5.2 FORMATION AND TRANSFORMATION OF HUMIC-LIKE SUBSTANCES (HULIS) IN ATMOSPHERIC AEROSOLS: RELATION TO CLIMATE FORCING

Nancy A. Marley*, Jeffrey S. Gaffney
University of Arkansas at Little Rock, Little Rock, AR

1. INTRODUCTION

Humic-like substances (HULIS) have been identified in the water soluble component of atmospheric aerosols, comprising as much as 50% of the water soluble aerosol species at both urban and rural sites (Cappiello, et al., 2003; Limbeck, et al., 1996). These substances have been found to resemble the aquatic humic and fulvic acids, which are known to play important roles in groundwater chemistry. These aquatic humic and fulvic acids are complex organic polymers that have strong uv-visible absorption profiles attenuating the penetration of UVB radiation in the water column (Gaffney et al., 1996; Yacobi et al., 2003). They also have strong IR absorptions that include intense carboxylate and ether bands between 800-1700 cm^{-1} (Gaffney et al., 1996; Marley et al., 1996; Kim et al., 1990). These materials are also known to complex metals and radionuclides very strongly leading to transport over much longer distances than previously estimated (Marley et al, 1993; Penrose et al., 1990).

The HULIS are similar complex organic polymers found in atmospheric aerosols and precipitation samples that have similar chemical functionalities and properties as the aquatic humic materials, although they are typically smaller in molecular weight (Graber and Rudich, 2006). The HULIS also have strong absorption bands in both UV-visible and IR spectral regions and are therefore of interest with regard to radiative balance and climate forcing (Andreae and Gelencser, 2006; Hoffer et al., 2006). The principal absorbing aerosol species has long been thought to be black carbon (BC) derived from incomplete combustion processes. The HULIS are an additional carbonaceous aerosol species that has the potential of contributing to the absorbing aerosols in addition to BC.

The HULIS can be formed by secondary photochemical reactions leading to water soluble species that can subsequently undergo organic condensation reactions resulting in the formation of these polymeric materials in acidic aerosols (Limbeck, et al., 1996; Holmes and Petrucci, 2006). HULIS can also be produced directly by primary combustion processes involving biomass burning (Hoffer et al., 2006). In addition, atmospheric oxidation and aging of the HULIS can also occur by reaction with ozone, OH and NO_3 radicals, as well as reaction with soluble oxidants such as H_2O_2, organic peracids, and organic peroxides (Jammoul, et al.,2008; Vione et al., 2006).

Past work on groundwater humic and fulvic acids has made use of diffuse reflectance spectroscopy to characterize key functional groups, particularly the carboxylate and hydroxy species (Marley et al., 1996). This same technique has been used to characterize the HULIS in atmospheric aerosols in the Mexico City area. These results are compared with the aerosol absorption profiles as well as carbon isotopic analysis. The likely HULIS formation processes are discussed along with a brief comparison of the spectral properties of these materials to the aqueous humic and fulvic acids.

2. METHODOLOGY

Fine mode (<1 micron) aerosol samples were collected in Mexico City in March 2006 as part of the Megacity Aerosol Experiment, Mexico City 2006 (MAX-Mex) sponsored by the U.S. Department of Energy (DOE). The samples were collected at the Instituto Mexicano del Petróleo (T0) located in the north central part of Mexico City and at the Technological University of Tecamac (T1) located north of Mexico City and 18 miles northwest of site T0. 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). The air samplers are equipped with brushless, three stage centrifugal fan blowers controlled by an electronic mass flow sensor that detects changes in the operators pre-set flow rate caused by changes in temperature, barometric pressure, and pressure drop due to dust loading on filter media. It compensates for these changes by adjusting the motor speed to maintain the pre-set flow rate at 40 scfm. The quartz filter samples were taken at 12-hour intervals from 5 am to 5 pm (day) and from 5 pm to 5 am (night). The volume of air sampled during the 12-hour time period averaged 740 m^3 with an average aerosol loading of 13 mg total carbon content.

Aerosol absorption was characterized in the infrared (IR) by using diffuse reflectance infrared spectroscopy (Nicolet 6700 FTIR with a Smart Collector Accessory). The aerosol samples were removed from the filter substrate by abrading with a small disk of silicon-carbide paper attached to a platen. The platen is placed directly into the diffuse reflectance accessory (Thermo Scientific Smart Collector). The accessory is

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**Corresponding author address:* Nancy A. Marley, University of Arkansas at Little Rock, 2801 S. University Ave., Little Rock, AR 72204-1099; e-mail: namarley@ualr.edu.

equipped with an integral gold mirror that is used as a background reference.

The aerosols samples were characterized in the UV-visible spectral range by using a research grade UV-visible-NIR spectrometer (Perkin Elmer Lambda 1050) equipped with an integration sphere reflectance accessory (Labsphere) for solid sample analysis. The integration sphere is designed to collect all the light scattered by the surface of the sample and direct it back to the detector, thus eliminating the scattering errors that can occur in light attenuation measurements on solid samples (Marley et al., 2001).

3. RESULTS

The FTIR spectrum of a humic acid is shown in Figure 1A. The prominent features in the humic acid spectrum are the broad band centered at 3400 cm^{-1} due to hydrogen bonded OH stretch, the carboxylic bands at 1700, 1610 and 1400 cm^{-1} (COOH, COO$^-$ asym, and COO$^-$ sym), and bands at 1170 (sym) and 1040 cm^{-1} due to C-O stretch of alcohols or polysaccarides. This can be compared to spectra of the fine aerosols collected in Mexico City shown in Figure 1B. The spectra very closely resemble that of humic acid in Figure 1A and the majority of the features can be attributed to the presence of HULIS in the aerosols. While the carboxylate bands are evident at 1620 and 1420 cm^{-1}, there is no evidence of the protonated acid band at 1700 cm^{-1} in the aerosol samples. The C-O stretching bands are present at 1020 and 1150 cm^{-1} and overlapping shoulders also appear in this region at 1100 and 1200 cm^{-1}, which are most likely due to aromatic ether groups.

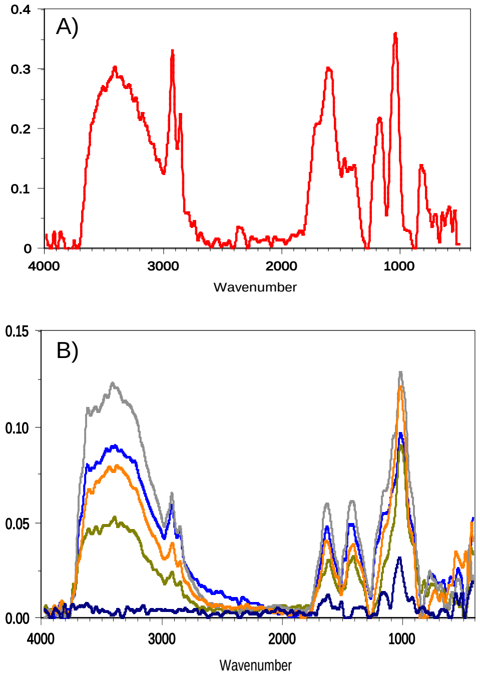

Figure 1. FTIR spectrum of a humic acid (A) and spectra of fine aerosols collected in Mexico City (B).

The evolution of these prominent functional groups in the aerosol samples can be followed by determining the band strengths. The presence of ether or alcoholic C-O groups in the organic aerosol species, as indicated by the intensity of the 1020 cm^{-1} band, is more predominant at site T0 than at site T1 and decreases at both sites during the later part of the study, when both sites were impacted by intense rain events (Marley et al., 2008a).

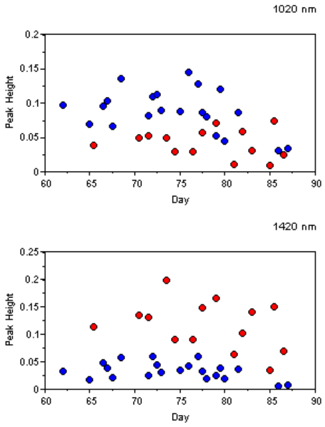

Figure 2. Changes in band strengths over time at 1020 cm^{-1} and 1420 cm^{-1} in the infrared spectra of fine aerosol samples collected in Mexico City at site T0 (blue) and T1 (red) in March 2006.

In contrast, the presence of carboxylate groups, as indicated by the intense symmetric COO$^-$ stretch at 1420 cm^{-1}, is more predominant in the aerosols collected at site T1 than at site T0. This is an indication of the production of HULIS in the aerosols at site T1 and can result either from chemical aging (i.e. oxidation by OH, ozone, NO_3, etc.) of the aerosols involving condensation reactions on acidic surfaces resulting in the formation of polyacids or from aerosols produced directly from biomass burning observed at site T1. These results are consistent with results obtained from carbon isotopic analysis that show higher fraction of modern carbon in aerosols at T1 than those at T0 (Marley et al., 2008b).

The aerosol absorption in the UV-visible range is described by $A = \beta\lambda^{-\alpha}$; where α is the absorption Ångstrom exponent (AAE) and β is the aerosol absorption at 1 µm. The value of α depends on the chemical composition of the absorbing aerosol (Bergstrom et al., 2007). Freshly emitted BC particles from diesel engines have an AAE of 1 (Bergstrom et al., 2002; Marley et al., 2001) while carbonaceous aerosols produced from biomass burning have much stronger wavelength dependence of absorption, with an AAE of 2 (Kirchstetter et al., 2004).

The AEAs determined from UV-visible spectra of aquatic humic acids were determined to be 1.5-2.4 while that for the smaller fulvic acids were 2.7-3.1. The aerosol AAEs determined on samples collected in Mexico City are shown in Figure 3. The AAEs observed at site T1 are higher than those observed at site T0, consistent with the presence of polycarboxyllic HULIS, which are also known to have increased UV absorbance over that due to black carbon alone (Hoffer et al., 2006).

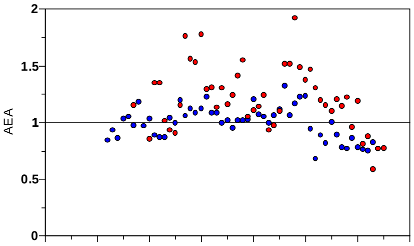

Figure 3. Fine aerosol Ångstrom absorption exponents determined on samples collected in Mexico City at site T0 (blue) and T1 (red) in March 2006.

4. CONCLUSIONS

The HULIS in atmospheric aerosols, like their aqueous counterparts, have strong absorptions in the UV and infrared spectral ranges. Their intense UV absorptions contribute to higher aerosol AEAs than BC aerosols resulting in more highly absorbing aerosols with larger than expected radiative forcing impacts.

The characteristic IR absorption bands can also be used to follow the formation and evolution of HULIS in atmospheric aerosols with time. Aerosols collected in Mexico City (site T0) have more C-O content and less carboxylate content than those obtained north of the city at site T1. This is consistent with higher AEAs at site T1 and a larger fraction of modern carbon as determined from radiocarbon analysis.

5. ACKNOWLEDGEMENT

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