Aerosol Chemical Composition at ESRL

**Emphases:**
- New capabilities
- Careful calibrations
- Process studies, mostly from aircraft
  *Build understanding of the entire atmosphere*

**Major instruments:**
- SP2: Single particle black carbon
  *Insights into climate forcing*
- AMS: Bulk, size-resolved composition
  *Fast, quantitative data to build correlations*
- PALMS: Single particle composition
  *Fundamental understanding of particles*
Aircraft

UND/NASA DC-8
0.2-12 km
PALMS

NOAA P-3
0.1-7 km
AMS, PALMS, SP2

Also many gas-phase instruments on each aircraft
Soot Photometer (SP2) Instrument

- Particles pass through intense laser beam
- Black particles heat to incandescence. Pure scatterers don’t.

Improvements:
1) Scatter signal hardware
2) Data processing
3) Aircraft operation

Gao et al. AS&T 2007
SP2 Calibration

- SP2 response is independent of soot morphology
- Good comparison to other techniques

![Graph showing calibration of SP2 instrument. The graph plots Refractory Mass/Particle (fg) against NOAA SP2 Incandescent Mass/Particle (fg). The data points are labeled for different values of φ: φ = 2.3, φ = 2.8, and φ = 3.5. A 1:1 line is also shown.]

SP2 Black Carbon Vertical Profile

- Here:
  - NASA WB-57F
  - Two flights, Nov. 2004
  - Over south-central US
  - Accuracy of 30%

- New measurements constrain global models
- Mass-based detection compares well to emission inventories

Schwarz et al. JGR, 2006
New Capability: Black Carbon Mixing State

Coatings on black carbon:
• Enhance absorption
• Influence lifetime

• Here:
  3 flights; Costa Rica in January
• Most black carbon in the UT/LS was coated
• More variable lower down
• High altitude particles had thicker coatings

Schwarz et al. JGR, 2007
Aerosol Mass Spectrometer (AMS)

- C-TOF version on NOAA P3
- Over 50 similar instruments worldwide

“Collection Efficiency”: Percentage of entering particles that hit and evaporate on hot target

Drewnick et al., Aerosol Sci. Technol., 2005
Here: 200 nm ammonium sulfate

- Phase (liquid or solid) changes AMS collection efficiency up to a factor of 4
- Measured mass loadings depend directly on collection efficiency.
- CE often assumed constant $\approx 50\%$
Apply to field data:
(2006 Houston TexAQS)

Using CE=0.5 for all data results in large scatter, systematic changes with acidity.

Using phase-dependent CE reduces scatter and systematic errors.

Agreement between independent measurements of volume and mass. (!!!)
Ammonium nitrate

In the future, ammonium nitrate is likely to become more important for climate.

- Houston 2006
- Gas-phase HNO₃, NH₃ Aerosol nitrate
  - Excluded region
  - More nitrate near stability region
- Work in progress
1) Particle enters vacuum. Trigger from light scattered from continuous laser.
2) Excimer laser beam hits particle.
3) Positive or negative ions analyzed with TOF mass spectrometer.
   - Size range about 0.25 to over 3 µm diameter

**Most of the mass and light scattering**

**Minority by number**
Challenge: Compare instruments without a good laboratory model for organic aerosols.

Solution: Use ambient data.

- Average (black) is captured by simple PALMS relative sensitivity (red)
- Biomass burning plumes identified from gas-phase acetonitrile (diamonds)
Average composition

The stratosphere

Smoke from forest fires
at 50000’!

Majority organics 20,000-45000’

Full range near the ground

pure sulfate  <----------->  pure organic

Murphy et al., JGR, 2006
The stratospheric laboratory:

- >95% of particles fall into 3 categories
- Limited gas-phase organic chemistry
- Long residence time

=> Understanding of processes
Stratospheric particles

Nucleation

Non-volatile CN

Mixing

Distinguish using metal ions
Compare carbon-containing ions

Organic-sulfate

Sulfuric w/ metals
Learning from the stratosphere

Obvious:
Particles formed in the troposphere have more carbon content.

Murphy et al., JGR, 2007
Lesson 1:

Limited acid-catalyzed polymerization with small organics like formaldehyde

Murphy et al., JGR, 2007
Learning from the stratosphere

Lesson 2:
Secondary organics even in the upper troposphere

Murphy et al., JGR, 2007
Learning from the stratosphere

Lesson 3:

Aerosol organics persist in the stratosphere against:
- loss of semi-volatiles
- loss of organic mass due to heterogeneous reactions with OH and O₃.

Murphy et al., JGR, 2007
Mixed organic-sulfate particles

- Most particles contain at least a little organic material
- Almost all also contain some sulfate (not shown)

Murphy et al., JGR, 2006
Importance of mixed particles for cloud activation

<10% organic is enough to get out of steep part of curve.
Great simplification for global models!

Mixing also helps AMS calibrations:

McFiggans et al., ACP, 2006
Field Studies for Specific Climate Issues

Why: (2006 - 07)
- Tropics are important
- Redistribution by deep convection

Some results:
- Black carbon profiles
- Organic content is different for outflow from continental or maritime convection

PALMS on B57, DC8
SP2 on B57
Field Studies for Specific Climate Issues

Why: (2008)
- Rapid Arctic changes
- Black carbon over snow and ice
- Different cloud feedbacks

Some results:
- ?
- ?
(end)