Progress on the Analysis of Aerosol Optical Properties from CARES

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Abstract

During June 2010, three multi-wavelength cavity ring-down extinction instruments were used at the T0 (Sacramento, CA) and T1 (Cool, CA) CARES ground sites to obtain aerosol optical properties and how they varied with size, relative humidity and thermo-denuding. Light absorption coefficients were also measured at T0 using a photo-acoustic instrument operating at two wavelengths both before and after thermo-denuding. Some analysis of the rich dataset has been completed and published, some is nearing completion, and some is planned for the near future. The analysis of the thermo-denuded aerosol extinction and absorption showed very little difference in the absorption when an optically significant amount of clear organic matter was removed from the particles (as judged by the change in extinction). This observation stands in contrast to the theoretical expectations that a clear coating on black carbon particles tends to increase the absorption coefficient via light focusing through lensing. Subsequent electron microscopy measurements suggest that a substantial fraction of the BC-containing particles sampled during CARES did not have a core-shell morphology (which leads to the largest enhancement factors), consistent with the optical measurements. In a separate line of investigation, the dependence of extinction or scattering on relative humidity, characterized by an optical hygroscopic aerosol growth factor, γ {where b_{ext} (%RH) = b_{ext} (dry) * (100% - %RH)$^{-\gamma}$} was found to depend strongly on particle size and composition, with some periods of higher than expected particle growth for mainly organic aerosols. The role of super-micron particles (D_p > 1.0 μm) in the observed optical growth is still being investigated and appears to have been important, but it still seems likely that some of the organic aerosols observed during CARES had greater than expected hygroscopicity. Planned future analyses also include the use of three-wavelength extinction coefficient data at both ground sites to produce a separation of fine and coarse mode scattering and an estimate of the effective radius for the observed particle distributions, potentially allowing a complete retrieval of size and hygroscopic growth, using only the optical data for future field campaigns and longer-term unattended monitoring applications.

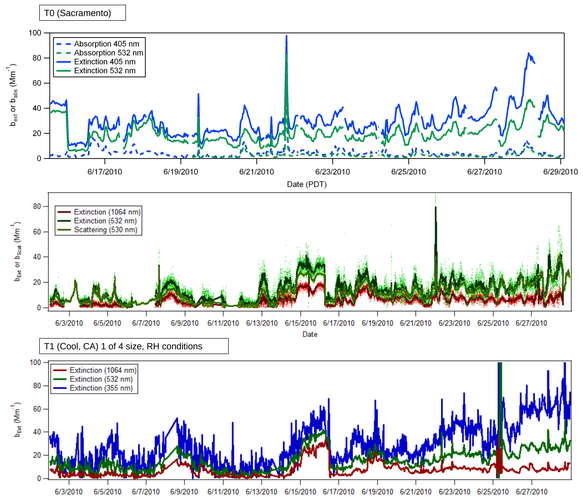

Figure 1: Optical Property Trends for the study duration. Much of the variation in the optical properties can be traced to changes in the large-scale flow in the Central Valley, as explained in the CARES overview paper and Fast, et. al.

Absorption Enhancement

The UC-Davis CRD and PAS instruments (405 and 532 nm) made aerosol optical extinction and absorption measurements with and without a thermodenuder (heated to 175 °C). This allows the possible role of non-absorbing organic components in enhancing the absorption of black carbon (the main absorber in atmospheric aerosols) to be directly determined by difference.

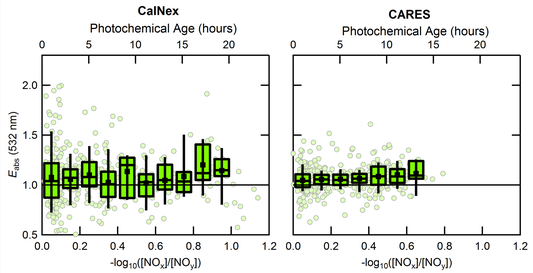

Figure 2: Direct observations of the absorption enhancement effect (of lack thereof) showing the relative change in the aerosol absorption coefficient following heating in the thermodenuder. There is little (~ 5%) change in the aerosol absorption following removal of non-absorbing organic components. The core-shell model predicts enhancements of 2.0 for atmospherically relevant mixtures of BC and organic aerosol components.

As shown above, there was a minimal decrease in the absorbance of the aerosol following heating. This was not because of a lack of non-BC volatile material, as demonstrated by the change in the optical extinction (not shown) and by results obtained with the SP-AMS (shown below). The logical conclusion is that the core-shell morphology that can be responsible for large absorption enhancements was not observed during CARES, as borne out by electron microscopy results.

There was an enhancement in the absorption of the near-UV (405 nm) with respect to the visible wavelength that could be removed by heating, which is attributed to a small amount of brown carbon absorption. The mass absorption coefficient for this material at 405 was determined to be ~0.2 m^2/g.

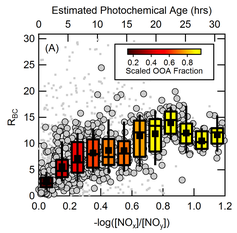

Figure 3: The observed increase in the coating thickness on the BC cores (as measured by the SP-AMS) with photochemical age. As shown above, the presence of volatilizable non-BC aerosol mass did not result in a change in absorption coefficient, so most of the observed decrease in extinction was due to loss of scattering material.

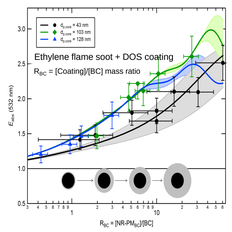

Figure 4: Laboratory measurements showing enhancement due to coating. There is reason to expect absorption enhancement based on theory and laboratory measurements.

Optical Hygroscopicity Measurements

Three instruments were deployed that could (in principle) obtain the optical hygroscopicity – the change in the extinction or scattering as a function of applied relative humidity. One instrument (PSU HC-CRDT) did not provide useful information, but the UC-Davis CRD-PAS at T0 and the MIT/PNNL Humidigraph at T1 provided nearly continuous records for the latter half of the CARES study period. The two instruments operated in different ways: the UC-Davis instrument lowered the incoming aerosol's RH to ~35% and then rehumidified to ~65% and ~85% in separate cavities, where the aerosol extinction coefficient was measured; the MIT/PNNL Humidigraph raised the incoming aerosol humidity to ~85% and then dried it to ~60% and ~ 30% in separate driers (Nafion diffusion type) and measured the scattering from the three RH aerosols using separate Aurora nephelometers.

The three extinction/scattering coefficients (b_{ext} or b_{scat}) are then log-transformed and a linear fit of ln (b) vs. ln (100% - RH) yields the optical hygroscopicity parameter γ, as shown in Figure 4 below.

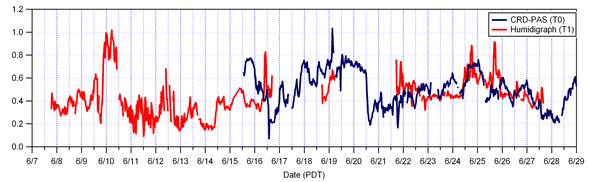

Figure 5: Derived optical hygroscopicity γ from the two RH-controlled instruments at the two ground sites. The data for the Humidigraph from the early part of the campaign was taken in a different mode than described above, so we chose to focus on the data that termporally overlapped the measurements at T0.

The optical hygroscopicity could not be well-modeled by simple consideration of the AMS-determined sub-micron composition, so we used a model that considered the temporally varying composition, size, and applied RH to predict the scattering for the lowest and highest relative humidity conditions. This model predicts the water uptake using the Petters and Kreidenweis kappa formalism and can achieve good agreement with the observations, as shown below.

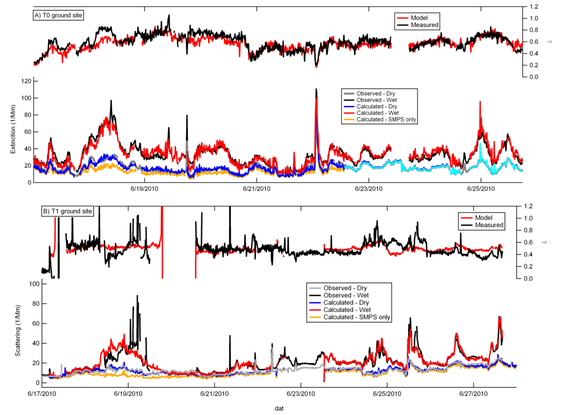

Figure 6: Results of size and composition resolved optical model (size-independent internal mixture assumption). The low RH scattering/extinction is well-represented after the super-micron mode is added. The high RH scattering/extinction agreement depends on the selection of kappa values for the OOA (oxidized organic aerosol) and for the super-micron fraction (unknown composition).

The next phase of the hygroscopicity measurement/modeling work is a realization that the mixing state of the different aerosol components is not completely characterized by the AMS. In the work shown, all of the components were assumed to be internally mixed with constant composition, independent of size. In fact, the AMS and single-particle instruments have determined that different size distributions are appropriate for the different components. Using the diurnal size distribution provided by Zhang and Setyan, we have constructed size distributions for three components (assumed to be ammonium nitrate, ammonium sulfate and the sum of the organic components (HOA + OOA + BC) which are being used to construct size dependent composition/refractive index/hygroscopicity, still assuming an internal mixture. Finally, we also plan to investigate the effect of assuming an external mixture on the modeled optical coefficients and optical hygroscopicity.

Using Multi-Wavelength and Multi-RH Measurements for Size and Composition

The effective radius of the aerosol fine mode can be obtained from a semi-empirical approach first demonstrated by O'Neill for the Aeronet/Aerocan ground-based sun photometer networks. The PSU HC-CRDT has extinction measurements at three wavelengths for each relative humidity condition, the minimum required for this approach. This could allow for a direct estimate of the growth factor, which could then be related to the sub-micron particle composition in an average sense (very hygroscopic inorganic vs. less hygroscopic organic modes). The CARES dataset offers the opportunity to attempt closure on these predictions with the AMS measurements. In this approach, the fine and coarse mode properties are separated and the fine mode effective radius can be predicted from the $\rho_{eff,f}$ parameter via the equation: $\rho_{eff,f} = 2\ (2\pi\ R_{eff,f} / \lambda)\ |m\text{-}1|$ assuming the refractive index is known.

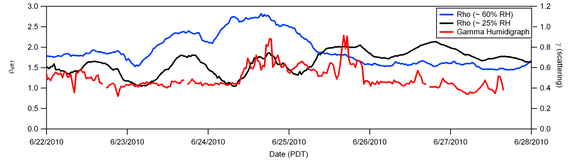

Figure 7: Effective radii for high and low relative humidity channels of HC-CRDT. The high RH in this instrument varied and only attained values of 60 – 65%. The red trace is the humidigraph's measurement of γ based on scattering measurements at ~80 and ~30 % RH.

Summary

- Little absorption enhancement observed in the thermodenuding experiments, despite abundant non-absorbing material associated with BC – core-shell morphology seems to not have been present.
- Some absorption enhancement at shorter wavelengths implicates the presence of brown carbon, albeit at low levels.
- The optical hygroscopicity of aerosols at T0 and T1 can be rationalized using collocated size and composition measurements and a model that predicts growth due to water uptake based on Petters and Kreidenweis kappa parameter.
- Ongoing work is examining the effect of different assumed mixing states in the optical hygroscopicity model.
- Future work will attempt to obtain self-consistent size and composition predictions from the multi-wavelength approach of O'Neill and the optical hygroscopicity model used here.

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