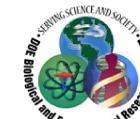




# The Effect of Aerosol Humic-like Substances (HULIS) on Aerosol Absorption.

Nancy A. Marley, Kristy L. Kelley, Amrita Sarkar, and Gail L. Bridges,  
Chemistry Department, University of Arkansas at Little Rock, Little Rock, Arkansas



## ABSTRACT

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 ( $\lambda^{-1}$ ) 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 hygroscopicity 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 reflectance 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<sup>3</sup>.

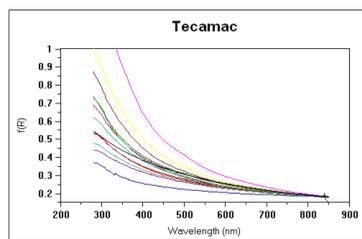
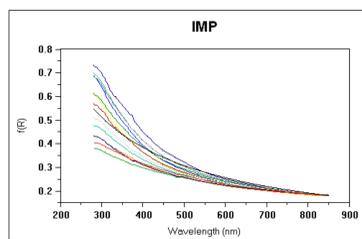
### Spectroscopy

UV-Visible spectra were obtained on the filter samples directly from 900 to 300 cm<sup>-1</sup> by using a 150 mm integration sphere coupled to a Perkin Elmer Lambda 850 spectrometer. AAEs were calculated from the UV-visible spectra in Kubelka-Munk format using all 2880 data points.

Kubelka-Munk theory defines the absorption and scattering components of the spectrum of highly scattering samples as a 2-flux radiative transfer problem and the K-M function is used to correct the diffuse reflectance spectrum to an absorption profile.

$$f(K-M) = (1-R)^2/2R$$

IR spectra were obtained on the aerosol samples after removing the particles from the filter substrate by abrading with a small disk of silicon-carbide paper attached to a platen. The platen is then placed directly into the diffuse reflectance accessory (Smart Collector) of a Nicolet 6700 FTIR Spectrometer equipped with a DLATGS/KBR detector.



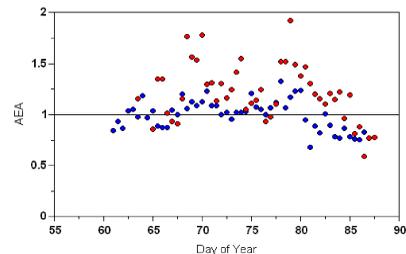
UV-visible absorption profiles from selected aerosol samples collected at IMP and Tecamac compared to that for BC (—).

**Wavelength Dependence of Aerosol Absorption**

The Ångström Absorption Exponent (AAE,  $\alpha$ );

$$A = \beta \lambda^{-\alpha}$$

Is determined by a linear fit to  $\ln(A) = \ln(\beta) - \alpha \ln(\lambda)$  using all 570 points in the UV-visible absorption profile.

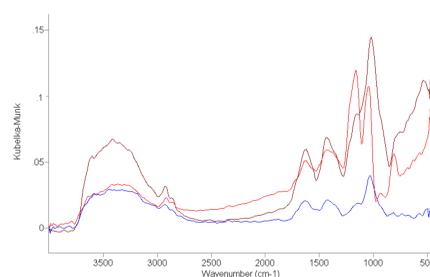


AAEs obtained from UV-visible spectra on aerosol samples collected at IMP (•) and Tecamac (•). AAEs are generally higher at Tecamac.

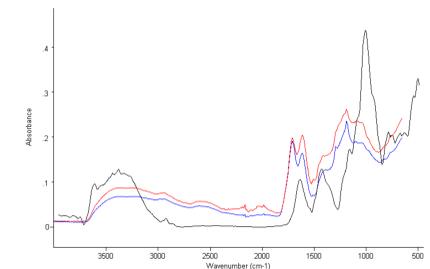
BC.....	1
BC + FA (1:10).....	1.5
BC + PAHs.....	1.1
BC + NPAHs.....	1.2
BC + FA + PAHs.....	1.6
BC + FA + NPAHs.....	1.7
Biomass Burning.....	2 <sup>a</sup>
HULIS.....	2-6 <sup>b</sup>
Aquatic Humic Acids.....	2
Aquatic Fulvic Acids.....	3

<sup>a</sup> Kirchstetter et al., JGR, 109, D21208  
<sup>b</sup> Andreae and Gelencser, ACP, 6, 3131.

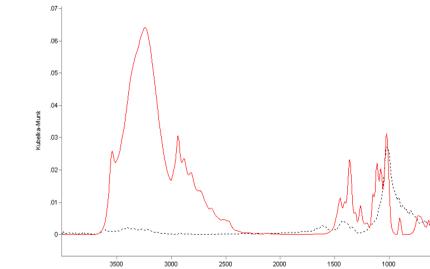
Aerosol AAEs calculated from UV-Visible spectra of aerosol standards.



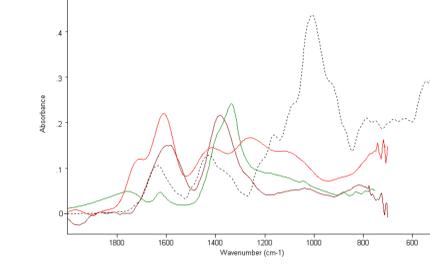
The FTIR spectra of most aerosol samples contained the broad OH stretching band from 3650-2750 cm<sup>-1</sup>, aliphatic CH stretching bands at 2921 and 2864 cm<sup>-1</sup>. The bands at 1625 and 1425 cm<sup>-1</sup> are typical of the COO<sup>-</sup> bend and CO asymmetric stretch of the carboxylate anion. The bands at 1157 and 1020 cm<sup>-1</sup> are assigned to the C-O-C stretch of an ester or polysaccharide.



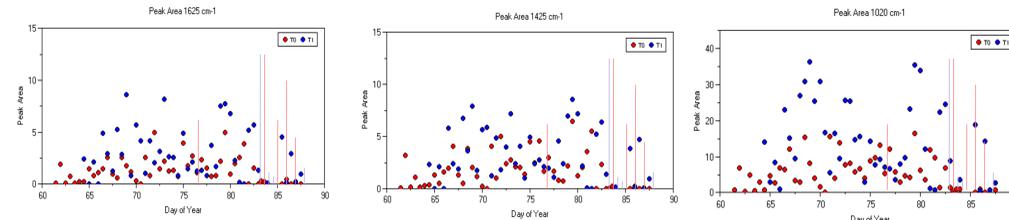
The FTIR spectrum of an aerosol sample (—) is compared to an aquatic humic acid (—), and an aquatic fulvic acid (—). The COOH bend and COH asymmetric stretch of the carboxylic acid appear at 1709 and 1613 cm<sup>-1</sup>.



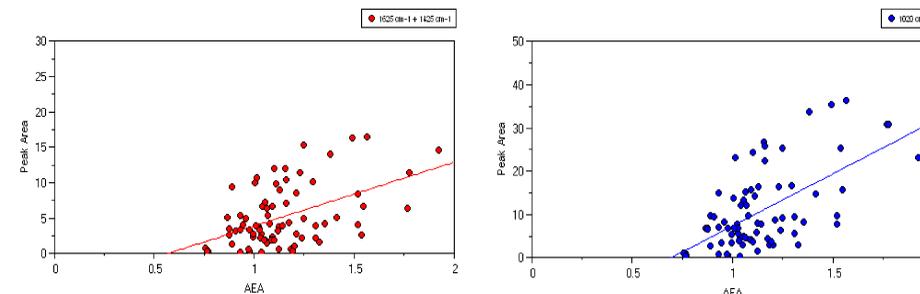
The FTIR spectrum of an aerosol sample (.....) is compared to glucose (—). The C-O-C stretch appears at 1020 cm<sup>-1</sup>.



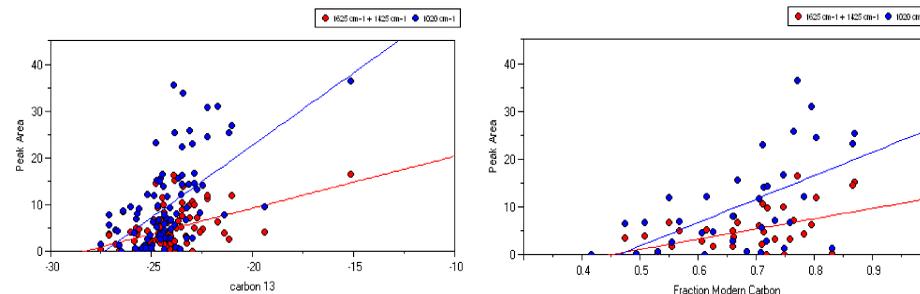
The FTIR spectrum of an aerosol sample (—) is compared to the aqueous solution spectra of an aquatic humic acid at pH 9 (—) and pH 11 (—) and the aqueous spectrum of the reaction product of  $\beta$ -caryophyllene with ozone (—).



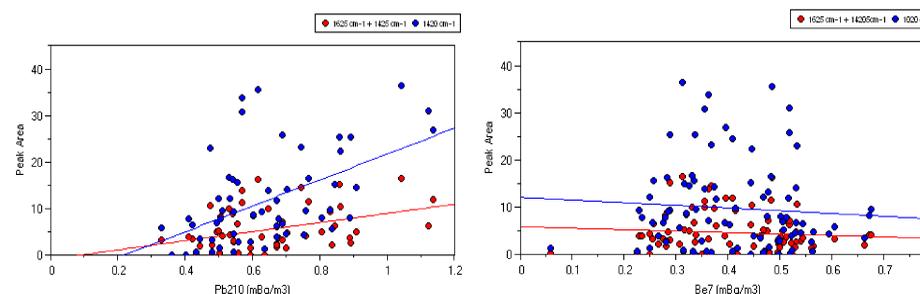
The peak areas of the carboxylate IR bands are generally higher at site T1 (•) than site T0 (•) indicating aging of the carbon aerosols. They are also generally lower during the rain events at T1 (—) and T0 (—) indicating possible washout of the more hydrophilic species. The peak area of the IR band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



The peak areas of the IR bands are correlated to the aerosol AAEs with correlation coefficients of 0.25 (1620, 1420 cm<sup>-1</sup>) and 0.4 (1020 cm<sup>-1</sup>). Indicating the oxidized organics are the source of the enhanced UV absorption. There is a stronger correlation with the polysaccharide C-O-C stretch (slope = 24) than for the carboxylate bands (slope = 9) indicating the importance of biomass burning aerosols to the enhanced aerosol absorption.



The peak areas of the IR bands are correlated to the aerosol carbon isotopic content (<sup>13</sup>C and <sup>14</sup>C) with correlation coefficients of 0.2 (1620, 1420 cm<sup>-1</sup>) and 0.3 (1020 cm<sup>-1</sup>) for <sup>13</sup>C and 0.3 for <sup>14</sup>C. Indicating the carboxylates are of biogenic origin.



The peak areas are also correlated with the concentration of the terrestrial isotope <sup>210</sup>Pb with correlation coefficients of 0.2 (1620, 1420 cm<sup>-1</sup>) and 0.3 (1020 cm<sup>-1</sup>). However, they show no correlation with the concentration of the cosmogenic isotope <sup>7</sup>Be.

## ACKNOWLEDGEMENT

This work was conducted as part of the Department of Energy's Atmospheric Systems Research Program. This work was supported by the Office of Science (BER), U.S. Department of Energy, Grant No. DE-FG02-07ER64328 and Grant No. DE-FG02-07-ER64329.