Quantitative Analysis of Volatile Organic Aerosols in the Atmosphere

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Introduction

An atmospheric research project was performed in conjunction with the Appalachian Atmospheric Interdisciplinary Research Program (AppalAIR) on the campus of Appalachian State University to quantify aerosols in the atmosphere. Organic aerosols may affect human health, cloud microphysical properties, as well as directly impacting the solar radiation budget. Sampling was performed from the main AppalAIR research site, which is collaborating with the National Oceanic and Atmospheric Administration (NOAA) to aid in a global network of aerosol monitoring. A program continues to be developed for quantification and identification of aerosols via Scanning Electron Microscopy (SEM) as well as by Gas Chromatography - Mass Spectrometry (GC-MS). Backward wind trajectories were used to perform a cluster analysis, yielding the origin of sampled air.

Methods

Measurements

Aerosol chemical analysis – Met One speciation sampler
Aerosol light scattering – TSI 3 λ integrating nephelometer Radiance Research integrating nephelometer
Aerosol light absorption – Radiance Research 3 λ PSAP; Magee Scientific 7 λ aethalometer and custom UV 6 λ aethalometer
Aerosol light extinction – CRD spectrometer
Aerosol number concentration – TSI CNC 3007
Trace gases – O_3, CO_2, and H_2O
Standard and Micro-meteorology

Chemical Analysis

Quartz fiber filters were used to collect 24 h aerosol samples for chemical analysis. A Headspace Solid Phase Microextraction (SPME) technique was developed and optimized for extraction of specific marker species. The GC-MS method was developed using an Agilent 689-N Network GC System with 5973 inert MS to separate and quantify seven marker species; SEM scans were performed on filter samples as well, using an Hitachi S4000 Force Emission Scanning Electron microscope (FESEM).

Cluster Analysis

The NOAA HYSPLIT model was used to calculate backward wind trajectories to determine the origins of the air sampled at the AppalAIR site. Seventy-two hour back trajectories were run every 8 hours for JJA at 500 m, 1000 m, and 1500 m AGL. Results were clustered using a clustering algorithm on the HYSPLIT model.

Results

Aerosol measurements were used to determine the particle scattering and absorption coefficients, as well as to calculate the corresponding single scattering albedo and Ångstrom exponent; time series plots are shown in Figure 1,a-d.

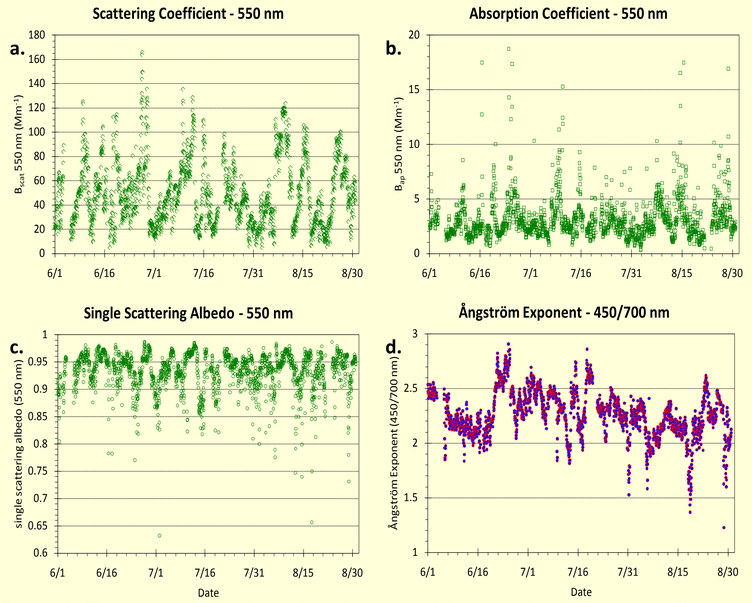

Figure 1: Time series data (June, July, August) of the particle scattering coefficient at 550 nm (a.), the particle absorption coefficient at 550 nm (b.), the single scattering albedo at 550 nm (c.), which is the ratio of the particle scattering coefficient to the total extinction due to particles, and the Ångström exponent (d.), which is inversely related to particle size.

Results from the optimization of the SPME/GC-MS method have determined that more marker species were efficiently extracted by a DVB/CAR/PDMS fiber, which contains both polar and non-polar polymer layers. The optimal extraction temperature and extraction time were 150°C and 30 minutes, respectively. A standard addition method is being developed to accurately quantify the seven marker species on continually sampled filters. Results of the SPME fiber optimization are displayed in Figure 2.

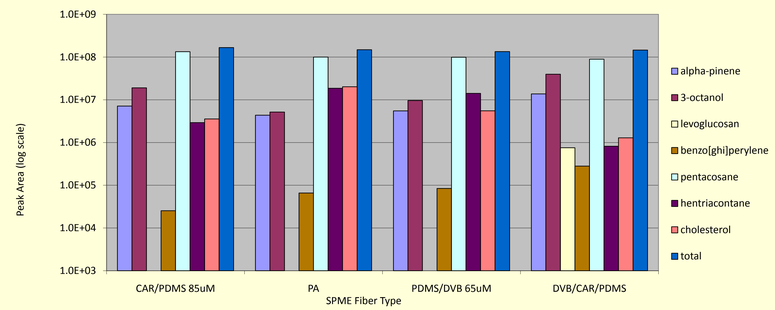

Figure 2) Bar graph of peak areas for marker species by extraction fiber

The average trajectories of the eight clusters (1000 m) identified by HYSPLIT are shown in Figure 3. An ANOVA was performed based on the cluster results to determine statistical differences among the clusters; the results from an ANOVA of particle scattering coefficient at 550 nm, the particle absorption coefficient at 550 nm, the single scattering albedo at 550 nm, and the Ångström exponent are shown in Figure 4..

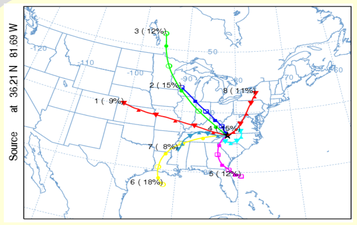

Figure 3: Calculated average back trajectory clusters at 1000 m

Initial results from FESEM scans of quartz fiber filter samples shows a wide variety of aerosol shapes and sizes; most aerosols during the summer months were sub-micron fractal agglomerates like those shown in Figure 5. Research continues towards developing rigorous SEM analysis.

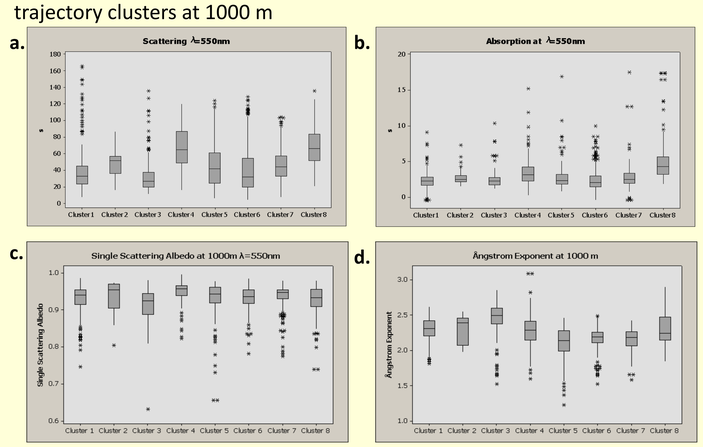

Figure 4: ANOVA results the particle scattering coefficient at 550 nm (a.), the particle absorption coefficient at 550 nm (b.), the single scattering albedo at 550 nm (c.), and the Ångström exponent (d.)

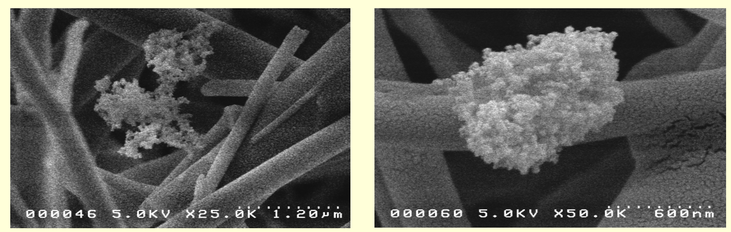

Figure 5: Examples from the SEM analyses of the 24 h filter samples collected at the AppalAIR site on 27 June, 2009. Many of the particles detected by the SEM analyses were sub-micron fractal agglomerates, such as those pictured.

Discussion

Initial results indicate small, highly absorbing, carbonaceous aerosols. These results differ from previous assumptions regarding eastern U.S. aerosol properties. The cluster analysis shows several meteorological regimes that impact the area and a wide range of aerosol influences. Optimization of the SPME/GC-MS chemical analyses is completed, and a quantification of the marker species will begin; a comparison between the SPME extraction method developed and various solvent extraction methods is planned. We will also commence calculations of the aerosol radiative forcing based on both the meteorological and chemical regimes.

Research continues towards an accurate source apportionment model to estimate source contributions of aerosols. Validation of the produced model will depend on comparisons with available aerosol source data; exploring uses of filter SEM analysis will continue to be developed through future work.

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References

Draxler, R.R. and Rolph, G.D., 2003. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). NOAA Air Resources Laboratory, Silver Spring, MD.