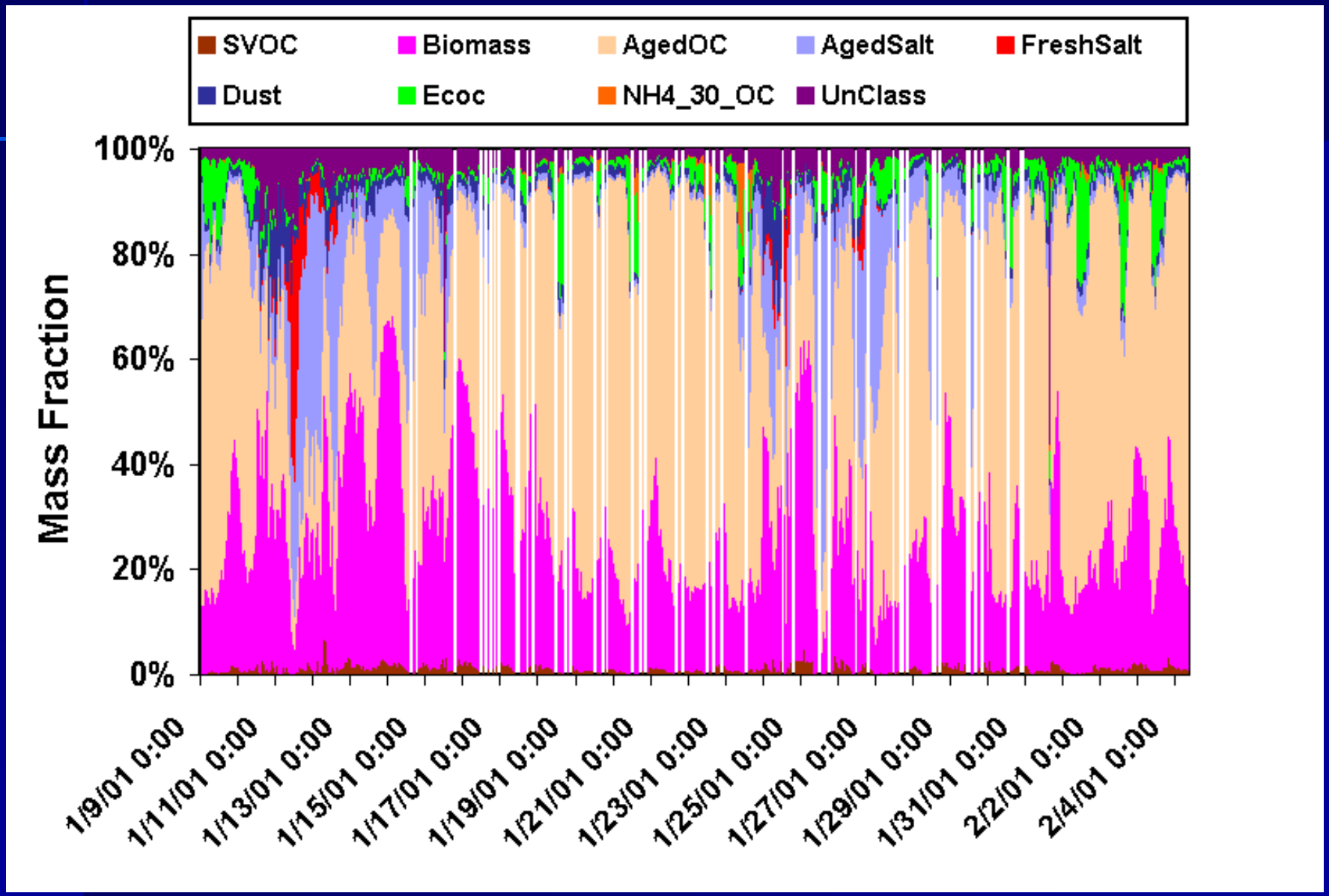
Angiola PM2.5 Measurements Comparison

R2	BAM	NEPH	AETH	ATOF-N
BAM	1.00	0.92	0.60	0.80
NEPH	0.92	1.00	0.77	0.88
AETH	0.60	0.77	1.00	0.63
ATOF-N	0.80	0.88	0.63	1.00

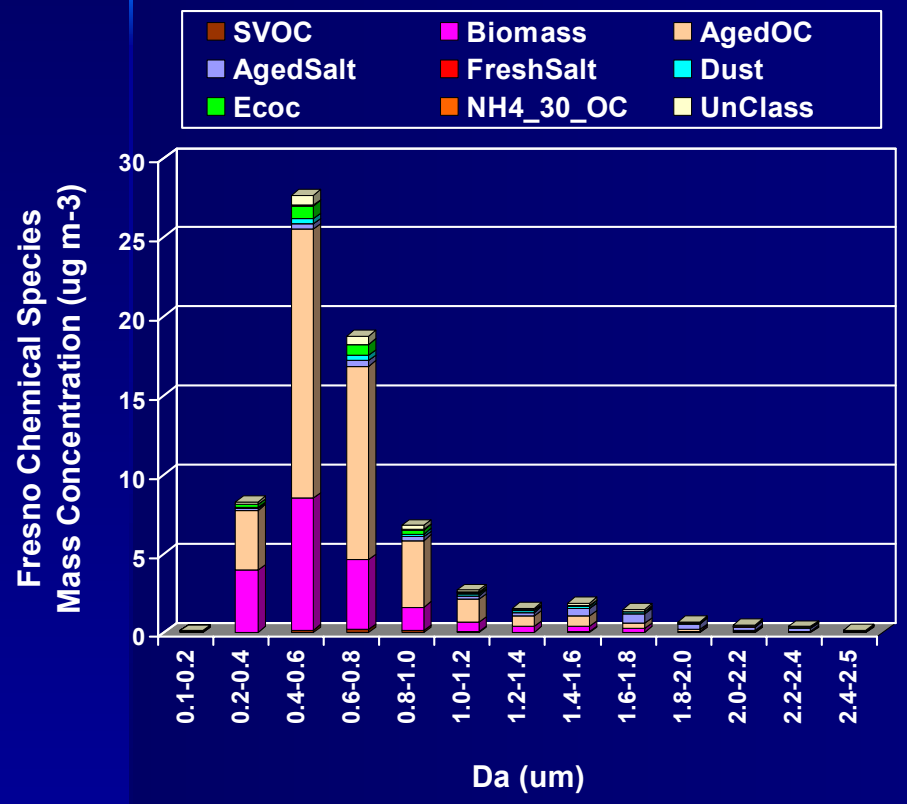
Fresno Temporal Variation of Chemical Types

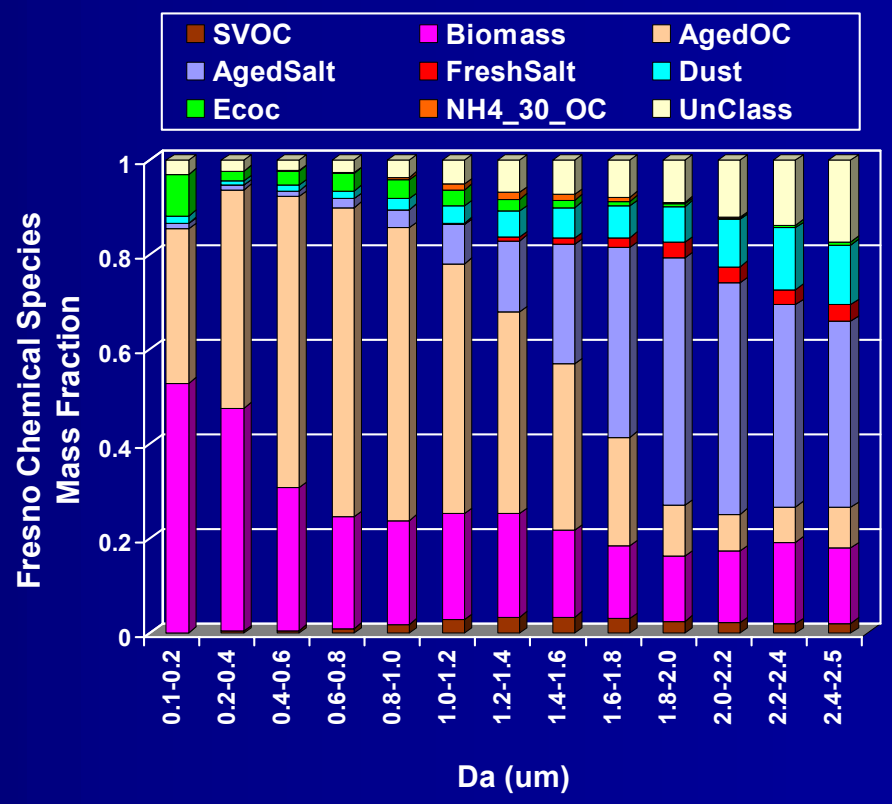


Fresno Temporal Variation of Chemical Types

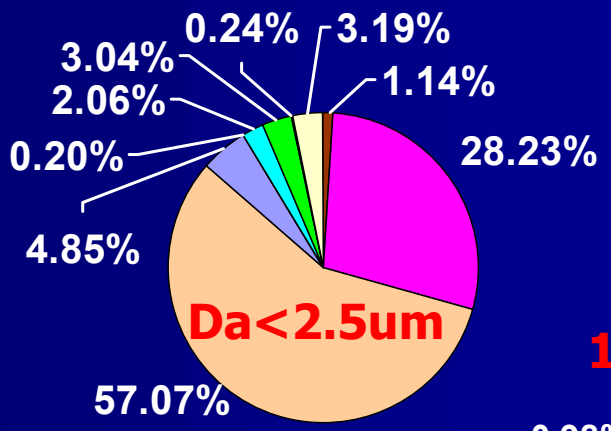


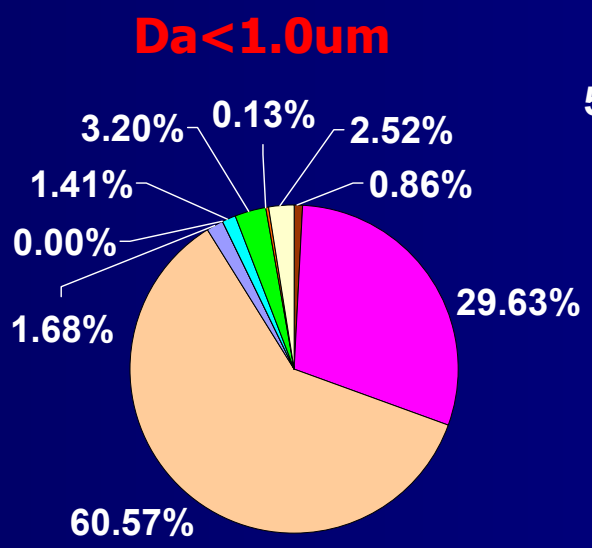
Fresno Size Resolved Fraction of Major Types

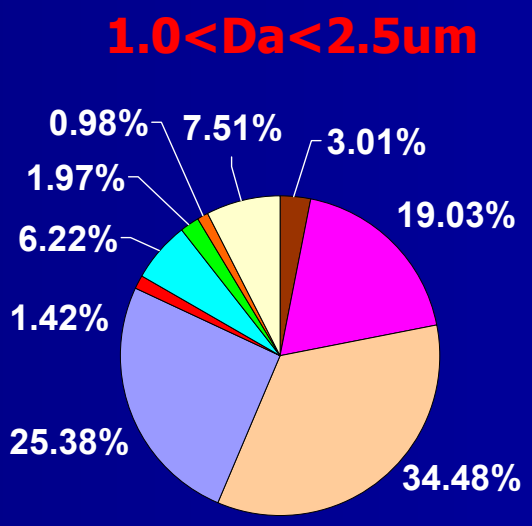




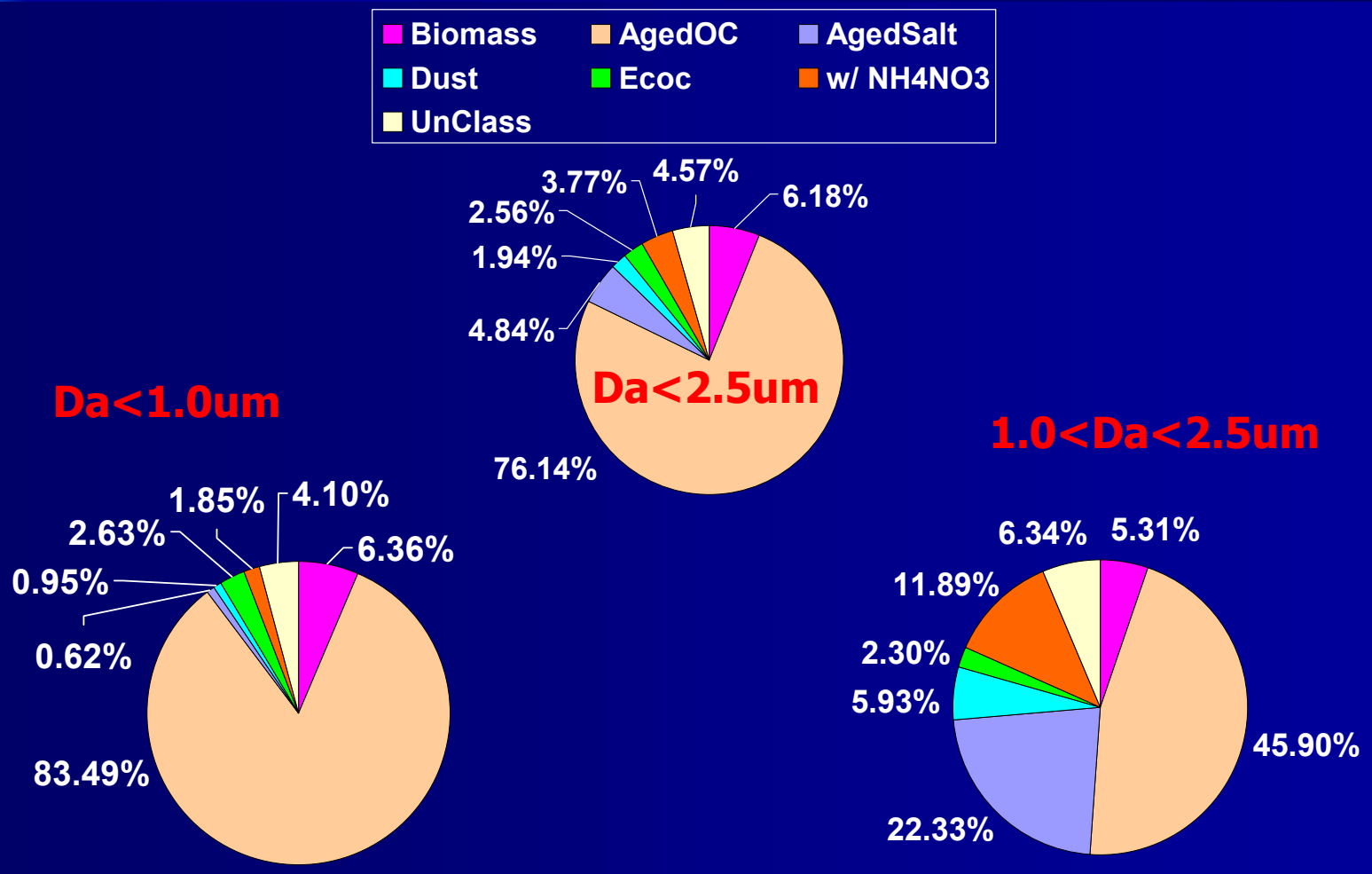
Fresno PM Chemical Composition Mass Fraction







Angiola PM Chemical Composition Mass Fraction



Conclusions

- **ATOFMS is able to provide size resolved, high temporal resolution, and quantitative information on ambient PM composition**
- **Carbonaceous particles account for more than 80% of the PM2.5 mass fraction in both Fresno and Angiola during the winter**
- **Higher fraction of fresh biomass emissions in Fresno**
- **Episodic periods with high amounts of ammonium and nitrate particles in Angiola**
- **Diurnal variation of particle chemistry**
  - Fresno: SVOC, biomass and aged OC peak at night
    EC/OC and NH_4NO_3-OC peak during the day
  - Angiola: PM with high levels of ammonium nitrate peak during day
- **To understand chemical variability and transformations will begin making comparisons with models (M. Kleeman, UC Davis)**

Acknowledgements

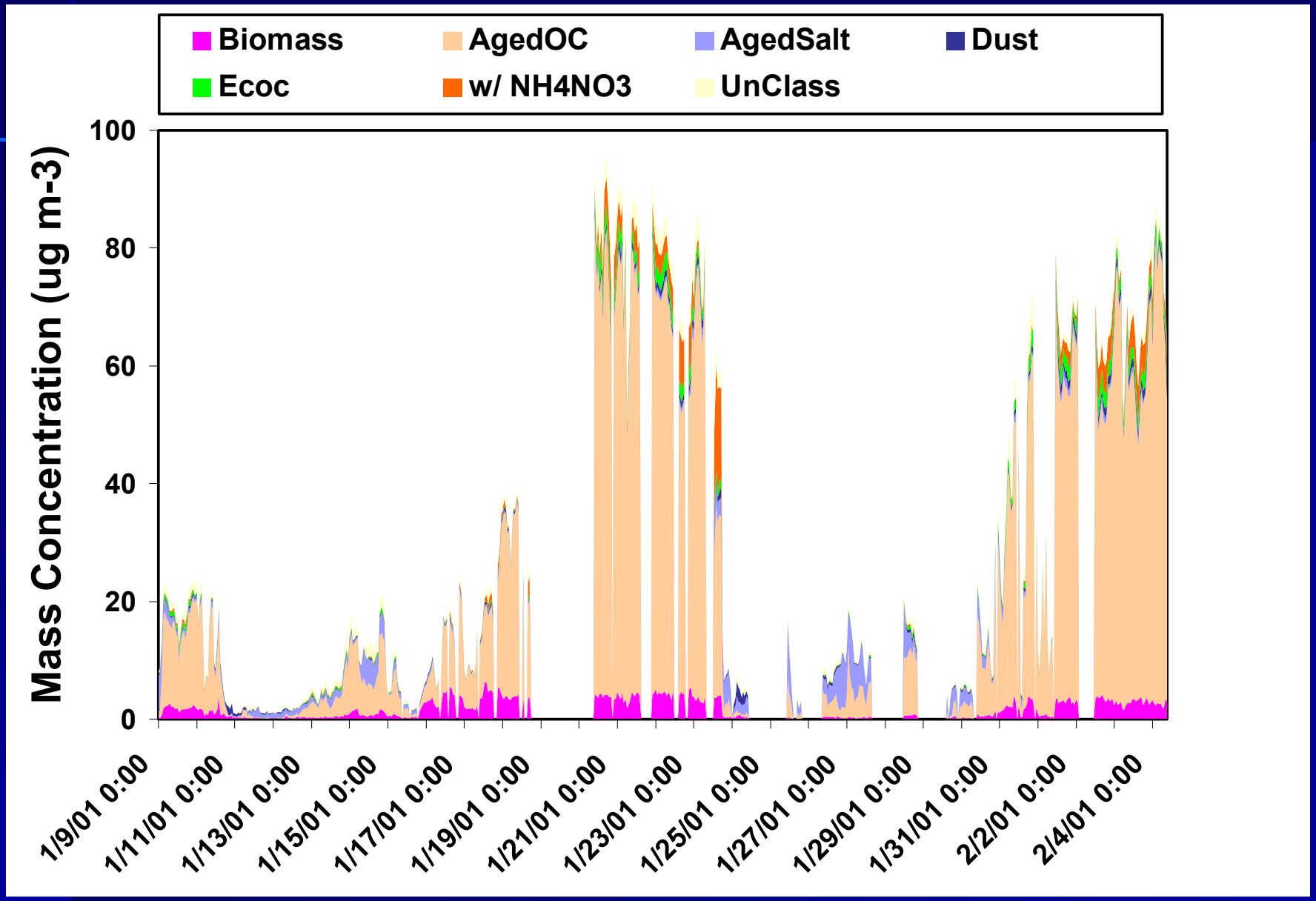
Dr. Jeffrey R. Whiteaker
Dr. Keith R. Coffee
Dr. George Khairallah
Dr. David T. Suess

The Prather Group

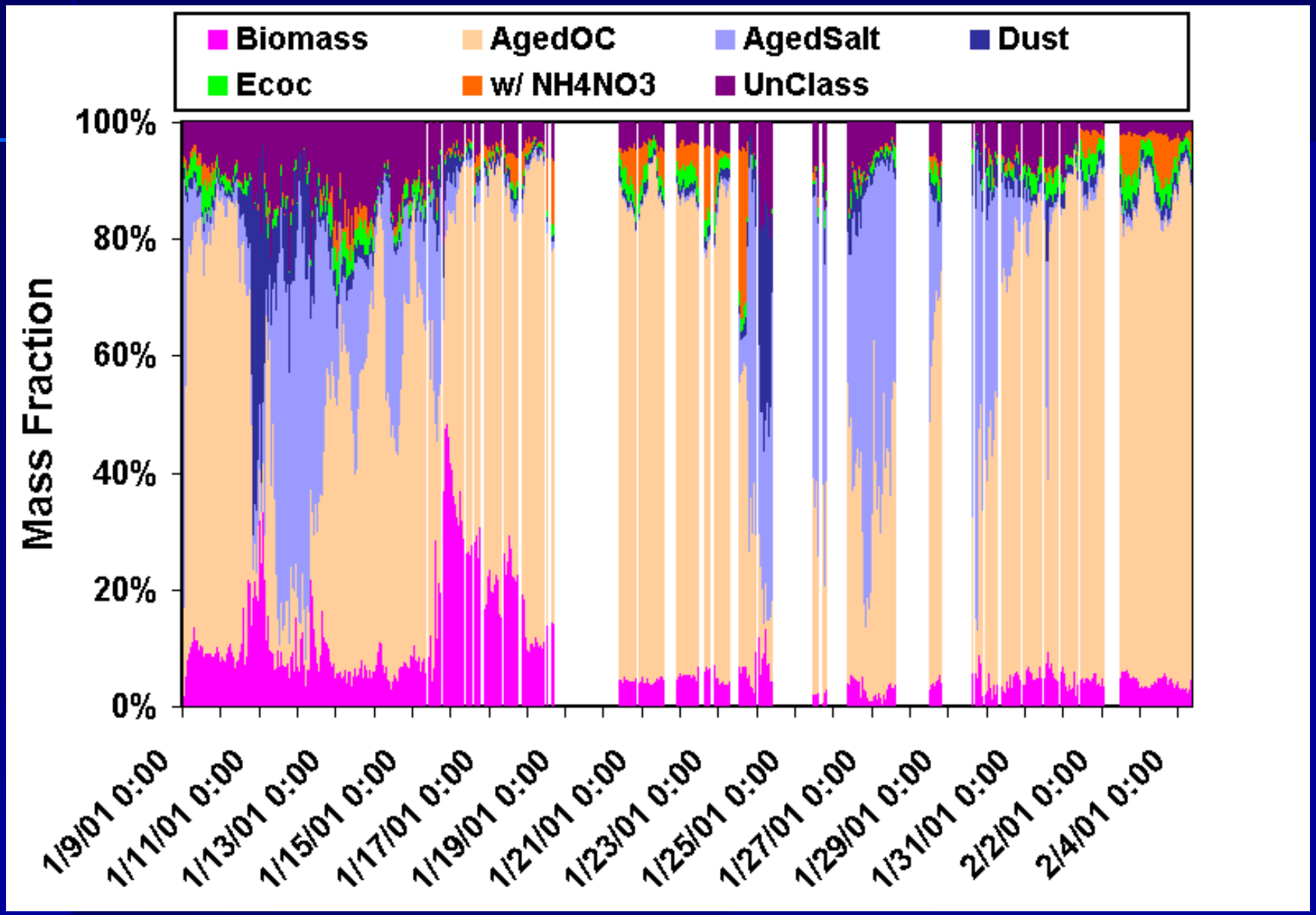
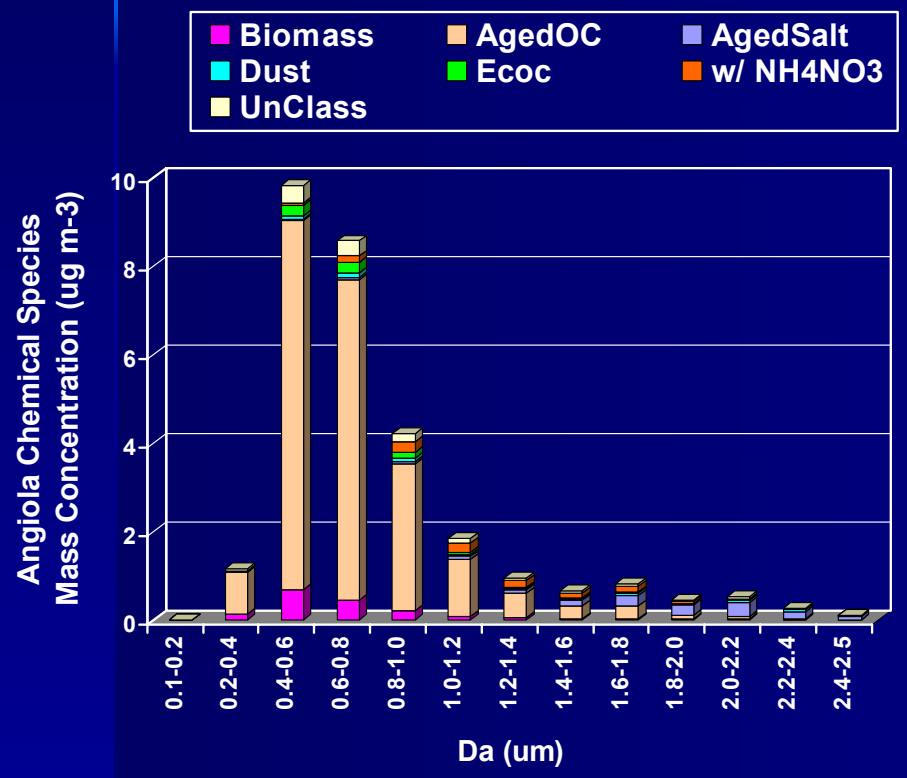
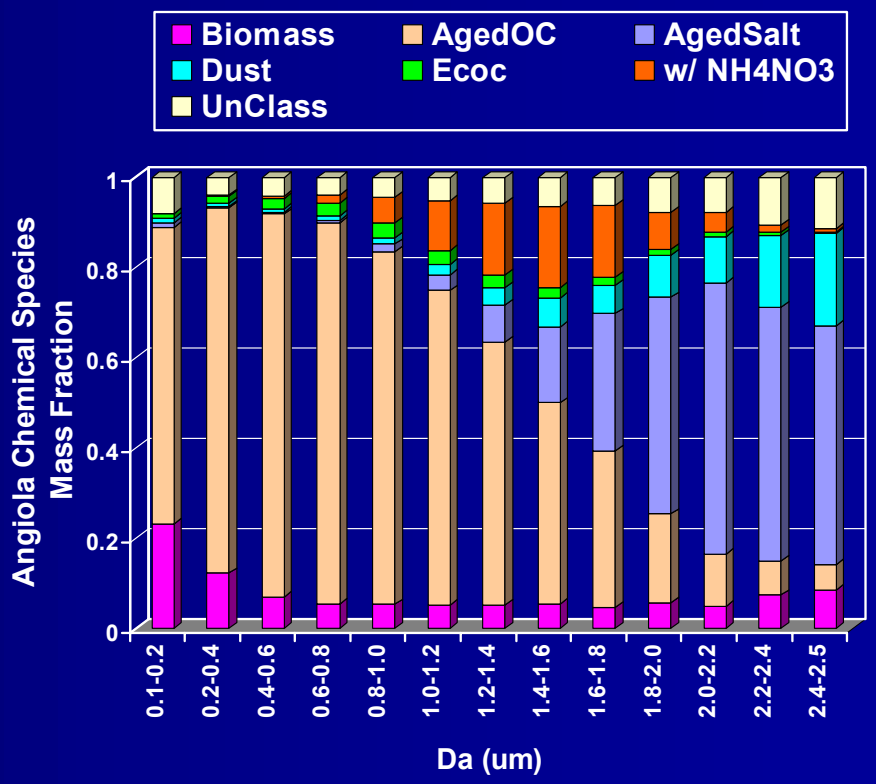
San Joaquin Valley Air Pollution District

California Air Resources Board

Angiola Temporal Variation of Chemical Types



Angiola Temporal Variation of Chemical Types



Angiola Size Resolved Fraction of Major Types