New York State Energy Research and Development Authority

Beyond OC—A Method to Extract and Interpret Additional Aerosol Organic Carbon Fractions from Thermal Optical Analysis of Filter-Based and Continuous Data

Final Report

November 2011

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Beyond OC—A Method to Extract and Interpret Additional Aerosol Organic Carbon Fractions from Thermal Optical Analysis of Filter-Based and Continuous Data

Final Report

Prepared for the

New York State Energy Research and Development Authority

Energy. Innovation. Solutions.

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Executive Summary

Carbonaceous particulate matter is ubiquitous in the ambient environment and comprises a major fraction of aerosol mass in New York State (NYS). Its sources are many and varied, including fixed and mobile combustion sources, biological sources, and atmospheric transformations of anthropogenic and natural hydrocarbon species from gaseous to condensed forms (SOA or secondary organic aerosol). The complexity of gaseous and condensed phase chemistry of carbonaceous particulate matter (PM) and its precursors presents a major challenge to measurement, modeling, and policy-related science.

Aerosol mass concentrations in general, and aerosol carbon in particular are subjects of great interest to regulators as well as scientists in NYS. Many areas of NYS are near or above the National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$. Carbon is a major fraction of the $PM_{2.5}$ mass, with carbonaceous compounds typically comprising 40% or more of the mass. New York State struggles to bring a number of downstate counties into compliance with the current $PM_{2.5}$ NAAQS, while at the same time there is pressure on the EPA to lower the standard, which may cause additional parts of the state to come into nonattainment. Given that carbon is a major component of fine aerosol (or $PM_{2.5}$), it is of critical importance to understand the identity of the carbon compounds in the $PM_{2.5}$ as well as their sources and transformations. This type of information is necessary for State Implementation Plans and for the protection of human health.

While the scientific community has methods to measure the overall amount of carbon (and in some cases carbonaceous compounds) in the $PM_{2.5}$ matrix, it is a significant challenge to identify individual carbon-containing compounds. While progress has been made in this area, only about 25% of the carbon-containing compounds in $PM_{2.5}$ have been uniquely identified. It is possible to assign compounds to broad classes, but since there may be hundreds or even thousands of individual compounds, unique identification of all carbon-containing compounds may not be an achievable or reasonable goal.

The most common carbon-specific measurement method for $PM_{2.5}$ is the thermal optical method, which thermally decomposes and oxidizes the particle-bound carbon before quantitatively detecting the carbon in various ways. The carbon is "split" into broad classes, empirically called OC for organic carbon, and EC for elemental carbon. Some implementations of the method divide the OC and EC classes into sub-classes, for example, OC1, OC2, OC3, OC4, EC1, and EC2. The method is "optical" because a laser, either in transmission or in reflectance, determines the split between OC and EC. Broad OC and EC classes, and the subclasses derived from them, are empirically determined by the method, and different implementations of the thermal optical method assign different values to the concentrations in various classes. This measurement difficulty leads to high levels of uncertainty regarding the sources of this important PM component, which in turn leads to uncertainty in the design and implementation of pollution control strategies for $PM_{2.5}$.

The goal of the project was to improve the measurement products, both through novel analysis and interpretation of the data produced by the method, and, if possible, through a better implementation of the measurement method to allow the mining of additional useful data from the measurements. The following accomplishments from this project will be explained further in the next sections of this report.

- A suite of organic (and inorganic carbonaceous) aerosols were generated in the laboratory and the thermograms produced by these pure species were measured using four different well-defined measurement protocols
- A series of experiments was performed using a Combustion Aerosol Standard (or CAST) system. The controlled combustion system allowed variable combustion conditions, while measuring detailed thermograms using one or more temperature protocols

- By combining the CAST system and an aerosol atomizer, detailed thermograms for mixed organic (combustion) and inorganic aerosols were measured
- Semi-continuous (hourly) thermogram data from Pinnacle State Park were analyzed using Positive Matrix Factorization (PMF). A five-factor solution yielded stable results with interpretable factors and small residuals
- The time series of the reported carbon fractions from the filter speciation data from the seven EPA network protocol sites in NYS were examined. This gives a pictorial display of the changing "volatility classes" of the aerosols at the different sites as a function of location and season

The policy relevance of this work to NYS comes from the pressing need to meet the requirements of air quality regulations for particulate matter ($PM_{2.5}$), and the important contribution of carbonaceous compounds to $PM_{2.5}$. Carbonaceous PM comes from many kinds of combustion activity, including an important contribution from fossil fuels burned in the process of electricity generation. A complete understanding of the sources of this carbon, its chemical properties, and the atmospheric processes involved in its transport and deposition, are necessary tools to achieve and maintain attainment with the air quality standards for all of New York State.

ASRC Laboratory Measurements

The emphasis for this task was on methods development and evaluation. Table 1 lists the compounds selected for laboratory tests. Many of these compounds had been generated to measure the AMS (Aerosol Mass Spectrometer) mass spectra. Compounds were selected to sample as wide a range of aerosol compounds as possible, considering the additional criteria of cost, safety and feasibility.

Table 1. Carbon-containing compounds selected for laboratory testing. (The two inorganic carbonates were added for completeness.)

Compound	Formula	MW	Class	Solubility
Glyoxylic Acid	$C_2O_3H_2$	74	Monocarboxylic Acid	Water
Oxalic Acid	$C_2H_2O_4$	90	Dicarboxylic Acid	Water
Malonic Acid	$C_3H_4O_4$	104	Dicarboxylic Acid	Water
Succicinic Acid	$C_4H_6O_4$	118	Dicarboxylic Acid	Water
Glutaric Acid	$C_5H_8O_4$	132	Dicarboxylic Acid	Water
DL-Malic Acid	$C_4H_6O_5$	134	Dicarboxylic Acid	Water
Adipic Acid	$C_6H_{10}O_4$	146	Dicarboxylic Acid	Water
Levoglucosan	$C_6H_{10}O_5$	162	Monosaccharide Anhydride	Water
Phthalic Acid	$C_8H_6CO_4$	166	Aromatic Dicarboxylic Acid	Water
cis-Pinonic Acid	$C_{10}H_{16}O_3$	184	Cyclo-monocarboxylic Acid	Water/ethanol
Palmitic Acid	$C_{16}H_{33}O_2$	256	Hexadecanioc Acid—saturated C_{16} fatty acid	Ethanol
Oleic Acid	$C_{18}H_{34}O_2$	282	Alkenoic Acid –mono-unsaturated C_{18} fatty acid	Ethanol
Fluoranthene	$C_{16}H_{10}$	202	PAH—4 ring	Ethanol
Benzo[a]pyrene	$C_{20}H_{12}$	252	PAH—5 ring	Hexane
5a-cholestane	$C_{27}H_{48}$	373	Sterane	Hexane
Sodium Carbonate	Na_2CO_3	106	Inorganic	Water
Calcium Carbonate	$CaCO_3$	100	Inorganic	Water (slightly)

These compounds represent a range of species known to be of importance in atmospheric aerosols. The first eight compounds are straight chain carboxylic or dicarboxylic acids, which may comprise a significant fraction of organic aerosol mass (Li and Yu; 2005; Kawamura et al., 2010). Levoglucosan and pinonic acid are biogenic compounds, and levoglucosan is widely used a marker for biomass burning aerosol. Palmitic acid and oleic acids are fatty acids strongly associated with, and used as markers for, meat cooking operations (and the associated carbonaceous aerosol produced in such operations). Fluoranthene and benzo[a]pyrene are four and five ring polyaromatic hydrocarbons, and cholestane is a commercially available sterane. Steranes (along with hopanes) are useful as biomarkers of motor oil emissions (Ruehl et al., 2011).

Four temperature methods were used to investigate the thermographical patterns (Table 2). Three of the methods are based on NIOSH 5040 method (the Pinnacle State Park (PSP) method, Aerosol Characterization Experiment-Asia (ACE-Asia) method, and Atmospheric Science Research Center (ASRC) method, and the fourth is the widely used IMPROVE method. The thermograms (defined as the measured carbon signal as a function of time) for the compounds in Table 1 using the four protocols in Table 2 are shown in Figures 1 through 4. These figures show both the differences between compounds, and those due to the different time and temperature steps for the methods.

Table 2. Experimental parameters of the thermal protocols

Temperature (°C)

Gas	ACE-Asia	IMPROVE	PSP	ASRC
He	340	120	1	100
He	500	250	600	150
He	615	450	840	300
He	870	550		450
He				600
He				750
He				840
He	Oven Off		Oven Off	Oven Off
He:O2	550	550	550	550
He:O2	625	700	650	650
He:O2	700	800	850	850
He:O2	775			
He:O2	850			
He:O2	900			
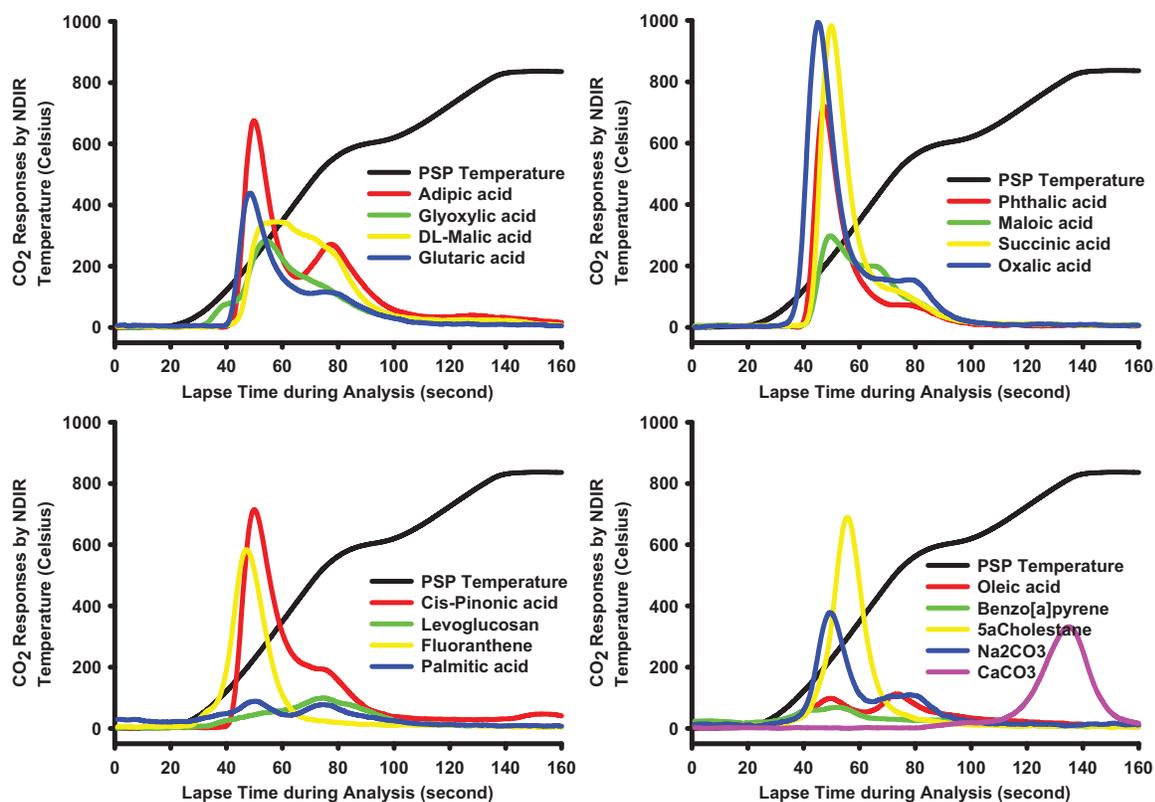
Figure 1. Spectrothermograms of compounds in Table 1 measured using the PSP temperature protocol.

Most of the carbon is measured in a single peak for nearly all the compounds. In addition, the major peak for the compounds is most often at or near the same time for a given method. There are exceptions to these general conclusions—and it is these exceptions that allow further investigation and differentiation of compounds based upon this method.
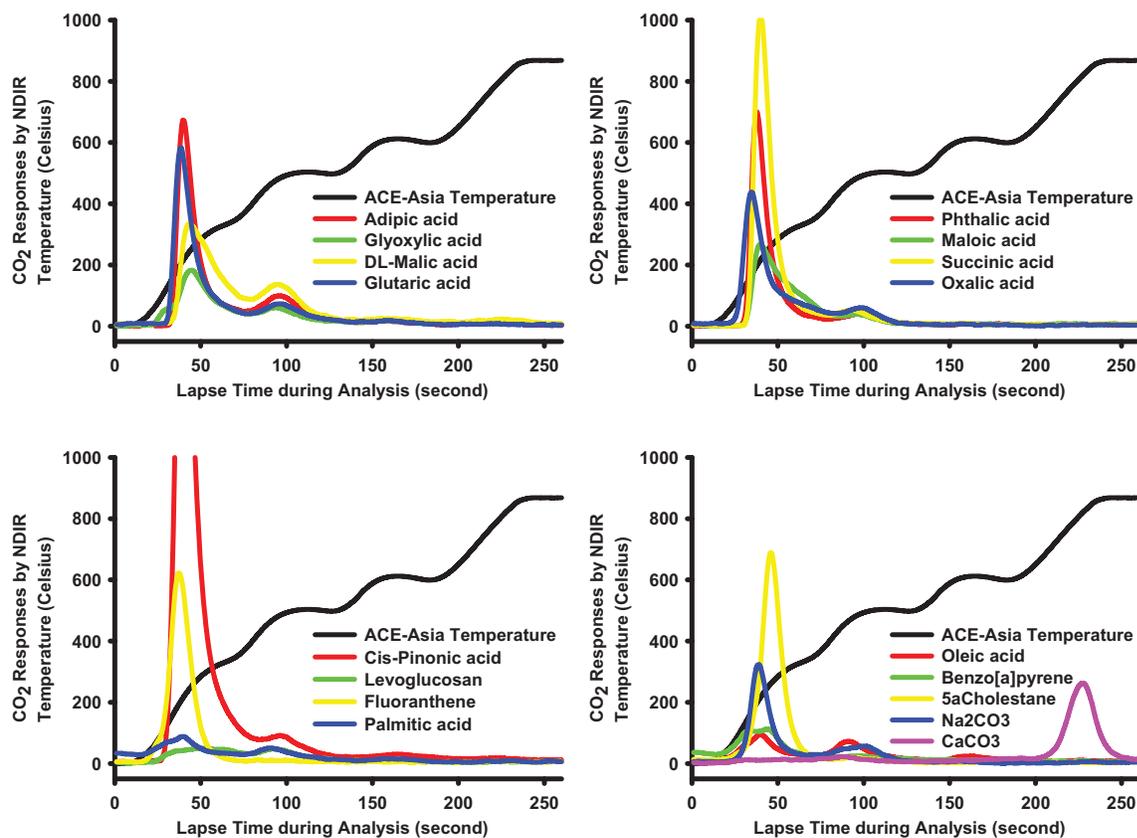
Figure 2. Spectrothermograms of compounds in Table 1 using the ACE-Asia temperature protocol.
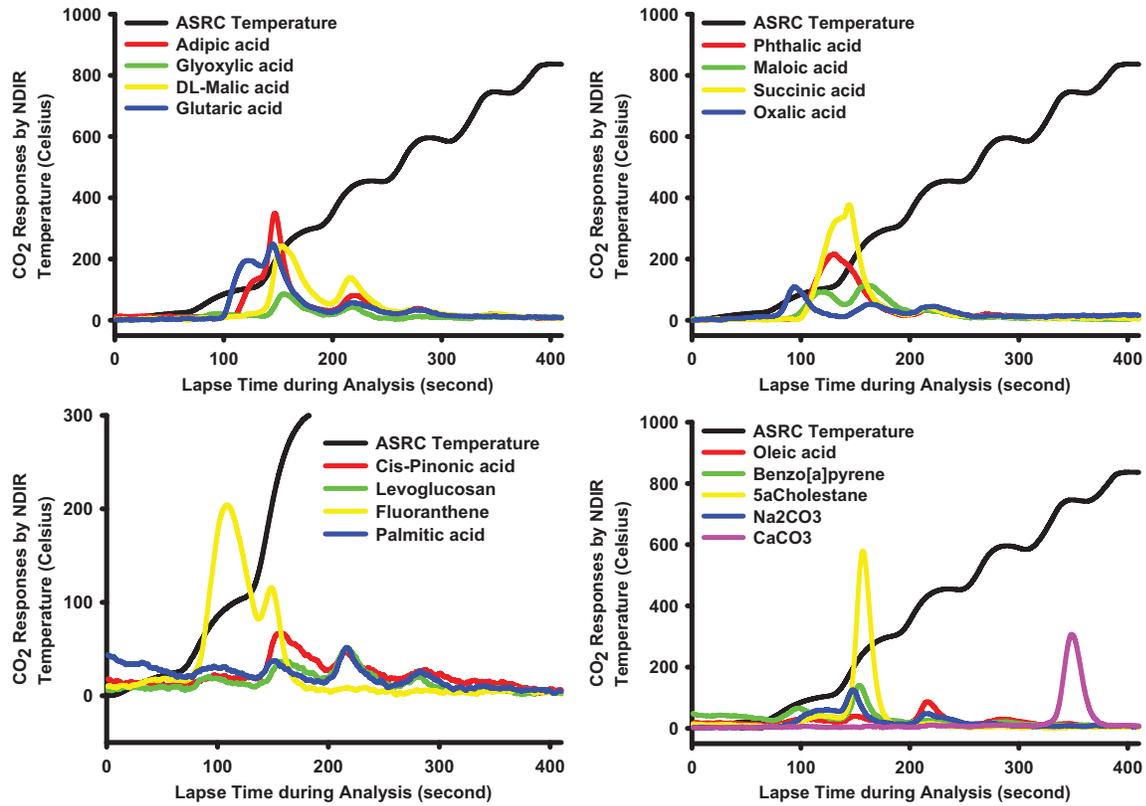
Figure 3. Spectrothermograms of compounds in Table 1 using the ASRC temperature protocol.
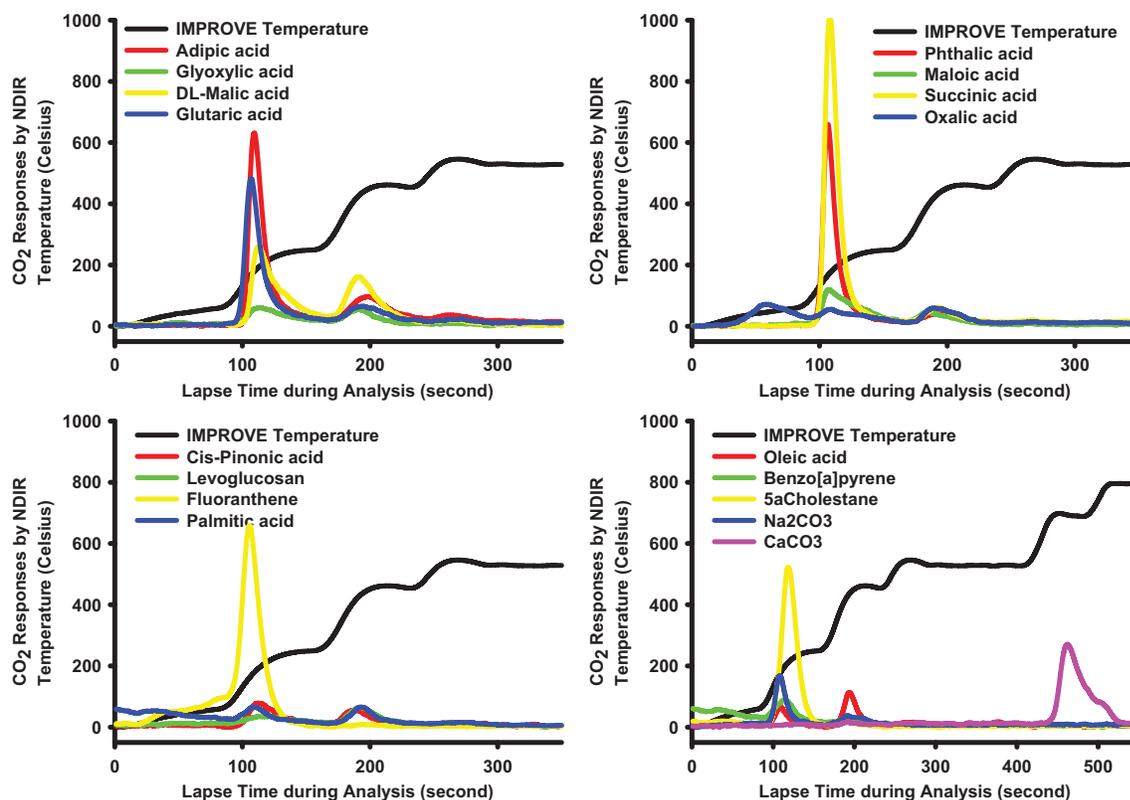
Figure 4. Spectrothermograms of compounds in Table 1 using the IMPROVE temperature protocol.

For example, the ASRC method, with its greater number of temperature steps in the OC measurement period (the analysis period during which only helium flows over the collected aerosol), exhibits a greater number of peaks, and greater separation of those peaks. Also, a clear (but generally smaller) secondary peak for the dicarboxylic acids is observed in Figure 4. Palmitic and oleic acids show a stronger second peak than first peak, and fluoranthene and benzo[a]pyrene exhibit quite different thermograms. Levoglucosan also has a distinct and later occurring peak.

We applied this more detailed knowledge of the method-specific temperature evolution of carbonaceous aerosol to data collected at Queens College in 2009. Panel a) of Figure 5 shows the raw carbon signal measured by Sunset ECOC analyzer operating under the PSP temperature protocol for the July—August intensive field study period. There are horizontal lines drawn through the time series contour plot at analyzer oven temperatures of roughly 350ºC and 540ºC. These temperatures correspond to two "peaks" in the carbon signal, which sometimes occur separately, and sometimes occur simultaneously. We did not have full speciation of this aerosol, but we did have HR-AMS (high resolution aerosol mass spectrometer) measurements at the same site beginning the 15th of July. Panels b), c), and d) of Figure 5 show the OOA (oxidized organic aerosol) measured by the HR-AMS, the $PM_{2.5}$ sulfate measured by a Thermo Instruments 5020i, and the HOA (hydrocarbon-like organic aerosol) measured by the HR-AMS, respectively.
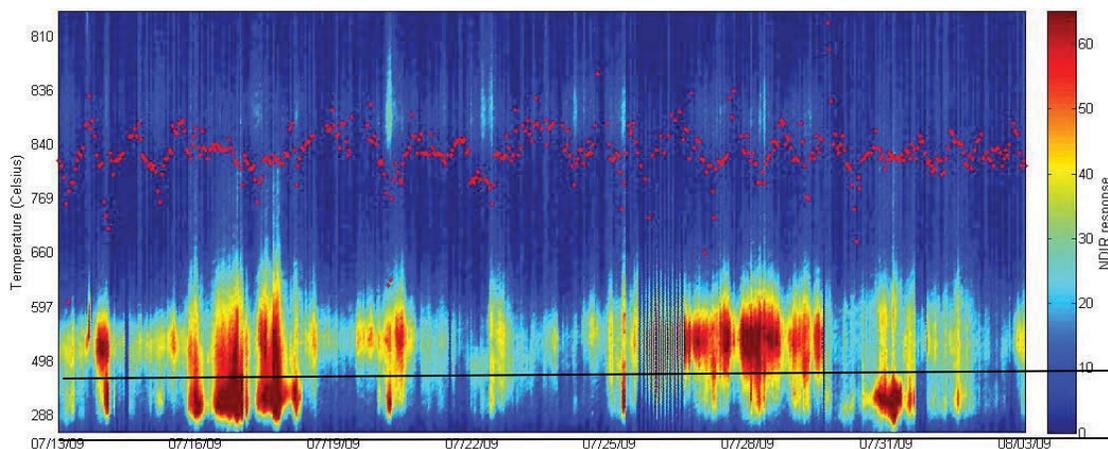
a)
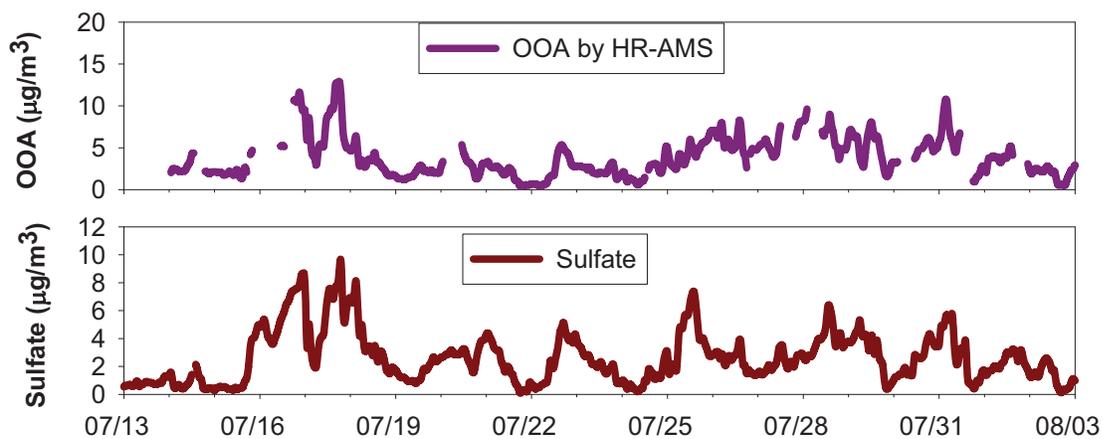
b) and c)
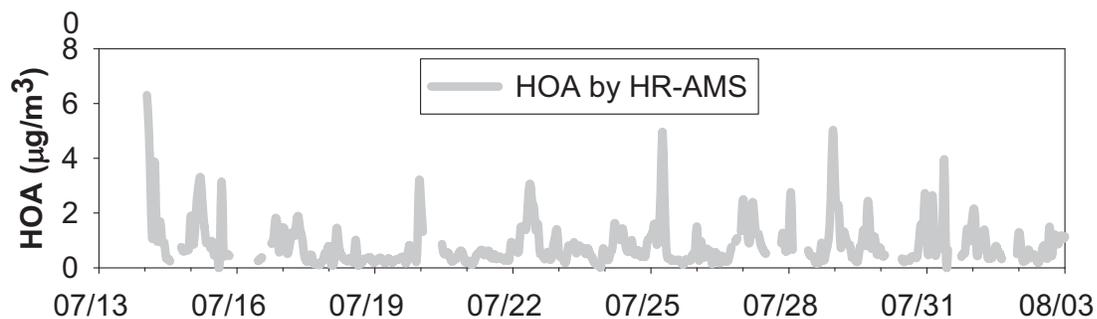
d)

Figure 5. Time series of a) carbonaceous aerosol thermograms, b) OOA measured by a HR-AMS, c) sulfate measured by a 5020i, and d) HOA measured by a HR-AMS during the 2009 Queens College field study.

Combining the laboratory measurements shown above, and the supporting measurements shown in panels b), c), and d) of Figure 5, additional information about the type of carbon-containing compounds that contribute to the two distinct peaks in panel a) is observed. Specifically, note the period around 7/26, where in panel a) the dominant peak is the later (higher temperature) peak. This corresponds to a period of relatively high OOA and sulfate, and lower HOA. July 31st, on the other hand, still was under the influence of OOA and sulfate, but also higher and more consistent HOA. This gives some indication that the first (low temperature) peak may have more influence from more volatile HOA compounds, while the second (higher temperature) peak may derive to a greater extent from less volatile and more highly oxidized organic aerosol (OOA).

Figure 6 summarizes the difficulty inherent in this analysis. The top panel shows the average thermogram for the 24-hour period centered on 7/28/2009 and the lower panel shows the average thermogram for the 24-hour period centered on 7/31/2009. These profiles are different, but not so distinctly different that they are easy to fully separate. In a later section of this report we report the use of Positive Matrix Factorization of these thermal profiles to attempt a better separation of "factors". The laboratory measurements described in this and the next section give us some of the baseline information necessary to interpret the factors.
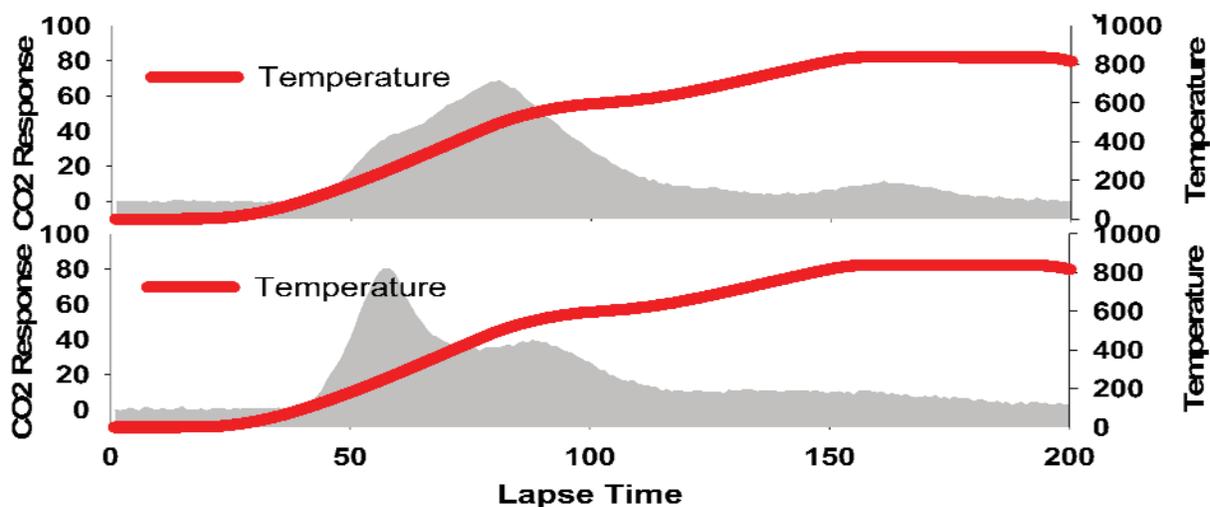

Figure 6. Average thermograms for the 24-hour period centered on 7/28/2009 (top panel) and 7/31/2009 (bottom panel).

Combustion Aerosol Measurements

The Combustion Aerosol Standard (CAST) system uses a carefully controlled propane flame to produce a stable stream of exhaust gas containing "soot" aerosol (Figure 7). There are five flow controllers providing gas flows to the CAST: propane and nitrogen are separately combined as the fuel flow, which together with a zero air flow feed the burner. Another flow of nitrogen gas acts as the quench flow, and a large dilution air flow provides a sheath flow for the exhaust. For a number of experiments, the aerosol flow was sampled directly from the CAST. Ten different setups were used for these experiments, and the undiluted CAST flow was sampled from four of these setups. For the other six conditions, a small portion of the CAST flow (typically 1 l/min) was diluted with HEPA filtered room air to provide aerosol concentrations more comparable to ambient levels, and to reduce the concentrations enough to allow use of condensation particle counters and a scanning mobility particle sizer for size and number characterization of the aerosol. Roughly a hundred experiments were run using the CAST generator, sometimes in combination with an atomizer for generating mixed organic/inorganic aerosol. A wealth of new data and information were produced through these experiments, and we will summarize a number of the most interesting findings in this section.
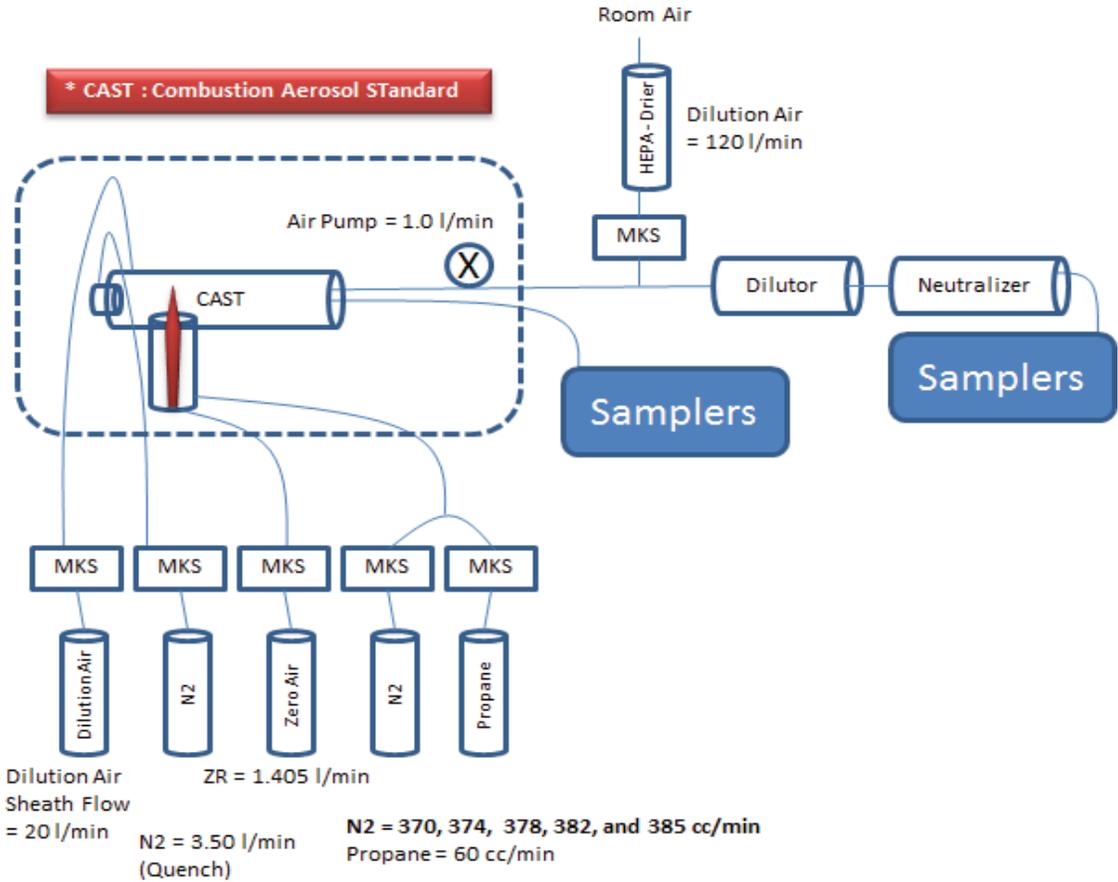

Figure 7. A schematic diagram of the Combustion Aerosol Standard system (left side of diagram), and the dilution system and two potential locations for sampling high concentration or diluted combustion aerosol.

The first set of experiments involved simple combustion aerosol sampled from a relatively lean flame. We call the flame "rich" or "lean" in these experiments, based on the measured OC/EC ratio of the aerosol sampled by the Sunset ECOC analyzer. OC/EC ratios above 3 will be considered lean for this work. Samples were drawn directly from the CAST for these experiments and three-minute sample times were sufficient to achieve enough sample for analysis (roughly 100 µg was collected in the three-minute period for these samples). Only minor adjustments were made to the flame conditions for these experiments, changing the N_2 fuel mixture flow from 370 to 385 cc/min—this variation kept the flame in a stable operating mode and was able to produce a noticeable change in the OC/EC ratio, with OC/EC increasing or becoming more lean as the N_2 flow increased. Details of the setup are shown in Figure 8.
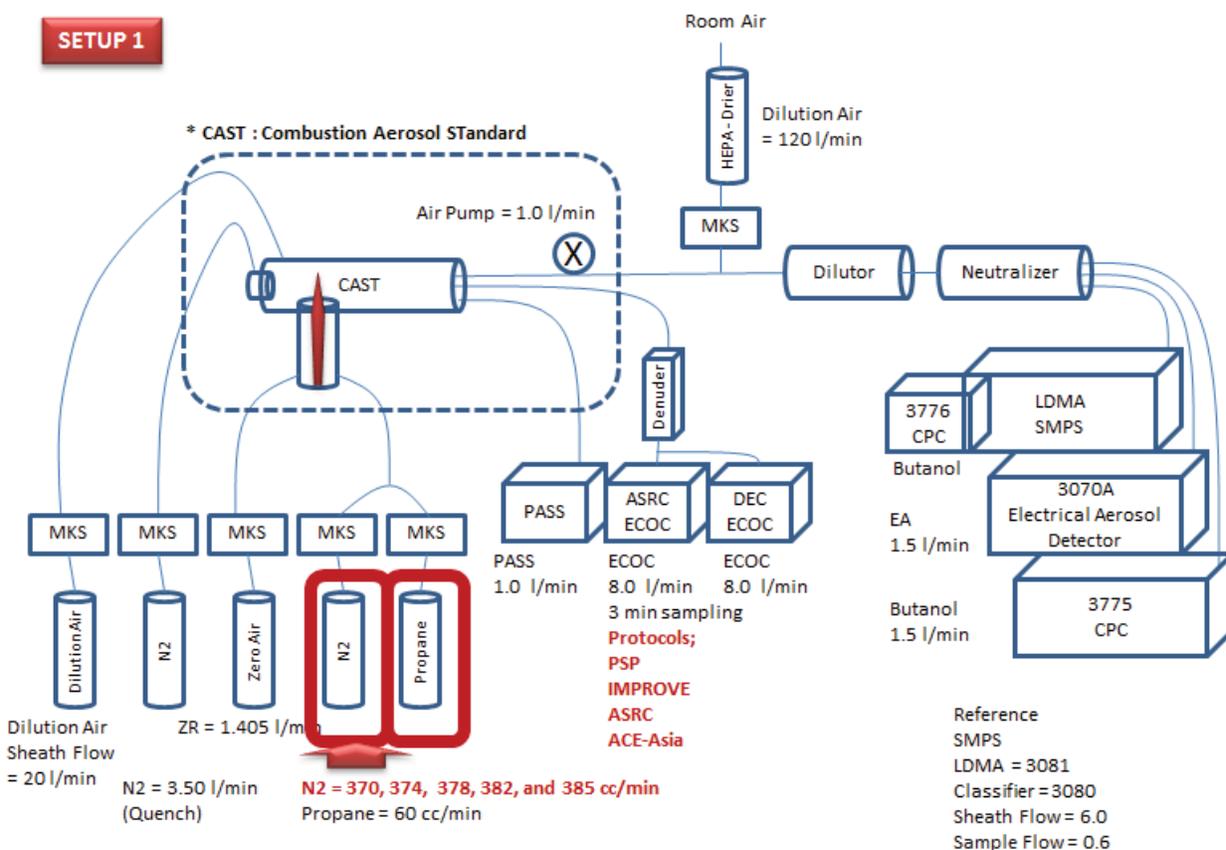
Figure 8. Details of the experimental system for the initial set of experiments.

Sample thermograms for the four measurement protocols are shown in Figure 9. The vertical lines more than half way through the analysis time represent the "split time" between OC and EC determined by the Sunset data analysis program for the four methods. One can visually discern up to six different peaks in the thermograms, which are an indication of the complexity of the aerosol mixture produced in the flame. The PSP protocol, with its shorter analysis time and fewer temperature steps has only one peak early in the analysis, whereas the other methods indicate two types of "OC" compounds with high volatility. The rather large spread in the OC/EC ratios determined for the four methods (from 2.6 to 4.2) is reason for concern, and has led some scientists to question the validity of the method-determined OC/EC ratios, and instead to focus on the total carbon (or TC) measured by the analyzer

(Watson et al. 2005; Rattigan et al., 2011). There was a definite systematic difference in our experiments in the OC/EC ratios for the different methods, with the ACE-Asia method determining lower OC/EC ratios than the other methods as in the bar graph panel of Figure 9.
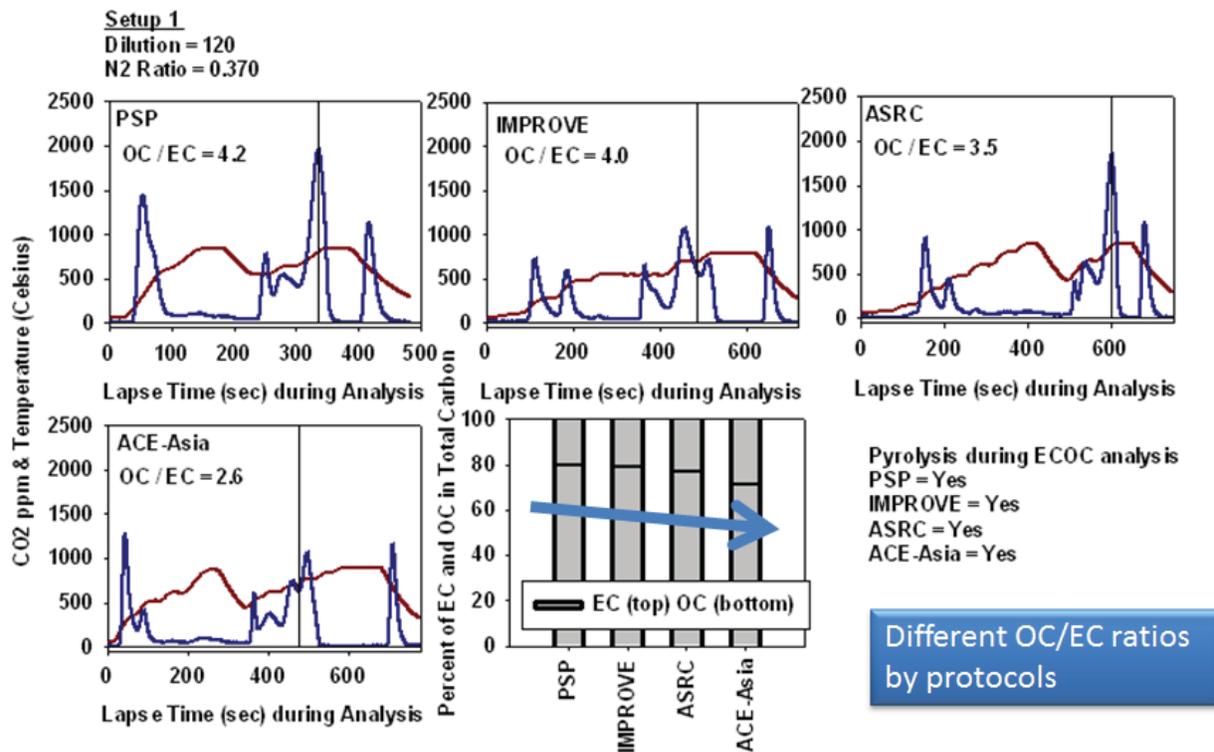

Figure 9. Thermograms and partitioning of OC and EC determined using the different measurement protocols for initial experiments with simple combustion aerosol.

The OC/EC split for the thermal optical method in general and this instrument in particular relies on the optical absorption properties of "EC type" aerosol. For the Sunset instrument it is optical transmission of the laser light that is used to determine the split time. The baseline transmission of the laser light through the unloaded filter is determined before sampling begins. As sample builds up on the filter, the EC causes a loss of transmission (the OC mainly scatters light without absorbing it, so its absorption is not considered). Still, after sampling stops and the analysis begins, the filter is progressively heated to high temperature and some fraction of the "OC" is pyrolyzed and converted to EC, which causes a further decrease in the transmission of the laser (while at the same time converting some of aerosol that was deposited as OC to now exist as EC on the filter). This method artifact is known as pyrolyzed carbon or PC. This PC is only burned off the filter during the analysis steps in which O_2 is introduced along with helium—the steps nominally intended to burn off and analyze the EC deposited as part of the ambient sample aerosol. The method "accounts" for this confounding PC by tracking the optical transmission through the filter, and assigning the split time to the point when the filter transmission returns to the baseline value determined at the end of sample period (the beginning of the analysis period). As noted in Figure 9, pyrolysis carbon is observed in each of the methods for this combustion aerosol, and is undoubtedly responsible for some, if not all, of the variability in the observed OC/EC ratios of the different analysis protocols.

The next set of experiments included the same combustion aerosol, but this time mixed with ammonium bisulfate (NH4HSO4) and sodium chloride (NaCl) aerosols from an atomizer (Figure 10). For ammonium bisulfate/ combustion aerosol mixtures, all four thermal protocols and the same full range of nitrogen fuel gas flow mixtures were employed. For sodium chloride, we only used the ASRC protocol.
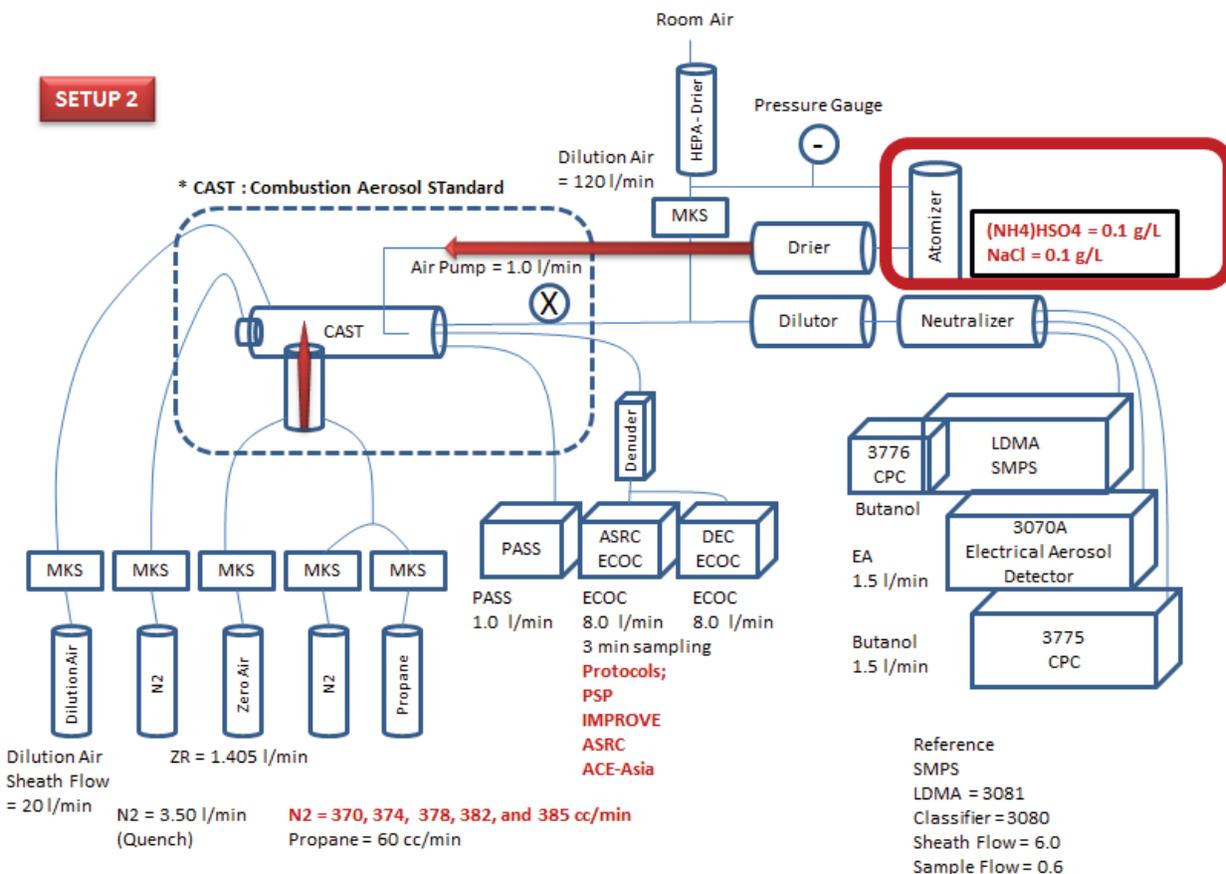

Figure 10. Experimental setup for producing a mixture of combustion and inorganic aerosol.

The mixed inorganic/combustion aerosol presented us with some surprising results. Figure 11 shows three thermograms—all using the ASRC temperature protocol, and all with the nitrogen flow set at 370 cc/min—but with and without inorganic aerosol. The first panel (Setup 1) is the same as was shown in Figure 9. The second panel (Setup 2) shows the result with ammonium bisulfate mixed in with the combustion aerosol, and the third panel (Setup 3) shows the result with sodium chloride mixed aerosol. With ammonium bisulfate mixed in there is a small, but noticeable change in the thermogram peak structure, but essentially no change in the split time. Nevertheless, for the mixture with sodium chloride, there is a dramatic change in both the thermogram peak signals, and in the method determined split time. It almost appears that the sodium chloride acted as a catalyst to "activate" more carbon than was seen in the other experiments, or alternatively, that the salt acted as a sorbent bed on the filter to capture additional carbon that had escaped due to its volatility in the other experiments. While this observation is very interesting from a scientific point of view, expending time and effort to further investigate was beyond the scope of this project.
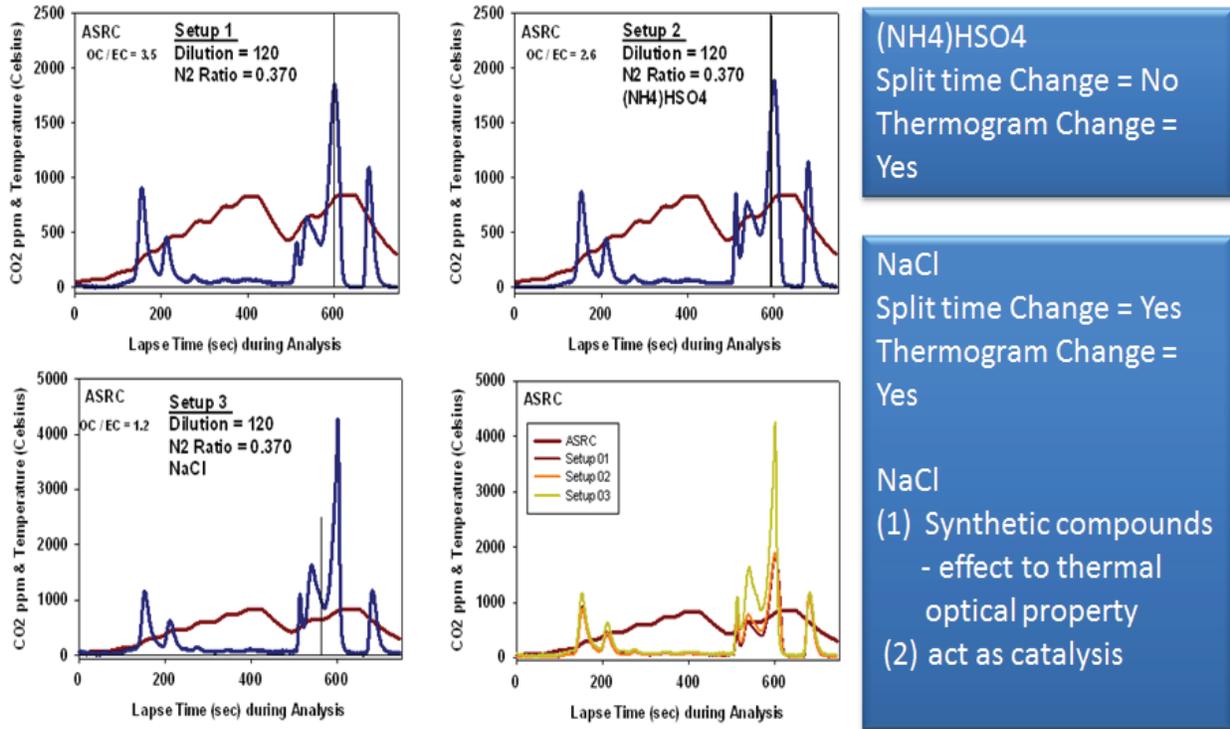
Figure 11. Thermograms for simple combustion aerosol (Setup 1); combustion aerosol mixed with NH₄HSO₄ (Setup 2); and combustion aerosol mixed with NaCl (Setup 3).

The next set of experiments involved mixing levoglucosan primary aerosol with combustion aerosol from the CAST. The levoglucosan was generated using an atomizer—properties of levoglucosan as a primary aerosol are displayed in Table 1 and Figures 1-4. The setup is identical to that shown in Figure 10 with levoglucosan in place of the inorganic compounds NH₄HSO₄and NaCl. All four thermal protocols and the same full range of nitrogen fuel gas flow mixtures were employed.

Results from the levoglucosan/combustion mixed aerosol experiments are shown in Figure 12. There is little difference in the split time and peak structure of the thermograms due to the addition of levoglucosan, which may not be unexpected since the levloglucosan signal in Figures 1-4 (pure levoglucosan form an atomizer in our ASRC lab) is small. The major difference is that the last OC peak (right before the vertical "split time" line) is noticeably larger when levoglucosan is mixed in.
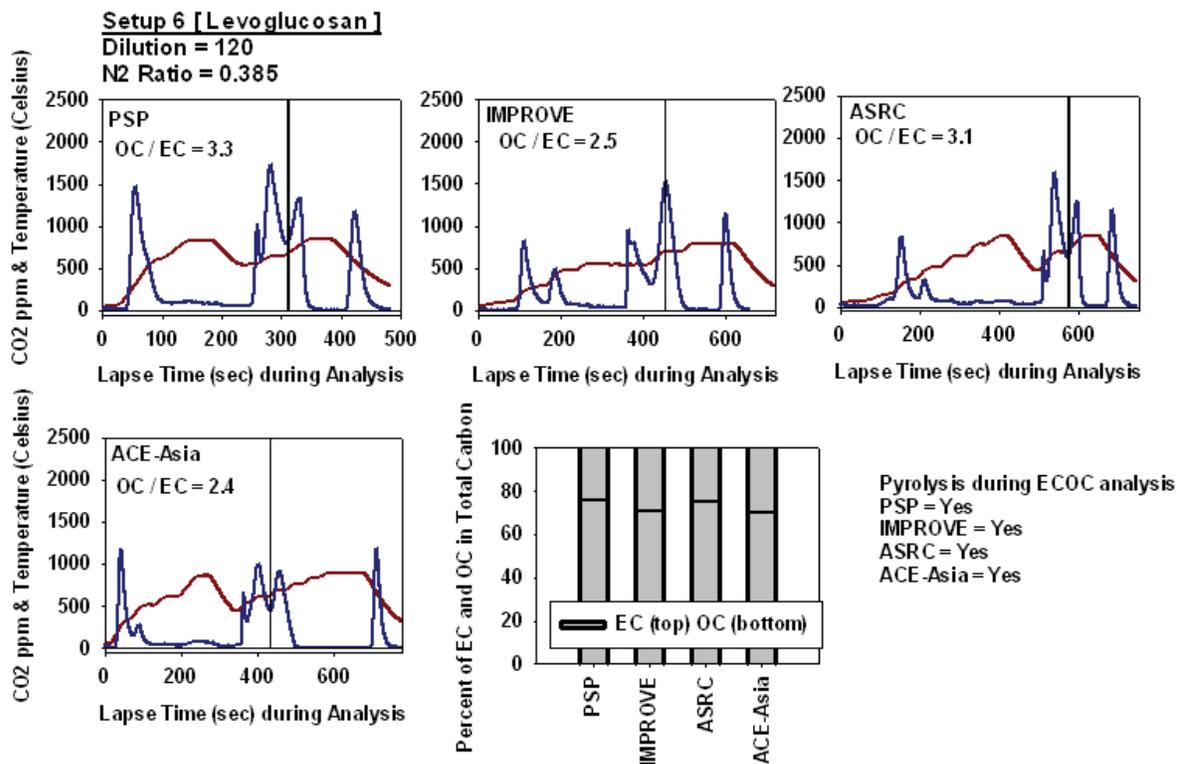
Figure 12. Thermograms for all four analysis protocols sampling a mixed aerosol containing levoglucosan and combustion mixed aerosol.

As noted above, the combustion aerosols measured and displayed in Figure 9 were sampled from a lean flame, with a small range of nitrogen flow in the fuel gas mixture. Operating the CAST at lower nitrogen flows created a richer flame with larger concentrations of aerosol that required additional dilution to collect reasonable (i.e., low enough) sample loading onto the filters. As shown in Figure 13, these "rich flame" experiments used lower N_2 flows in the fuel mixture, and the Sunset OCEC analyzer sampled the aerosol only after dilution with an additional 15 l/min of filtered room air. Sample collection time was doubled to collect an adequate amount of aerosol for analysis, and only the ASRC temperature protocol was used.

Results of these experiments are shown in Figure 14. The final peak in the thermogram is the calibration peak, and is the same (within a narrow experimental error) for all runs. Two significant changes were observed as the flame changes from lean (N_2 flow = 370 cc/min) to rich (N_2 flow = 310 cc/min). The total signal, or amount of carbon sampled increases dramatically from about 12 to about 46 µg for the 6 min sample period. Also, the OC/EC ration declines dramatically and uniformly from 4 to 0.6. For the last four conditions, the OC changes very little, and the EC increases at each step. This is shown in the bottom two panels of the figure.
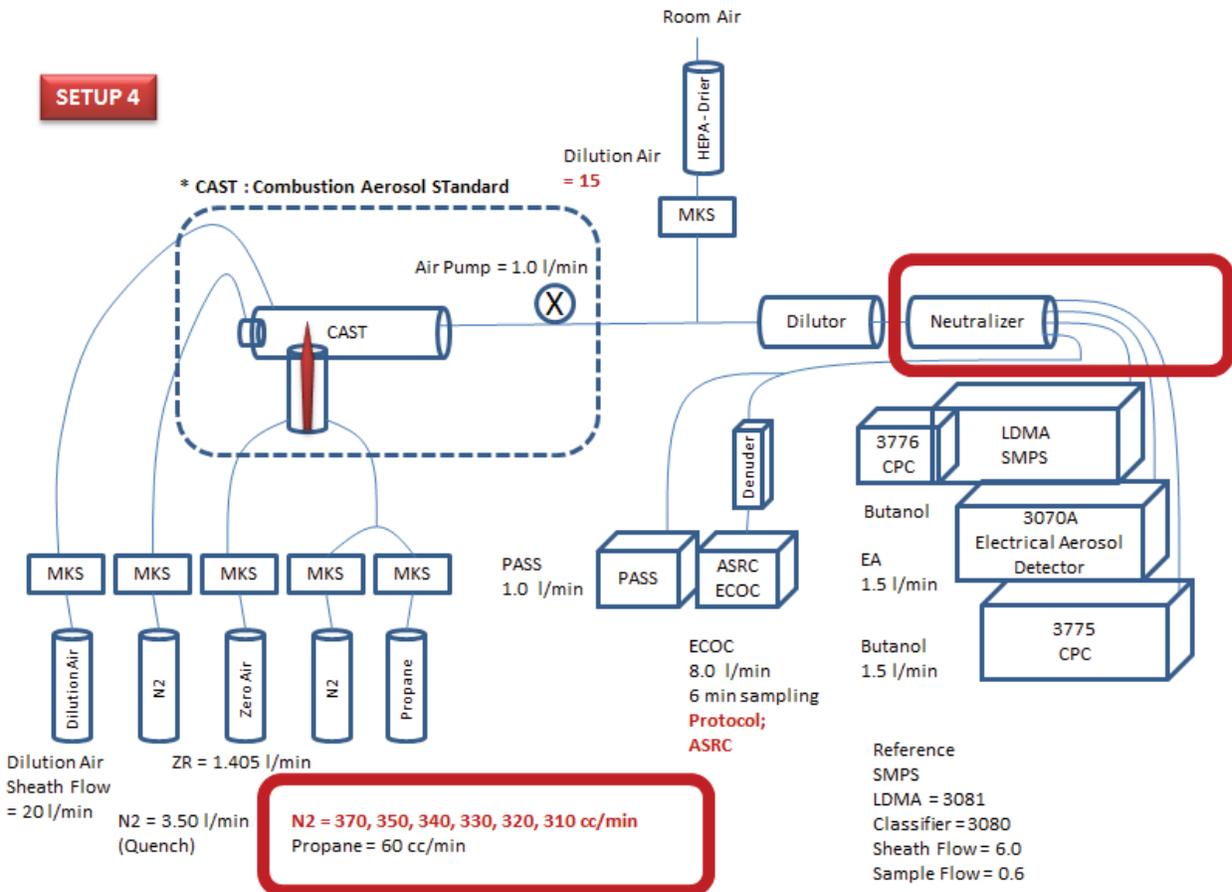
Figure 13. Experimental set up for sampling of rich flame combustion aerosol. For these experiments the Sunset ECOC analyzer samples the aerosol after an external dilution system that mixes in filtered room air with the CAST output.
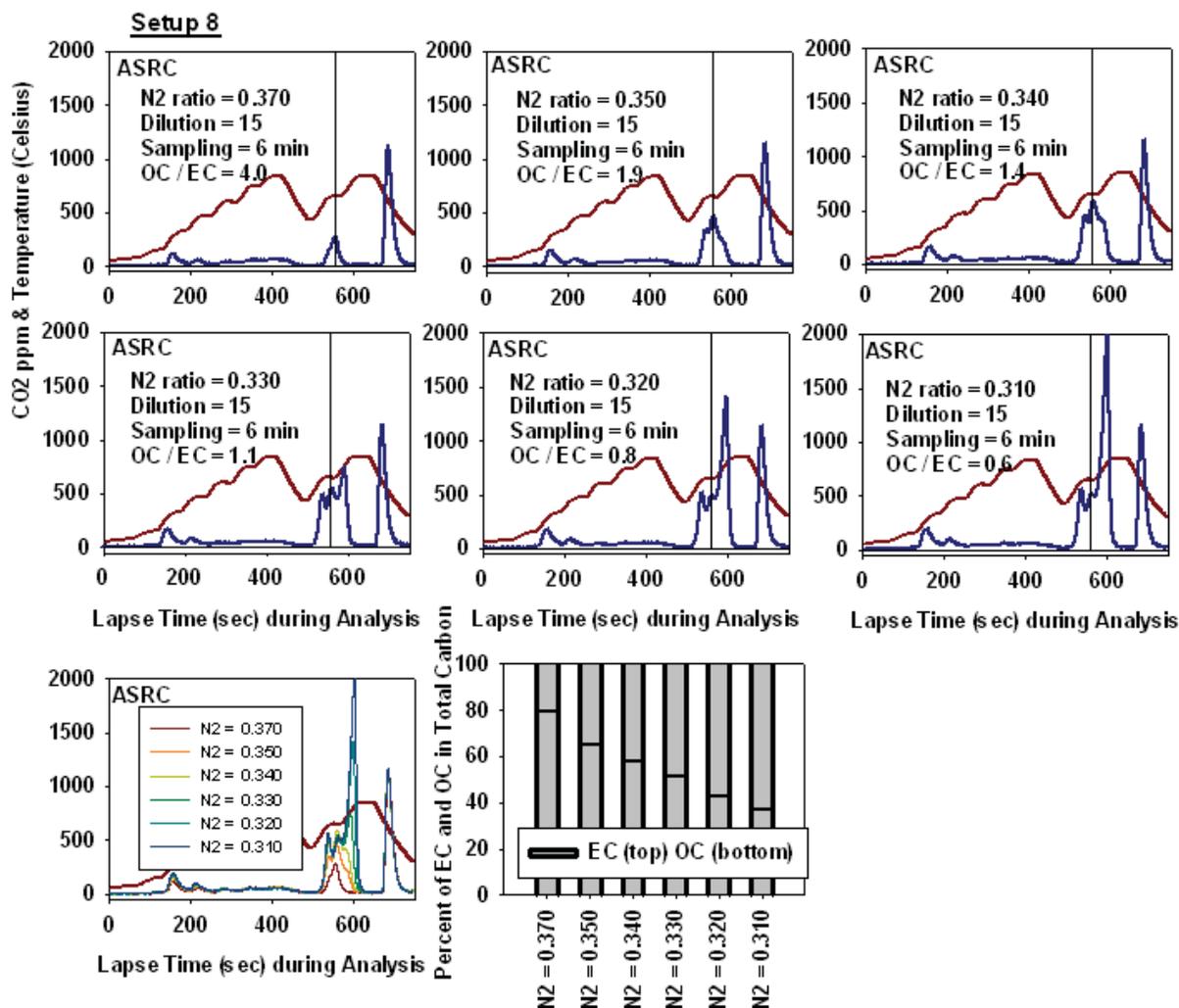
Figure 14. Thermograms and OC/EC ratios for the rich flame experiments.

For the final set of CAST experiments we sampled a very rich flame, with a N_2 fuel dilution flow of 200 cc/min. The very sooty and concentrated combustion aerosol required a greater amount of external dilution to be in range of the instruments, so the external dilution was set to 120 l/min. The setup was as shown in Figure 13 with these two changes (N_2 fuel flow dilution and external dilution flow). Sampling time was increased to 10 minutes to attain adequate sample. In this case there was a predominate EC signal, but rather low OC signal. All four thermal protocols were used to analyze this very rich, or "soot rich" combustion sample. The results are shown in Figure 16. Split times are very much earlier for all but the IMPROVE protocol. PSP, ASCR, and ACE-Asia protocols have multiple peak structure in the Helium-Oxygen step or EC analysis period. These measurements cannot by themselves determine if this indicates different characteristics of the aerosol, or simply method-induced features due to carbon mass loading and specifics of the temperature steps and hold times.
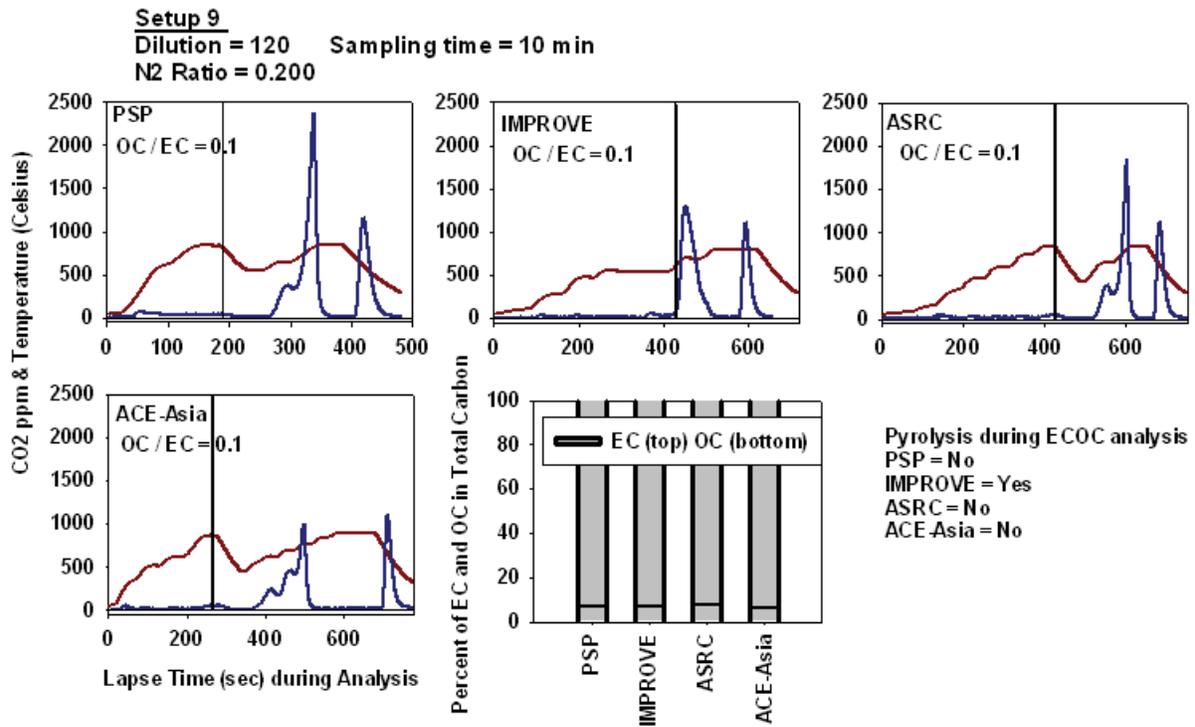
Figure 15. Soot rich aerosol as measured using four temperature protocols.

PMF Analysis Method for Carbon Aerosol Time Series Data

There are indeed different characteristics to the measured thermograms for different carbonaceous materials and different analysis temperature protocols. While this was positive information, and confirmed (to an extent) our hypothesis and motivation for proposing and carrying out this study, the observed differences were smaller and more subtle than anticipated—and did not lend themselves to easy or unambiguous interpretation. Still, this study has yielded additional information which we applied to ambient atmospheric data sets.

A useful and very powerful analysis method for complicated time series data sets is Positive Matrix Factorization, which attempts to detect and quantify recurring features (called factors) in a data set. For this work we used the EPA PMF model version 3, which is freely available on the EPA web site (EPA, 2011). PMF is widely used for attribution of pollution sources based on a series of detailed measurements at a "receptor" site. Our application is a variation on this idea. We used a month-long time series of hourly measurements taken with the Sunset ECOC analyzer. For each hourly measurement the analyzer raw data is a "thermogram" consisting of the detector signal as a function of analysis time. There were two challenges to address before applying the PMF model to the ambient data: 1) background CO_2 is also measured and reported by the instrument, so for each set of raw thermogram data we needed to determine a baseline and subtract that baseline from the detector data; 2) the PMF model only accepts 120 data points (or "species" in the model terminology) for each input sample; so we needed to average the raw data to reduce the number of "analysis time" steps from roughly 360 to 120.

With these adjustments to the data, PMF runs of the time series analyzer measurements were performed. We ran the model many times to test the sensitivity of the results to changes in input parameters. Ten base runs were performed for each execution of the model. Another key parameter is the number of factors the model is allowed to consider during execution. The model was challenged with 3 to 15 factors, and anything over eight factors gave poor results. (That is, the object function Q gave unacceptable values.) The first goal in factor selection is good optimization results (low values of Q), and the second goal is to identify an association of the computed factors with source compounds that make sense from the ambient data. This is where some operator expertise is useful, and the combination of these two criteria in factor selection led us to settle on a five-factor solution to the PMF model.

The data set as reported by the Sunset ECOC analyzer is presented in Figure 16. The left panel is the instrument reported OC data and the right panel is the instrument reported EC data. We used the optical EC data because of its much higher signal to noise (the thermal EC data is at or below the detection limit more than 50% of the time at this rural location).
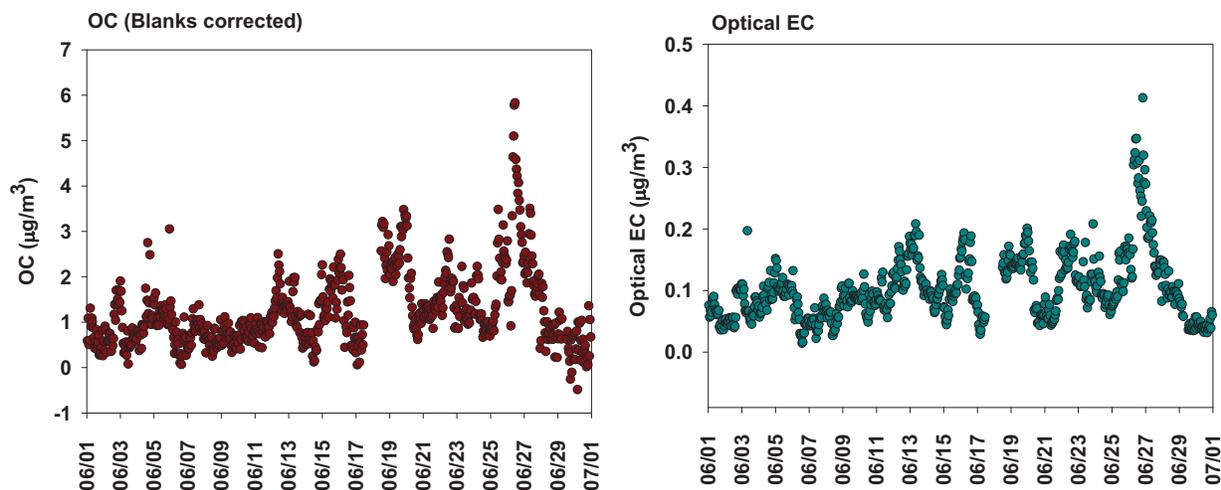
Figure 16. Thermal OC and optical EC data as measured and reported hourly for June 2010 at the Pinnacle State Park research site.

After the adjustments to the raw data discussed above, we obtained the time series of measured carbon data shown in Figure 17. Temperature is along the vertical axis, time along the horizontal axis, and detector CO_2 signal above the baseline is the color contour. The red band near the top of this plot is the calibration signal, and the calibration data was excluded from the PMF analysis. The high carbon aerosol concentration period on June 27 is clearly visible in both Figure 16 and Figure 17.
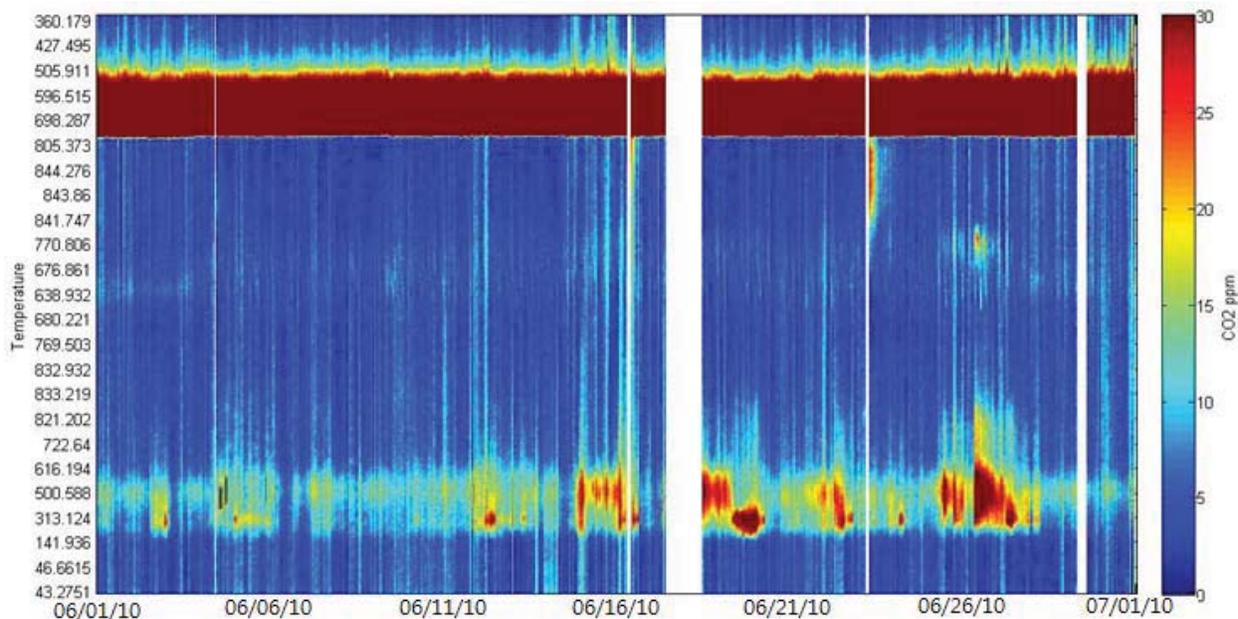
Figure 17. Contour plot of the time series "thermogram" plots, that is, of detector signal (above baseline) as a function of analysis time (temperature).

As noted above, the model obtained a stable solution with five factors, and we were able to make a tentative assignment of the factors, drawing as much help as we could from the laboratory measurements presented earlier in this report. Figures 18 a) through 18 e) present the model-determined factor profiles and factor contributions. The factor profile shows the concentration of carbon (measured by the instrument as ppm of CO_2) attributed to the factor as a blue bar, and the percent of carbon at each time step apportioned to the time step as a red dot. The factor contribution graph shows the contribution of the factor to the total carbon signal.
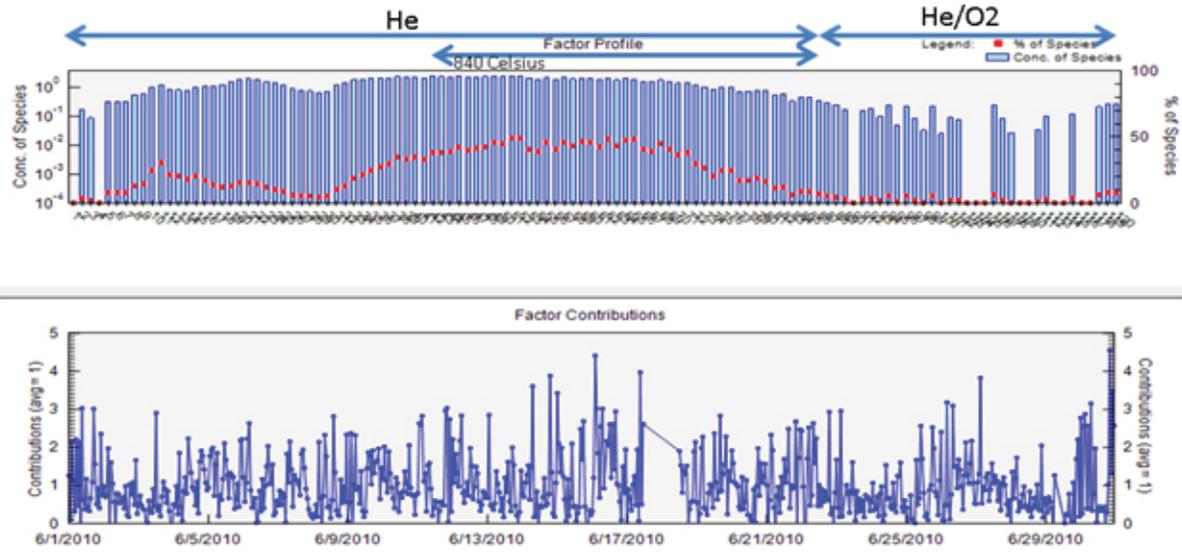
Figure 18a). Factor 1 profile and contributions.
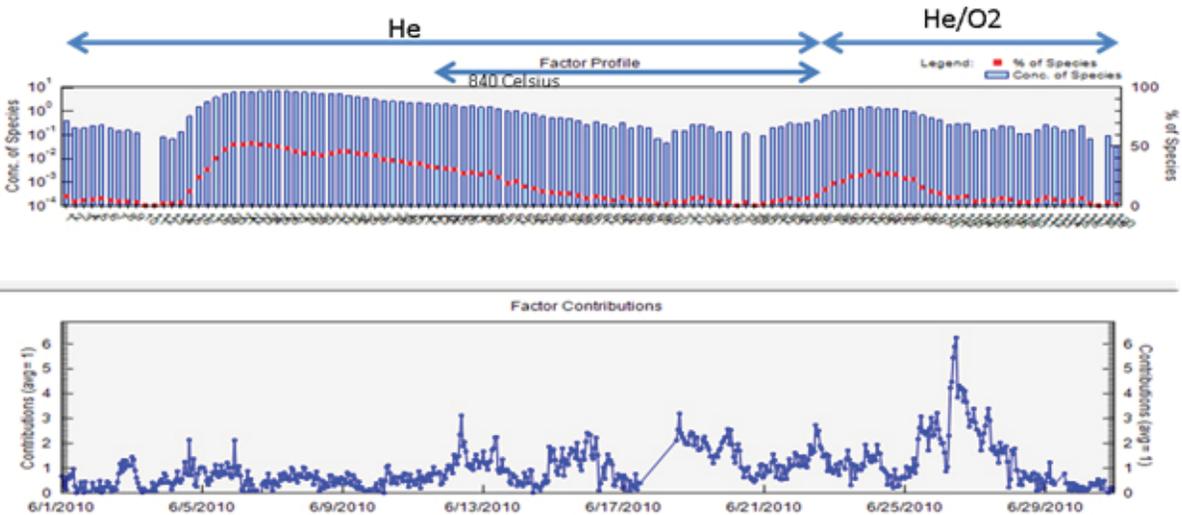
Figure 18b). Factor 2 profile and contributions.
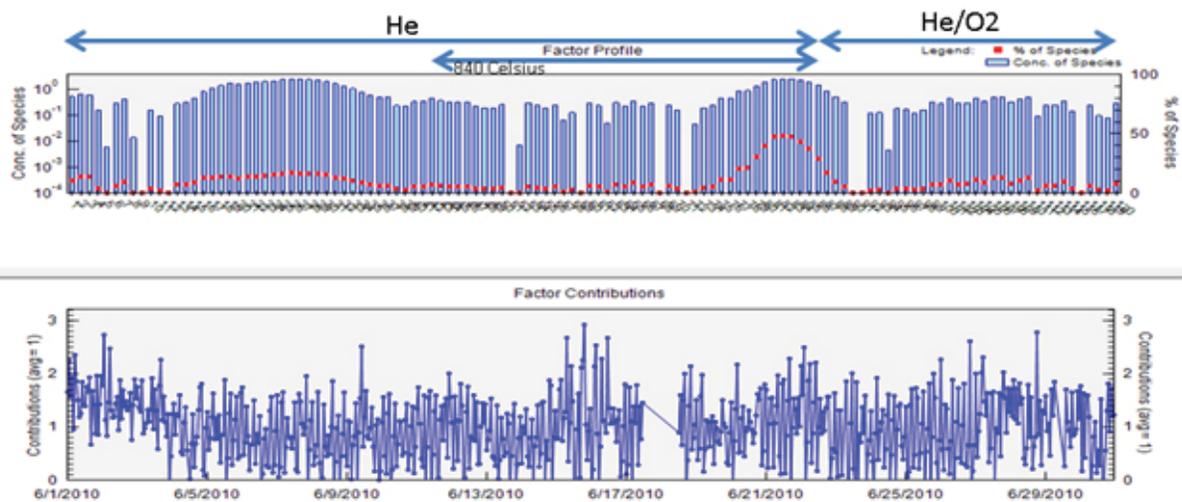
Figure 18c). Factor 3 profile and contributions.
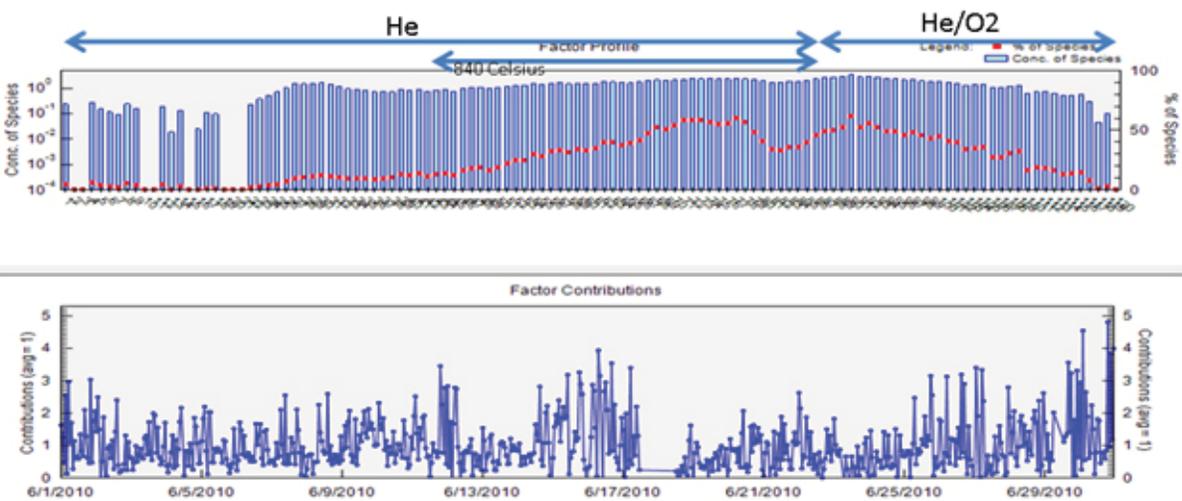
Figure 18d). Factor 4 profile and contributions.
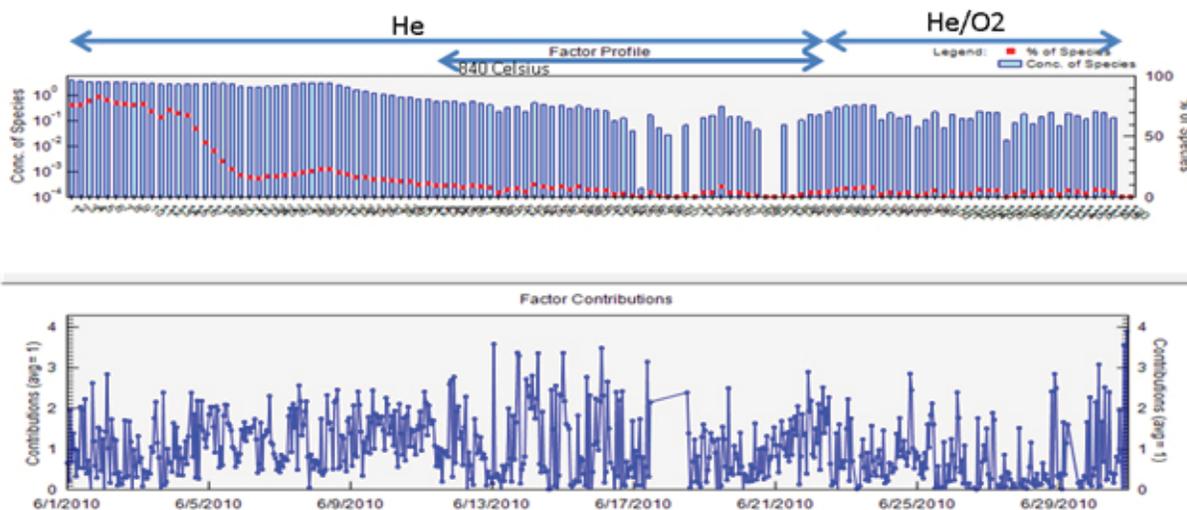
Figure 18e). Factor 5 profile and contributions.

The first factor determined by the model has two broad peaks during the helium only (or OC) analysis period, and very little during the helium-oxygen (or EC) analysis period. The second factor has a broad peak midway through the "OC" period, and a second, smaller peak during the "EC" period. The third factor has a peak near, but a little "sharper" than the second factor OC peak, and a second, more isolated peak at the end (or highest temperature part) of the helium only (OC) portion of the analysis. The fourth factor has very little attributed to it early in the analysis period, but increases steadily and accounts for a good fraction of the carbon detected late in the "OC" period and early in the "EC" period. Finally, the fifth factor is heavily weighted to the early eluting OC species. The broad structure of the factor profile peaks complicates their interpretation, but is not all that surprising given that many of the compounds measured in the laboratory experiments exhibited broad peaks in their thermograms as well.

With this in mind we propose the following interpretation for the five factors determined by the PMF model:

- Factor 1—Secondary Organic Aerosol of relatively low volatility;
- Factor 2—is dominated by a low volatility OC peak and is assigned as semi-volatile oxidized organic aerosol compounds (similar to those measured in the ASRC laboratory);
- Factor 3—has a small contribution similar to that of Factor 2, and a much larger contribution near the transition from helium to helium-oxygen analysis periods that leads us to assign it to pyrolyzed carbon;
- Factor 4—has its largest contribution at high temperature in the OC analysis period and we assign it to highly oxidized or low volatility oxidized organic aerosol;
- Factor 5—is dominated by very early emissions and we assign it to highly volatile primary emissions at this site.

A pie chart showing the how much of the carbonaceous aerosol is accounted for by the five factors is shown as Figure 19. The measured carbon is generally spread evenly among the five factors, with Factor 2 (SV-OOA) being slightly larger than the others, and Factor 3 (pyrolyzed carbon) being slightly smaller. Oxidized aerosol (as opposed to primary emissions) makes up more than 80% of the measured carbon in this analysis, which is consistent with our understanding of the nature of carbonaceous aerosol during the summer at this rural receptor site.
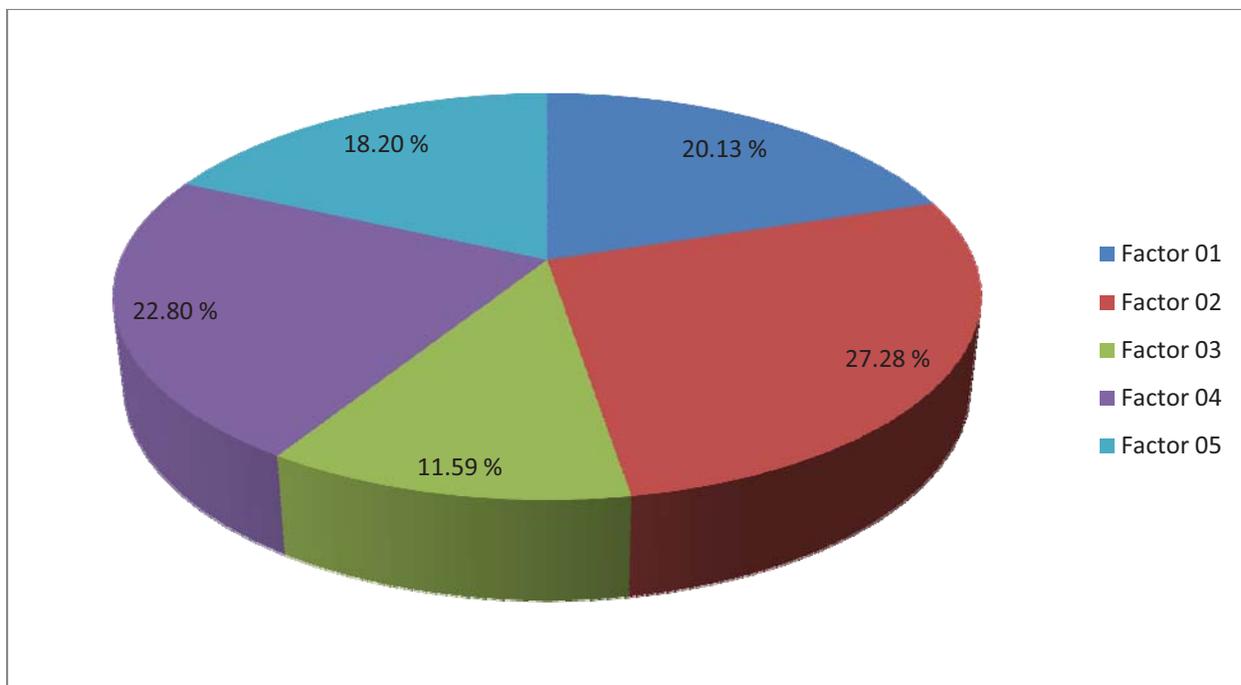
Figure 19. Distribution of carbon among the five factors resolved by the PMF model.

Analysis and Interpretation of Carbon Filter Data from New York State

In light of improved understanding of carbon aerosol fractions from our laboratory and previous analytical work, we have performed detailed analyses of aerosol carbon data collected throughout NYS as part of the New York State Department of Environmental Conservation PM$_{2.5}$ speciation sampling program. The seven sites, four upstate and three in New York City are shown in Figure 20 and listed in Table 3.
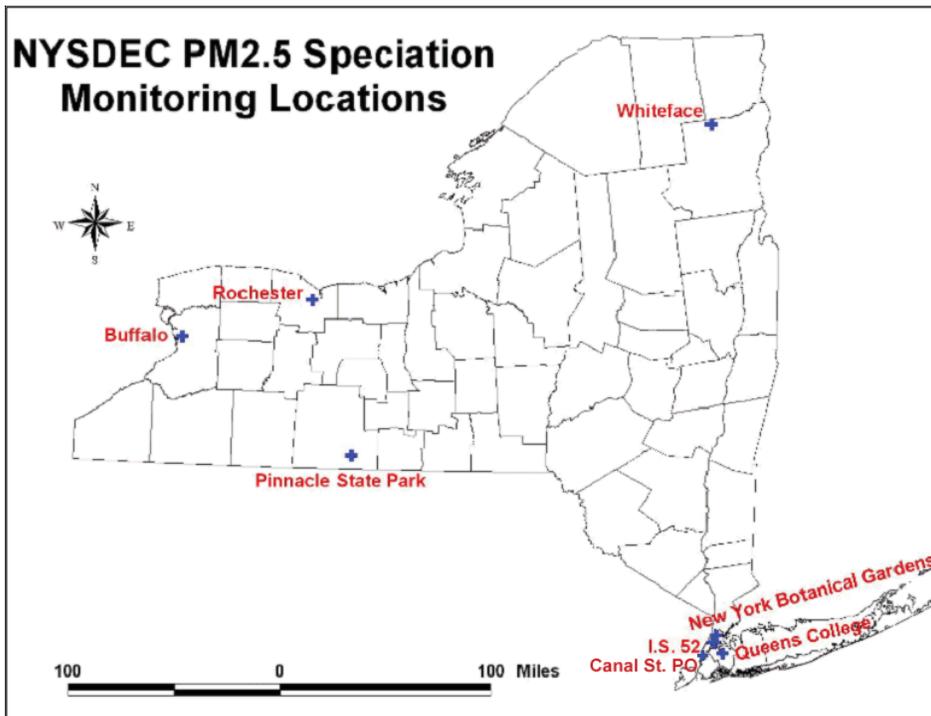
Figure 20. PM$_{2.5}$ speciation monitoring sites in New York State.

Table 3. PM$_{2.5}$ speciation monitoring sites used in this study and abbreviations used for the sites. *CAM—Continuous Air Monitoring (site)

Buffalo CAM *	BUFF
Whiteface Base CAM *	WHTE
Rochester CAM *	RCH2
Pinnacle State Park	PSP
South Bronx Intermediate School 52	IS52
Queens College II (PS 219)	QCII
Canal Street Post Office	CANL

Filters are collected using an EPA protocol and shipped in coolers to keep them cold (and retain volatile components) to a laboratory under contract with EPA to perform the analysis. Relevant to this work is the quartz filter, which is analyzed at the EPA contract lab using a NISH 5040 thermal protocol—this protocol is almost identical to the ACE-Asia protocol described above as part of our laboratory experiments. This protocol consists of four temperature steps under pure helium flow, and five steps under the helium/oxygen mixture flow. Thermograms are not available for these samples, only the final reported data, which consists of TC, OC, EC, and six "fractions". It is these fractions that provide the "additional information" we seek as part of this project, and allow the possibility of additional interpretation. The reported fractions are labeled OC1, OC2, OC3, OC4, PC, and EC. EC needs no further explanation, and PC represents pyrolyzed carbon. Pyrolyzed carbon originally was sampled as organic carbon, but charred as the oven heated up. The sample then converted to "black carbon", which evolved during the helium/oxygen phase. In short, the PC is another organic carbon fraction. OC1 through OC4 are organic carbon fractions that evolve sequentially as the temperature increased. That is, OC1 is the most volatile of these four organic carbon fractions, and OC4 is the least volatile of these four fractions. It is difficult to assign a volatility class to PC, but as shown below, it is not a big contributor to the mix, and doesn't require too much attention.

To explore this very rich data set, we have extracted two years of the filter speciation data (2006 and 2007) for all of the sampling sites. The filters were collected every third day for five sites (ROCH2, PSP, IS52, QCII, and CANL), and every sixth day for the other two. We present the data graphically as a time series of these filter samples with time (i.e., date) as the x-axis and carbon fraction along the y-axis. Measured concentration in micrograms of carbon per cubic centimeter is displayed as a color contour, with warmer colors (red) representing higher concentration values. A plot of the data from PSP is shown as Figure 21. There is some similarity with the much shorter time series of continuous data in Figure 17, but the discrete data and greater number of temperature steps resulted in a larger variety of fractions.
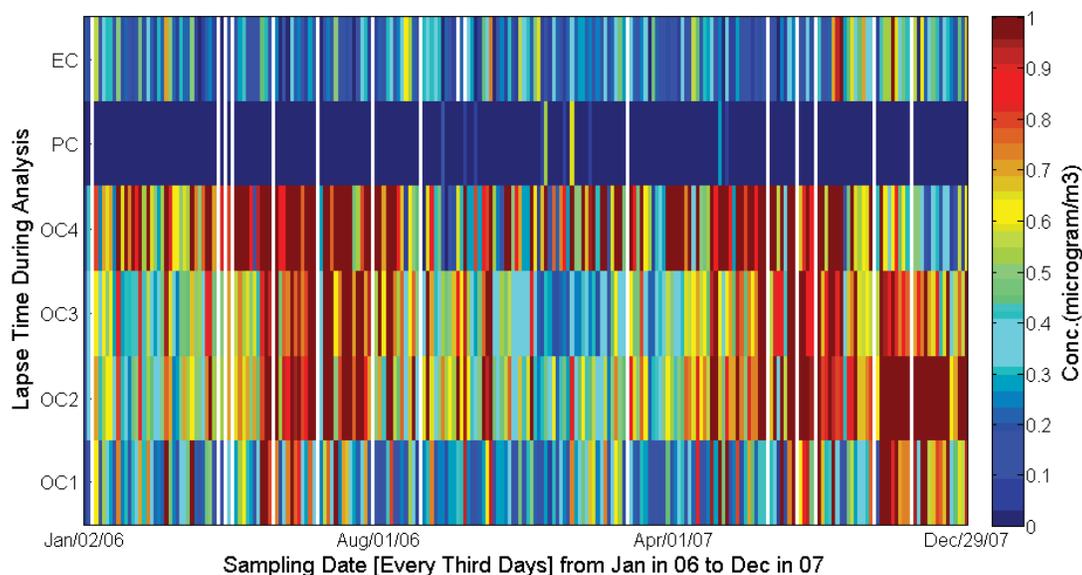

Figure 21. Time series of carbon fractions from filter speciation data sampled at Pinnacle State Park during 2006 and 2007.

Results for other sites are shown in Figures 22 a)—f). The concentration scale is matched to the site for these figures, and there is a factor of two differences between WHTE and CANL. The seasonal dependence is also apparent, but is strongest at the PSP and WHTE rural sites.
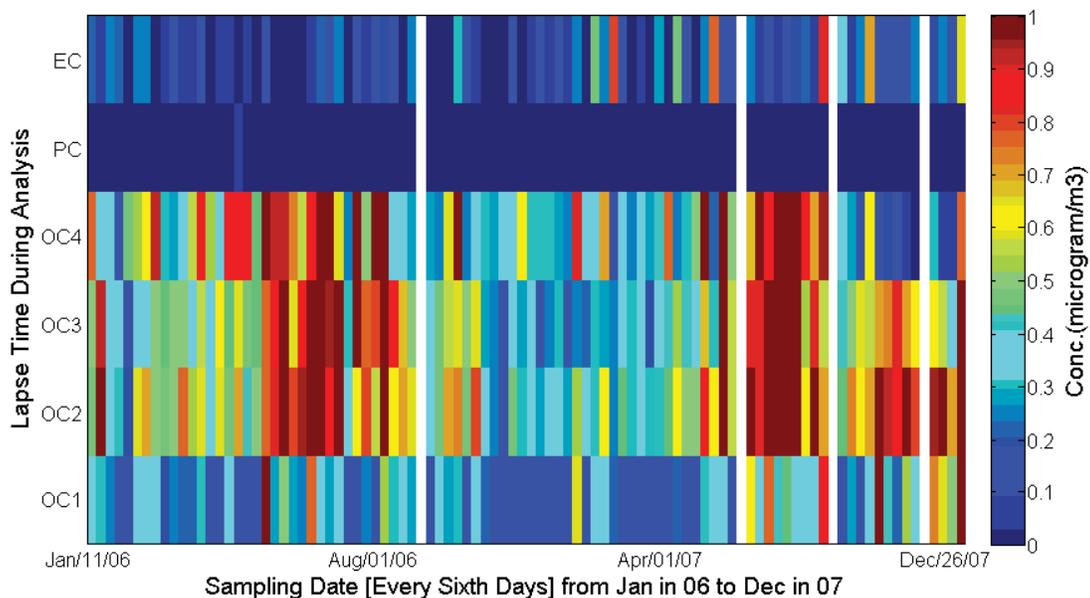

Figure 22 a). Time series of carbon fractions from filter speciation data sampled at Whiteface Mountain during 2006 and 2007.
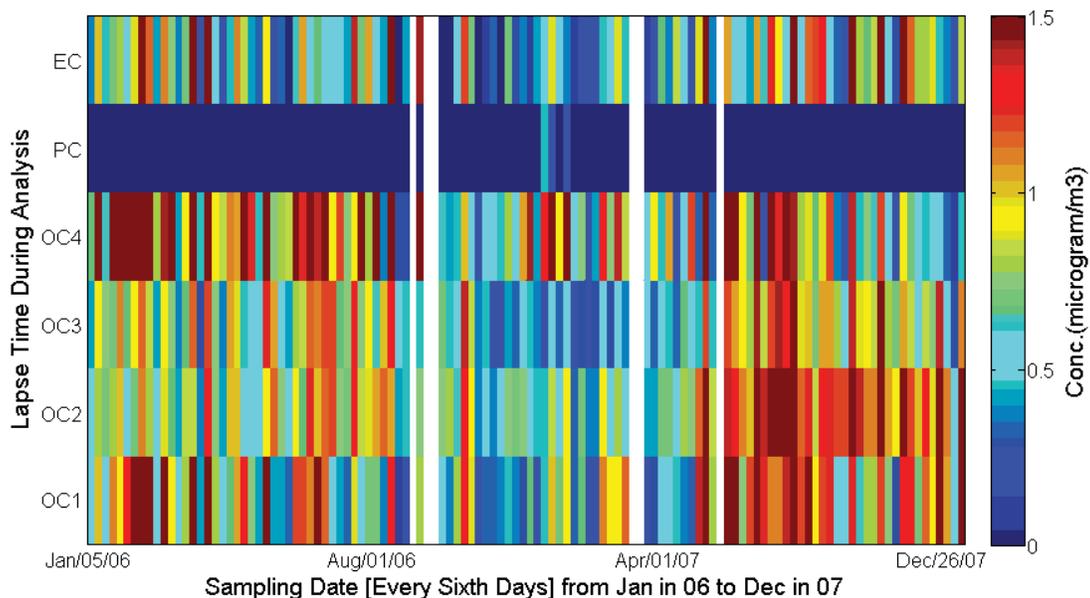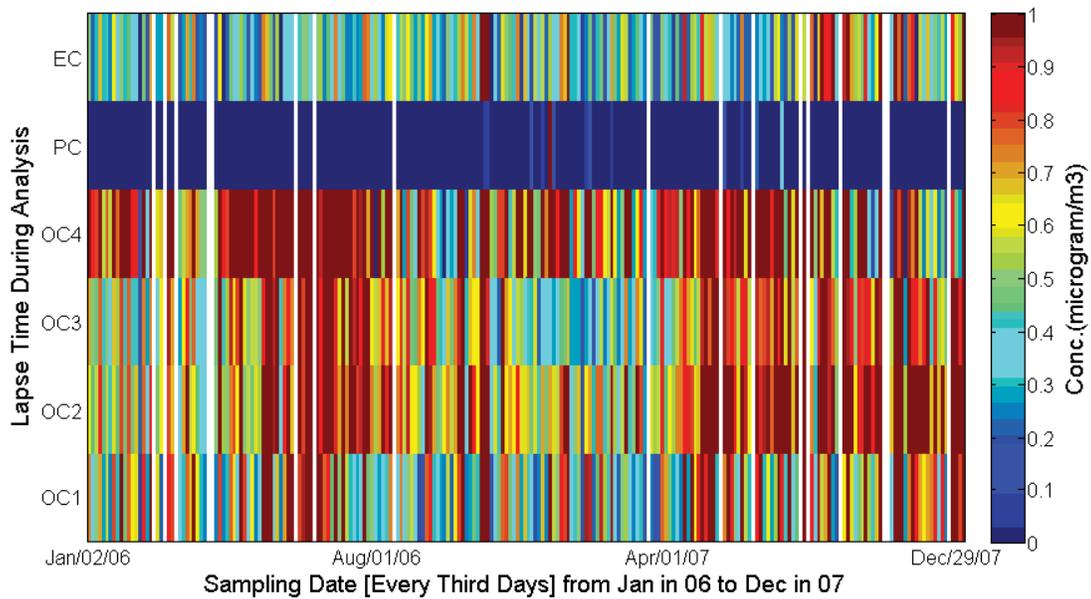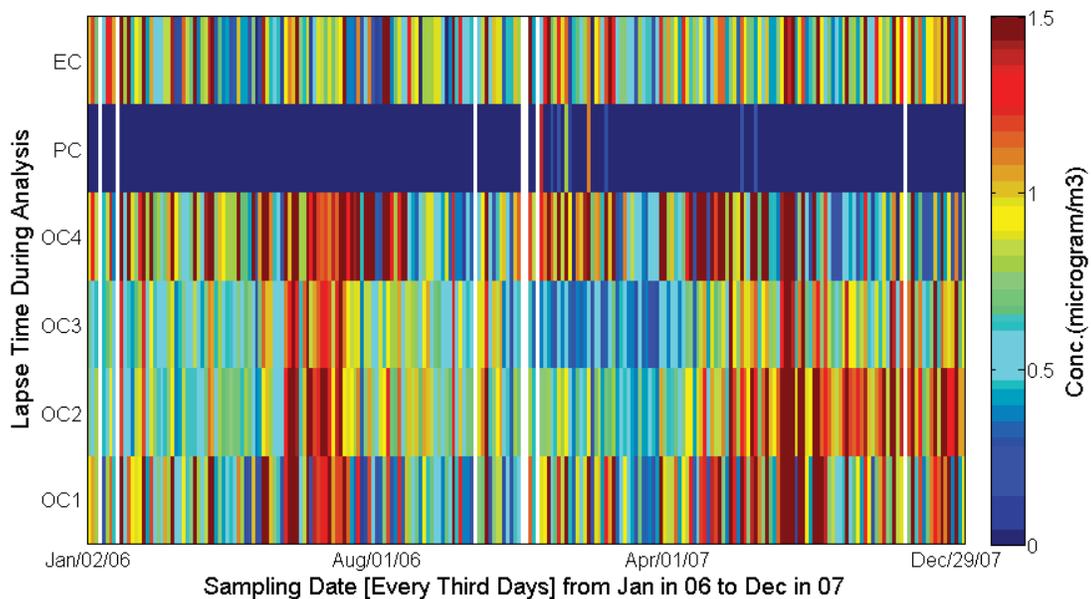

Figure 22 b). Time series of carbon fractions from filter speciation data sampled at Buffalo during 2006 and 2007.

Figure 22 c). Time series of carbon fractions from filter speciation data sampled at Rochester during 2006 and 2007.

Figure 22 d). Time series of carbon fractions from filter speciation data sampled at Queens College during 2006 and 2007.
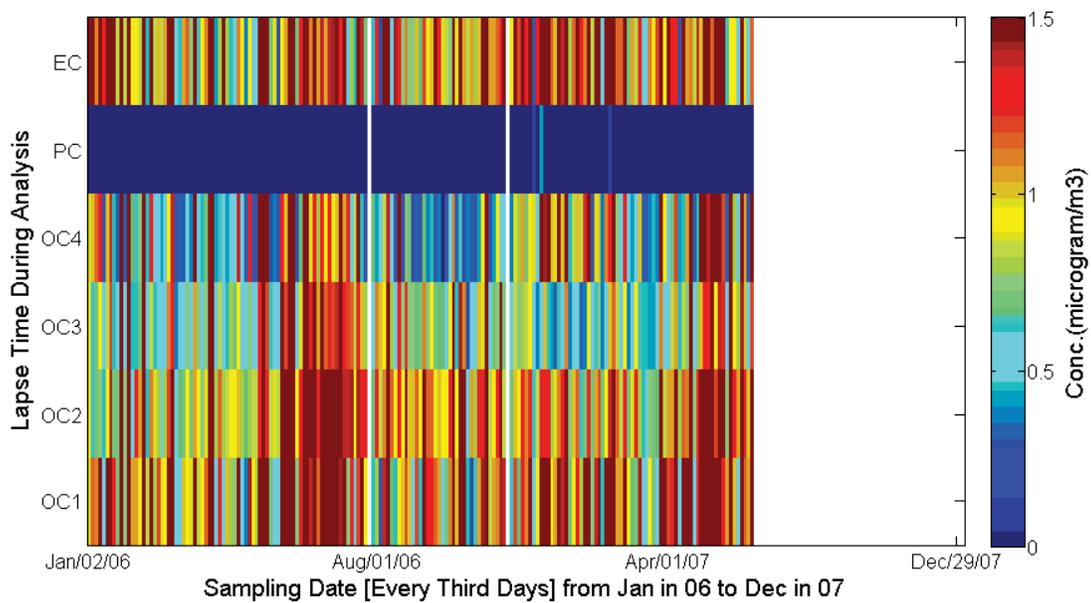
Figure 22 d). Time series of carbon fractions from filter speciation data sampled at South Bronx Intermediate School 52 during 2006 and 2007.
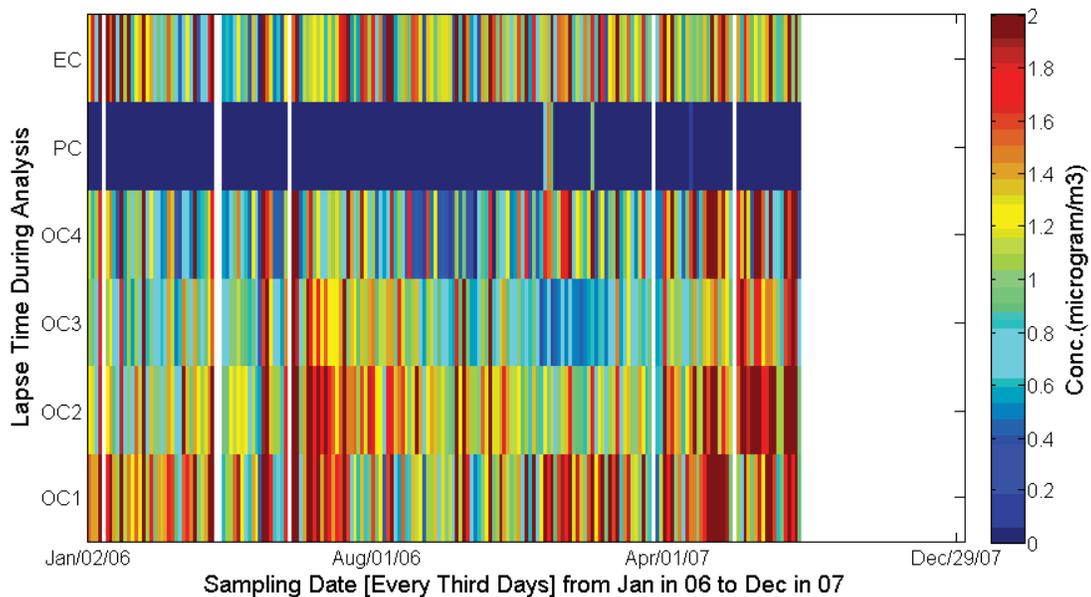

Figure 22 e). Time series of carbon fractions from filter speciation data sampled at Manhattan Canal Street during 2006 and 2007.

We have combined the two years of data to produce an annualized picture of the carbon fractions. At the same time, we have combined the data into monthly averages and normalized all of the data to a single concentration scale to show the differences between the sites more clearly. These plots are shown as Figures 23 a)—g), starting with the most rural site (WHTE) and ending with the most urban (CANL).
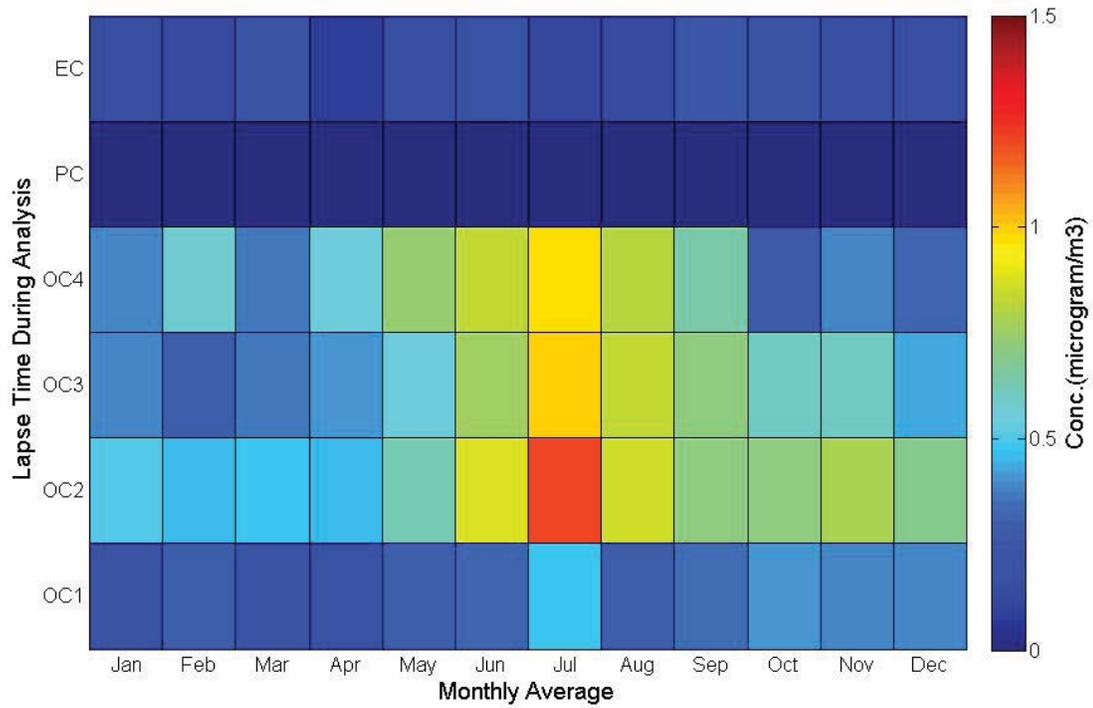

Figure 23 a). Monthly averages of PM$_{2.5}$ carbon fractions reported by the EPA Speciation Network for Whiteface Mountain in 2006 and 2007.
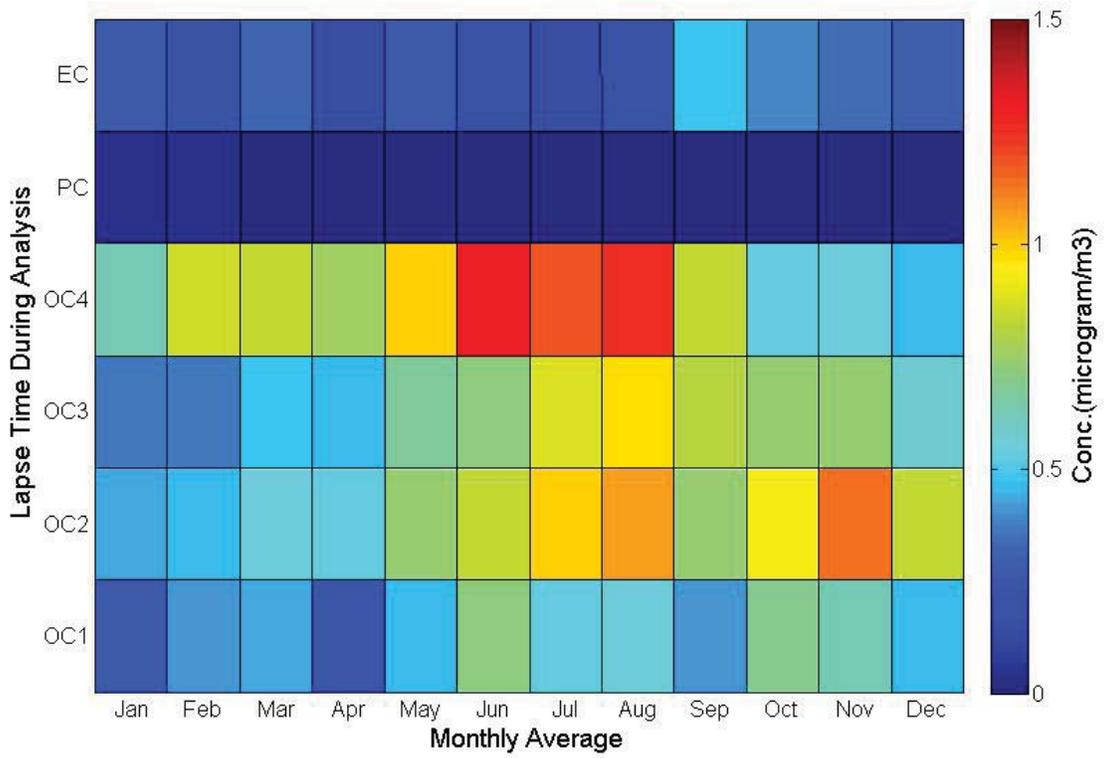
Figure 23 b). Monthly averages of PM$_{2.5}$ carbon fractions reported by the EPA Speciation Network for Pinnacle State Park in 2006 and 2007.
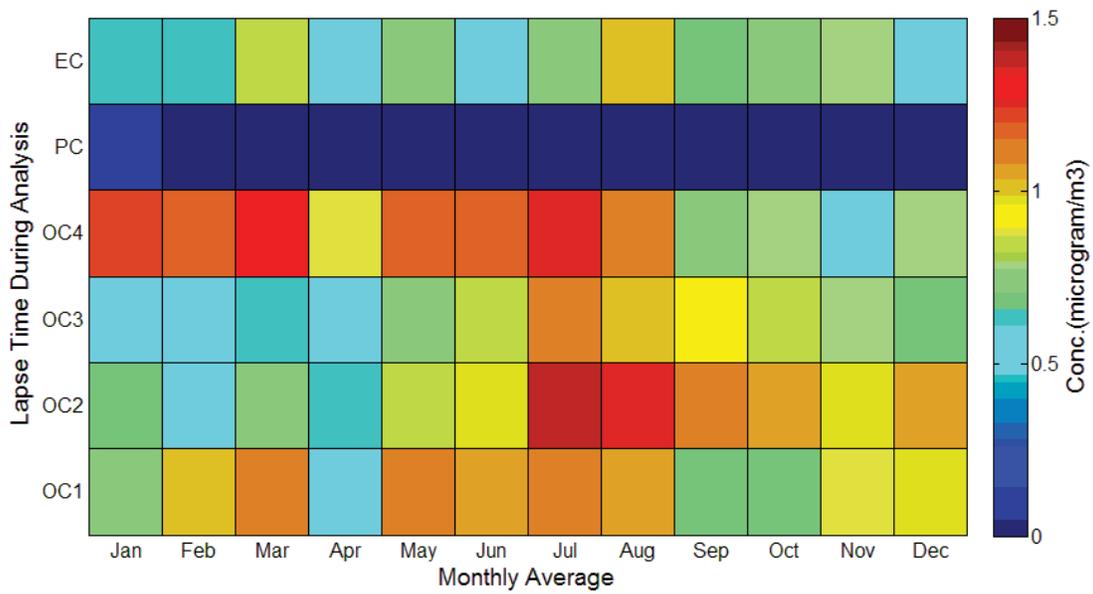
Figure 23 c). Monthly averages of PM$_{2.5}$ carbon fractions reported by the EPA Speciation Network for Buffalo in 2006 and 2007.
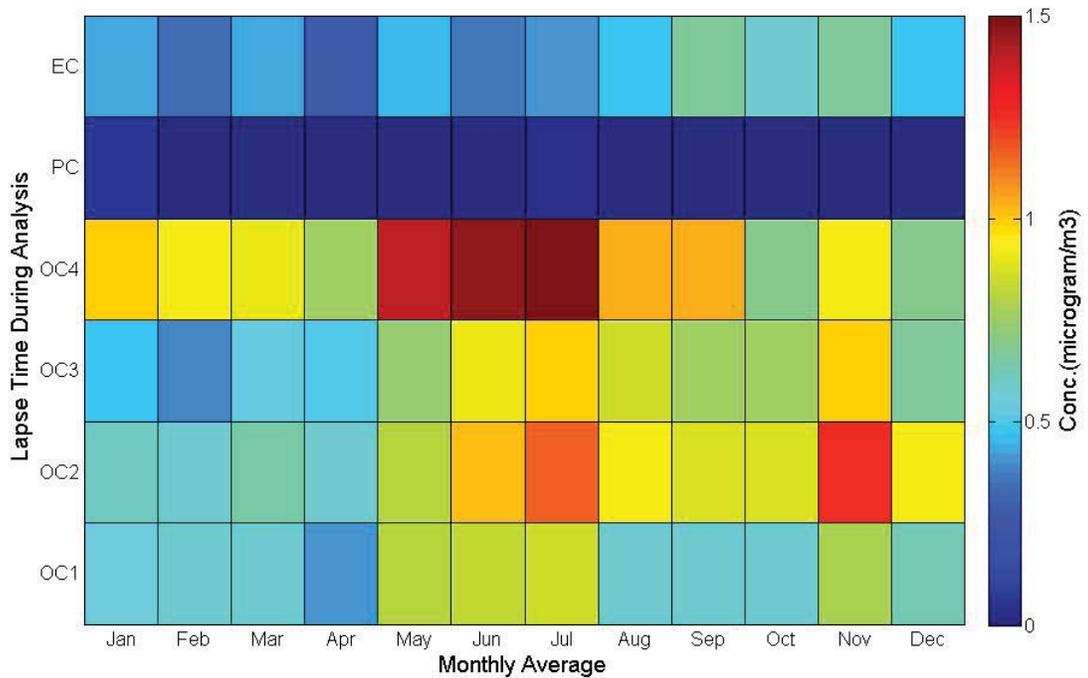

Figure 23 d). Monthly averages of PM$_{2.5}$ carbon fractions reported by the EPA Speciation Network for Rochester in 2006 and 2007.
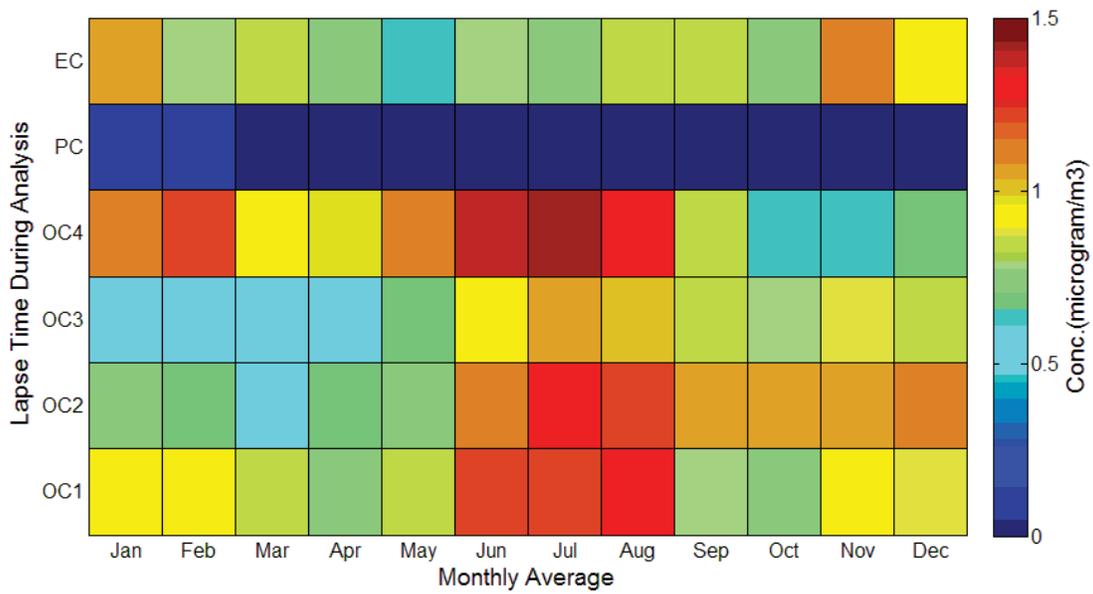
Figure 23 e). Monthly averages of PM$_{2.5}$ carbon fractions reported by the EPA Speciation Network for Queens College in 2006 and 2007.
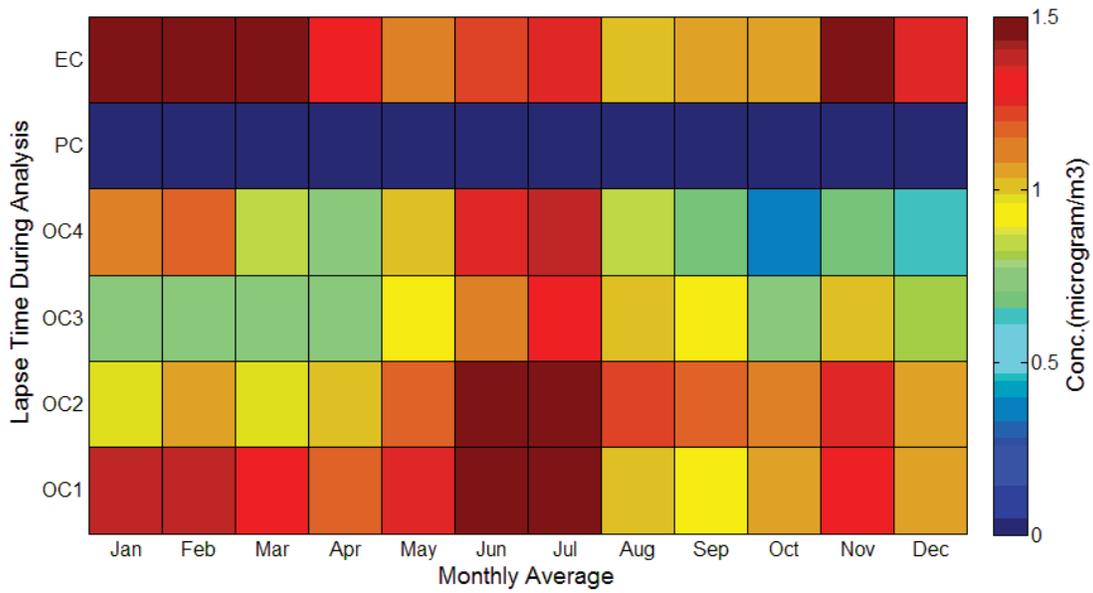

Figure 23 f). Monthly averages of PM$_{2.5}$ carbon fractions reported by the EPA Speciation Network for South Bronx Intermediate School 52 in 2006 and 2007.
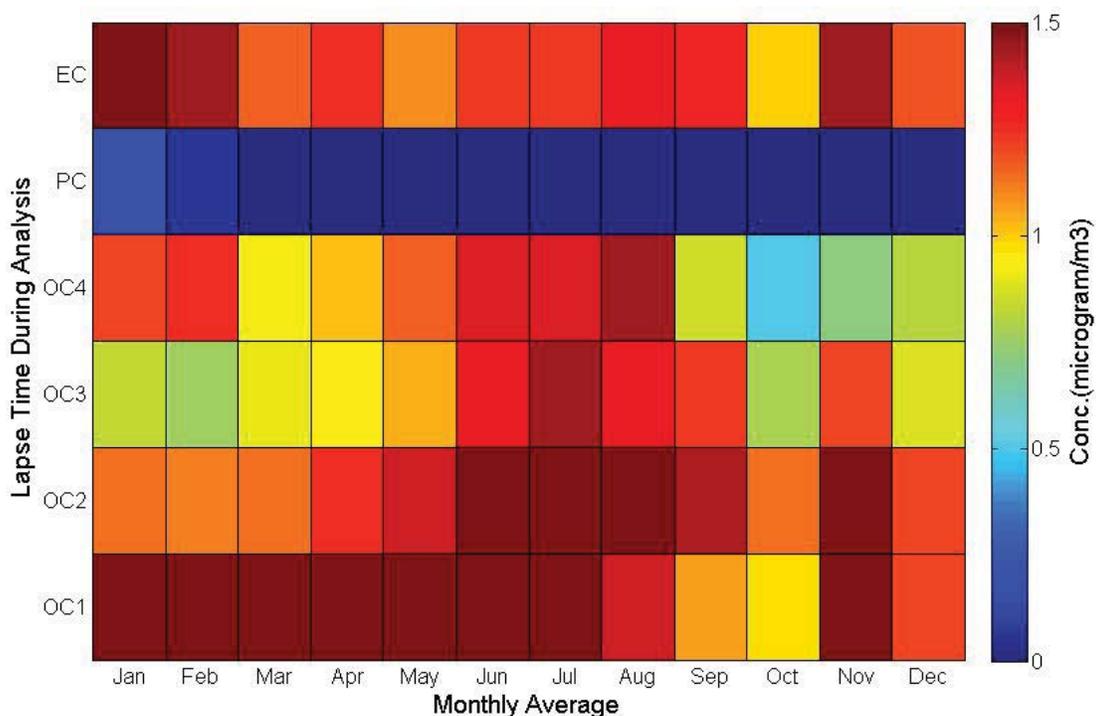
Figure 23 g). Monthly averages of PM$_{2.5}$ carbon fractions reported by the EPA Speciation Network for Canal Street in 2006 and 2007.

A number of points of emphasis suggest themselves from inspection and analysis of Figures 23 a) through g). First, there is a large difference in concentration levels comparing the rural site at Whiteface and sites located in New York City, which is not unexpected. Second is a very strong seasonal dependence—specifically a summer maximum—that is most noticeable in the rural (WHTE and PSP) data, but present in the data from all seven sites. The PSP, BUFF, RCH2, and even QC11 data have very significant OC4 fractions in the summer, which based on laboratory studies and other evidence, we attribute to a well-aged secondary organic aerosol contribution. This is in contrast to the large OC1 contribution at the most traffic-impacted sites of IS52 (South Bronx) and CANL (Manhattan). Again referring to laboratory measurements we attribute this OC1 fraction in these sites to primary organic aerosols, highly volatile fresh emissions from motor vehicles in particular. Note that the OC1 fraction is essentially absent from the rural sites, but that it is very evident in BUFF. The EC contribution is unimportant for the rural sites. There some evidence for EC fractions in BUFF, and it is significant at the IS52 and CANL sites. This is consistent with the OC1 fraction. The OC1 and particularly the EC have strong winter contributions. The observations of strong wintertime EC concentrations is consistent with our previous work (Rattigan et al., 2010).

Another significant observation from the study of these measurements is that the exact location of the measurement site can make a rather large difference for carbonaceous aerosol "fractions". Consider the Buffalo and Rochester measurement data. The Metropolitan Statistical Areas (MSAs) for these two cities are quite close in total population (roughly 1.1M for the Buffalo MSA and 1.05M for the Rochester MSA), but the concentrations and partitioning of carbon is quite different. Upon closer inspection, one finds that the Buffalo measurement site is located approximately 100 meters from Interstate I-90 and industrial sources (http://www.dec.ny.gov/chemical/54370.html#Buffalo), while the Rochester site is in the middle of a field located

at a utility substation and nearly 300 meters from a major interstate highway (http://www.dec.ny.gov/chemical/54367.html#Rochester). It is difficult to understand why this makes the large difference observed for these sites, but some difference is to be expected based on our understanding of the evolution of carbonaceous aerosol. Fresh exhaust emissions (like those captured as OC1 at BUFF) rapidly dilute, and undergo evaporation and oxidation. The oxidized products are less volatile and recondense, and these products are captured by this method in the OC2, OC3, or OC4 fraction. This added complexity of transformation (on relatively short time and space scales) adds to the difficulty in assigning carbonaceous aerosol into fractions, and more importantly, for the comparison of these fractions in a quantitative way between measurement locations.

Conclusion

The goal of this project was to increase the characterization and understanding of sources and evolution of carbonaceous species. As has been detailed in this report, we have been successful in meeting this goal: we have characterized laboratory generated aerosols, combustion aerosols, and mixed aerosols using the most widely deployed measurement method for carbon-containing aerosols, the thermal optical method. We have applied the knowledge gained in these experiments to perform a detailed analysis that is to extract and interpret additional carbon fractions from a semi-continuous data set; and two years of $PM_{2.5}$ carbon data from 24-hour filter measurements.

Measurement of carbonaceous aerosol and interpretation of the data remain a major challenge for scientists and regulators. Carbonaceous materials emitted as condensed phase material, can in some cases evaporate and be transformed into different forms (both gaseous and condensed) on rather short time and space scales. The information and knowledge collected in the performance of this research provide additional tools to inform the problem of carbonaceous aerosol.

References

EPA, 2011, "EPA Positive Matrix Factorization (PMF) 3.0 Model", located at EPA website:
http://www.epa.gov/heasd/products/pmf/pmf.html

Kawamura, K., H. Kasukabe, and L.A. Barrie, 2010: Secondary formation of water soluble organic acids and α-dicarbonyls and their contributions to total carbon and water-soluble organic carbon: Photochemical aging of organic aerosols in the Arctic spring, J. Geophys. Res., 115, D21306, doi:10.1029/2010JD014229.

Li Y.-C., and Y.Z. Yu, 2005: Simultaneous determination of mono- and dicarboxylic acids, oxocarboxylic acids, midchain ketocarboxylic acids, and aldehydes in atmospheric aerosol samples, Environ. Sci. Technol., 39, 7616-7624.

Rattigan, O.V., H.D. Felton, M.-S. Bae, J.J. Schwab, and K.L. Demerjian, 2010: Multi-year hourly $PM_{2.5}$ carbon measurements in New York: Diurnal, day of week and seasonal patterns, Atmos. Environ., 44, 2043-2053, doi:10.1016.j.atmosenv.2010.01.019.

Rattigan, O.V., H.D. Felton, M.-S. Bae, J.J. Schwab, and K.L. Demerjian, 2011: Comparison of long-term $PM_{2.5}$ carbon measurements at an urban and rural location in New York, Atmos. Environ., 45, 3228-3236, doi:10.1016/j.atmosenv.2011.03.048.

Ruehl, C.R., W.A. Ham, and M.J. Kleeman, 2011: Temperature-induced volatility of molecular markers in ambient airborne particulate matter, Atmos. Chem. Phys., 11, 67-76, doi:10.5194/acp-11-67-2011.

Watson, J.G., J.C. Chow, and L.-W. Anthony, 2005: Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons, Aerosol Air Qual. Res., 5(1), 65-102.

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Beyond OC—A Method to Extract and Interpret Additional Aerosol Organic Carbon Fractions from Thermal Optical Analysis of Filter-Based and Continuous Data

Final Report
November 2011