Chemistry as an aid in characterizing aerosol sources, evolution, and properties during 2008 VOCALS

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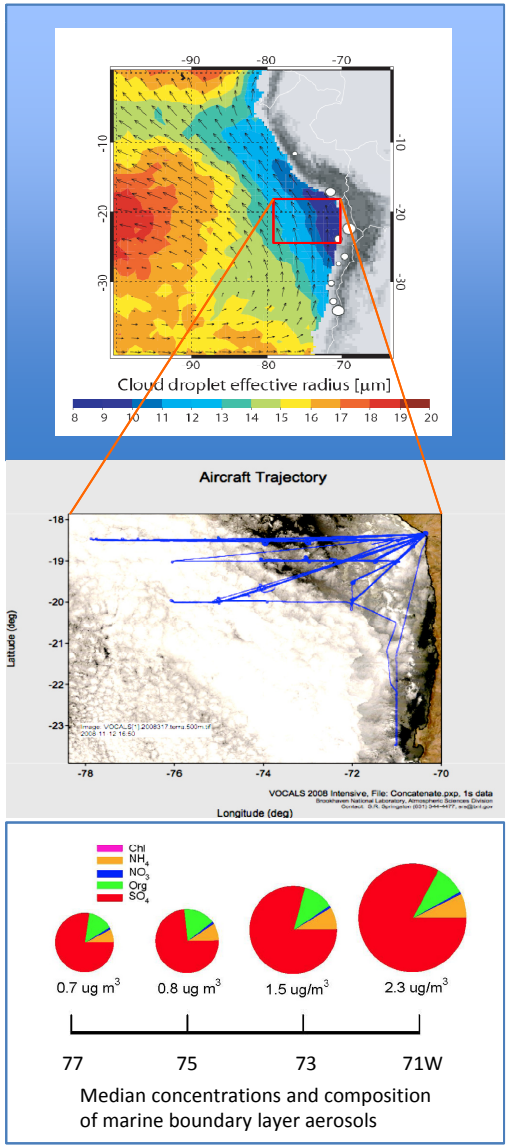
Introduction



- Previously reported:
  - SO_4^{2-} dominated aerosol mass
    - strong land-to-sea concentration gradient
    - highly acidic (~1/4 neutralized)
    - Anthropogenic, with little contribution from DMS
  - Organics, like NH_4^+, accounted for <15% of aerosol mass
  - Sea-salt particles, uniform longitudinally, contributed up to ~1/2 aerosol mass off-shore (-78° Lon)
  - SO_4^{2-} and sea-salt aerosols externally mixed
  - The progressively smaller effective cloud droplet size toward the coast observed by satellite in this region was due to an increased aerosol loading from man-made sources
- In this presentation, we report further insights into aerosol sources and evolution based on overall data patterns.

*VOCALS Rex: VAMOS (Variability of American Monsoon System) Ocean-Cloud-Atmosphere-Land Study Regional Experiment

Chemical Measurements on the G1 and Aerosol Life Cycle Characterizations

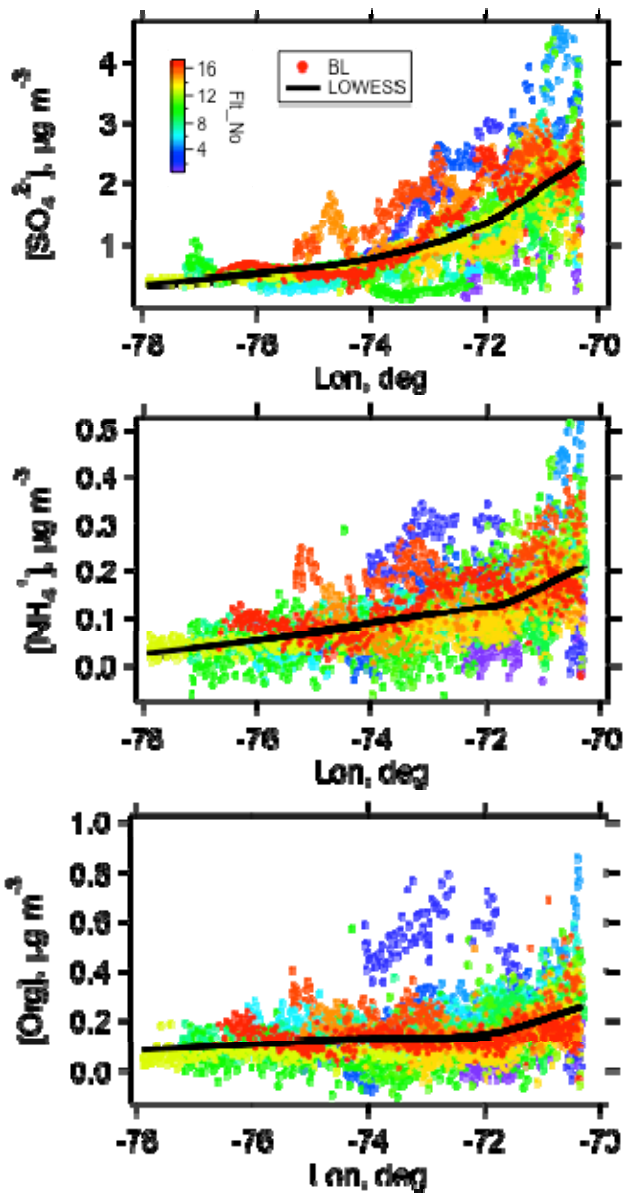
Trace Species Measured on the DOE G1:

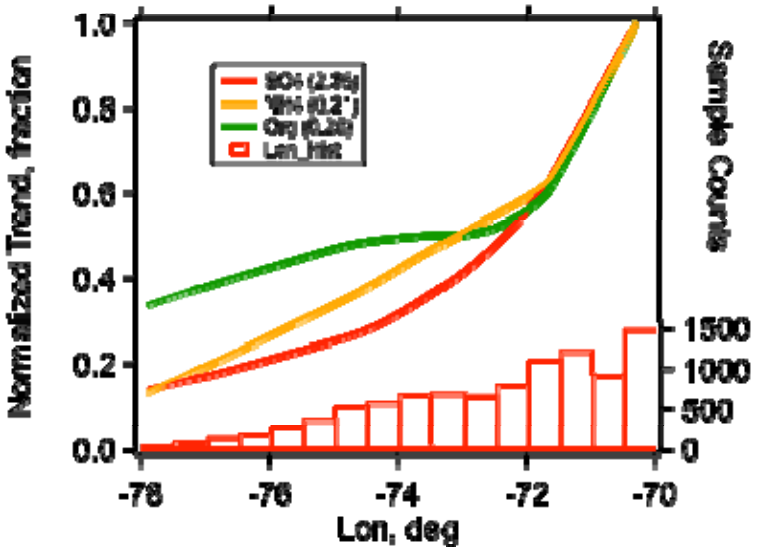
- Aerosol phase:
  - SO_4^{2-}, NH_4^+, *Org* by cToF-AMS (22 s)
  - SO_4^{2-}, NH_4^+, NO_3^-, Na^+, Cl^- , $CH_3SO_3^-$ K^+, and Ca^{2+} by PILS-IC (180 s)
- Gas phase:
  - *CO* by VUV fluorescence
  - O_3 by UV absorption
  - SO_2 by pulsed fluorescence
  - $(CH_3)_2S$ by PTR-MS

Aerosol Properties:

- Sources
- Transport and mixing (horizontal and vertical)
- Gas-aerosol reactions
- In-cloud aerosol reactions

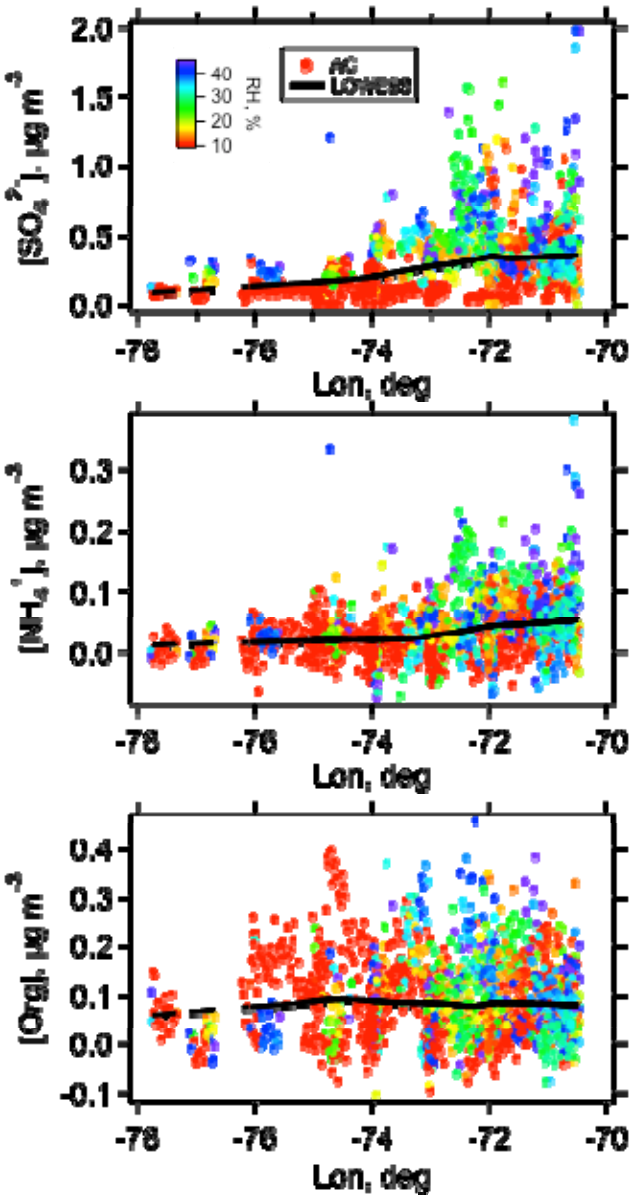
Longitudinal Distributions of SO_4^{2-}, NH_4^+, and Org - Below Cloud

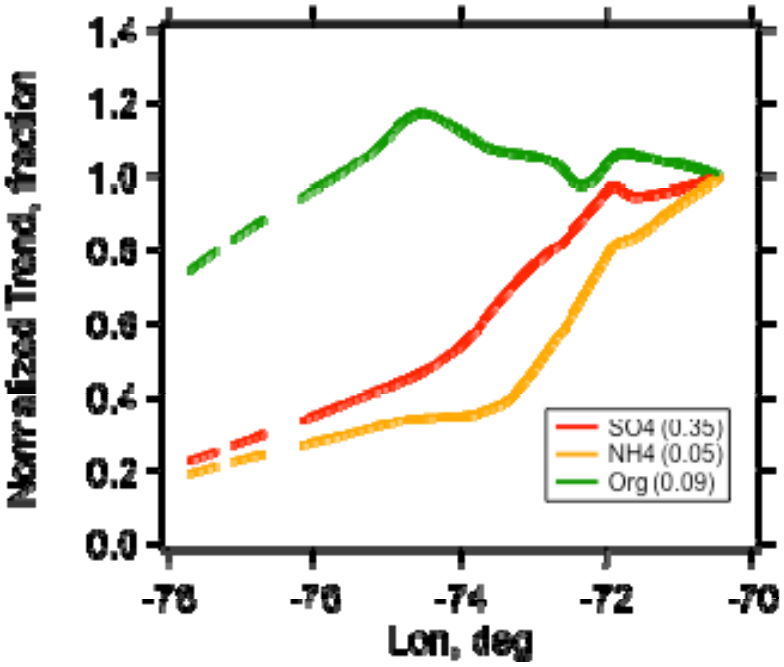




- LOWESS smoothing, approximating median, for pattern comparison
- Data segregated into below-cloud (BL) and above-cloud (FT) groups
- All 3 species show same source attributes near the shore
- Org showed enhancement relative to SO_4^{2-} into the open ocean, indicating changes in source characteristics
  - mixing from FT?
  - primary aerosol from the ocean?
  - SOA formation from oceanic/terrestrial precursors?
    - Gas-phase formation
    - In-cloud production

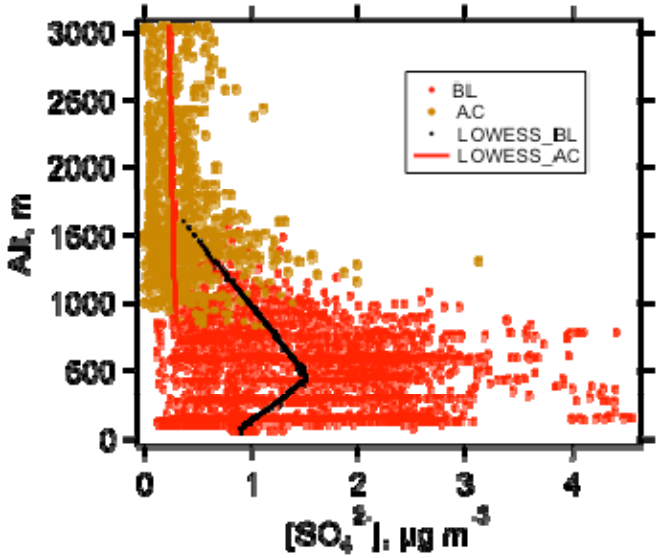
Longitudinal Distributions of SO_4^{2-}, NH_4^+, and Org – Above Cloud

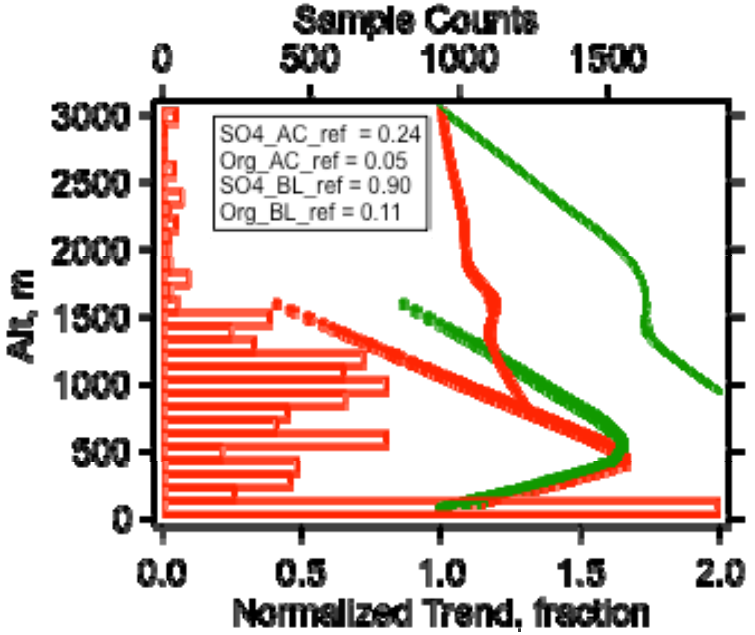


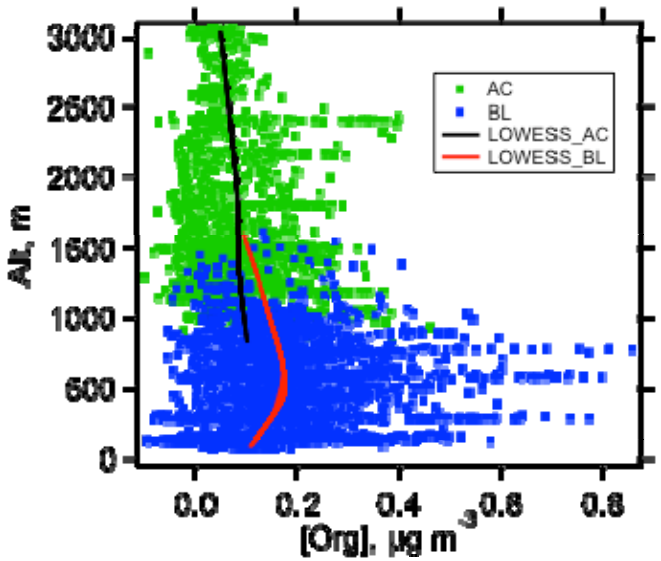


- Above-cloud, Org enriched over SO_4^{2-} away from shore
- Fairly uniform longitudinal distribution of Org (and CO) suggests long distance sources in addition to local sources?
- Source of BL organic aerosols?

Vertical Distributions of Aerosol SO_4^{2-} and Org

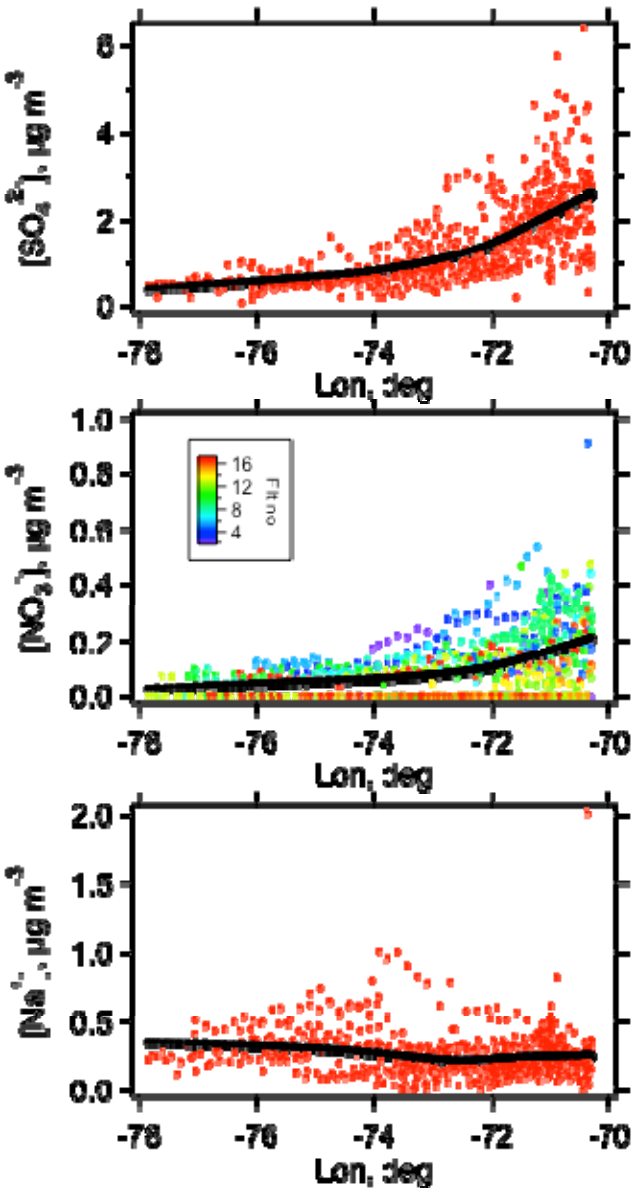


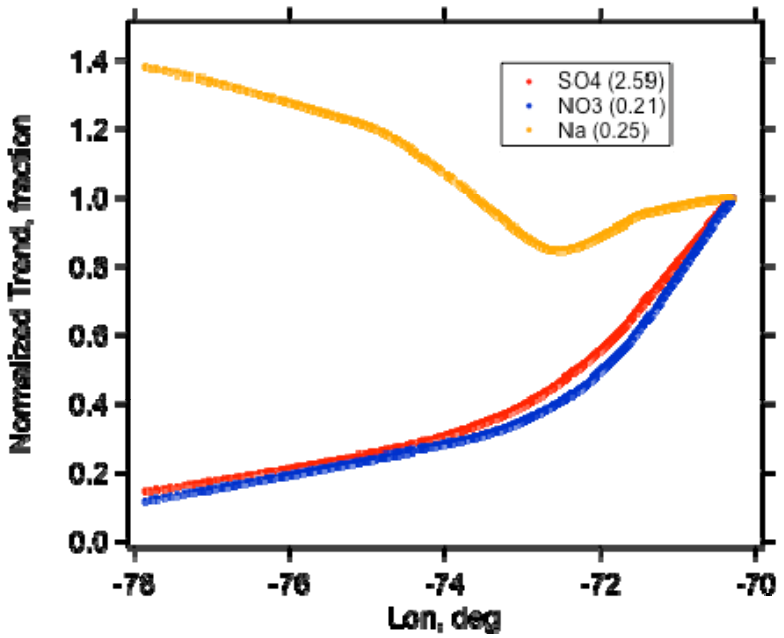




- SO_4^{2-} greater in BL than FT
- In contrast, Org showed a smaller difference between BL and FT
- Downward mixing can result in Org enrichment over SO_4^{2-} in BL
- In-cloud SOA production possible
- No indication of primary Org aerosol from ocean (mass wise)

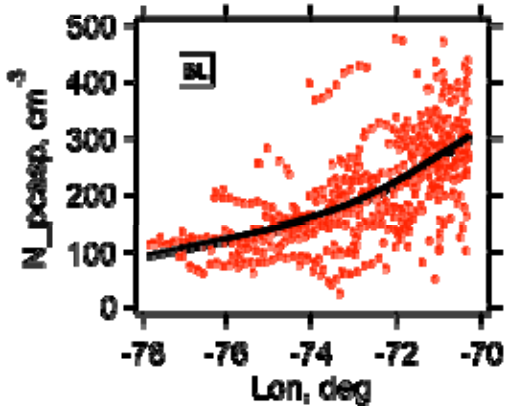
Longitudinal Distributions of Na^+ and NO_3^- – BL

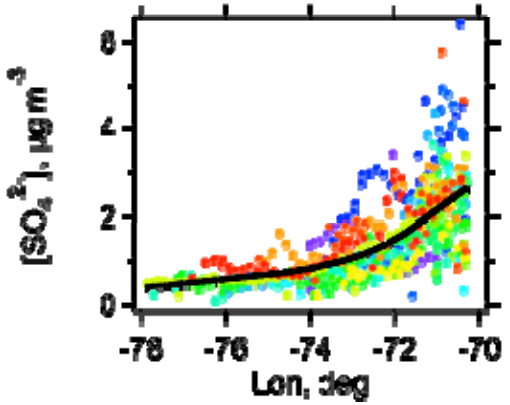


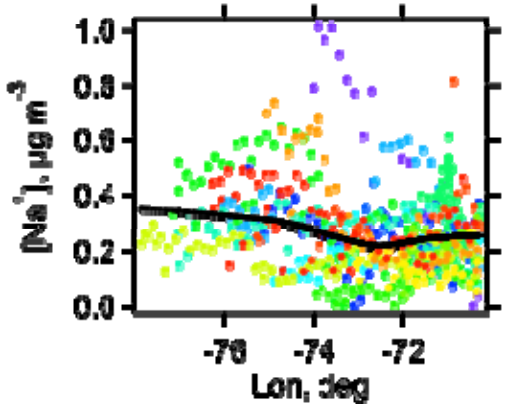


- Sea-salt concentration increases off-shore
- Uptake of HNO_3 on sea-salt particles was fast
- Life times of SO_4^{2-} and sea-salt aerosols are comparable unless HNO_3 formation continues to take place
- NO_3^-, and therefore SO_4^{2-}, are dominated by terrestrial sources

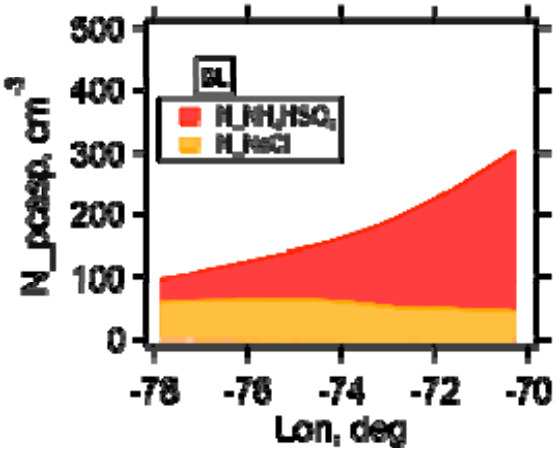
Estimating Sea-Salt Particle Concentrations (a ***loose*** upper limit)

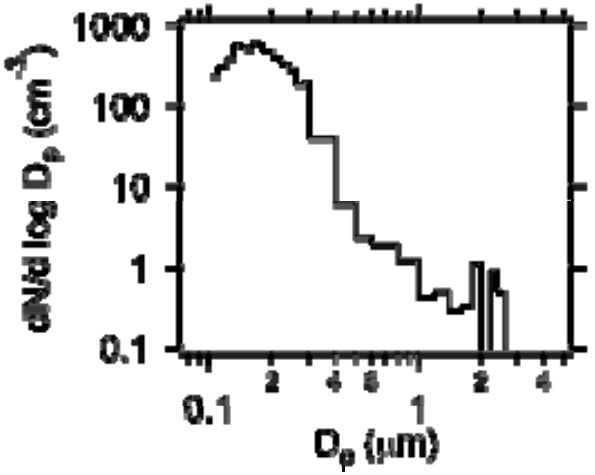


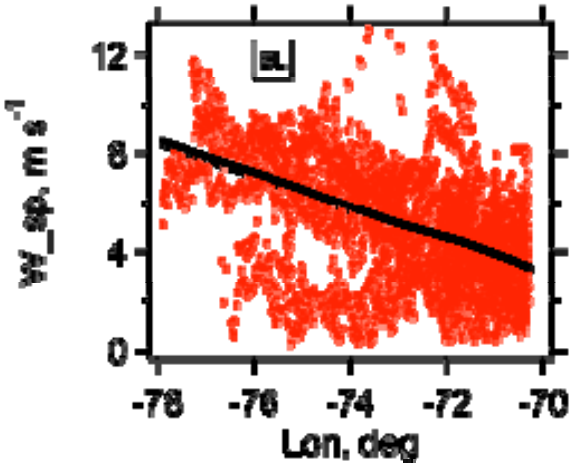


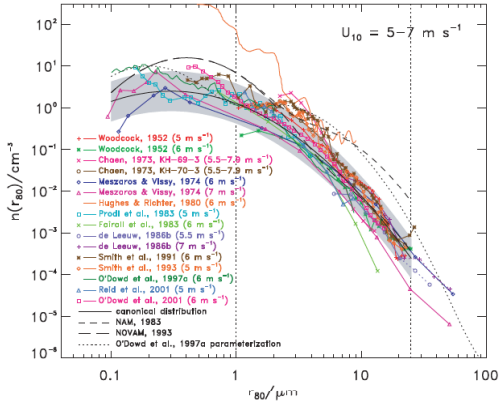


Assuming SO_4^{2-} and sea-salt have the same size distribution

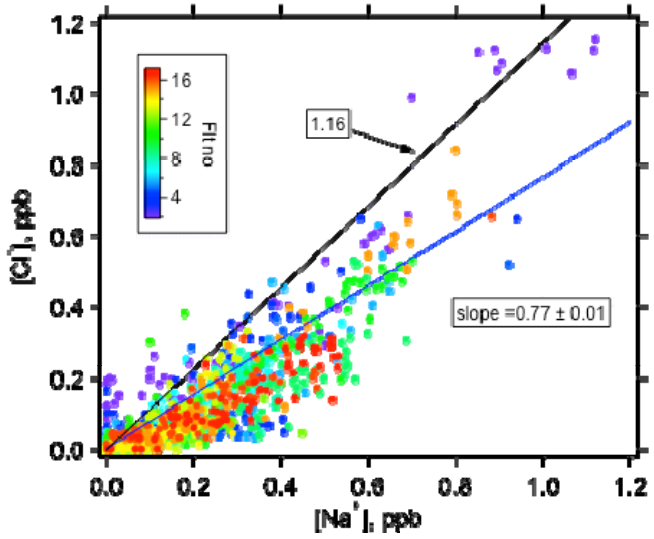


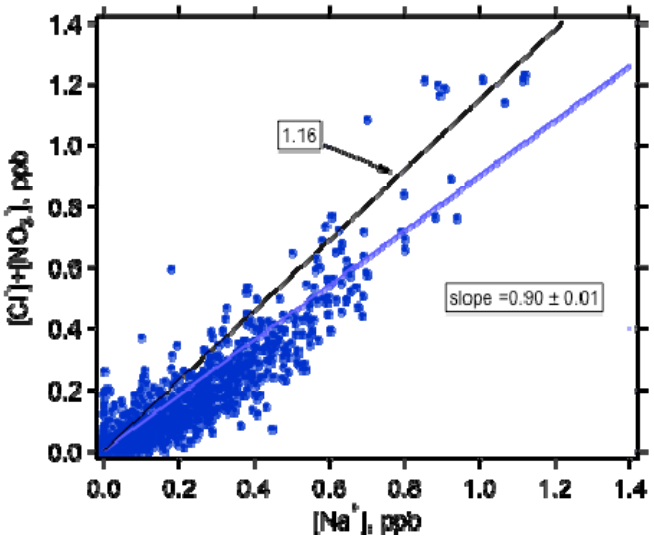




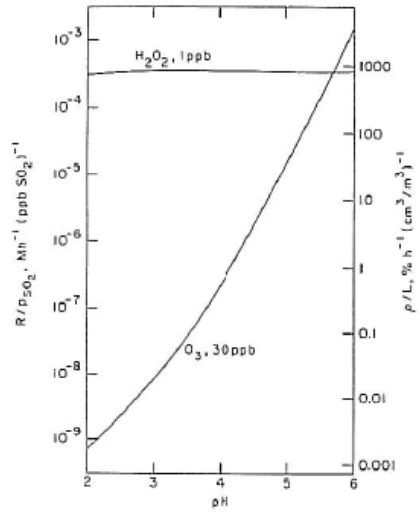


Processing of Sea-Salt Particles

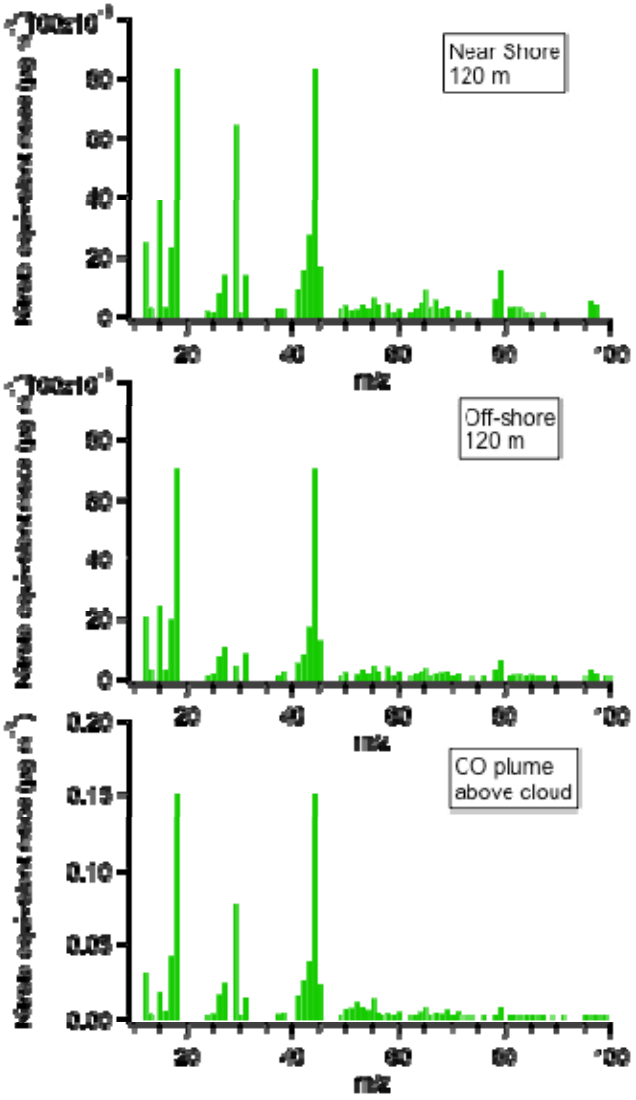


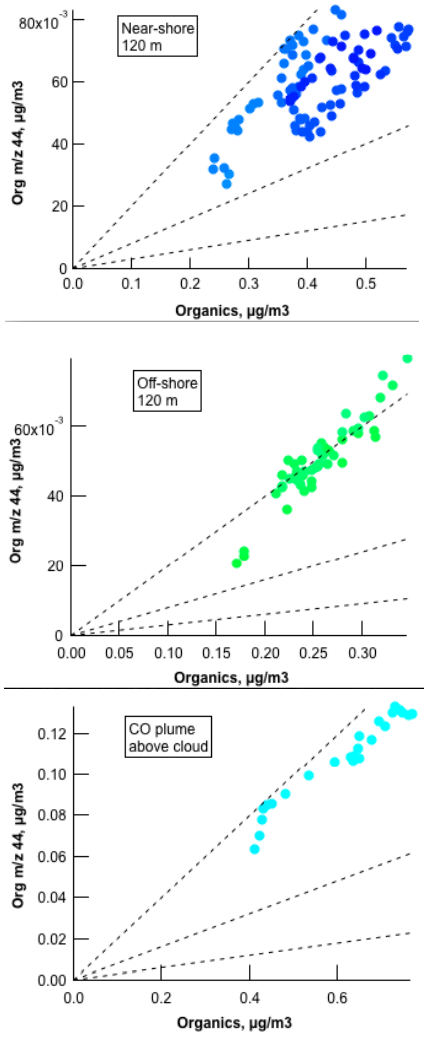


- Acidification:
  - uptake of HNO_3
  - uptake of H_2SO_4 (slow)
  - in-cloud H_2O_2-S(IV) reaction
  - in-cloud O_3-S(IV) reaction (pH>5)
  - coagulation with H_2SO_4 aerosol (slow)
- A good in-cloud S(IV) oxidation indicator
  - need concentrations of SO_2 and H_2O_2



Sources and Processing of Organic Aerosol





Data from 10/25/08

- Near shore BL organics less oxidized
- Off shore BL organics highly oxidized
- No evidence of primary oceanic organic aerosol
- Organic aerosol in CO plume above cloud resembles that in near shore BL, but was more oxidized and aged in comparison

Summary

- Aerosol chemical composition was characterized in detail during VOCALS using a cToF-AMS and the PILS-IC technique
- Terrestrial sources dominated MBL SO_4^{2-} of the G1 study regime, to -78° Lon
- Org aerosol increased relative to SO_4^{2-} away from shore, suggesting additional sources
  - SOA formation, conceivably in-cloud, judging from Org vertical gradient
  - Gas-phase precursors (oceanic vs terrestrial) unknown
  - No evidence for primary oceanic organic aerosol
- Sea-salt particles undergo acidification from uptake of gaseous HNO_3, and are useful as an indicator for in-cloud S(IV) oxidation process
- Future field studies:
  - Cross wind transects at varied distances from source region
  - Characterization of FT air
  - Characterization of source regions and over land
  - Determine H_2O_2 as well as SO_2 with high sensitivity (LOD <50 ppt)
  - Characterization of organic aerosol (e.g., O:C ratio)