Characterizing the Formation of Secondary Organic Aerosols

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Research Team

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Objective

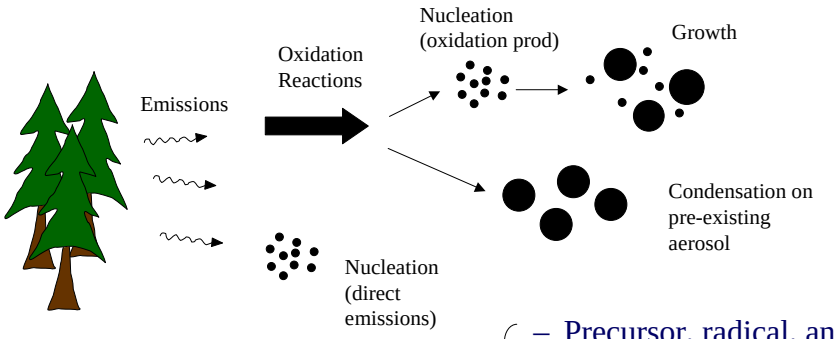
To investigate SOA formation under actual field conditions to establish a rich data set that will be analyzed to characterize SOA formation from hydrocarbon emissions from a number of sources, at the regional scale.

What is Secondary Organic Aerosol?

SOA is formed in the atmosphere by the mass transfer to the aerosol phase of low vapor pressure products formed from oxidation of organic gases (emissions).

The oxidation products of volatile organic emissions are less volatile than their precursors; hence the products partition between the gas and particle phase.

Biogenic SOA Formation



SOA formation from biogenic precursors depends upon

- Precursor, radical, and aerosol concentrations
- Volatility of products and precursors
- Ambient conditions

SOA Significance

- SOA production is very difficult to estimate well
- SOAs are important particle sources in the Central Rocky and Gulf of Mexico regions
- SOAs contribute to visibility degradation in scenic wilderness areas where oil and gas E&P activities occur
- SOAs and other aerosols influence atmospheric processes at the urban, regional, and global scales and affect ozone, visibility, ambient PM concentrations, climate, and human health

Regional Haze Rule

- Natural visibility conditions represent the ultimate goal of the regional haze rule
- Must be able to distinguish natural (biogenic) emissions from anthropogenic emissions
- Must be able to model their formation, processing, and source strength to comply with regional haze rule.

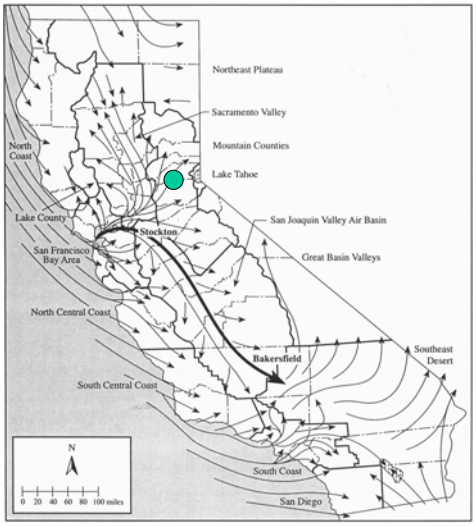
This is currently not possible

Experimental Approach

- Collect simultaneously aerosol, VOC, other trace gases, and meteorology data
- Use measures of black carbon, CO, and other tracers to distinguish anthropogenic- and biogenic-influenced air masses
- Examine and characterize relationships between particle concentrations and size distributions, VOCs, NOy, O_3, and important meteorological factors.

Blodgett Air Parcel Contributors

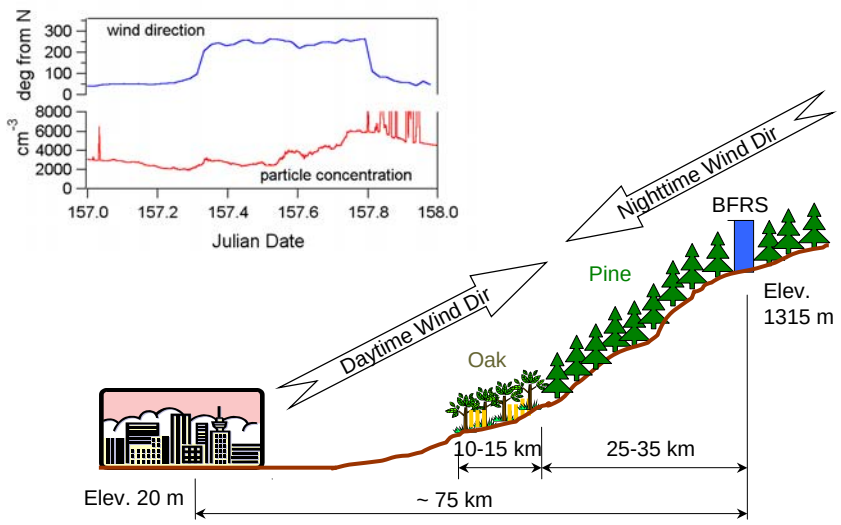
- Clean coastal inflow
- Urban outflow-Bay Area
- Agricultural outflow upwind of Sacramento
- Urban outflow-Sacramento
- Night-time Inflow from Sierra Nevada



Site Description

- Heavily forested site on western slope of Sierra Nevada, CA
- 38.9˚ N, 120.6˚ W; elev. 1315 m-75 km NE of Sacramento
- Primary species is ponderosa pine - known terpene emitter
- Consistent wind patterns
  - Carried biogenic and anthropogenic emissions during day and primarily biogenic emissions at night
- Field measurements: Fall 2000, summer and fall 2001, spring, summer 2002, and summer, fall 2003.

Air parcel behavior



Task I

- Review and asses SOA models and studies to identify areas of impact with experiment.
- Status: Considerable effort devoted, summarized in recent report, and ongoing for life of project.
- Summary: Have reviewed smog chamber experiments, modeling studies of SOA formation, models, chemical kinetics of reactive hydrocarbon species, thermodynamics of condensed phase organics, and advances in partitioning theories.

Task II

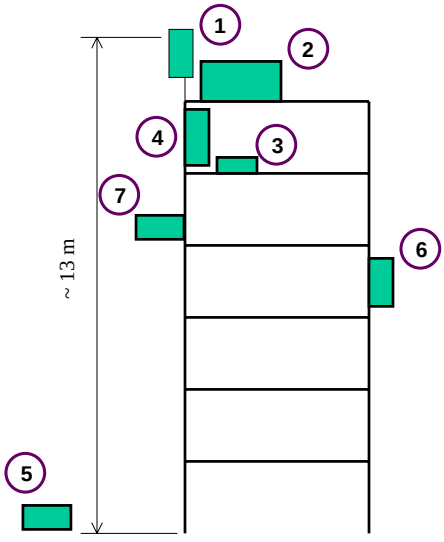
- Plan and prepare for field measurements
- Status: Completed
- Summary: This task involved considerable coordination with other investigators and has been completed. Added new instruments and filter measurements in second year, plus an aethelometer at an upwind urban site.

Task III

- Conduct experimental campaign in summer/fall 2002 and 2003
- Status: Task III has been completed—results are shown in next few slides.
- Exciting results! Characterized particle growth events and transport and fate of forest fire emissions and their effect upon local particle loading and visibility.

Instrumented Tower

Aerosol Instrumentation



1. 2.5 μm cut-point cyclone inlet
2. Aethalometer: Black Carbon (ng/cm^3)
3. Condensation Particle Counter: Total Particle Counts (#/cm^3)
4. Scanning Mobility Particle Sizer: Particle Size Distributions (10-400 nm)
5. Optical Particle Sizer: Particle Size Distributions (0.1 – 2.5 μm)
6. Nephelometer: Scattered Light (km^{-1})
7. Filter Samplers: Particle mass and chemistry

Aerosol Instrument Operation

	2000	2001	2002	2003
CPC	10/5 – 11/21	7/12 – 10/20	5/9 – 11/13	8/6 – present
Nephelometer	10/5 – 11/11	7/12 – 11/5	5/9 – 11/13	8/6 – present
Aethalometer	9/28 – 11/21	7/12 – 10/24	5/9 – 11/12	6/23 - present
SEMS	N/A	7/12 – 10/24	5/29 – 11/13	7/31 – 11/19
Lasair	N/A	N/A	5/9 – 11/13	N/A

VOC and Meteorology Measurements

- Over 20 VOCs of size C_2-C_{10} measured with a gas chromatograph-flame ionization detector and proton transfer mass reaction mass spec.
  - Time resolution: 30 min avg each hour
  - Primarily biogenic: terpenes and isoprene
  - Biogenic oxidation products: Methacrolein and methyl-vinyl ketone
  - Primarily anthropogenic: Toluene
- CO, ozone, temp, RH, rain, PAR, wind direction and wind speed
- NO_2, PAN, and HNO_3 with thermal dissociation-laser induced fluorescence

Task IV

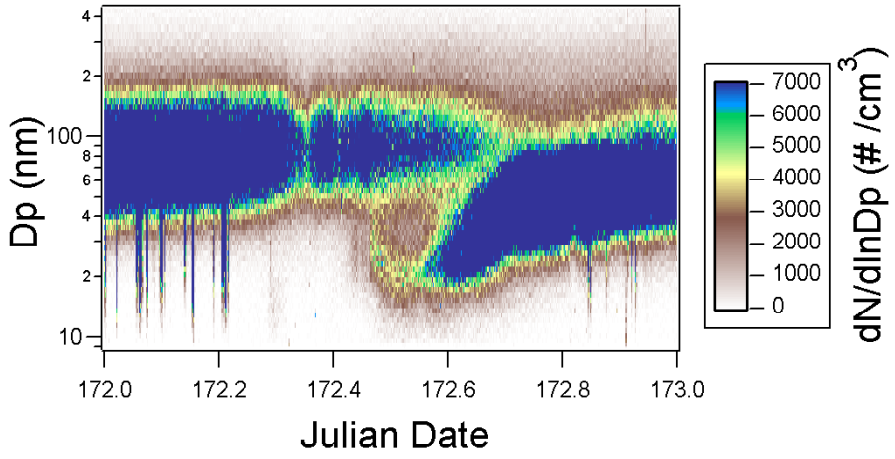
- Analyze data from field experiments
- Status: Ongoing and will be major focus of third year.
- Summary: Particle data sets are at level I and level II. Limited hydrocarbon data for 2002. A protocol for removing on-site diesel particle loading has been developed.
- ***Interesting results on particle growth events and on forest fires.***

Task V: Technology Transfer

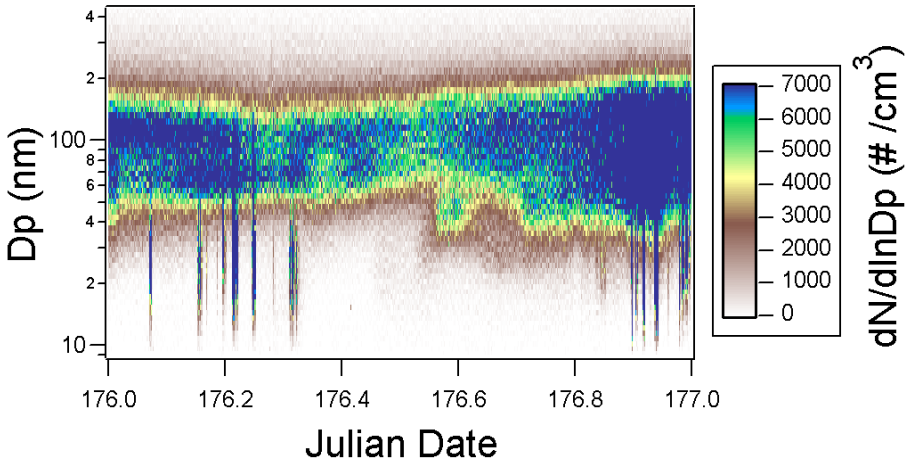
- Presentation of research results at meetings and forums: American Association of Aerosol Research, November 2002 and October 2003. Telluride workshop on aerosols, August 2002. DRI Workshop on SOAs, November 2002. Washington seminar, May 2003. California Air Resources Board seminar, June 2003.
- Report describing the work conducted in first 18 months submitted to sponsors
- Bimonthly progress reports to DOE

Particle Growth Event

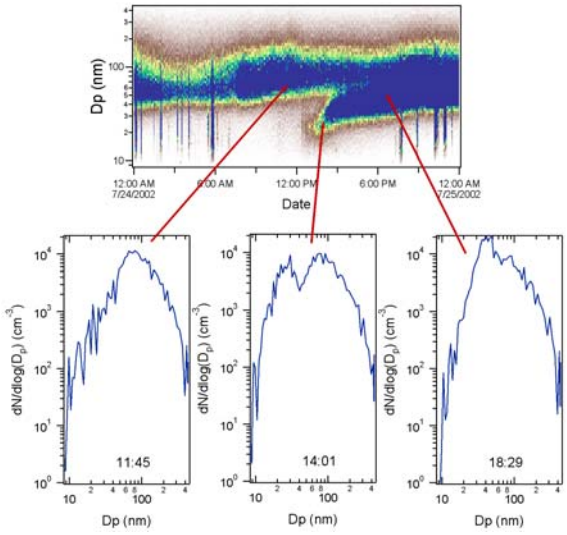
Mobility size distributions recorded every 3 minutes for 21 June 2002.



No growth June 25, 2002



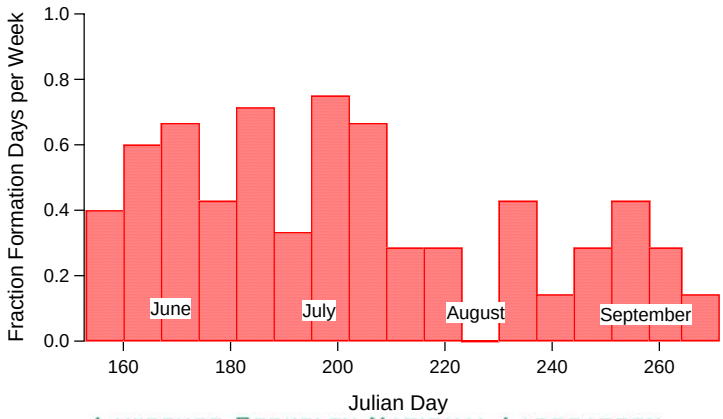
Size Distribution Evolution-6/24/02



Formation Events in 2002

Average daily maximum temperature

	June	July	August	September
Formation	**21.1**	**24.3**	**23.0**	**21.7**
No Formation	**25.0**	**28.7**	**26.5**	**24.8**



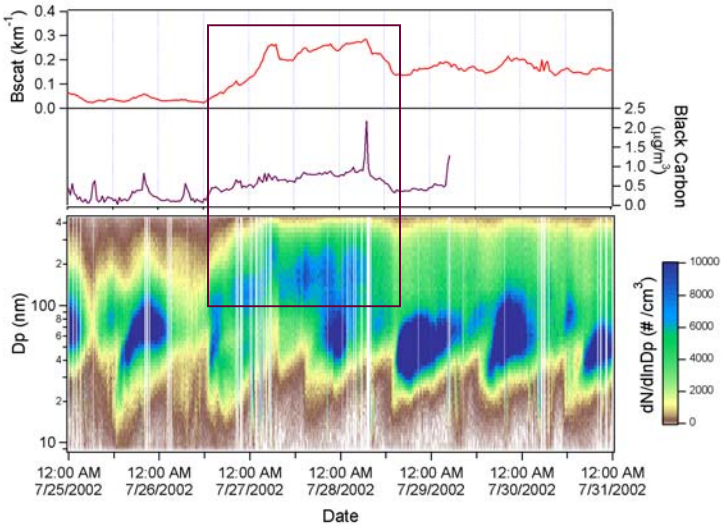
Growth Events

- Temperature is very influential
- Particle growth correlates in time with decreasing temperatures
- Total particle number is dominated by smaller particles
- Volume of particles in nuclei mode can be as high as 10 % of total particle volume
- Lifetime calculations show growth processes occur in forest

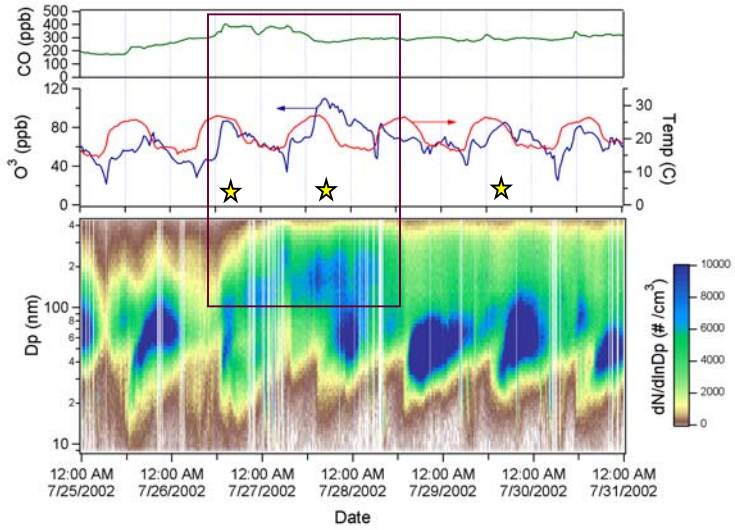
Growth Events

- Coagulation of small particles with larger ones is significant pathway of SOA into ambient aerosol
- Aerosol mass associated with growth events is same order of magnitude of measured concentrations of hydrocarbon oxidation processes.

Fire emissions lead to decreased visibility

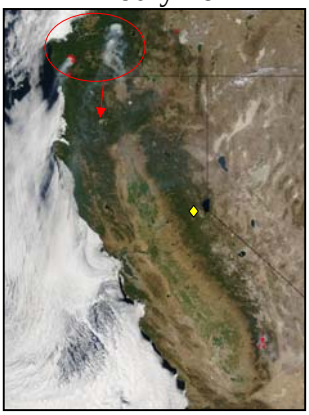


Fire events increase O_3 and CO



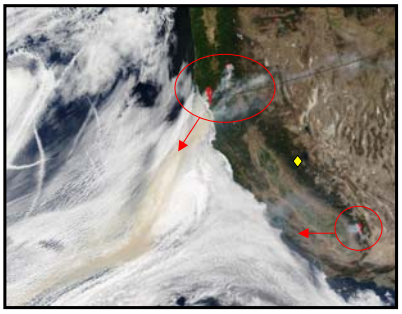
Meteorology lead to the effects seen on July 26 – 28, 2002

July 26



July 27

July 29



♦ Blodgett location
Red areas denote active fires

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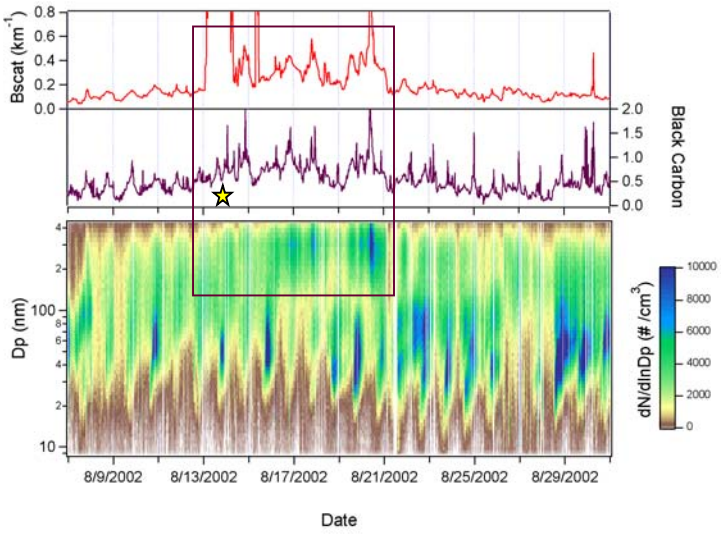
Much of August affected by fire



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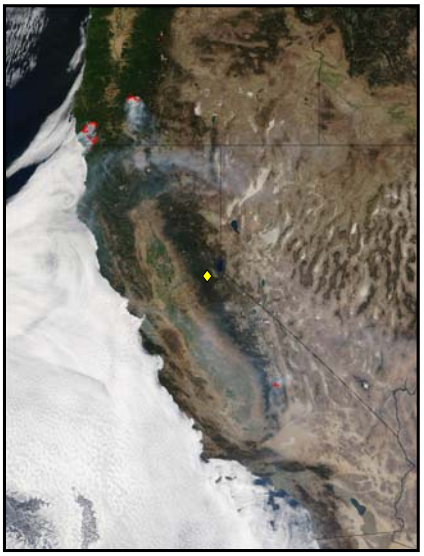
Fires in Oregon and California significantly effect air quality in the state

Aug 14, 2002



♦ Blodgett location

Red areas denote active fires

Summary and Conclusions

- Planned and conducted extensive set of field measurements
- Met deliverables and reporting requirements
- Current and Future research directed toward analysis and model validation
- Interesting results of consequence to visibility debate