Ship Sampling Objectives

- Emissions
- Transport and Transformations
- Aerosol Radiative Forcing
Emissions

1. Improve Emission Inventories

Source and emissions characterization during TexAQS from Ronald H. Brown

Houston Ship Channel

Galveston Bay
First Pass Through the Houston Ship Channel

Styrene, 3.2 ppbv
i-Pentane, 40 ppbv
n-Pentane, 20 ppbv

Date and Time
18:00 8/2/2006
00:00 8/3/2006
06:00
12:00

Percentage of Minimum OH reactivity (100%)

J. Gilman
NOAA ESRL
Emissions

1. Improve Emission Inventories

   - Mobility of the ship and ability to position near sources allows for measurements of:
     - Ratios of co-emitted pollutants
     - Absolute amounts of emitted pollutants
     - Spatial patterns of emissions
     - Temporal variations in emissions strength and composition

   - Data will be compared with estimates based on existing emissions inventories and with gas and aerosol concentrations calculated using high resolution chemical transport models.
Emissions

2. Sulfate Formation over California Coastal Regions – Contributing Sources and Controlling Processes

DMS emissions

- Coastal upwelling – eddies are locations where DMS concentrations are often high.
- Survey regions of upwelling while continuously measuring seawater and atmospheric DMS.
Surface Seawater DMS Concentrations
West Coast of U.S. for the Months of May through July

http://saga.pmel.noaa.gov/dms/
SO$_2$ emissions within California.

- Near shore survey tracks near Los Angeles/Long Beach will be conducted when polluted continental air is transported into the surface marine layer (most likely night time, early morning, or late in the day).
- Investigate transport of Mexican emissions into coastal southern California during transit to study region.
SO$_x$ from Marine Vessel Emissions (MVE)
Emissions

3. Marine Vessel Emissions

Concentrate on:

- San Francisco/Oakland
- Los Angeles/Long Beach
- Santa Barbara Channel

- Near shore measurements downwind of ships under conditions of onshore flow to characterize emissions.

- Measurements during offshore flow to evaluate downwind and land-sea breeze processing of ship emissions.
Measurement of ship emissions from *Ronald H. Brown* during TexAQS 2006

Conditions for this experiment:
- Night time (no photochemistry)
- Constant wind field
- Target ship at anchor

- Determine emissions factors for gas phase (NO, NO2, SO2, CO, CH2O, VOCs (<C9), CO2, and NH3) and particulate phase species (NR SO4=, NR NO3-, NR NH4+, NR POM, and BC).

E. Williams, NOAA ESRL
Measurements of Ship Emissions during TexAQS

Aerosol Properties

Gas Phase Species

Lack et al., 2008

Williams et al., 2008
<table>
<thead>
<tr>
<th>Vessel Engine Classification</th>
<th>$SO_4^{2-}$ (g kg$^{-1}$) Avg. ± S.D.</th>
<th>Pnts</th>
<th>OM (g kg$^{-1}$) Avg. ± S.D.</th>
<th>Pnts</th>
<th>LAC (g kg$^{-1}$) Avg. ± S.D.</th>
<th>Pnts</th>
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<tbody>
<tr>
<td>Slow Speed Diesel (SSD)</td>
<td>1.55 ± 1.10</td>
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<td>1.57 ± 0.83</td>
<td>28</td>
<td>0.41 ± 0.27</td>
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<tr>
<td>Medium Speed Diesel (MSD)</td>
<td>0.79 ± 0.70</td>
<td>12</td>
<td>0.65 ± 0.44</td>
<td>12</td>
<td>0.97 ± 0.66</td>
<td>51</td>
</tr>
<tr>
<td>High Speed Diesel (HSD)</td>
<td>0.53 ± 0.46</td>
<td>3</td>
<td>0.75 ± 0.22</td>
<td>3</td>
<td>0.36 ± 0.23</td>
<td>8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vessel Type</th>
<th>$SO_4^{2-}$ (g kg$^{-1}$) Avg. ± S.D.</th>
<th>Pnts</th>
<th>OM (g kg$^{-1}$) Avg. ± S.D.</th>
<th>Pnts</th>
<th>LAC (g kg$^{-1}$) Avg. ± S.D.</th>
<th>Pnts</th>
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</thead>
<tbody>
<tr>
<td>Tankers (SSD)</td>
<td>1.42 ± 1.36</td>
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<td>1.42 ± 0.98</td>
<td>20</td>
<td>0.38 ± 0.27</td>
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<tr>
<td>Container (SSD)</td>
<td>3.58 ± 3.20</td>
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<td>2.10 ± 0.92</td>
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<td>0.80 ± 0.23</td>
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<tr>
<td>Cargo Carriers (SSD)</td>
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<td>0</td>
<td>-</td>
<td>0</td>
<td>0.40 ± 0.23</td>
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<tr>
<td>Bulk Carriers (SSD)</td>
<td>0.79 ± 0.70</td>
<td>5</td>
<td>1.90 ± 1.26</td>
<td>5</td>
<td>0.38 ± 0.16</td>
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<tr>
<td>Tug Boats (MSD)</td>
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<td>0.65 ± 0.44</td>
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<td>0.97 ± 0.66</td>
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<tr>
<td>Passenger Boats (HSD)</td>
<td>0.53 ± 0.46</td>
<td>3</td>
<td>0.75 ± 0.22</td>
<td>3</td>
<td>0.36 ± 0.23</td>
<td>8</td>
</tr>
</tbody>
</table>
TexAQS 2006: Emission factor for $\text{SO}_4^{\text{2-}}$ as a function of fuel sulfur content. (Triangles = MSD vessels; Circles = SSD vessels)

Lack et al., 2008
• Surveys of SO₂ and SO₄⁻ in harbor areas and during alongshore transects will help in the evaluation of sulfur sources and transformations in areas that are difficult to sample without a ship.

• The ship will be able to assess compliance to the mandated reduction of marine fuel-S used within 24 miles of shore.
1. Marine boundary layer structure and dynamics
   • Coastal jet
   • Coastal oscillations (land-sea breezes)
   • Southerly surges

Experimental approach

• Transects parallel and perpendicular to the coast (extent and magnitude)

• Time series at fixed locations (diurnal variations)

• Surveys at key inflow locations (Los Angeles basin and the Central Valley through San Francisco Bay)
2. Transport and transformations of polluted air masses advected offshore

Sample plumes offshore at successively further distances downwind to examine transformations related to plume aging in the marine boundary layer.

NEAQS cruise track colored by aerosol light scattering. The red portion indicates plume location. The bottom panel shows changes in aerosol properties along the cruise track as the distance from the source region increased.

Quinn et al., 2006.
Transport and Transformation

3. Night time chemistry, halogen activation and chemistry

TexAQS 2006: Night time production of CINO₂ through the uptake of N₂O₅ on Cl⁻ containing aerosol particles

Filling a radical gap:

\[ \text{N}_2\text{O}_5 \rightarrow \text{CINO}_2 \text{ on sea salt} \]

- longer photochemical day
- enhanced O₃ production

Osthoff, Roberts et al., 2008
Ronald H. Brown will provide continuous measurements to assess night time chemistry and chlorine activation in near coastal environments impacted by ship, urban, and sea salt emissions.

Land-sea breeze conditions will be targeted as the

- Night time land-breeze transports NO$_x$ into the MBL for interaction with sea salt and the
- Mid-morning sea breeze delivers photochemically active products back to shore.
Ship Sampling Objectives - Transport and Transformation

- SOA Formation
  - Measure downwind of areas with urban or rural emissions. The ship can be positioned to observe SOA formation in an environment with no significant additional input of VOCs.

At the time of emission gas-phase species dominate the budget, but after two days OVOCs and POM form a significant fraction of the total organic carbon mass.

de Gouw et al., 2005
Radiative Effects of Aerosols

1. Aerosol direct radiative forcing

• Since the concept of aerosol-radiation-climate interactions was first proposed around 1970, substantial progress has been made in determining the mechanisms and magnitudes of these interactions.

• Yet aerosols still pose the largest uncertainty in calculations of radiative forcing of the climate system (IPCC, 2007).

• *In situ* instruments that have been developed over the past decade allow for the measurement of relevant aerosol properties with high accuracy and fast time resolution (AMS, PAS, CRD).

• The result is:

  • an improvement in regional aerosol chemical, microphysical, and radiative property characterization and

  • strong constraints for satellite retrievals and model simulations of aerosols and their direct radiative forcing.
Locations and timing of measurements relevant to aerosol direct radiative forcing

Brown
June’ish

P3
May 1 – June 15

DOE G1, NASA B-200
June
# Measurements relevant to aerosol direct radiative forcing

<table>
<thead>
<tr>
<th>Platform</th>
<th>In situ aerosol properties (composition, size distribution, $\sigma_{ep}$, $\sigma_{sp}$, $\sigma_{bsp}$, $\sigma_{ap}$, $b$, $\omega$, $f(RH)$)</th>
<th>Aerosol Optical Depth</th>
<th>Radiative Fluxes</th>
<th>Tracer Species (CO, CH$_3$CN,....)</th>
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</thead>
<tbody>
<tr>
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<tr>
<td>CARES: DOE G1. NASA B-200</td>
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</table>
Radiative Effects of Aerosols

- Aerosol direct radiative forcing

Provide data for improving chemical transport – radiative transfer models.

Measurement – model comparisons

- chemical composition
- direct radiative effect

Bates et al., 2006.
Radiative Effects of Aerosols

1. Aerosol direct radiative forcing

Develop/improve empirical-based parameterizations for use in coupled chemical transport – radiative transfer models.

Increasing organic mass fraction →

Quinn et al., 2005.
The effect of chemical composition on the relative humidity dependence of light scattering for the NEAQS study region

Increasing organic mass fraction
Radiative Effects of Aerosols

1. Aerosol direct radiative forcing

Add to regional data base of aerosol chemical, physical, and optical properties for testing models and linking aerosol sources to climate impacts.

Aerosol composition (source) \(\rightarrow\) Light extinction

Quinn and Bates, 2005
<table>
<thead>
<tr>
<th>Campaign</th>
<th>λ Range (nm)</th>
<th>Mean (W m⁻²)</th>
<th>Std. Dev (W m⁻²)</th>
<th>Reference</th>
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<td>350-1670</td>
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<tr>
<td>INDOEX</td>
<td>400-700</td>
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<td>Meywerk and Ramanathan, 1999</td>
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<td>Bush and Valero, 2002</td>
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<td>ACE-Asia</td>
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<td>-42.2</td>
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<td>Bush and Valero, 2003</td>
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<td>INDOEX</td>
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<td>ACE-Asia</td>
<td>300-3810</td>
<td>-73</td>
<td>9.6</td>
<td>Bush and Valero, 2003</td>
</tr>
</tbody>
</table>
All as a function of:
- RH
- altitude
- meteorological conditions
- sources
- distance from sources
- …

Calculated direct radiative forcing for the CalNex study area
2. Aerosol indirect radiative forcing

Stratus and stratocumulus clouds are expected to persist offshore during much of the CalNex time period. Regions where local pollution sources and recirculation events lead to the coincidence of aerosol and clouds will be targeted.

Ship tracks off the west coast of the US (Durkee et al., 2001)
Radiative Effects of Aerosols

2. Aerosol indirect radiative forcing

Determine the albedo response of marine stratiform clouds to aerosols in the study region.

- A combination of surface and remote observations can be used to determine the magnitude of the effect of aerosol on cloud optical and microphysical properties.

- Compare measured and model-derived cloud drop concentrations where modeled values are based on measured aerosol properties.

McComiskey et al., 2008.
SSFR: eff. radius, optical thickness, LWP
Spectral actinic flux

In-cloud droplet conc, LWC

Above-cloud aerosol properties, mixing

SSFR: cloud optical depth
μwave radiometer: LWP

Doppler lidar: w, w'

Cloud radar: structure, precip

Below-cloud CCN, aerosol properties

Below-cloud CCN, aerosol properties
Observations vs. LES: Comparison of PDFs of various cloud and dynamical fields

Jiang et al. 2008
Ship Logistics

- Instrumentation
- Communication
- Schedule/Transit times
- Operating areas
2006 TexAQS GoMACCS

PMEL VAN3 -
Aerosol composition:
Organic speciation (PTR-MS)
NR composition (WTOF-AMS)
Radiometers

PMEL VAN1 -
Aerosol composition:
Ions (PILS-IC)
Water sol. organics (PILS-TOC)
Organic speciation (PILS-LCMS)
NR speciation (AMS)
OC/EC
CCN
SO2, O3

PMEL VAN2 -
Aerosol parameters:
Number and size distribution
Light scattering (Neph)
Scattering f(RH) (Neph)
Light absorption (PSAP)
Light extinction (CaRDS)
Extinction f(RH) (CaRDS)
Light absorption (PAS)
Composition (impactors)
Functional groups (FTIR)
Radon

ESRL VAN3 -
NO; NO2; NOy; PANs; HNO3; O3; CO;
CO2; SO2; jNO2; jO3; jNO3; met; GPS/AIS

ESRL VAN2 -
VOCs: GC-MS; PTR-MS; CH2O
Alkyl N; NO3; N2O5; HO2/RO2

ESRL VAN1 -
Gas-phase inlets and radiometers tower
High-Resolution Doppler Lidar (HRDL)
Winds; 360° scanning; zenith to horizon

AL Storage
PMEL Storage
3 mm Doppler Radar Microwave Radiometer
Charleston to Panama – 1700 nm, 6 days
Puerto Rico to Panama – 670 nm, 2.5 days
Panama to San Diego – 3000 nm, 11 days

Currently have 49 DAS including transit
May – July
Most likely in the study region in June
San Diego to LA - 74 nm
LA to SF – 390 nm
Preliminary Schedule

49 DAS, May – July (May be decreased to ~ 40 but could buy additional days if the resources are available)
Includes the transit time from where we pick up the ship to a U.S. west coast port (14 – 17 days)

Most likely in the study region during June

End at a west coast port

Communications

Internet access – 24/7
Cell and satellite phones
VHF radios
Ship Sampling Objectives - Transport and Transformation

- Halogen chemistry
  - Efficiency of halogen activation by nitrogen oxides
  - Impacts of this halogen activation on ozone production
  - Effects of halogens on aerosol production
  - Importance of halogen oxidation of VOCs.
  - Sources of reactive Cl (ClNO2…)
  - Importance of shipping NOx relative to urban NOx as a halogen source
<table>
<thead>
<tr>
<th>Category</th>
<th>Parameters to Measure</th>
<th>Instrument(s)</th>
<th>Status</th>
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<tbody>
<tr>
<td>Gas phase species</td>
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<td>CO₂</td>
<td>Nondispersive IR</td>
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<tr>
<td></td>
<td>SO₂</td>
<td>Pulsed UV fluorescence</td>
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</tr>
<tr>
<td></td>
<td>NO</td>
<td>Chemiluminescence</td>
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<td>NO₂</td>
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<td>NO₃</td>
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<td>HCHO, NH₃</td>
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<td>VOCs</td>
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<tr>
<td>Aerosol properties and species</td>
<td>Number concentration</td>
<td>CPC, UCPC</td>
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<td>Number size distribution</td>
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<td>Spectral absorption (EBC)</td>
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<td>NR SO₄, NO₃, NH₄, POM</td>
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<td>NR SO₄, NO₃, NH₄, POM</td>
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<td>Seawater species</td>
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<td>GC-chemiluminescence</td>
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<tr>
<td>MBL dynamics, plume structure</td>
<td>MBL winds</td>
<td>HRDL</td>
<td>X</td>
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## Measurements Required to Accomplish Transport and Transformation Objective

<table>
<thead>
<tr>
<th>Category</th>
<th>Parameters to Measure</th>
<th>Instrument(s)</th>
<th>Status</th>
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<td>NO$_y$</td>
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<td>Aerosol properties and species</td>
<td>Number concentration</td>
<td>CPC, UCPC</td>
<td>X</td>
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<tr>
<td></td>
<td>Number size distribution</td>
<td>DMPS, APS</td>
<td>X</td>
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<tr>
<td></td>
<td>Inorganic ions (Na, Cl)</td>
<td>PILS/IC, Impactors/IC</td>
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<tr>
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<td>NR SO4, NO3, NH4, POM</td>
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<td>Absorption (EBC)</td>
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<td>Seawater species</td>
<td>DMS</td>
<td>GC-chemiluminescence</td>
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<td>Radiation</td>
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<td>MBL dynamics, plume structure</td>
<td>MBL winds</td>
<td>HRDL</td>
<td>X</td>
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</tbody>
</table>
Aerosol and Cloud Microphysics

- **Aerosol measurements**: in-situ
- **Cloud microphysics**:
  - Cloud optical depth $\tau_c$:
    - Solar Spectral Flux Radiometer (SSFR; Pilewskie) and/or
    - NFOV radiance measurement
  - Liquid water path: $\mu$wave radiometer
  - Drop effective radius $r_e$ (radar + $\mu$wave or SSFR)

Feingold et al. 2003
Drizzle---VOCALS (RB) Radar Measurements
Univ. Miami W-Band and X-Band Radars

- **W-Band**—Bistatic Mode (no dead zone) - Reflectivity and Doppler Spectra
  - Radar returns from cloud top to within 30 m of surface
  - Drizzle characterization (size distribution retrieval)
  - Sub-cloud drizzle evaporation
  - Turbulence—Resolved and within radar sampling volume
  - Back up for ESRL/ETL cloud radar
- **X-Band**—Reflectivity and Doppler Spectra
  - Dual-wavelength drizzle characterizations
Land/Sea Breeze observations with Doppler Lidar

Barbour’s Cut
Galveston Bay
Gulf

Wind barbs point into the wind
Line color indicates wind speed

Nocturnal Low Level Jet
Land breeze
sunrise
Bay/Sea breeze (changing ship location)
Onshore flow

Observations close to Houston
Ship Sampling Objectives – Radiative Effects of Aerosols

1. Aerosol direct radiative forcing

   • Determine the direct radiative effect of aerosols in the CalNex region.
Determine the albedo response of marine stratiform clouds to aerosols within the CalNex study region

Assuming a coupling between clouds at the top of the boundary layer and surface aerosol:

- *In situ* observations of surface aerosol properties
- Ship-based remote observations of updraft velocities just below cloud base (HRDL) and cloud liquid water path (microwave radiometer), optical depth (SSFR) and effective radius (cloud radar).
- P3 observations of FT aerosol entrained into the tops of clouds.
Ship Sampling Objectives – Radiative Effects of Aerosols

2. Aerosol indirect radiative forcing

- Determine the impact of aerosol composition on the formation of cloud condensation nuclei.
  - Compare measured CCN spectra with those calculated by thermodynamic models of aerosol activation based on observed aerosol size distributions and composition.
- Determine the relationship between aerosol properties, cloud microphysics, and precipitation formation.
- Effects of clouds on aerosol size distribution and chemical properties
## Measurements Required to Accomplish Aerosol Radiative Forcing Objective

<table>
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<th>Parameters to Measure</th>
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<td>EC</td>
<td>Impactors</td>
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<td>OC</td>
<td>Impactors</td>
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<td>POM</td>
<td>Q-AMS</td>
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<td>Impactors</td>
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<td><strong>Aerosol and Cloud Physical and Optical Properties</strong></td>
<td>Number concentration</td>
<td>CPC, UCPC</td>
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<td>Number size distribution</td>
<td>DMPS, APS</td>
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<td>Spectral absorption</td>
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<td>Spectral scattering and backscattering</td>
<td>Nephelometer</td>
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<td>Spectral extinction</td>
<td>CRD</td>
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<td>f(RH) – scattering</td>
<td>Nephelometers</td>
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<td>f(RH) – extinction</td>
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<td>Aerosol hygroscopic growth</td>
<td>H-TDMA</td>
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<td>Lidar backscatter profiles</td>
<td>MPL</td>
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<td>CCN concentration f(S)</td>
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<td>Cloud liquid water path</td>
<td>Microwave radiometer</td>
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<td>Cloud effective radius</td>
<td>Cloud radar</td>
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## Measurements Required to Accomplish Aerosol Radiative Forcing Objective

<table>
<thead>
<tr>
<th>Category</th>
<th>Parameters to Measure</th>
<th>Instrument(s)</th>
<th>Status</th>
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<tr>
<td><strong>Radiative Properties</strong></td>
<td>Spectral AOD</td>
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<td>Radiative fluxes</td>
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<td>Cloud optical depth</td>
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<td>Cloud reflectance</td>
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<tr>
<td><strong>MBL dynamics</strong></td>
<td>Updraft velocity</td>
<td>HRDL</td>
<td>X</td>
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</tbody>
</table>
Sub-cloud vertical velocity observations (HRDL)

Cloud layer

Mean horizontal wind profiles

Vertical velocities in “clear” air

Cool colors → falling air/particles

Warm colors → rising air

HRDL zenith signal strength (relative aerosol backscatter)

HRDL vertical velocity

Cloud radar can see vertical motion inside clouds

S. Tucker