Ambient Observations of Aerosol Optical Properties During TexAQS II Using Cavity Ring-Down

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Introduction

Whenever the air quality in a state or region does not meet National Ambient Air Quality Standards (NAAQS), the area is designated by the U.S. EPA as a non-attainment area. Any state with areas that are not in attainment must submit a State Implementation Plan (SIP) that explains how the state will comply with Clean Air Act air quality standards. Texas has 39 counties, including the Houston-Galveston Area (HGA), that are non-attainment areas or areas of high concern, and therefore must update the current SIP. In order to address high priority SIP-relevant questions, the Second Texas Air Quality Study (TexAQS II), an 18 month-long field campaign in Texas, in 2005and 2006, was conducted to supply the needed scientific and air quality information.

Figure 1: Aerial Photograph of HGA. The approximate location of the Moody Tower site can be seen in relation to Downtown Houston and the Houston Ship Channel. With over 5.2 million people in the HGA, it is classified as the seventh largest urban area in the United States. The metropolitan center of the HGA is located at latitude 29.75 and longitude -95.35. The climate of this location is semi-tropical with typically hot, sunny, humid summers. A combination of the meteorology and highly concentrated chemical and petrochemical industrial activities in the area make it particularly susceptible to air quality concerns.

As part of the TexAQS II sub-study, TRAMP (TexAQS II Radical and Aerosol Monitoring Project,) the Atkinson research group used a tandem pulsed cavity ring-down transmissometer/nephelometer (CRDT/N) to make aerosol optical property measurements on the 200-foot tall Moody Tower at the University of Houston from August 14, 2006 to September 27, 2006. (Figure 1) The optical property data from this well mixed site can serve as an indicator of the local background concentration of fine aerosols ($PM_{2.5}$) and help determine the effect of regional transport on the air quality of non-attainment areas in and downwind of Houston. In addition, the real-time optical property measurements can be used to determine urban air quality patterns and as an input to improve predictive and exposure models.

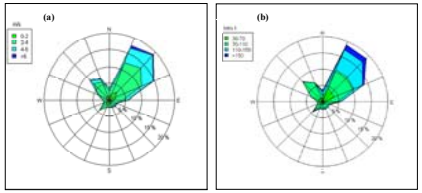

Figure 2: Wind Roses for Moody Tower. a) Data collected between September 1, 2006, 00:00:00 CST and September 6, 2006 23:59:59 averaged over two minute intervals, were used to plot wind speeds versus wind directions. Data for the entire study duration was unavailable. During the six day period shown here, wind speeds ranged between 0 and 10 m/s, with 2-4 m/s as the predominant speed. The wind direction in relation to the Moody Tower measurement station was dominated by the winds from the NE, NNE, and ENE. **b)** An extinction wind rose for the same time period shows that the extinction is dominated by particles that originate from the NE. This direction corresponds to the location of the ship channel and several petrochemical plants. The city of Houston lies to the NW.

Instrumentation and Methods

To understand the background particulate conditions and evaluate air quality trends in Houston, average particulate optical properties were calculated from the data. The whole study average provides insight into the composition and levels of ambient $PM_{2.5}$ in Houston. Daily averages can be used to evaluate if there are any clear population-linked trends in the particulate concentrations. Hourly averages help to show the diurnal variations in the background levels and can be compared to emission inventories, traffic data and meteorological data to understand the impact of these sources on the Houston air quality. Comparison of CRDT/N results with other instruments is not in the scope of this poster, but could be helpful in evaluating the potential of the CRDT/N technique for regulatory use.

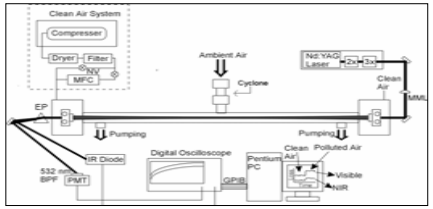

Figure 2. Schematic of the CRDT used. This technique uses two high reflectivity (>99%) dielectric mirrors to "trap" light in a cavity where the light makes thousands of passes between the mirrors. With each pass the light intensity decreases due to absorption and scattering as well as mirror losses. By measuring the decay rate of the light as it passes through a sample and comparing it to the corresponding decay rate of filtered air, the fractional losses in intensity due to the particles can be measured. This instrument is also coupled to a Radiance Research Nephelometer (530) and a TSI condensation particle counter. Validation studies show that the CRD measures the extinction coefficient while the nephelometer measures the scattering coefficient. With the tandem instrument it is possible to obtain the absorption coefficient by subtraction.

Results

The optical property time series data for the TRAMP study in Figure 4 show that the particulate matter concentrations in HGA have both daily and long term trends. Since ambient measurements of pollutants are thought to be an indicator of emissions, analysis of the data for cycles can help determine major sources of particulate matter. Spectral analysis of this data set in Figure 5 shows that the particulate patterns in Houston exist on a five day pattern, but a longer sampling time is needed for complete understanding of the trend for HGA. Smaller 24-hour and 12-hour cycles were also indicated by the analysis.

Typically a seven day cycle with weekday highs and weekend lows is expected in a densely populated urban area. Houston's deviation from this pattern could be due to either high levels of industrial emissions that mask trends due to transportation, wind patterns and other variable meteorological conditions or a combination of both. Further analysis and model studies on larger data sets would help to clarify the emission sources responsible for the observed trends.

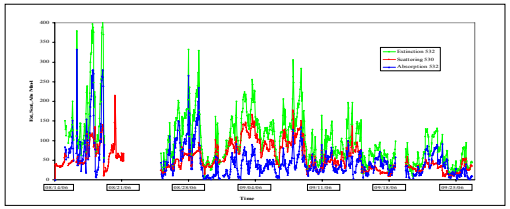

Figure 4: Optical Property Hourly Averages and Trends for the study duration. High and low cycles can be observed throughout the study but there is no clear weekly pattern.

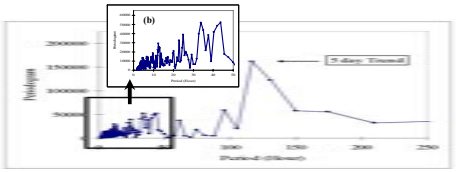

Figure 5: Spectral Analysis of Absorption Time Series Data. Spectral analysis was performed on all three optical properties and results for absorption are shown. Extinction trends were similar to absorption. Scattering trends were less obvious, an indication that the cycles noted in the extinction measurements are caused primarily by absorbing particles. The major trend that could be determined was approximately a five day, or 117 hour, trend. **b) (inner graph)** Several less dominant short term absorption cycles were visible with truncated x and y-axes. These occur at approximately 12, 24 and 34-37 hours.

Table 1: Daily Averaged Measured Values With Calculated Absorption and Mass Concentration. In response to studies that linked $PM_{2.5}$ exposure to increased risk of premature death in sensitive populations, decreased lung function, and development of chronic respiratory problems in children the EPA strengthened the 24-Hour $PM_{2.5}$ standard from 65 $\mu g/m^3$ to 35 $\mu g/m^3$ in 2006. The annual standard, which determines long term exposure, remained at 15 $\mu g/m^3$. (Values that exceed this level have been highlighted red.) Since these NAAQS standards are in units of concentration, the optical measurements must be converted from $b_{scattering}$ and $b_{absorption}$ to $\mu g/m^3$. Since the mass scattering and absorption coefficients for the Houston area are not yet available to the public, well documented values that represent general urban conditions were chosen for this analysis. To convert $b_{absorption}$ to mass concentration of light absorbing carbon (LAC,) the value of 7.5 m^2/g was used as suggested by Bond et al. The conversion of $b_{scattering}$ to mass was accomplished by dividing the scattering coefficient by 6.73 m^2/g. This value was calculated for the conversion of scattering from ammonium sulfate and particulate organic matter to mass at a relative humidity of 60% by Sciare et al.

Day Of the Week	532 Extinction Mm-1	530 Scattering Mm-1	Scattering PM $\mu g/m^3$	532 Absorption Mm-1	SSA	LAC $\mu g/m^2$	PM 2.5 $\mu g/m^3$
Monday	98.9±5.4	49.6±2.1	7.4	47.6±4.0	0.5	6.3	13.7
Tuesday	94.3±4.9	53.5±2.2	8.0	41.7±3.5	0.6	5.6	13.5
Wednesday	79.1±4.8	49.5±2.0	7.3	33.6±3.6	0.6	4.5	11.8
Thursday	126.7±7.5	70.8±3.1	10.5	57.5±5.5	0.6	7.7	18.2
Friday	118.7±6.4	65.8±3.3	9.8	54.1±4.1	0.6	7.2	17.0
Saturday	102.8±5.5	49.8±3.0	7.4	52.5±3.4	0.5	7.0	14.4
Sunday	98.1±6.2	54.9±3.8	8.2	47.9±3.0	0.6	6.4	14.5
Study Average	102.7±2.3	56.3±1.1	8.4	47.8±1.5	0.6	6.4	14.7

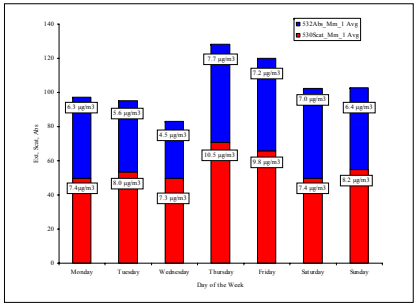

Figure 6: Daily Average Optical Properties for TRAMP 2006. The overall average is slightly below the NAAQS annual standard of 15 $\mu g/m^3$ but there were over 50 hours where this standard was exceeded over the course of the study. The averages for both Thursday and Friday are also above the standard, indicating that specific $PM_{2.5}$ control strategies will be necessary in the Houston area.

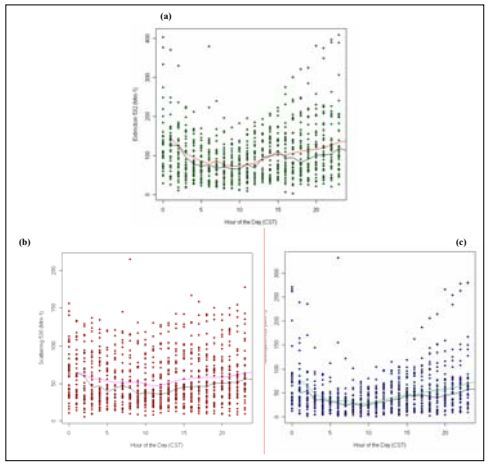

Figure 7 :Hourly Averages of Optical Properties for an "Average" Houston Day With Mean and Median Lines. a) The mean line (red) and the median line (black) for particle extinction both indicate a pattern where the highest levels of extinction are at night and the low occurs around sunrise. **b)** The mean line (pink) and median line (black) for scattering show that particulate scattering in the Houston area is relatively constant on a daily basis. **c)** The Absorption trend has a similar fluctuation as the extinction since both the mean (green) and median (black) lines have nighttime highs. The fluctuations observed in the daily extinction patterns are most likely due to changes in levels of absorbing particles.

Summary

- Spectral analysis indicated a five day optical property trend that was dominated by levels of absorbing particles.
- The daily average particle extinction at 532 nm in Houston from August 14 to September 28, 2006 varied between 79.1 ± 4.8 Mm^{-1} and 126.7 ± 7.5 Mm^{-1} depending on the day of the week.
- The daily average scattering at 530 nm was 56.3 ± 1.1 Mm^{-1}, which corresponds to an average concentration of 8.4 $\mu g/m^3$ scattering particles over the course of the study.
- The 532 nm particle absorption and single scattering albedo (SSA) are also derived from the measured extinction and scattering coefficients.
- The average SSA during the study period was 0.55.
- Daily average absorption coefficients ranged between 33.6 Mm^{-1} and 57.5 Mm^{-1}. The study period average was 47.8 Mm^{-1}, which corresponds to a mass concentration of 6.3 $\mu g/m^3$ for light absorbing carbon.
- The calculated scattering and absorbing particle concentrations indicate that HGA had an average particle concentration of 14.7 $\mu g/m^3$ during the six week TexAQS II study.

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