Chair's Air Pollution Seminar

November 20th, 2007

Wintertime Particulate Matter in the San Joaquin Valley: Concentrations, Mechanisms, and Sources

Jorn Dinh Herner, Ph.D.
Research Division

Air Resources Board

Acknowledgements

- Professor Michael Kleeman – Advisor, UC Davis
- Professor Daniel Chang, Qi Ying, Oliver Gao, Jeremy Aw – UC Davis
- Karen Magliano – California Air Resources Board

Definitions

- **PM_{10}** – Particulate Matter with aerodynamic diameter of 10μm or less. Often referred to as coarse PM
- **$PM_{2.5}$** – Particulate Matter with aerodynamic diameter of 2.5μm or less. Also known as Fine PM.
- **Ultrafine PM** – Particulate Matter with aerodynamic diameter of 0.1μm or less.

Human hair	~ 100μm diameter.
Red Blood cell	~ 7.5 μm diameter.

1 μm = one millionth of a meter

California Regional Particulate Air Quality Study

CRPAQS

The California Regional PM10/PM2.5 Air Quality Study is a multi-year effort of meteorological and PM air quality monitoring, emission inventory development, data analysis, and air quality modeling. Field work consisted of 14 months of monitoring, between December 1999 and February 2001

This work:

Filter-based and cascade impactor data collection and analysis for 15 intensive sampling days at five sites during winter 2000/01

California Regional Particulate Air Quality Study

Motivation

Ambient particulate matter pollution has been linked to several undesirable health outcomes, such as:

- increased respiratory symptoms, such as
- irritation of the airways, coughing, or difficulty breathing, for example;
- decreased lung function;
- aggravated asthma;
- development of chronic bronchitis;
- irregular heartbeat;
- nonfatal heart attacks; and
- premature death in people with heart or lung disease.

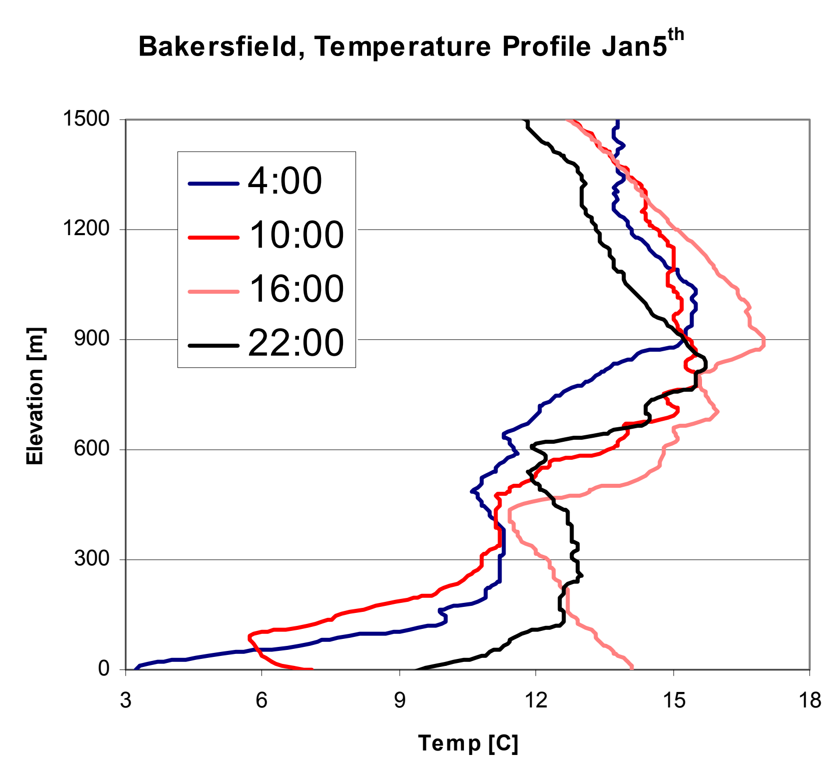
The San Joaquin Valley has some of the highest PM concentrations measured in the nation, and exceeds the National Ambient Air Quality Standard for $PM_{2.5}$

Why the high winter-time PM ?

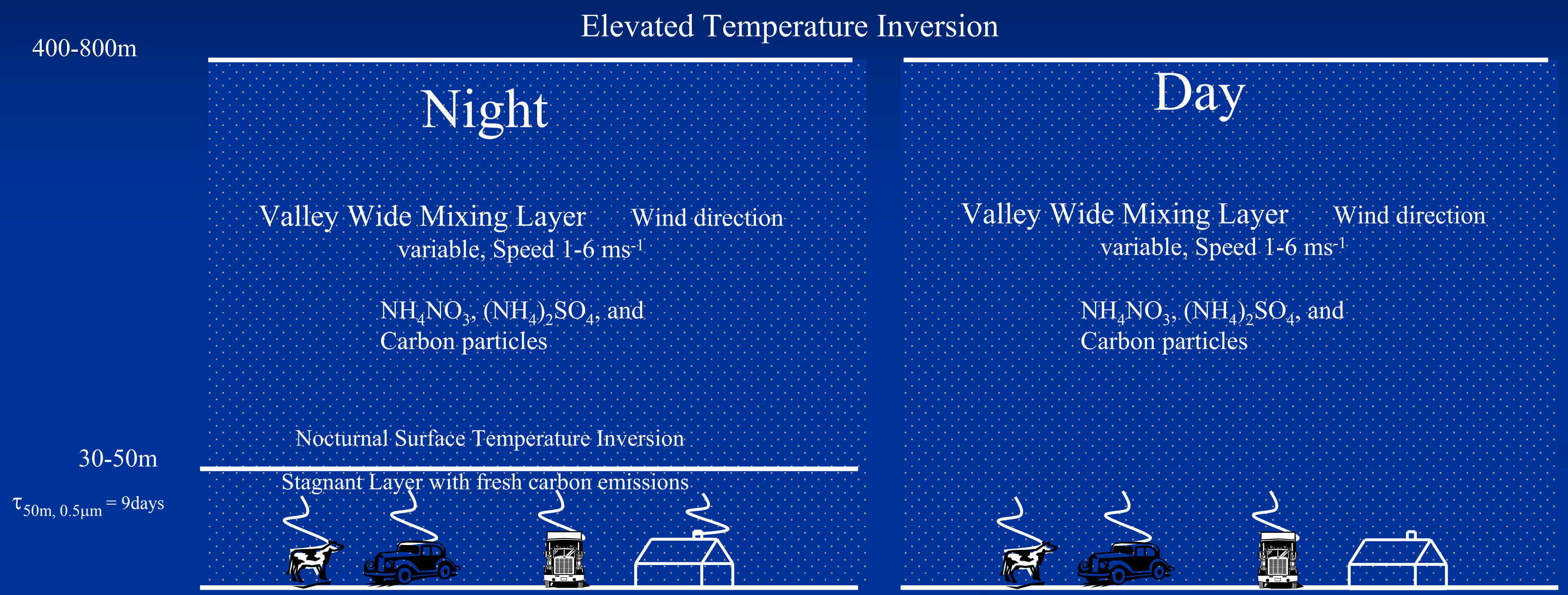
- Geography – SJV enclosed by mountains
- Meteorology – Stagnant winter conditions

Conceptual Model for Winter PM Formation:

- Great Basin High – limited exchange with neighboring airsheds.
- High temperatures aloft (850mb) combined with low ground level temperatures create shallow nighttime inversion layer (30-50m) with low wind speeds. Above inversion layer windspeeds 1-6m s^{-1}
- During the daytime solar radiation breaks down the inversion, creating a single layer (400 – 800m)

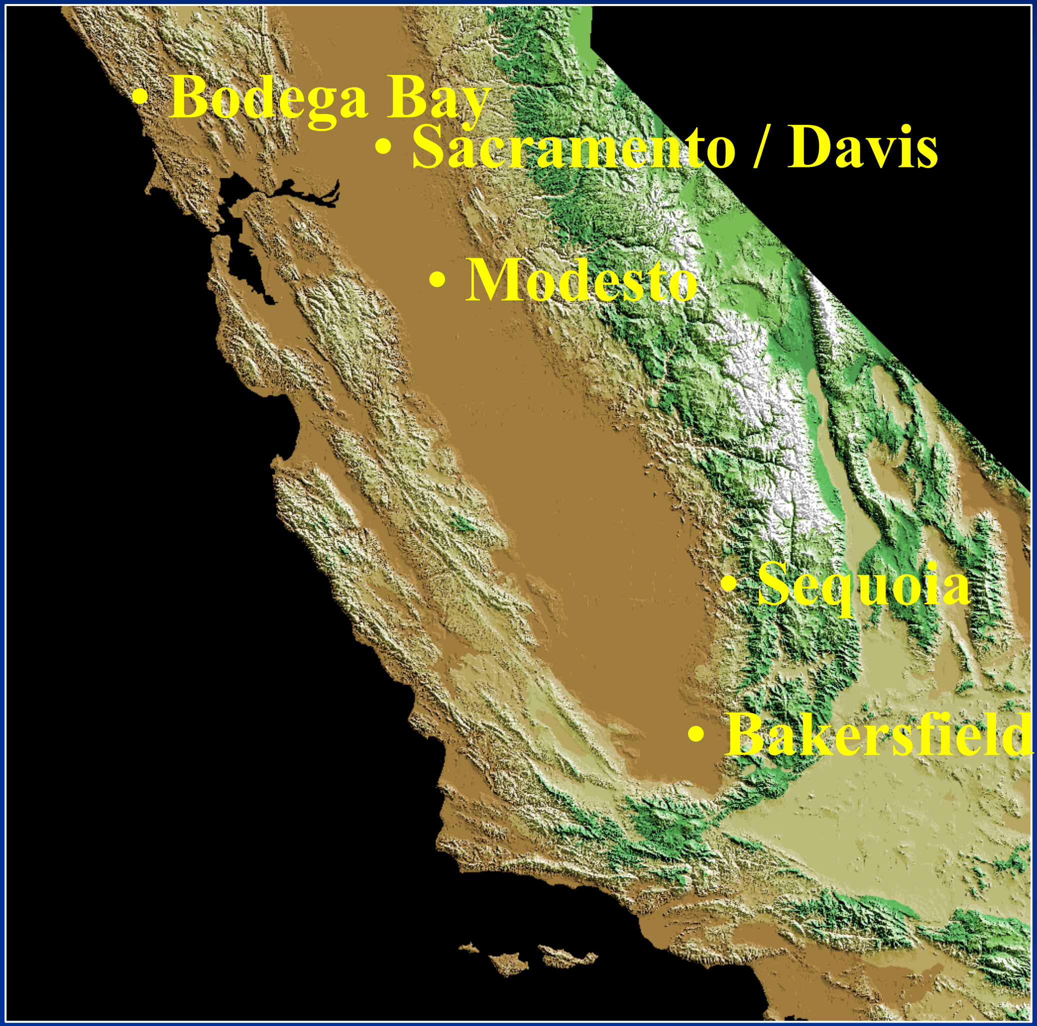


Conceptual Model for Winter PM Formation:



- When repeated for days or weeks this cycle promotes mixing and pollutant buildup in the San Joaquin Valley

UCD Sampling Sites and Times



Site Name	Elevation [m]
Bakersfield	119
Bodega Bay	17
Davis	30
Modesto	28
Sacramento	26
Sequoia	535

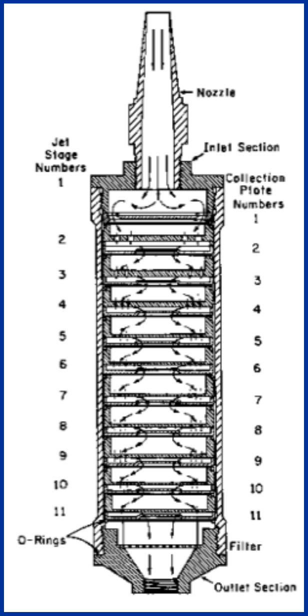
Urban Sites, Bakersfield, Modesto, Sacramento
10:00 – 18:00
20:00 – 08:00

Background Sites, Bodega Bay, Davis, Sequoia
00:00 – 22:00

* These sampling sites were embedded within the much broader CRPAQS network

Sampling Instrumentation

- Filter based PM_{10} and $PM_{1.8}$
  Andersen RAAS 400 + PM_{10} Head
- Cascade Impactors
  MSP MOUDI series 110

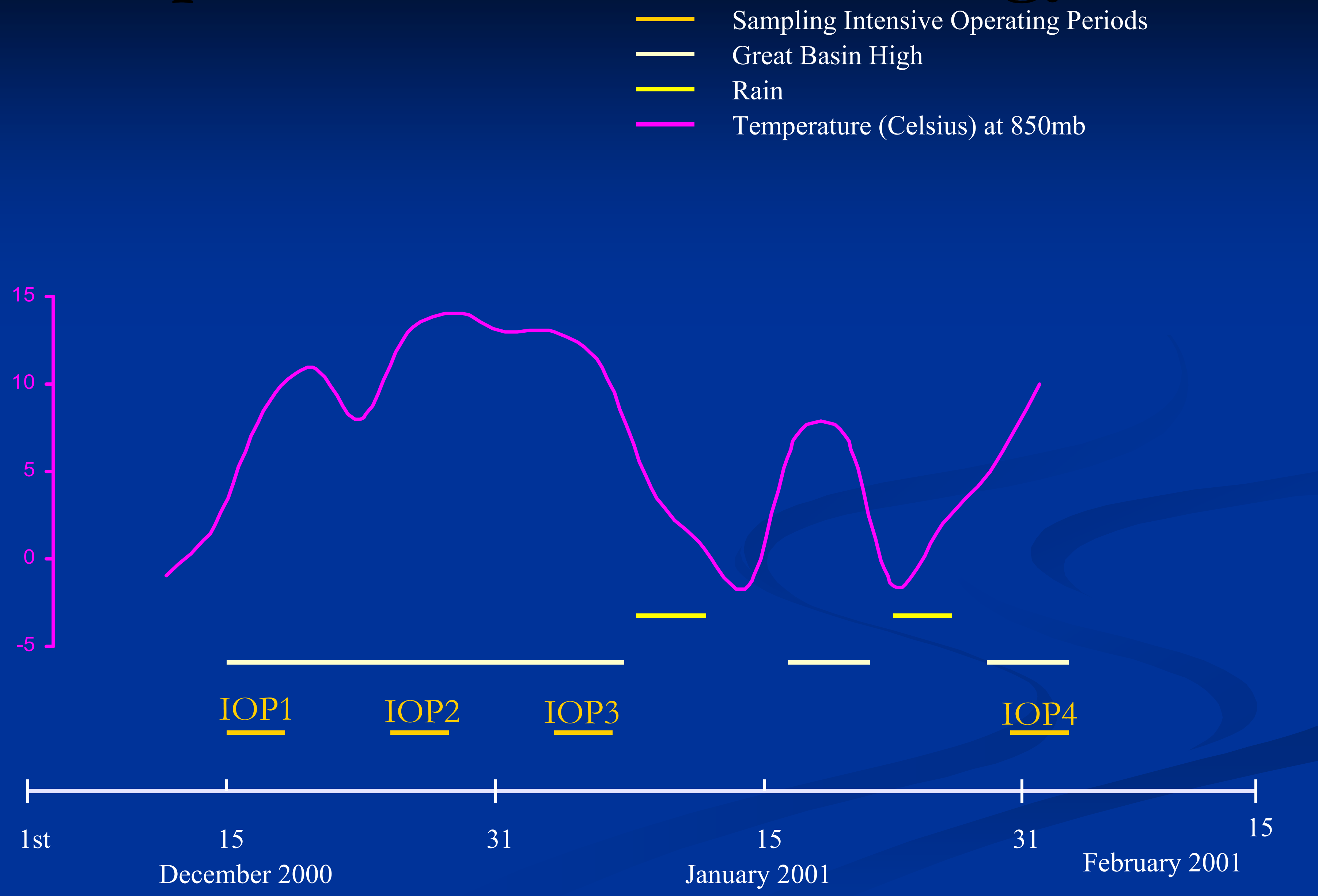


Size Segregated sample collection

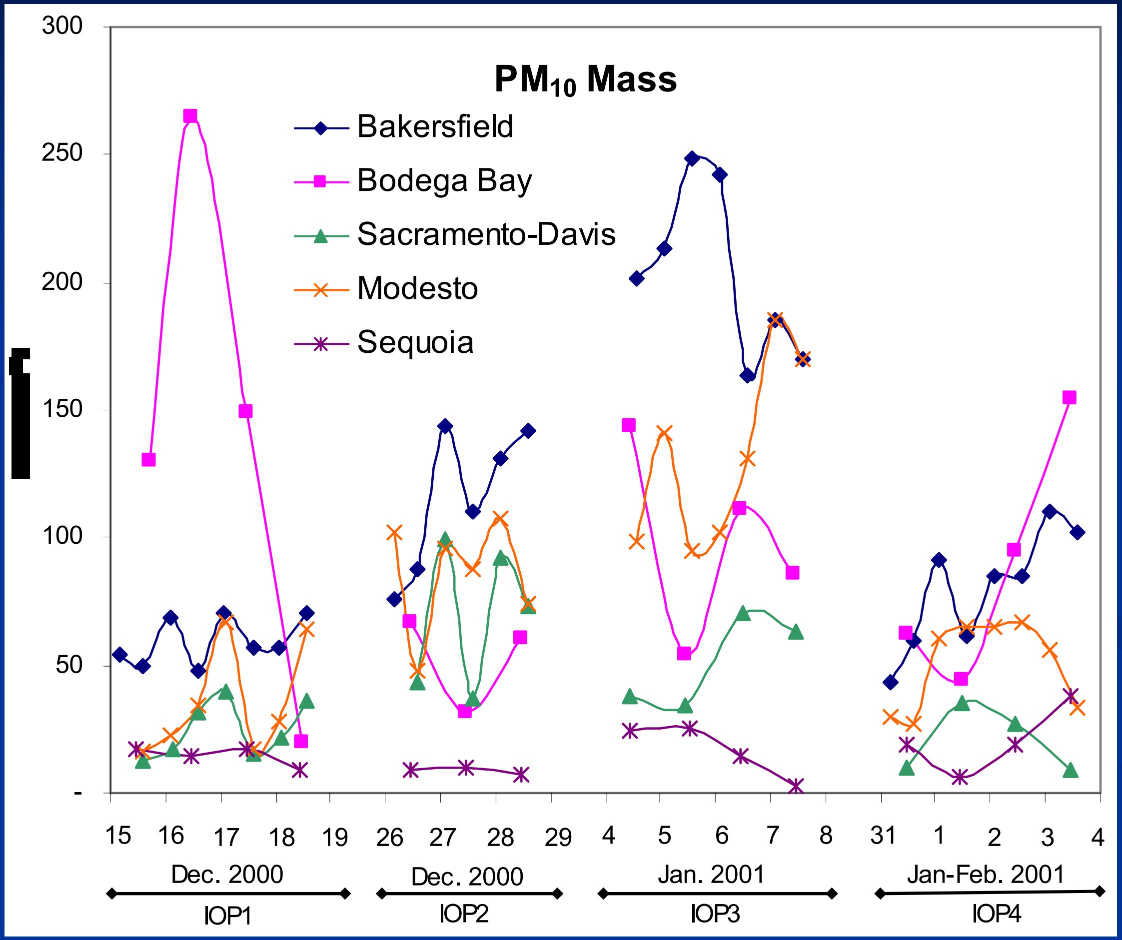
Stage 5: 1.8 – 1.0 µm
Stage 6: 1.0 – .56 µm
Stage 7: .56 – .32 µm
Stage 8: .32 – .18 µm
Stage 9: .18 – .10 µm
Stage 10: .10 – .056 µm

Can add all six stages to get a second measure of $PM_{1.8}$

Sample Times and Meteorology

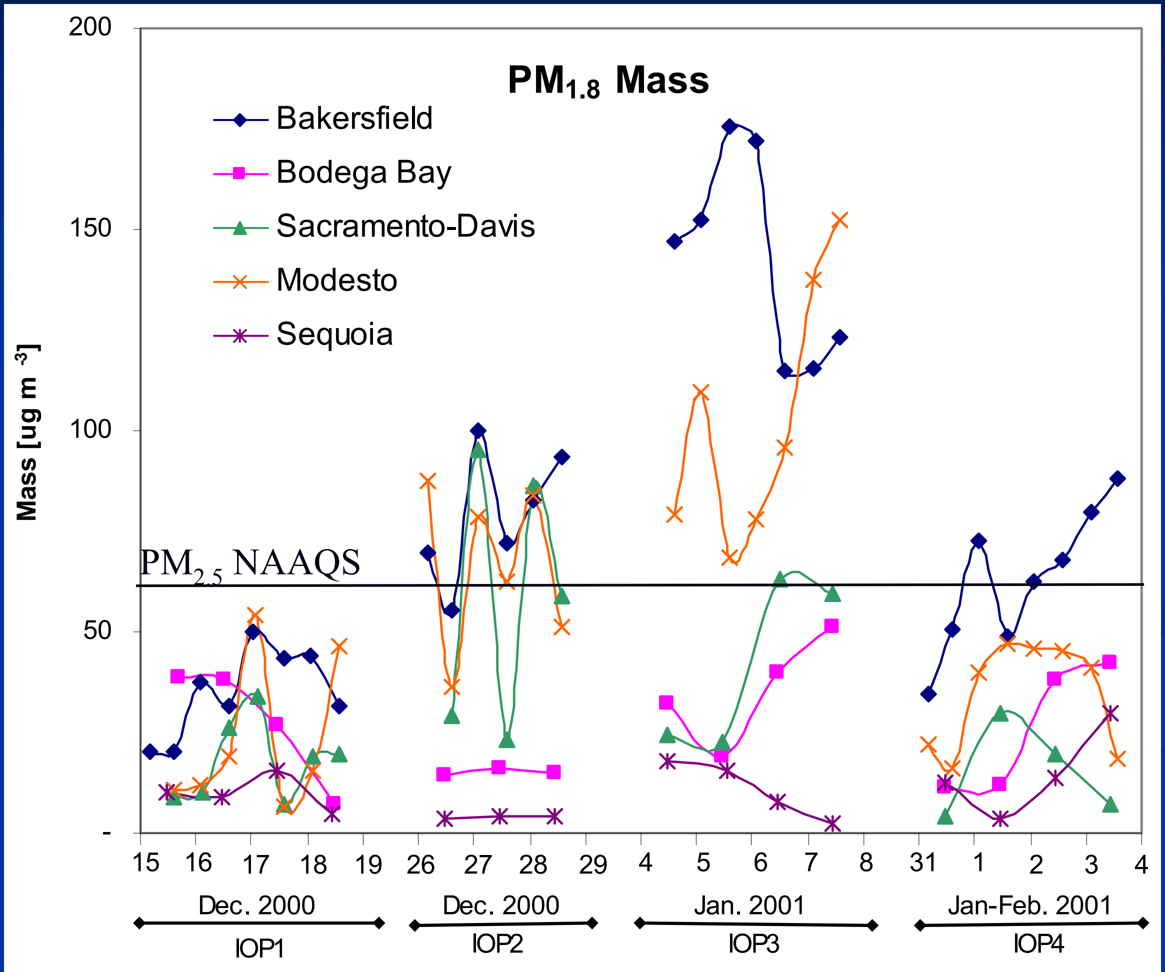


Gravimetric PM_{10} Results



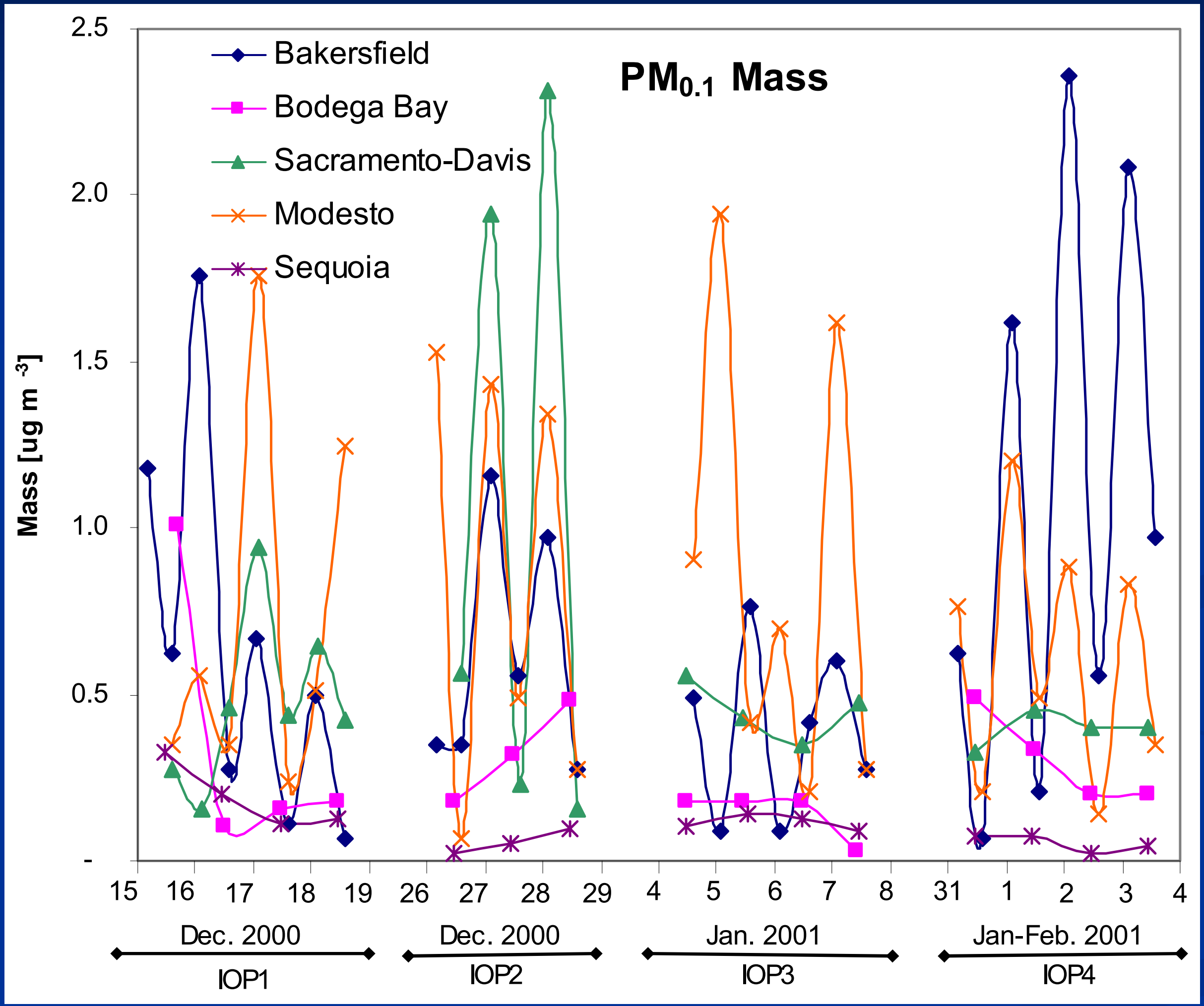
- Increase in PM levels over the course of stagnation events in the SJV
- No discernable diurnal pattern
- Sea-salt at the coast and very low levels at Sequoia

Gravimetric $PM_{1.8}$ Results



- Similar pattern to that seen for PM_{10}, less sea salt at Bodega Bay
- Most of PM_{10} is $PM_{1.8}$
- Increase in PM levels over the course of stagnation events in the SJV
- No discernable diurnal pattern, except for IOP2 on the valley floor
- NAAQS exceeded by a factor of 2-3

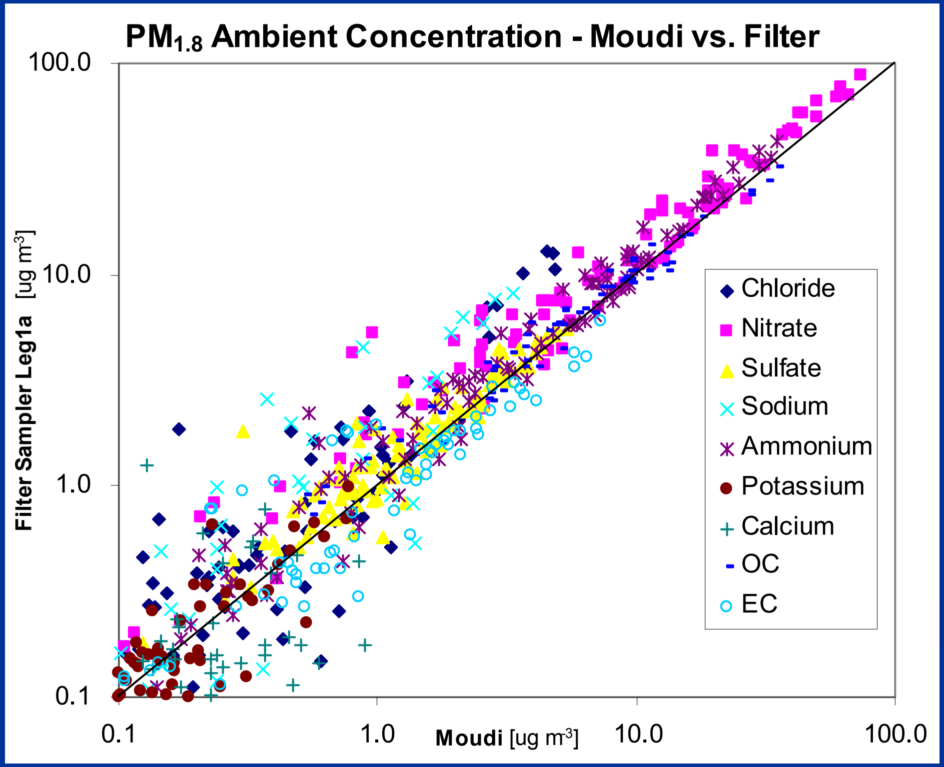
Gravimetric $PM_{0.1}$ Results



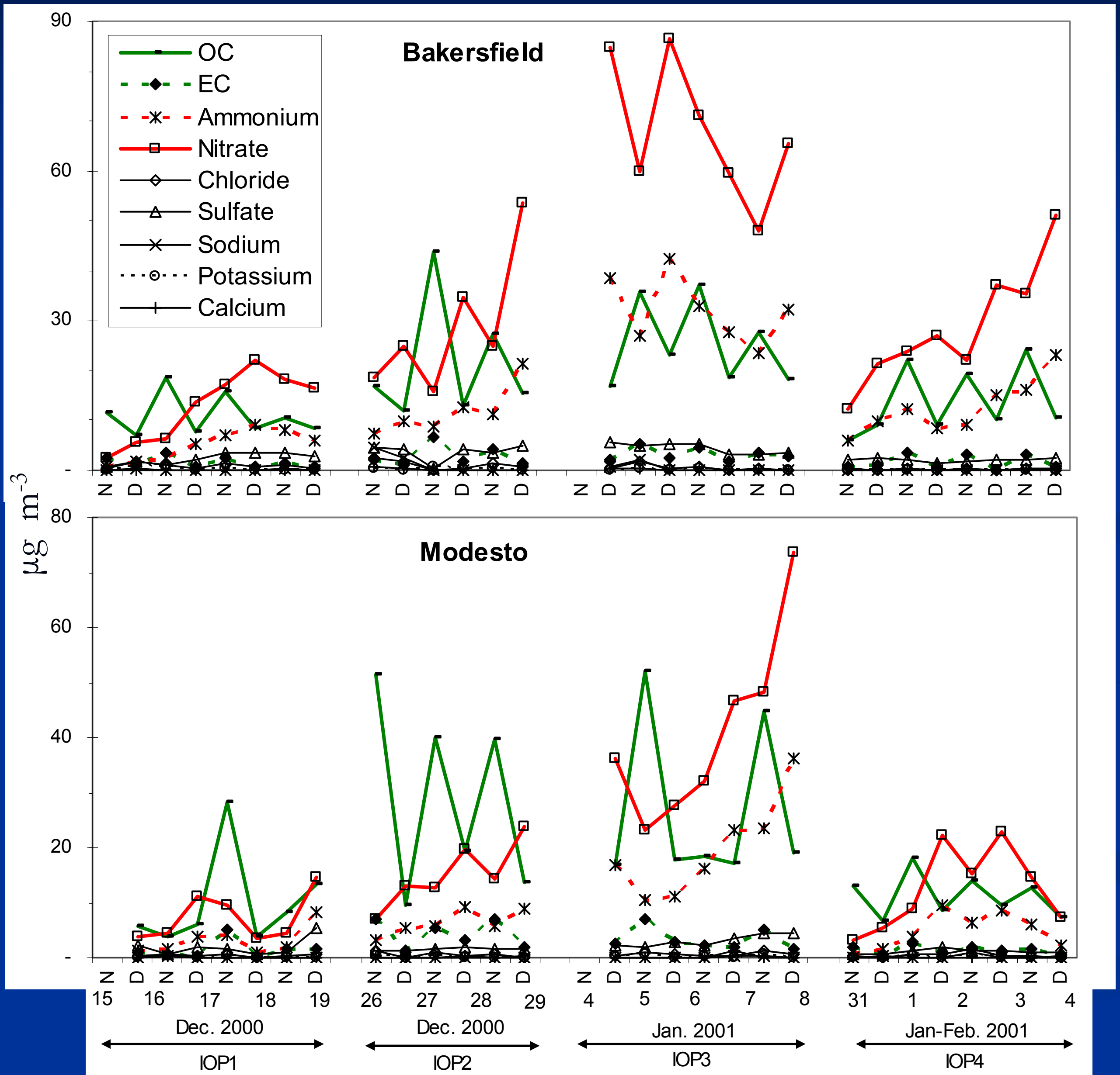
- Pattern very different from that seen for PM_{10} and $PM_{1.8}$
- While levels are high when compared to previous measurements they are only a small fraction of $PM_{1.8}$
- Concentrations are highly diurnal with higher night time measurements
- Concentrations do not increase during stagnation events. At Bakersfield they *decrease*

Chemistry

- Organic and Elemental Carbon analysis – Niosh
- Water soluble ions – Ion Chromatography
- Trace metals - ICPMS

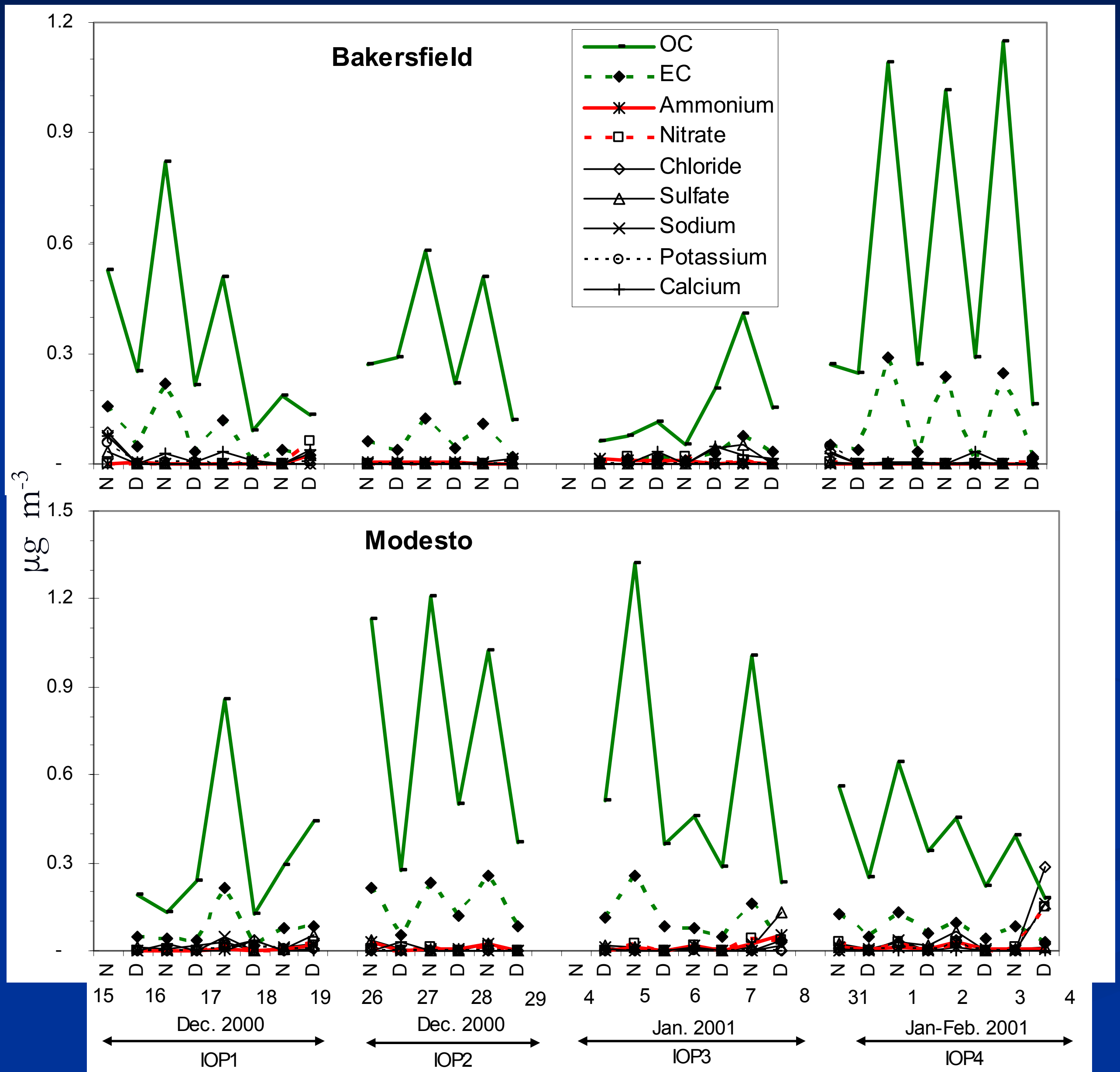


$PM_{1.8}$ Chemical Composition



- Ammonium and nitrate
  - most abundant species
  - weakly diurnal with higher daytime concentrations
  - increase during stagnation
- Carbon OC and EC
  - diurnal with higher nighttime concentrations
  - less increase during stagnation

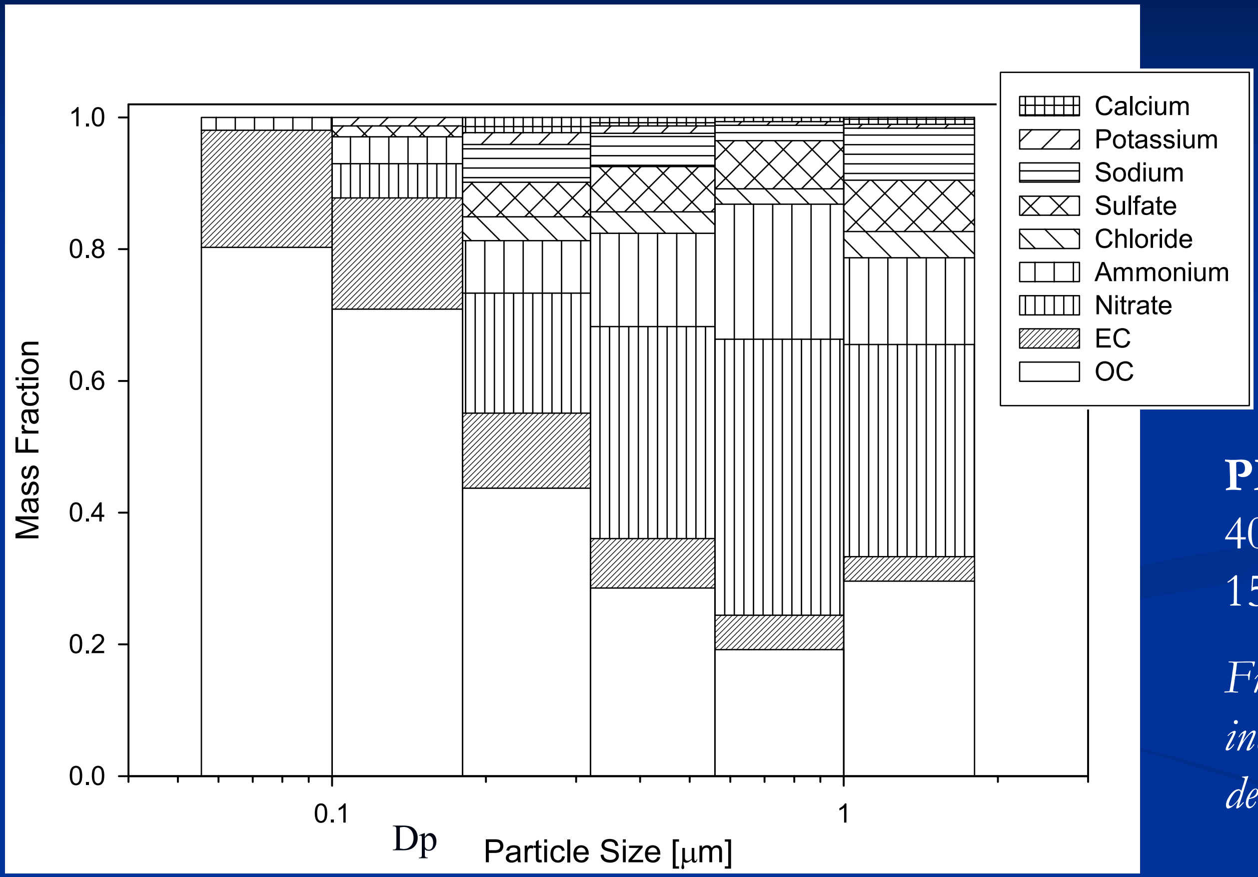
$PM_{0.1}$ Chemical Composition



- Ammonium and nitrate
  - barely measurable

- Carbon OC and EC
  - diurnal with higher nighttime concentrations
  - no increase or decrease during stagnation

Size Dependent Particle Composition



$PM_{1.8}$
40-75% Ammonium nitrate
15-50% Carbon

Fraction of ammonium nitrate increases, while fraction carbon decreases, with $PM_{1.8}$

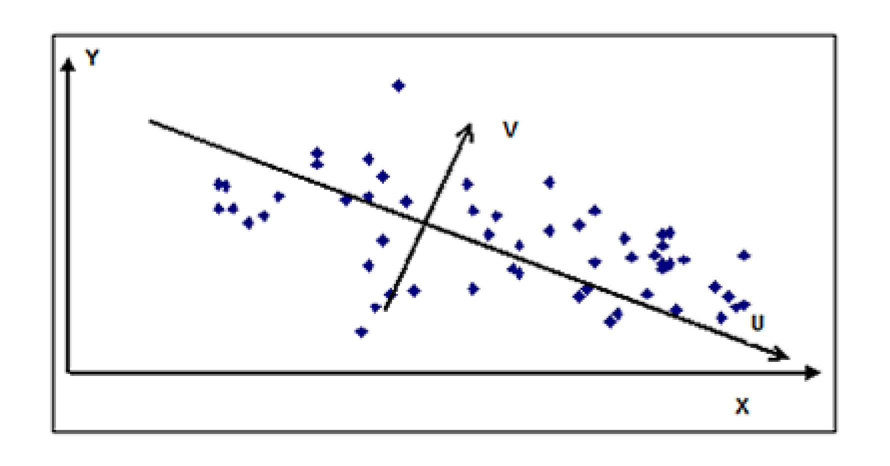
$PM_{0.1}$
98% Carbon,
irrespective of concentration

Principal Component Analysis

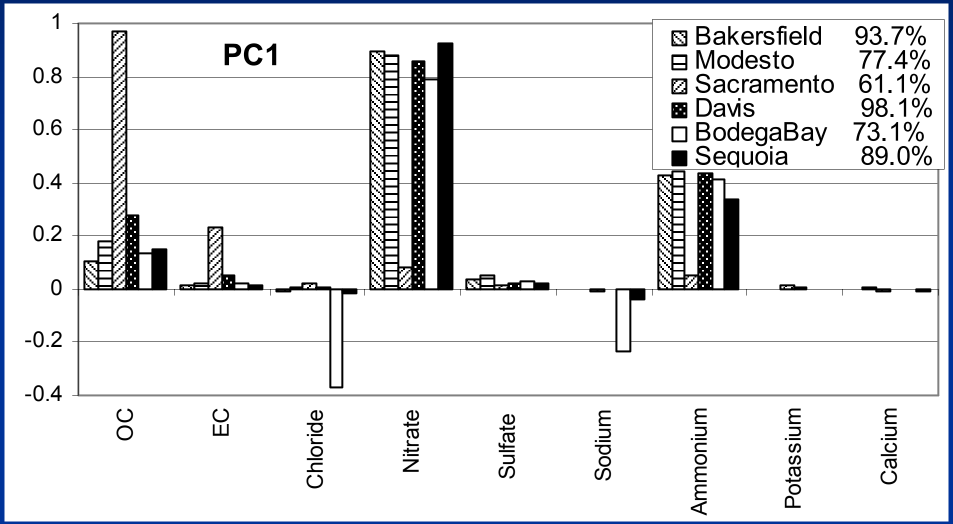
- Two separate particle types – carbon and ammonium nitrate. Use PCA.

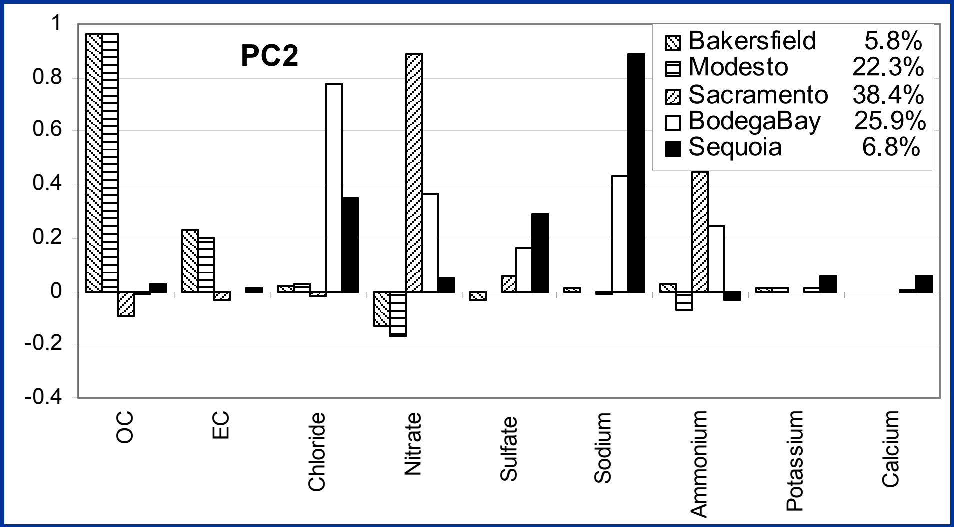
The central idea of principal component analysis is to reduce the dimensionality of a data-set consisting of a large number of interrelated variables, while retaining as much as possible of the variation present in the dataset. This is achieved by transforming to a new set of variables, the principal components (PC's), which are uncorrelated, and which are ordered so that the first *few* retain most of the variation present in *all* of the original variables.

I.T. Jolliffe on
Principal Component Analysis



Principal component analysis of $PM_{1.8}$

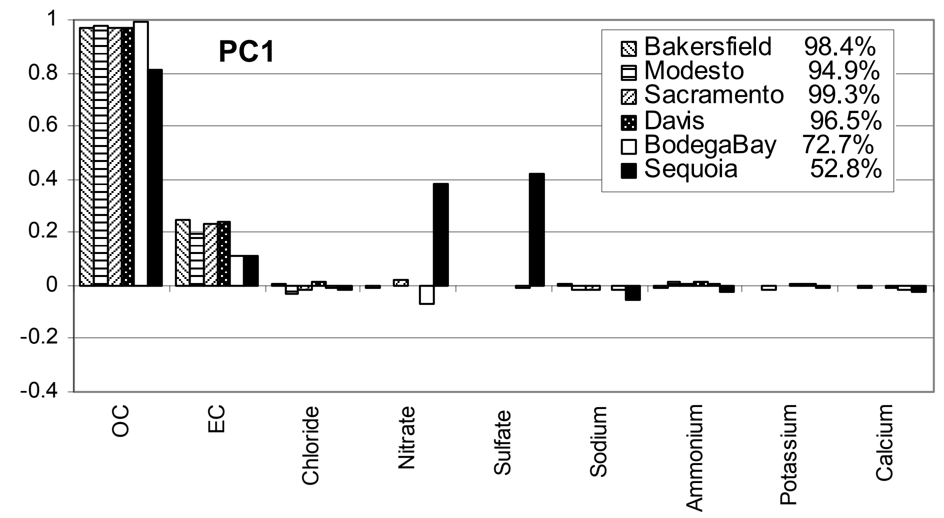


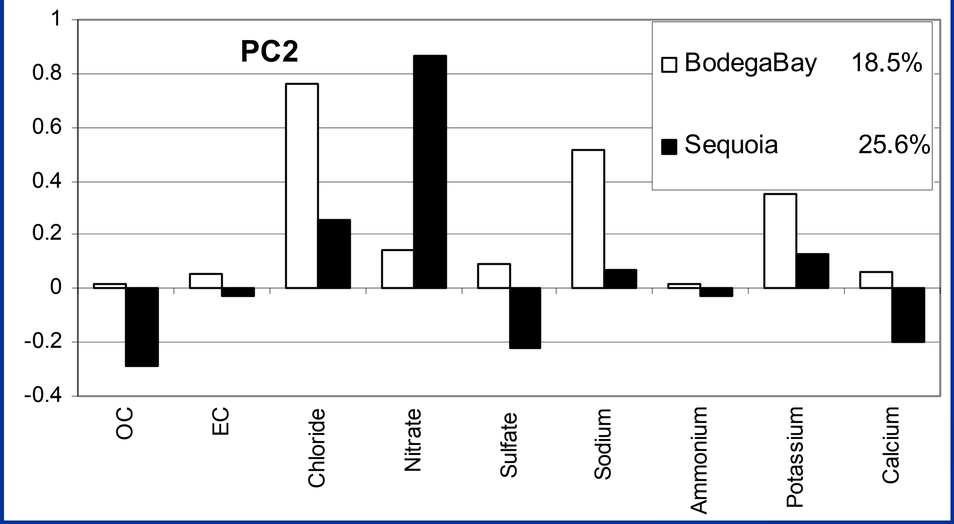


- PC1 is dominated my ammonium nitrate and to a lesser degree carbon, ***almost in the same ratio as found in*** $\boldsymbol{PM_{1.8}}$
- PC2 explains a much smaller fraction of total variance

*The percentage of variance explained by each principal component is shown in the key adjacent to the sampling location.

Principal component analysis of $PM_{0.1}$





- PC1 is dominated my carbon, and almost all the variance is contained in PC1
- PC2 explains a much smaller fraction of total variance. Some sea salt seen at Bodega Bay

*The percentage of variance explained by each principal component is shown in the key adjacent to the sampling location.

Two particle types:

Ammonium Nitrate is a secondary particle species:

$$NH_{3(g)} + HNO_{3(g)} \leftrightarrow NH_4NO_{3(p)}$$

Equilibrium between gas and particle phase in dependent on temperature and RH.

$T\downarrow$, $RH\uparrow$ $\rightarrow$ particle phase

$T\uparrow$, $RH\downarrow$ $\rightarrow$ gas phase

Wintertime temperature and RH in the SJV favors the particle phase even during the day.

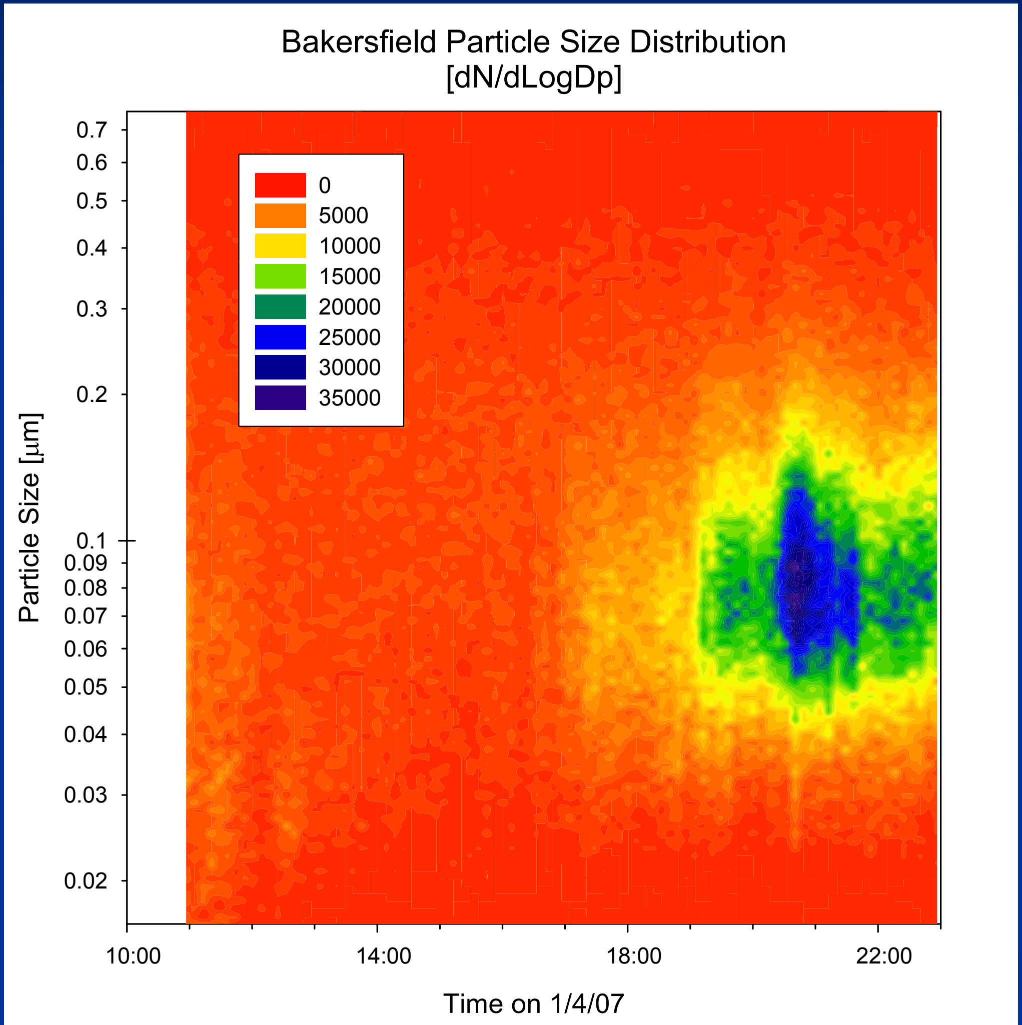
Two particle types:

Carbon is a primary particle species:

Source	MOUDI Stage	Particle Size [µm]
Gas Vehicle - Cat	Stage 9-10	0.056 – 0.18
Woodburning (pine,oak,eucalyp)	Stage 9	0.1 – 0.18
Medium Duty Diesel	Stage 9	0.1 – 0.18
Gas Vehicle – Non Cat	Stage 8	0.18 – 0.32
Meat Charbroiling	Stage 8	0.18 – 0.32
Cigarette Smoke	Stage 7	0.32 – 0.56

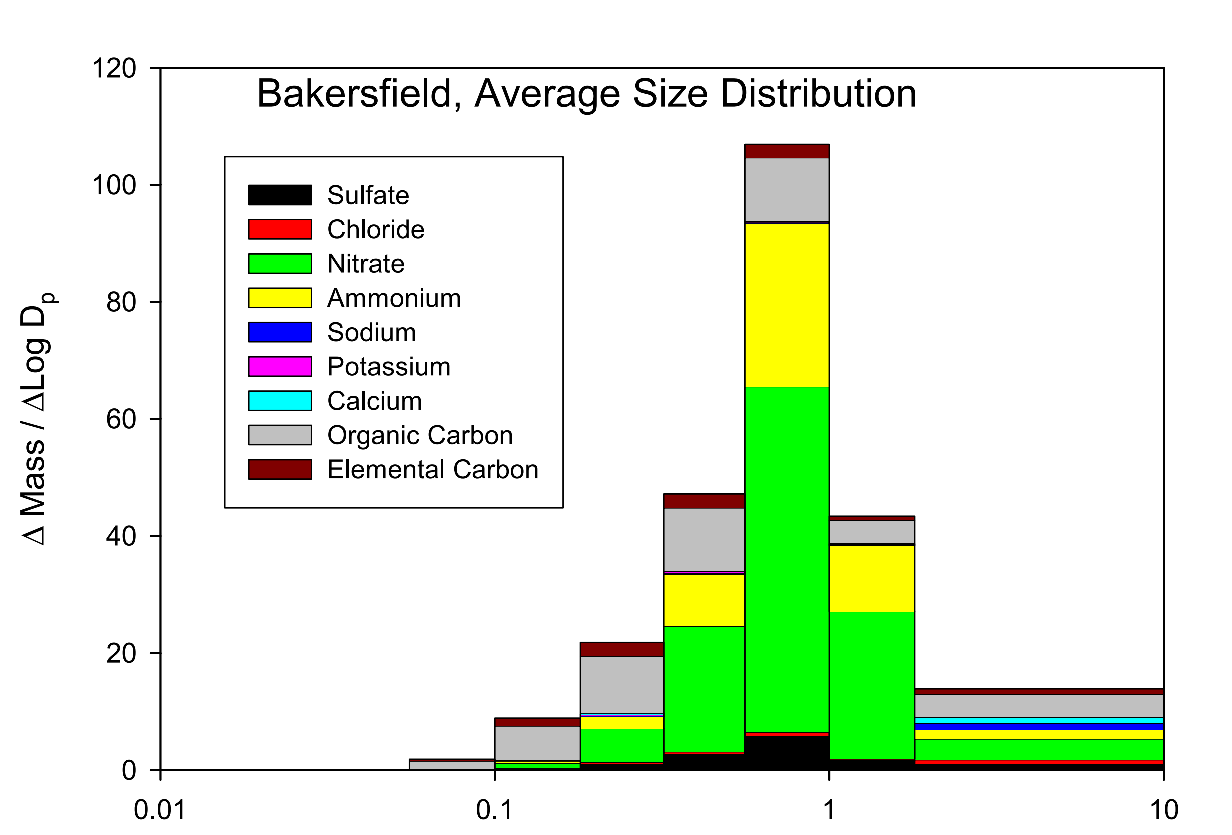
Source: Kleeman et al.

Particle Number Size Distribution



- Particle number measurements peak late in the evening, 21:00, and in the size range where we would expect mostly organic and elemental carbon
- This is consistent with $PM_{0.1}$ comprising mainly directly emitted carbon particles from combustion such as traffic and wood burning.

Bakersfield, Average Particle Size distribution

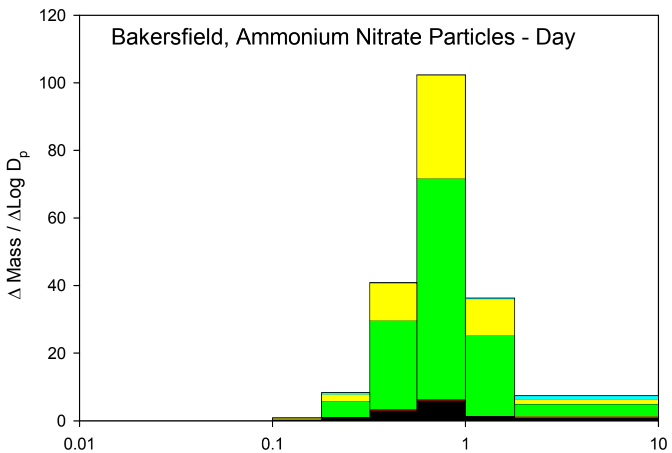


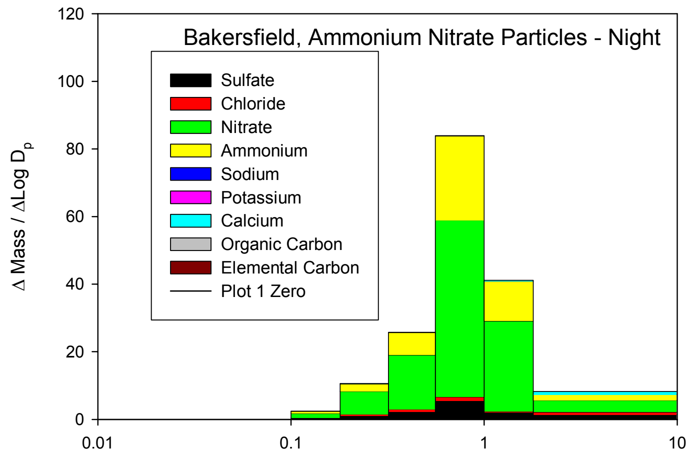
- During winter time stagnation events PM is dominated by ammonium nitrate with a peak in the mass distribution between 0.56-1.0μm
- Carbon and other species play an important but much smaller role.

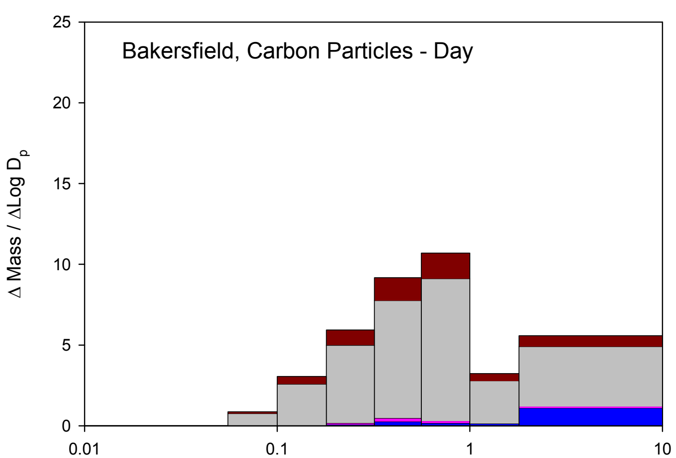
Bakersfield, Average Particle Size distribution

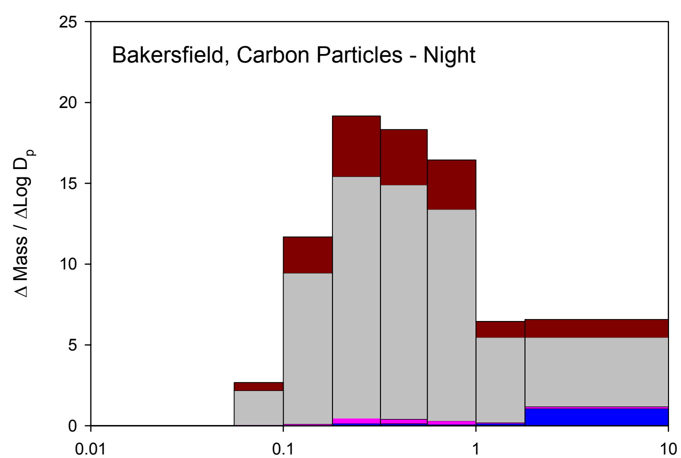
Day

Night









Ammonium Nitrate

- Peak at 0.56-1.0μm
- Slightly greater concentrations during day

Carbon

- Peak at 0.56-1.0μ during day, at 0.18-0.32 μm during night
- Greater concentrations during day, by a factor of 2 or 3

Processes that effect particle size distribution:

- Condensation

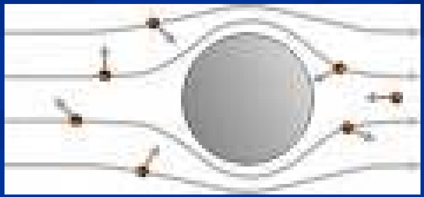
  Condensation is the change in matter of a substance to a denser phase, such as a gas (or vapor) to a liquid

- Deposition

  The removal of particles to the earths surface due to gravitational settling

- Coagulation

  colliding particles tend to adhere forming a single large particle. Coagulation rates is larges between different sized particles

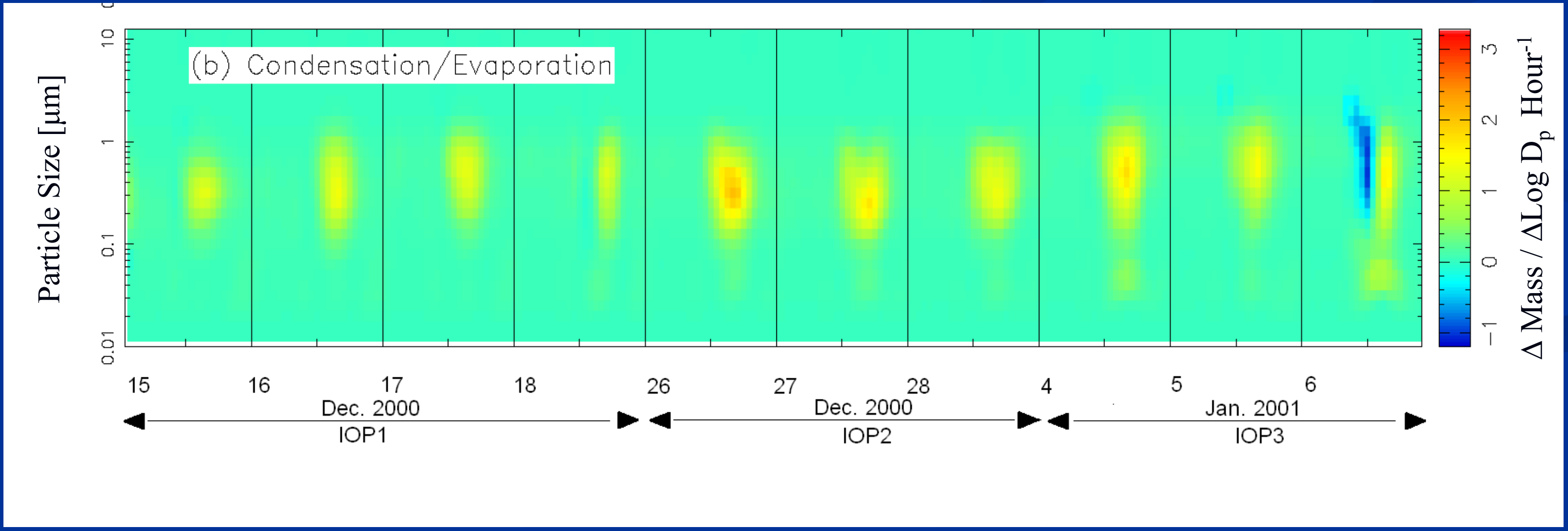


Processes that effect particle size distribution:

- Condensation

Ammonium – Nitrate – Sulfate is considered hygroscopic and condensation onto those particles may explain their growth.

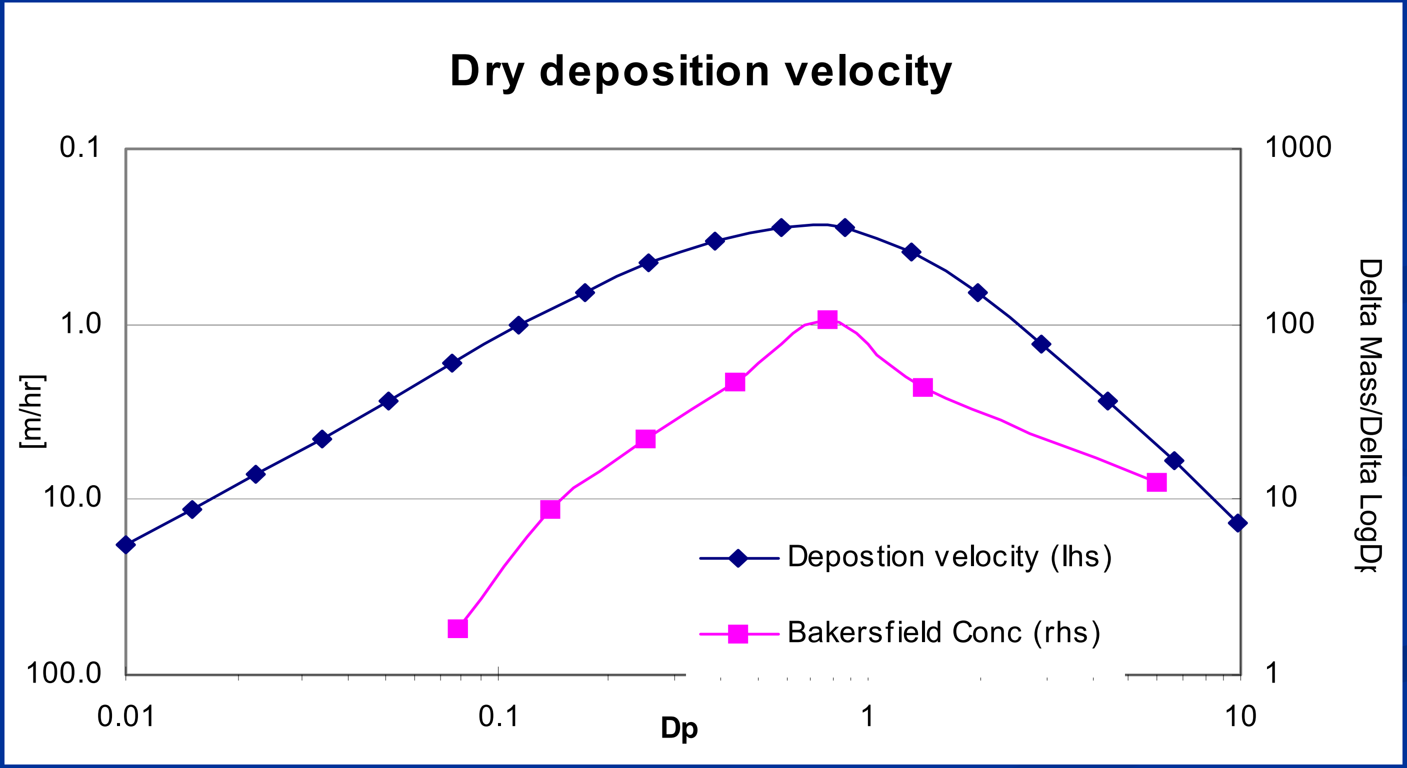
Ammonium – Nitrate to Carbon ratio in 560-1000nm range does not suggest carbon particles become part of the accumulation mode via condensation of ammonium nitrate exclusively.



Processes that effect particle size distribution:

- Deposition

The shape of the ammonium nitrate particles is determined by dry deposition



Conclusions
Ammonium – Nitrate – Sulfate Particles

- Grow through condensation of gas-phase NH_3 and HNO_3, possibly initially onto sulfate particles.

•Deposition gives us peak in 560-1000nm size

•Temperature and RH favors particles phase of ammonium nitrate at all times during winter in the SJV

•The daytime coupling of atmospheric layers brings additional ammonium nitrate from the upper layer to both urban and rural areas.

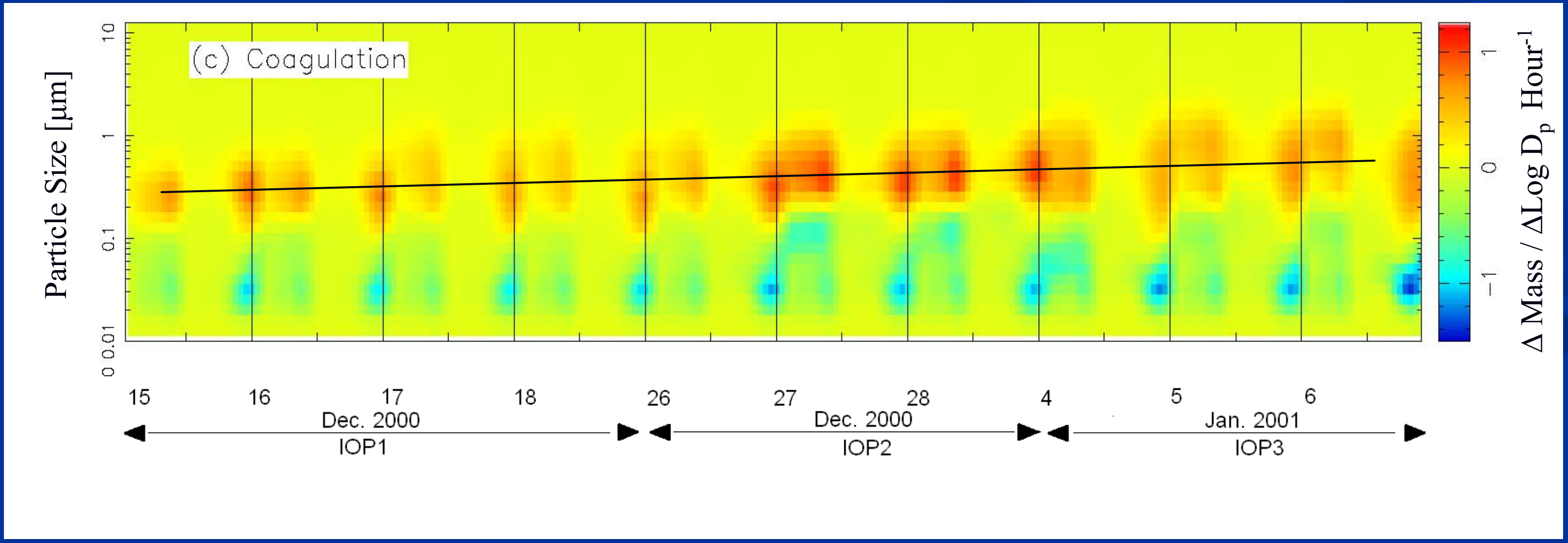
•Daytime photochemistry assist in the conversion of NOx to HNO3, which in turn forms additional ammonium nitrate particles

Processes that effect particle size distribution:

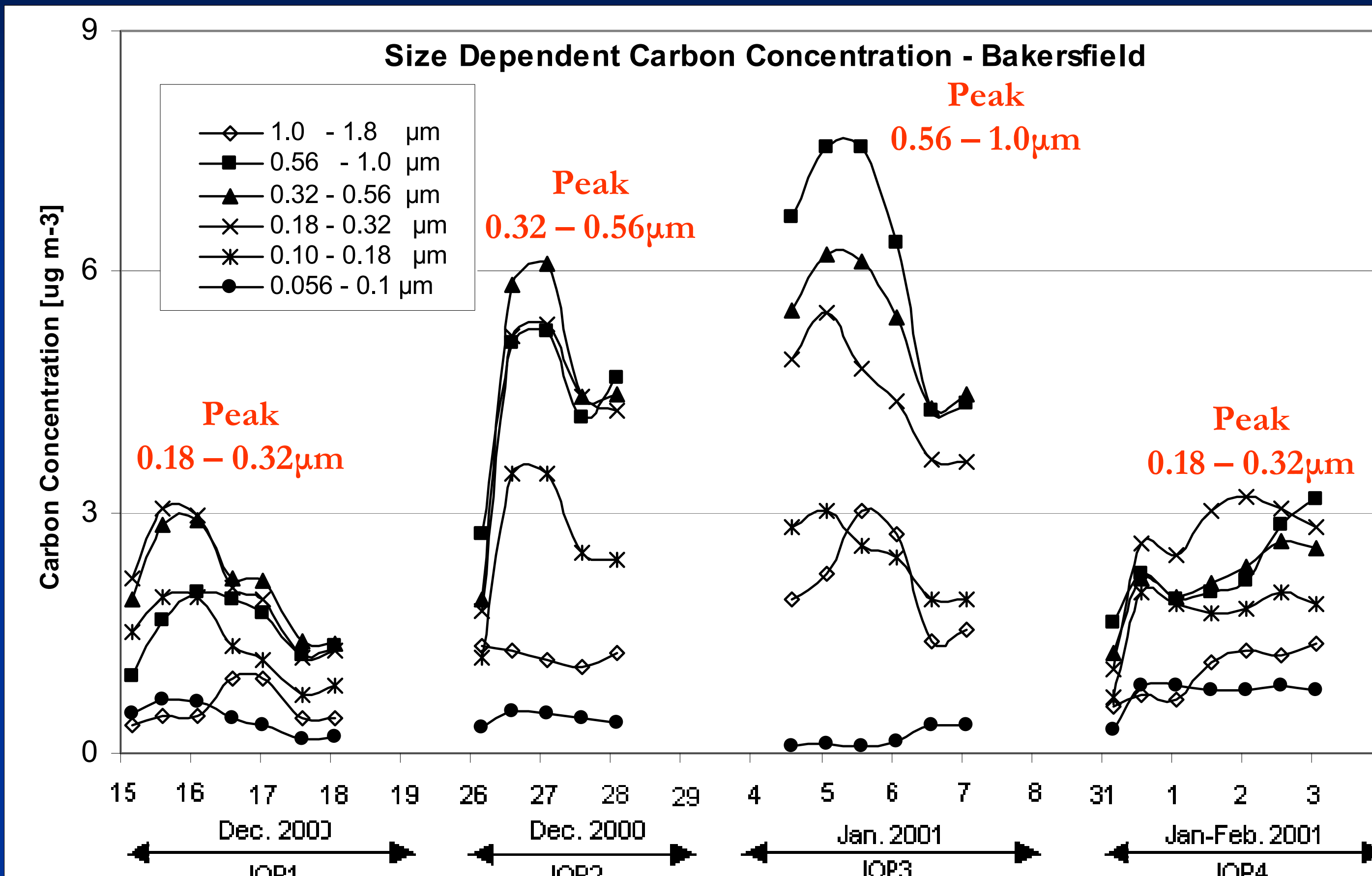
- Coagulation

The small directly emitted carbon particles are transferred to larger sizes via coagulation, especially during peak emissions at night and early mornings

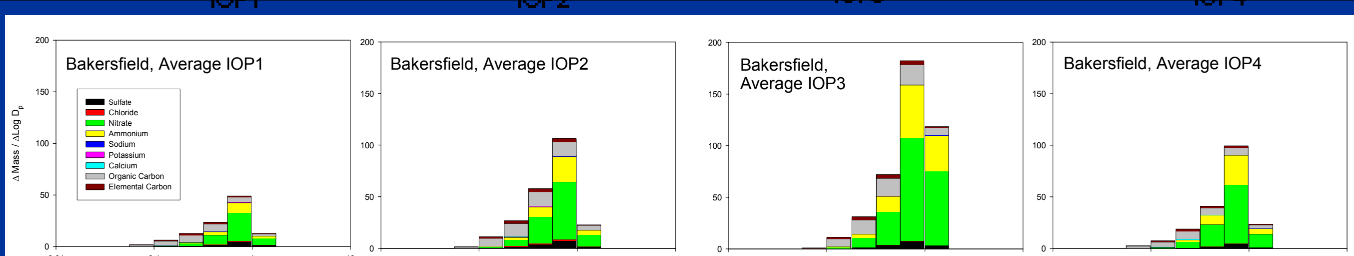
As the stagnation event continues the ammonium nitrate particle size distribution takes shape and affect the size of particles carbon coagulates with.



Size Dependent Average Daily Carbon Concentrations



- The size of the carbon peak concentration changes during the stagnation events
- The peak is dependent on coagulation with existing size distribution and growth.



Bakersfield, average size distribution by IOP ↑

Conclusions - Carbon Particles.

- Are primary particles emitted as small particles mainly at night (traffic, home heating) and early morning (traffic)

- “Grows” mainly due to coagulation with existing particles

- Long residence times in the upper layer allows a shift in the size distribution which is brought to the ground level during daytime.

Overall Conclusions

•Data corroborates the conceptual model developed earlier

•Box model suggest the formation of secondary organic aerosol is negligible under cool winter conditions

• Duration of winter-time stagnation events determine the final maximum particle mass concentration

•Carbon particles and ammonium/nitrate/sulfate particles exist separately in the San Joaquin Valley until coagulation mixes them in the accumulation mode

•Separate strategies will be needed to reduce these two types of particles

Achieving PM Reduction

- Reduce sources of carbon or sources of ammonium nitrate ?

- What has occurred since CRPAQS ?

Reductions in Carbon Emissions

RULE 4901 WOOD BURNING FIREPLACES AND WOOD BURNING HEATERS
(Adopted July 15, 1993; Amended July 17, 2003)

This has reduced PM in the form of organic and elemental carbon in the San Joaquin Valley

Ammonium Nitrate ?

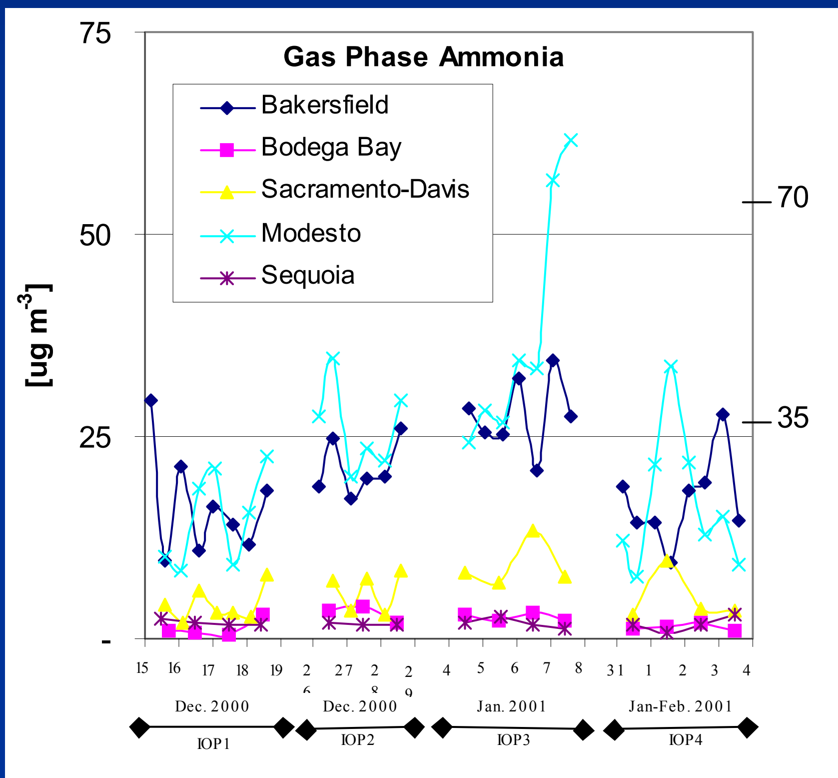
Ammonium Nitrate is a secondary particle species:

$$NH_{3(g)} + HNO_{3(g)} \leftrightarrow NH_4NO_{3(p)}$$

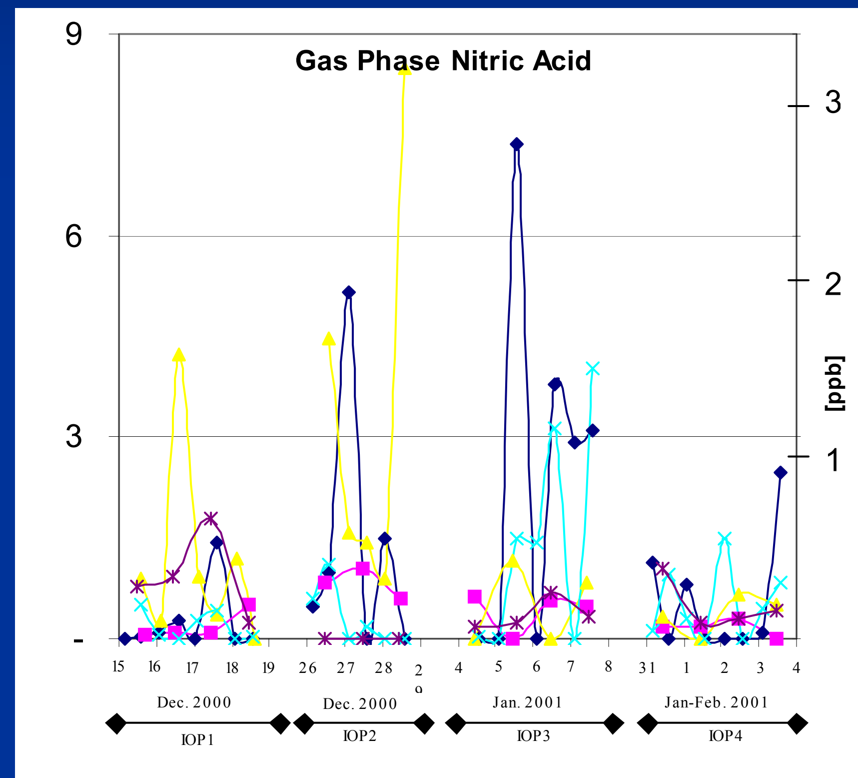
- Source of ammonia – dairies
- Source of nitric acid – transportation
  - $NO_2 + OH \rightarrow HNO_3$
  - $N_2O_5 + H_2O \rightarrow 2HNO_3$
  - $NO_2 + H_2O \rightarrow HNO_3 + HONO$

Ammonium Nitrate Precursors

Ammonia



Nitric Acid

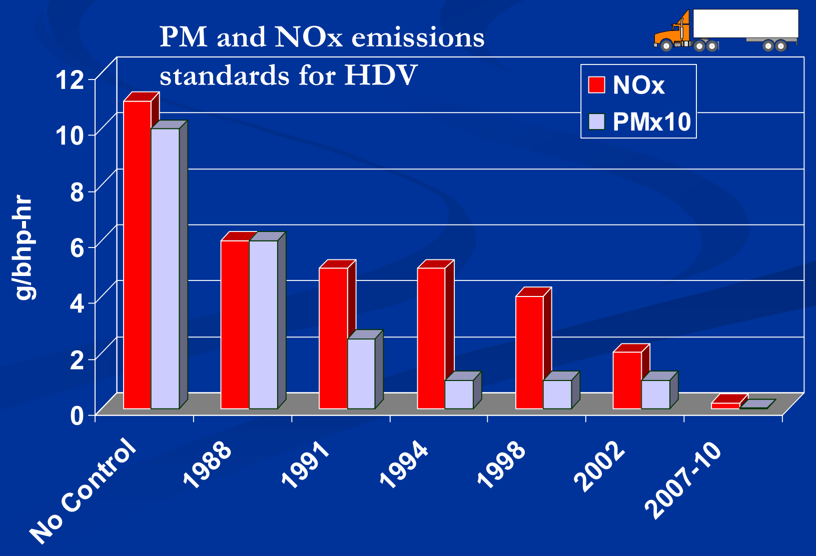


The production of ammonium nitrate is limited by nitric acid.

Need to reduce NOx emissions

Ammonium Nitrate

- The challenge continues to reduce ammonium nitrate.
  - Emissions standards for heavy duty diesels reduced by 90% by 2010
  - Agricultural electrification
  - Regulations aimed at reducing NOx to meet ozone standards are numerous and will also help in meeting the PM_{10}, $PM_{2.5}$ standards



Thank you

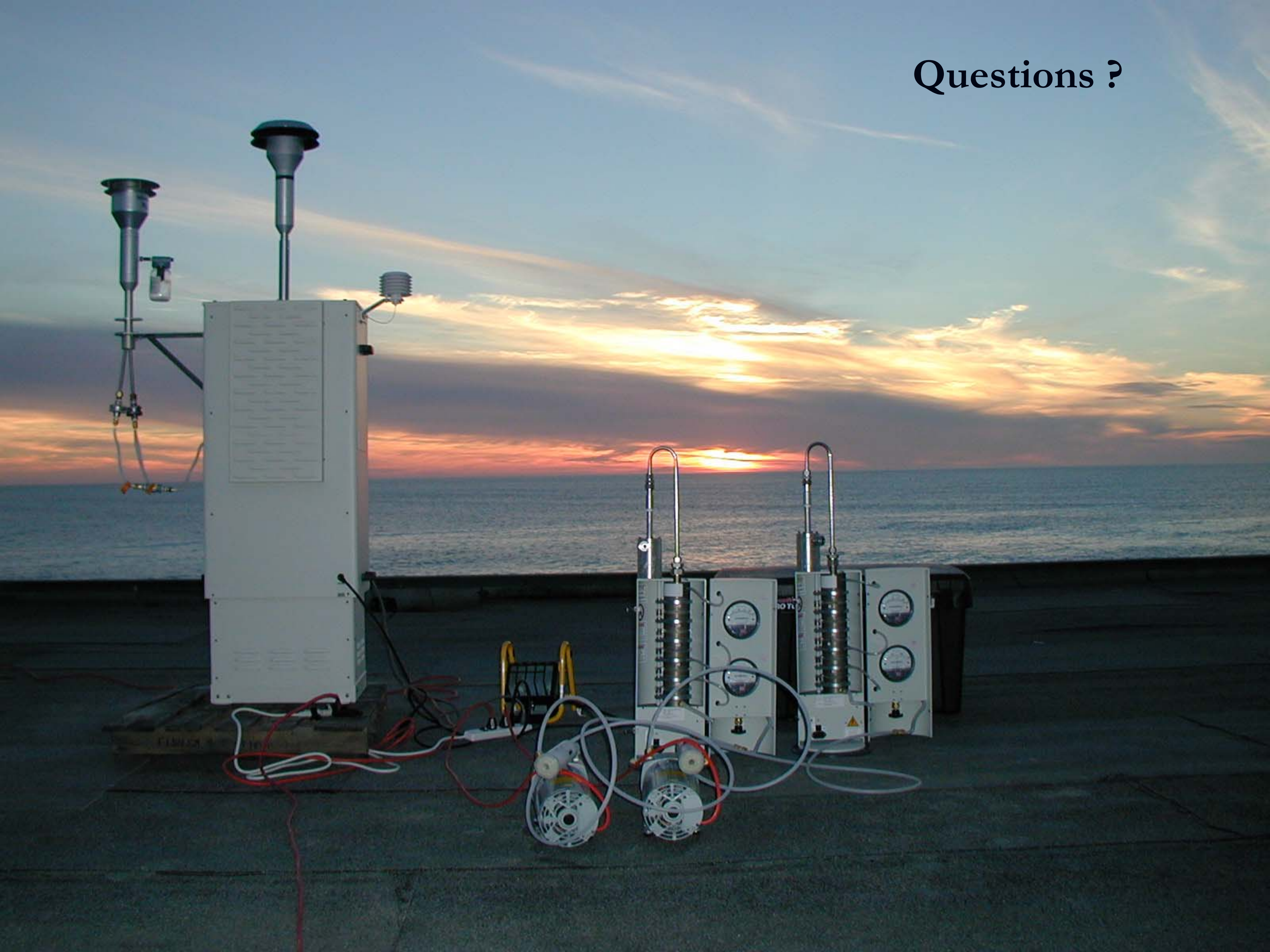
For more information contact

Jorn Dinh Herner
California Air Resources Board
Research Division
1001 “I” Street. PO Box 2815
Sacramento, CA 95812
Ph# 916.324.9299
email: jherner@arb.ca.gov

See also

Herner, Jorn D., Qi Ying, Jeremy Aw, Oliver Gao, Daniel P.Y. Chang, and Michael J. Kleeman (2006). Dominant Mechanisms that Shape the Airborne Particle Size and Composition Distribution in Central California. *Aerosol Science and Technology.* Vol. 40 Issue 10, p827-844.

Herner, Jorn D., Aw, Jeremy, Gao, Oliver, Chang, Daniel P., Kleeman, Michael J. (2005). Size and Composition Distribution of Airborne Particulate Matter in Northern California: I--Particulate Mass, Carbon, and Water-Soluble Ions. *Journal of the Air & Waste Management Association*, Jan2005, Vol. 55 Issue 1, p30-51


Questions ?