DISCOVER-AQ Baltimore: Measurements of Aerosol Composition from the NASA P-3B

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Motivation

During the first phase of the DISCOVER-AQ project, aerosol measurements were made from the NASA P-3B. These include aerosol number concentration, size, optical properties and composition. This poster focuses on aerosol composition, specifically:

1) Relative abundances of black carbon, inorganic and organic aerosols
2) Variation in composition
   a) amongst flights
   b) diurnally, and
   c) spatially
3) Effects of changes in composition on optical properties
4) Properties and sources of black carbon and aerosol absorption

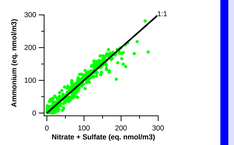
Preliminary Conclusions

- In general, aerosol mass was composed of approximately 60% organics and 40% ammonium sulfate. However, this ratio changed with aerosol loading (ammonium sulfate dominated on highly polluted days). This changes the hygroscopic nature of the aerosols.
- Meteorological conditions drove gas-particle partitioning for nitric acid (more work is needed to study partitioning of organics).
- Sulfate increased during the day while organics decreased. Edgewood had the highest loadings for most compounds. Bay spirals did not enter the marine boundary layer.
- Black carbon emissions driven by efficient combustion except during RF08.
- Organic coatings enhanced the absorption of black carbon. This enhancement was similar to that seen during previous campaigns. Absorption enhancement will alter aerosol SSA.

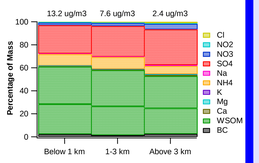
Mission Overview

Measured aerosols were composed of:

- 36% $(NH_4)_2SO_4$, 3% NH_4NO_3 and 2% other inorganics
  - no significant aerosols from sea salt, crustal or fire sources
- 58% water-soluble organic matter (WSOM)
  - assuming a WSOM/WSOC ratio of 1.8 (Hand, JGR '07)
  - non-water soluble organics were not measured
- 2% black carbon (BC)



Ammonium completely neutralized sulfate (as $(NH_4)_2SO_4$) and nitrate

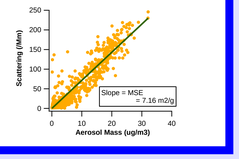


Aerosol mass decreased with altitude

- Slight decrease in relative abundance of organics
- Decrease in relative abundance of black carbon

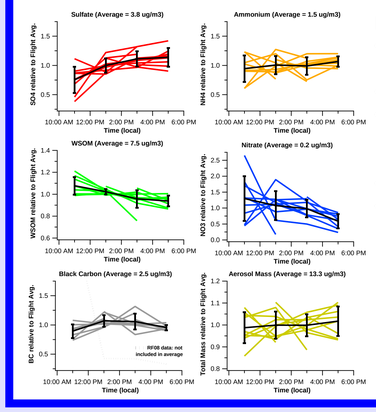
An average mass scattering efficiency of 7.2 m^2/g was measured

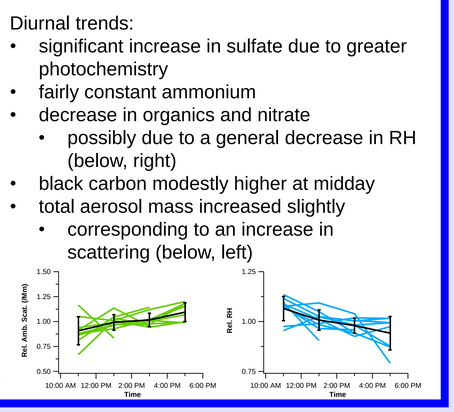
- 8.4 m^2/g if the WSOC to WSOM conversion is not used
- An average aerosol density of 1.53 g/cm^3 was also found by correlating aerosol mass versus aerosol volume (measured by a UHSAS)



Temporal Variation

Temporal variation in composition found by determining the diurnal cycle for each flight and then normalizing by the average concentration for that flight. Samples were binned into four 2-hour time periods.

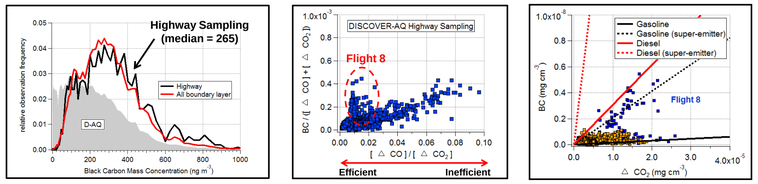




Diurnal trends:

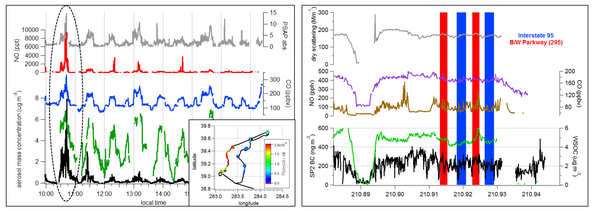
- significant increase in sulfate due to greater photochemistry
- fairly constant ammonium
- decrease in organics and nitrate
  - possibly due to a general decrease in RH (below, right)
- black carbon modestly higher at midday
- total aerosol mass increased slightly
  - corresponding to an increase in scattering (below, left)

Black Carbon: Highway Sampling



High levels of BC were measured during the highway sampling

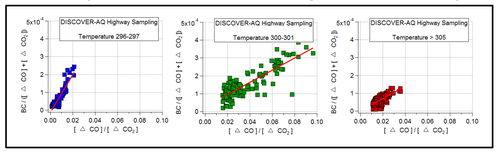
- generally, more inefficient combustion (based on CO emissions) produced higher BC
- during RF08, high BC was measured despite low CO emissions (center)
- this case was seen to have emissions closer to a diesel engine
- no clear explanation is known (RF08 was a weekday with high aerosol loading)
- the highest BC corresponded to a spike in NO during the first highway sampling of RF08 (below left, circled and shown in inset)

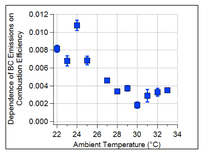


No clear difference was observed between the 95 and 295 sampling (RF14, shown in the right-most figure)

Ambient Temperature Effects

- At low ambient temp., BC emissions were highly dependent on combustion efficiency
- This dependence decreased at higher ambient temperatures



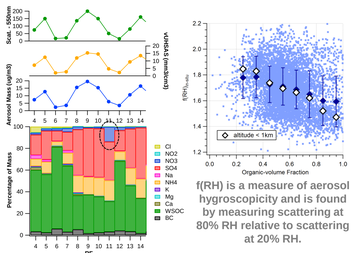


Variation Amongst Flights

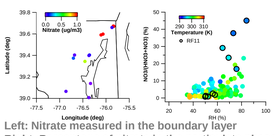
Distinct difference in composition with aerosol loading.

High loading days had:

- Higher RH
- A greater abundance of ammonium sulfate relative to organics
  - shift in composition could be the result of RH effects on gas-to-particle partitioning.
- Lower organic mass fraction corresponds to a lower f(RH)
  - Means that scattering/AOD is more dependent on changes in RH



f(RH) is a measure of aerosol hygroscopicity and is found by measuring scattering at 80% RH relative to scattering at 20% RH.



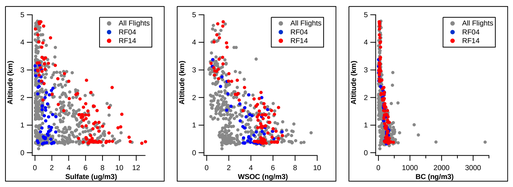
Left: Nitrate measured in the boundary layer
Right: Percentage of nitrate in the particulate phase for all flights colored by temperature (RF11 circled)

High ammonium nitrate concentrations measured during RF11

- Corresponds to a period of high nitric acid, high RH and low temperatures
- Highest gas-to-particle partitioning of nitrate measured during the campaign.

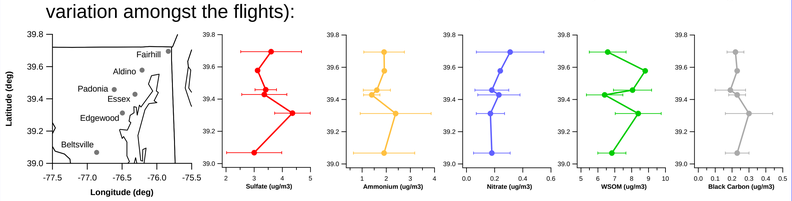
Aerosol mass decreases with altitude

- RF04 & RF14 chosen as examples of low and high loading days
- No difference in BC altitude profile between the low and high loading days – suggests no difference in primary aerosol sources amongst the days while secondary sources differ



Spatial Variation

Average boundary layer (<1 km) mass concentrations (normalized by aerosol loading variation amongst the flights):

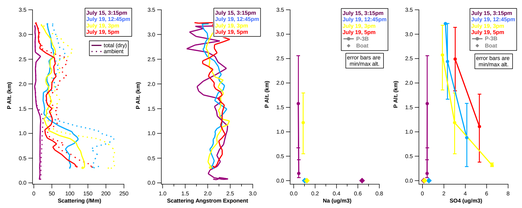


- As expected, Edgewood had the highest mass loadings for ammonium, sulfate and black carbon.
- Organic mass elevated at Padonia, Aldino and Edgewood.
- Nitrate elevated at Fairhill largely due to the high ammonium nitrate measured at the site during RF11 (left side panel). All other sites had similar nitrate loadings.

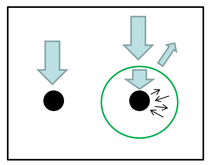
Delaware II Spirals

Four spirals performed on two days

- Increase in scattering in lowest km
- But the P-3B did not sample in the marine boundary layer
  - No change in scattering angstrom exponent
    - sea salt typically has an Angstrom exponent below 1
  - Sodium values measured on the P-3B were typically below the limit of detection
    - measurements on the boat were an order of magnitude higher
  - Non-sea salt inorganics (such as sulfate) were lower in the marine boundary layer



Absorption Enhancement

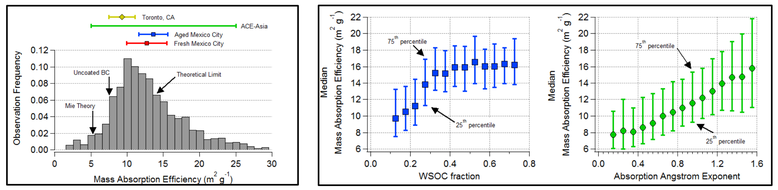


The mass of black carbon is related to absorption via it's mass absorption efficiency (MAE) with units of m^2/g.

- measured MAE for bare carbon = 7.5±1.2 (Bond, AS&T '06)
- coating on soot particles tend to increase the absorption by acting as a 'lens' for the incoming radiation ($MAE_{coated} = MAE_{bare} + abs_{coating}$)
- this increased absorption changes the single scattering albedo of the aerosol

Measured MAEs were found to be considerably higher than MAE_{bare}

- Similar range as measured in Mexico City (but slightly higher than in Toronto)
  - similar coatings as seen in Mexico City?
- MAE increased with the WSOC fraction and absorption angstrom exponent (AE_{abs})
  - AE_{abs} uses solely optical measurements
  - Deriving MAE from AE_{abs} would allow for a better understanding of aerosol absorption and composition based on solely-optical methods (such as remote sensors)



This poster includes the following measurements:

- P-3B CO and RH from DACOM (PI: G. Diskin, LaRC)
- P-3B CO_2 from AVOCET (PI: S. Vay & M. Yang, LaRC)
- P-3B NO from Chemiluminescence Instrument (PI: A. Weinheimer, NCAR)
- P-3B HNO3 from TD-LIF (PI: R. Cohen, UC Berkley)
- Delaware II aerosol Na^+ and SO_4^{-2} from IC analysis (C. Jordan, UNH)