In past work, black carbon (BC) produced from incomplete combustion has been assumed to be the only major absorbing species in atmospheric aerosols. BC absorption follows a broad band spectral profile with an inverse wavelength dependence ($\beta$) from the UV to the near IR. This wavelength dependence is described by the Ångström absorption exponent (AAE), which is 1 for BC. Recent work has identified other absorbing aerosol species that can add to the absorption of BC resulting in enhanced absorption primarily at shorter wavelengths yielding AAEs greater than 1. Other important absorbing aerosol species other than BC are the water soluble organic compounds including humic-like substances, or HULIS. These aerosol species can become internally mixed with black carbon as the combustion aerosols age resulting in larger AAEs, enhanced hydropyrolysis and removal of the aerosols through cloud formation and rainout.

By using surface reflection spectroscopy, the absorption spectra of atmospheric aerosols were obtained in the UV-visible for accurate determination of aerosol AAEs. These results are compared to total aerosol carbon content, carbon isotopic analysis, and aerosol HULIS content measured by diffuse reflection FTIR spectroscopy. These results indicate that the aerosol HULIS content increases as the aerosols age and that this is primarily responsible for the observed enhanced UV absorption yielding overall aerosol AAEs from 1-2. In addition, carbon isotopic measurements show that the aerosol HULIS are biogenic in origin arising from biomass burning and/or SOA formation from biogenic precursors.

## EXPERIMENTAL METHODS

### Sample Collection

Samples of fine (<1.0 micron) aerosols were collected in Mexico City during the MILAGRO field study from March 1 (day 60) – 28 (day 88), 2006 at site T0 (IMP) and site T1 (TECAMAC). The Aerosol samples were collected on quartz fiber filters by using high volume samplers (Hi-Q Environmental. Products, Model HVP-3800AFC) equipped with cascade impactors (Thermo Anderson). Samples were taken at 12-hour intervals from 05:30 to 17:30 and from 17:30 to 05:30 local standard time (LST). The volume of air sampled during the 12-hour time period averaged 740 m$^3$.

### Spectroscopy

UV-Visible spectra were obtained on the filter samples directly from the UV-visible spectra in Kubelka-Munk format using all 2880 points in the UV-visible absorption profile. The FTIR spectra of most aerosol samples contained the broad OH stretching band from 3650-2700 cm$^{-1}$, aliphatic C-H stretching bands at 2921 and 2864 cm$^{-1}$. The bands at 1625 and 1425 cm$^{-1}$ are typical of the COO- bend and CO asymmetric stretch of the carboxylic acid. The bands at 1175 and 1025 cm$^{-1}$ are assigned to the C-O-C stretch of an ester or polysaccharide.

### Wavelength Dependence of Aerosol Absorption

[Figure showing wavelength dependence of aerosol absorption]

The Ångström Absorption Exponent (AAE, $\beta$) is determined by a linear fit to $\ln(A) = \ln(A_0) - \beta \lambda$ using all 570 points in the UV-visible absorption profile.

### UV-visible Absorption Profiles

UV-visible absorption profiles from selected aerosol samples collected at IMP and Tecamac compared to that for BC: $\beta = 1$.

### FTIR Spectra

The FTIR spectra of aerosol samples contained the broad OH stretching band from 3650-2700 cm$^{-1}$, aliphatic C-H stretching bands at 2921 and 2864 cm$^{-1}$. The bands at 1625 and 1425 cm$^{-1}$ are typical of the COO- bend and CO asymmetric stretch of the carboxylic acid. The bands at 1175 and 1025 cm$^{-1}$ are assigned to the C-O-C stretch of an ester or polysaccharide.

### FTIR Spectrum of Aerosol Sample

The FTIR spectrum of an aerosol sample (—) is compared to an aqueous humic acid (...) and an aqueous fatty acid (...) and to total aerosol carbon content, carbon isotopic analysis, and aerosol HULIS.

### Aerosol AAEs

Aerosol AAEs calculated from UV-Visible spectra of aerosol standards.

### Carbon Isotopic Measurements

The peak areas of the IR bands are generally higher at site T1 (+) than site T0 (—) indicating aging of the carbon aerosols. They are also generally lower during the rain events at T1 (+) and T0 (—) indicating possible washout of the more hydrophilic species. The peak areas of the IR band at 1025 cm$^{-1}$ is much higher at site T1, possibly due to emissions of polysaccharides from grass fires in the area.

### FTIR Spectrum of Aerosol Sample

The FTIR spectrum of an aerosol sample (—) is compared to an aqueous humic acid (...) and an aqueous fatty acid (...) and to total aerosol carbon content, carbon isotopic analysis, and aerosol HULIS.

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