

Evaluation of Wood Smoke Contribution to Particle Matter in Connecticut



Connecticut Department of Environmental Protection
Bureau of Air Management
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Acronyms and Abbreviations

AQI – Air Quality Index
AQS – Air Quality System
CAA – Clean Air Act
CFR – Code of Federal Regulations
CO – carbon monoxide
CTDEP – Connecticut Department of Environmental Protection
CV – coefficient of variance
DAS – data acquisition system
DQA – data quality assessment
DQO – data quality objective
EPA – Environmental Protection Agency
FEM – Federal Equivalent Method
FRM – Federal Reference Method
GC – gas chromatography
GC/MS – gas chromatography/mass spectrometry
GIS – geographical information systems
GPS – global positioning system
HAP – hazardous air pollutant
HPLC – high performance liquid chromatography
ICP/MS – inductively coupled plasma/mass spectrometry
IMPROVE – Interagency Monitoring of Protected Visual Environments
IO – Inorganic
IT – information technology
LAN – local area network
LMP – limited maintenance plan
MQO – measurement quality objectives
MSA – metropolitan statistical area
NAAQS – National Ambient Air Quality Standards
NIST – National Institute of Standards and Technology
NO_x – nitrogen oxides
NO_y – reactive oxides of nitrogen
NPAP – National Performance Audit Program
OAQPS – Office of Air Quality Planning and Standards
OWB – Outdoor Wood Boilers
PAMS – Photochemical Assessment Monitoring Stations
P&A – precision and accuracy
PM_{2.5} – fine particulate matter (2.5 microns)
PM₁₀ – respirable particulate matter (10 microns)
PM_{10-2.5} – coarse particulate matter (PM₁₀ – PM_{2.5})
QA – quality assurance
QA/QC – quality assurance/quality control
QAPP – quality assurance project plan
QMP – quality management plan
RH – relative humidity
RPD – relative percent difference
SIP – State Implementation Plan
SLAMS – state and local monitoring stations
SO₂ – sulfur dioxide
SOP – standard operating procedure
STN – Speciation Trends Network
SQL- Structured Query Language (Database Language)
TSP – total suspended particulate

VOC – volatile organic compound

WSPM – wood smoke particulate matter

This project was conducted by the Connecticut Department of Environmental Protection (CTDEP) and funded by the United States Environmental Protection Agency (US EPA) through a 2005 Local-Scale Air Toxics Ambient Monitoring Grant Solicitation (RFA NO: OAR-EMAD-05-16). This is the final report submitted to EPA to fulfill the final grant obligation. Below is the project title, category and applicant information by which the proposal for this project was submitted for consideration.

Project Title: Evaluation of Wood Smoke Contribution to Particle Matter in Connecticut

Category: Source Identification and Characterization (Bin 1)

Applicant Information: Connecticut Department of Environmental Protection, Bureau of Air Management

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Executive Summary

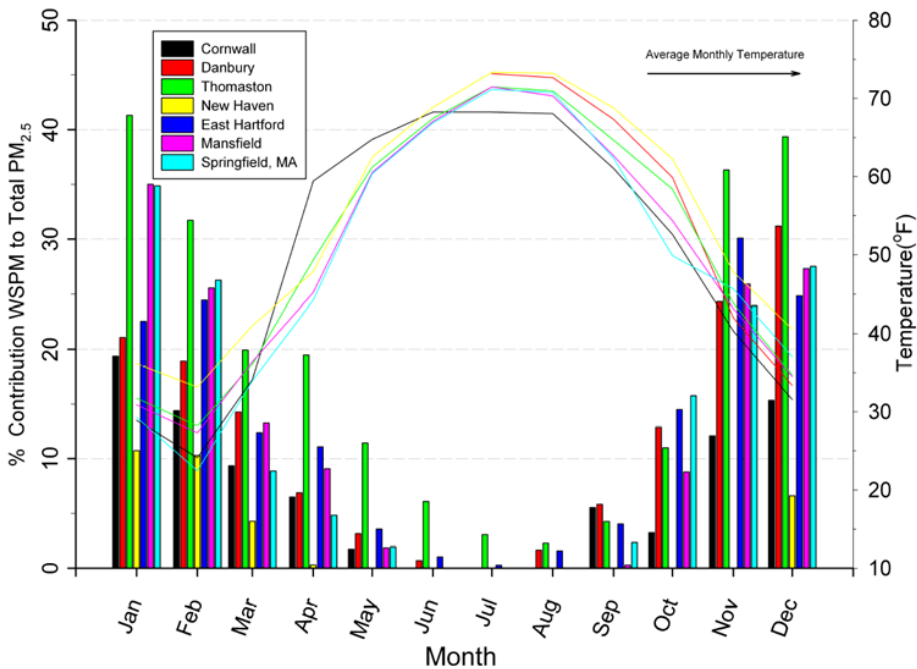
The CTDEP conducted an ambient air monitoring study from September 2006 through April 2008 that characterized the contribution of particulate matter from wood burning sources. Monitoring was conducted at seven sites and modeling was applied to the data collected to apportion the sources and quantify wood smoke particulate matter (WSPM) concentrations.

This study confirmed that the 2-channel Aethalometer™ (Magee Scientific) does provide a real-time wood smoke indicator. Using modeling, a scaling factor was derived to quantify wood smoke concentrations. This scaling factor was somewhat variable from site to site; however, a reasonable approximation of WSPM concentrations could be determined.

The impetus for this work was to compare emission inventory estimates of WSPM in Connecticut to actual ambient air monitoring measurements. The 2002 Mid-Atlantic Regional Air Management Association (MARAMA) emission estimates for WSPM was that 38% of Connecticut PM_{2.5} emissions are from wood burning sources. Results from this study indicate that on an annual average, the WSPM contribution to total PM_{2.5} measurements range from 1.7 to 17.3% for the six Connecticut sites evaluated in this study (10.8% for Springfield, MA). Even though these are estimates for only six distinct sites in Connecticut, these sites are representative of Connecticut as a whole with rural, urban, valley and non-valley sites represented.

As one would expect, the contribution of WSPM is strongly linked to the season, with highest contributions in the colder, winter months and much lower contributions during the warmer, summer months. For all sites, maximum monthly average WSPM contributions in the winter ranged from 10.8 to 41.3%, while maximum monthly summertime averages ranged from near zero to 6.1% (See Figure ES-1).

Figure ES-1: Average Monthly Percent Contribution of WSPM to Total PM_{2.5}



In addition to approximating average annual WSPM contributions in Connecticut, another objective of this project was to determine WSPM contributions when total PM_{2.5} observations are elevated. This is significant given the new daily PM_{2.5} standard of 35 µg/m³ and with the probability of the establishment of a sub-daily PM_{2.5} standard in the future. Understanding the sources that contribute to elevated PM levels is key for effectively developing and evaluating control strategies.

WSPM contributions were evaluated for daily PM_{2.5} concentrations above 15 µg/m³. This level corresponds to the “Moderate” breakpoint for the Air Quality Index. When the 24-hr average temperature was less than 45 degrees Fahrenheit (°F) and the daily PM_{2.5} concentrations were greater than 15 µg/m³, the average WSPM contribution was 23.9% (range of 8.9 to 38.0%) of the average total PM_{2.5} concentrations. When the 24-hr average temperature was greater than 45°F and the daily PM_{2.5} concentrations were greater than 15 µg/m³, the average WSPM contribution was 4.2% (range of 0.9 to 5.5%) of the average total PM_{2.5} concentrations.

A similar evaluation was conducted for WSPM contributions when hourly PM_{2.5} concentrations were greater than 30 µg/m³. When the hourly average temperature was less than 32°F and the hourly PM_{2.5} concentrations were greater than 30 µg/m³, the average WSPM contribution was 36.3% (maximum of 56.8%) of the average total PM_{2.5} concentrations. When the hourly average temperature was less than 45°F and the hourly PM_{2.5} concentrations were greater than 30 µg/m³, the average WSPM contribution dropped to 22.8% (maximum of 45.0%) of the average total PM_{2.5} concentrations. When the hourly average temperature was greater than 45°F and the hourly PM_{2.5} concentrations were greater than 30 µg/m³, the average WSPM contribution was 1.7% (range of 0.6 to 3.5%) of the average total PM_{2.5} concentrations.

Although the objective of this study was to quantify the contribution of Connecticut WSPM emissions primarily during the wintertime, wood-burning season, it also provided valuable information on the effects of summertime forest fire transport events. Analysis in this report shows that these forest fire events can significantly contribute to both PM_{2.5} and ozone exceedance days. These WSPM methodologies could also prove useful in documenting future exceptional events.

Modeling conducted through this project not only provided a highly time resolved profile for wood burning sources, but also resulted in valuable profile and contribution information for other sources such as fresh and aged mobile sources, home heating oil and secondary aerosols with hourly time resolution. Understanding the contributions of these sources and the diurnal and seasonal patterns can greatly enhance the ability to develop control strategies to address these sources, as well as, determine the effectiveness of both current and future mitigation efforts. Therefore, future analyses of the other sources could provide useful information on where appropriate mitigation efforts could be applied in the most effective manner.

Introduction

The Connecticut Department of Environmental Protection (CTDEP), Bureau of Air Management, was awarded a US EPA grant to assess wood smoke contributions to fine particle matter (PM_{2.5}) in Connecticut, and also to conduct monitoring and testing to characterize the emissions for an emerging source known as outdoor wood furnaces (OWFs), outdoor wood boilers (OWBs), or hydronic heaters.

The first part of this project utilized ambient measurements to evaluate the portion of PM_{2.5} concentrations that can be attributed to wood burning. The second part of this project characterized the PM_{2.5} emissions associated with OWBs, an emerging, uncontrolled and unregulated source that has been largely uncharacterized up to this point.

Although this was one grant award, the findings are presented in two separate reports; this report addresses the findings relative to the ambient air monitoring portion of the study and NESCAUM has prepared the final report for the OWB source characterization portion of the study.¹

The main objective of the wood smoke monitoring portion of this study was to better characterize the contribution of wood smoke to ambient PM_{2.5} concentrations in Connecticut. This was accomplished by selecting monitoring sites that are representative of areas that are impacted by wood smoke sources. The ambient wood smoke monitoring effort: 1) characterized the impact of wood burning on PM_{2.5} concentrations; 2) assessed the contribution of wood smoke to PM_{2.5} during wintertime inversion events; 3) assessed emission inventory estimates; 4) evaluated modeling results with monitoring data; 5) provide information that could prove useful in developing future control and reduction strategies.; and 6) built upon new techniques that quantify PM_{2.5} concentrations from wood smoke on a real-time basis. This study will provide valuable information as the CTDEP looks to identify risk reduction strategies and develop PM_{2.5} and Regional Haze State Implementation Plans (SIPs).

Background Information

The severity of potential health effects and magnitude of populations affected by wood smoke pollutants have led health scientists to conclude that exposure to it should be minimal. Wood smoke is comprised of numerous constituents including PM_{2.5}, carbon monoxide (CO), volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). Some VOCs and PAHs are respiratory irritants and also have carcinogenic and mutagenic properties, while carbon monoxide exposure has been associated with adverse respiratory and cardiac effects^{2, 3, 4, 5}. Exposure to PM_{2.5} may play a large role in observed health effects

¹ Contribution of Wood Smoke to Particle Matter Levels in Connecticut – Source Characterization of Outdoor Wood Furnaces. Prepared by NESCAUM in conjunction with this project. September 9, 2008.

<http://www.nescaum.org/documents/source-characterization-of-outdoor-wood-furnaces/ctdep-owb-test-report.pdf>

² http://www.epa.gov/burnwise/pdfs/woodsmoke_health_effects_jan07.pdf

³ [Simpson](#), Christopher D. and [Luke P. Naeher](#). 2010. Biological Monitoring of Wood Smoke. Inhalation Toxicology. Vol 22 (2).

related to wood smoke. Fine particles are of health concern because of their association with serious cardiopulmonary health outcomes and their impact on a large number of susceptible population subgroups, including young children, asthmatics, persons with respiratory or heart disease, diabetics, and the elderly.⁶

There is increasing concern regarding the impact of wood smoke from residential wood combustion (RWC) sources on air quality. According to the 2002 Mid-Atlantic Regional Air Management Association (MARAMA) emissions inventory, wood smoke contributes 38% of the PM_{2.5} emissions in Connecticut. Woodstoves are now available that are EPA-certified; however, the majority of the woodstoves in operation are older units with no pollution control devices. As fuel prices have risen, so have the sales of woodstoves and OWBs⁷.

A pilot study conducted in Rutland, VT in 2003 looked at evaluating an approach that quantified, in near real-time, the contribution of wood smoke to PM_{2.5} concentrations (WSPM).⁸ The pilot project succeeded in apportioning the PM_{2.5} into several source categories. The Rutland study also identified ways in which this approach could be improved upon in future studies; the key concept of using the delta C signal as a marker for real-time woodsmoke emissions is integrated in this proposal.

Project Design

The CTDEP conducted wood smoke monitoring that was comprised of one newly established core site and six satellite sites. Monitoring was conducted from September 2006 through April 2008. A full range of parameters were operated at the core site while the six satellite sites collected appropriate data to assess WSPM using information obtained and applied from the core site. See Figure 1 for a map of the monitoring sites used in this study.

Core site: The core site was in the Thomaston area, located in western Connecticut. Thomaston is located in the Naugatuck Valley and is prone to wintertime inversions, which trap pollutants close to the ground. The emphasis was placed on collecting highly sensitive, highly time-resolved data to best characterize and apportion sources. A comprehensive selection of pollutants were measured at this site to best assess the PM_{2.5} contributions from wood smoke. Continuous PM_{2.5}, along with volatile and non-volatile fractions of PM_{2.5}, were measured in addition to continuous speciation methods to obtain highly time-resolved organic carbon (OC), elemental carbon (EC), sulfate (SO₄), and the optical absorption of PM at two wavelengths

⁴ [Noonan](#), Curtis W. and [John R. Balmes](#). 2010. Biomass Smoke Exposures. *Inhalation Toxicology*. Vol 22(2)

⁵ Lewtas, Joellen. 2007. [Air pollution combustion emissions: Characterization of causative agents and mechanisms associated with cancer, reproductive, and cardiovascular effects](#). *Mutation Research*. Vol 636 (1-3)

⁶ http://www.epa.gov/burnwise/pdfs/woodsmoke_health_effects_jan07.pdf

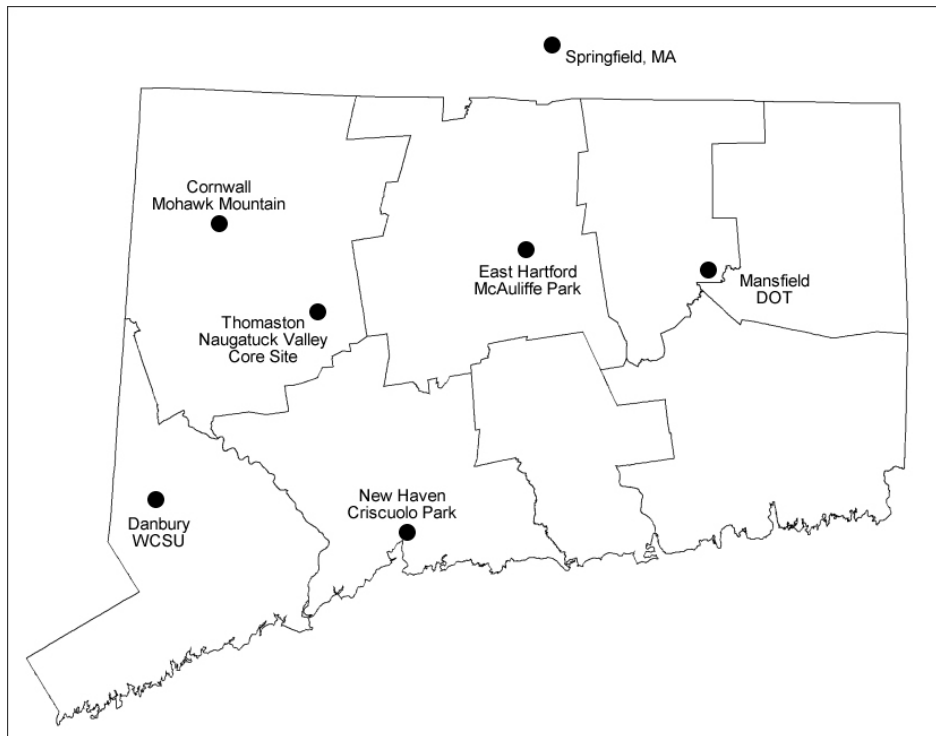
⁷ NESCAUM. 2006. Assessment of Outdoor Wood-Fired Boilers.

⁸ Allen, George A., Babich, Peter C. and Poirot, Richard L. Paper No. 16. "Evaluation of a New Approach for Real Time Assessment of Wood Smoke PM." Air & Waste Management Association Visibility Specialty Conference on Regional and Global Perspectives on Haze: Causes, Consequences and Controversies. Asheville, NC, October 25-29, 2004.

(370 and 880 nm). Trace-gas analyzers were used to obtain carbon monoxide (CO), sulfur dioxide (SO₂), and reactive oxides of nitrogen (NO_x). Highly time-resolved measurements of trace metals and PAHs were collected, as well. This information was used to quantify WSPM and to relate the measurements to other wood smoke markers (i.e., potassium) and other pollutants (i.e., PAHs).

Satellite sites: A total of five satellite sites in Connecticut and one satellite site in Massachusetts were included in the wood smoke monitoring network. Three of the sites were located in Danbury, East Hartford and Mansfield. These sites were selected based on the fact that they are located in valleys that are prone to wintertime inversions and are located in western, central and eastern Connecticut, respectively. A two-wavelength Aethalometer™ were deployed to each site to provide semi-quantitative, real-time WSPM estimates. These WSPM measurements will be better quantified using analysis performed on data obtained from the core site. The other two Connecticut sites were located on Mohawk Mountain in Cornwall and at Criscoolo Park in New Haven. Both Mohawk Mountain and Criscoolo Park are established sites that are recently approved NCORE sites with a comprehensive selection of parameters currently being measured. The Cornwall Mohawk Mountain site is a rural background site located well above inversion boundary layers and is in the Mid-Atlantic/Northeast Visibility Union (MANE-VU) Rural Aerosol Intensive Network (RAIN). The New Haven Criscoolo Park site is a coastal urban site which is prone to inversion conditions, but is presumably more heavily impacted by mobile sources relative to wood smoke sources. The final satellite site selected was the Springfield, MA site based on its proximity to Connecticut and that a comprehensive suite of measurements were already being obtained at this established site that could be utilized for WSPM estimates.

Figure 1: Wood Smoke Monitoring Network



WSPM: A two-wavelength Aethalometer™ (Magee Scientific Models AE21 and AE22) was operated at all seven sites. The Aethalometer™ was used to measure the optical absorption of PM at 880 nm (BC) and 370 nm (UV-C). The Aethalometers™ at all sites were operated at 2 LPM with a PM-1 (BGI/Magee Scientific SCC 0.732) size selective inlet. Field studies have shown that BC measurements are strongly correlated with thermal elemental carbon (EC) measurements.^{9,10,11} The difference between the UV-C and BC channels (Delta-C) has been shown to be a specific, semi-quantitative indicator of wood-smoke related PM. The Rutland study showed that the Delta-C measurement was specific to WSPM even in presence of PM associated with mobile sources. The Aethalometer™ was configured to capture five-minute measurements.

Continuous PM_{2.5}: An FDMS-B TEOM (Thermo Series 8500) was operated at the core site to obtain hourly PM_{2.5} concentrations, as well as volatile and non-volatile fractions of PM_{2.5}, which is valuable in terms of source apportionment. An FDMS-B TEOM was also operated at the New Haven Criscuolo Park and East Hartford McAuliffe Park sites. MetOne BAMs were operated at the Cornwall, Danbury, New Haven and Springfield, MA sites to obtain continuous PM_{2.5} measurements.

Continuous Speciation: A continuous OC/EC analyzer (Sunset Laboratory Model 3) was deployed to the core site to collect two-hour OC and EC measurements. A continuous SO₄ analyzer (Thermo Environmental Model 5020 SPA) was deployed at the core site to obtain 15-minute sulfate averages. Both of these analyzers were also operated at the Cornwall site.

Gaseous Pollutants: Trace-gas analyzers were deployed at the core site for CO (Thermo Environmental Model 48C-TLE) and SO₂ (Thermo Environmental Model 43C-TLE). The utilization of trace instrumentation is important in order to increase the sensitivity, which allows increased confidence in assessing source contributions. NO, NO₂ and NO_x were also obtained at the core site. Gas analyzers were also operated at other satellite sites to allow additional source apportionment modeling to be conducted to compare with results from the core site in Thomaston.

Trace Metals: A slotted 3-Drum Impactor (DELTA Group) was deployed at the core site to obtain high-resolution trace metal and optical attenuation measurements for three size ranges. Among the target metals to be measured are high priority HAPs that include arsenic, beryllium, cadmium, chromium, manganese and nickel.

PAHs: A continuous PAH analyzer (EcoChem PAS 2000) was deployed at the core site to obtain real-time particle-bound PAH measurements.

⁹ Hansen, A.D.A., Rosen, H., Novakov, T. **1984**. The Aethalometer™ - an instrument for the real-time measurement of optical absorption by aerosol particles. *Sci. Total Environ.* **(36)** 191.

¹⁰ Allen, George A., Lawrence, Joy and Koutrakis, Petros. **1999**. Field validation of a semi-continuous method for aerosol black carbon (Aethalometer) and temporal patterns of summertime hourly black carbon measurements in southwestern Pennsylvania. *Atmos. Environ.* **(33)**817-823.

¹¹ Babich, Peter C., Davey, Mark E., Allen, George A. and Koutrakis, Petros. **2000**. Method comparisons for particulate nitrate, elemental carbon, and PM_{2.5} mass in seven U.S. cities. *J. Air & Waste Management Assoc.* **50** (8).

Meteorological Parameters: A meteorological system (Climatronics) was operated at the core site to obtain wind speed, wind direction, ambient temperature, barometric pressure and dew point. Similar meteorological systems were also operated at the six satellite sites.

Data Management and Analysis: Ambient monitoring data related to this project was managed in a SQL Server database located on a server at CTDEP Headquarters in Hartford, CT. Data was polled, stored, validated and then generated into Air Quality System (AQS) files for reporting to the US EPA. The monitoring data was analyzed to characterize spatial resolution, concentration gradients and source signatures of air pollutants specific to wood smoke sources. The analysis performed on the data obtained in this study built upon results from the pilot study conducted in Rutland, VT. Unmix modeling was applied to apportion measured PM_{2.5} from the core site located in Thomaston into several source categories. The resulting factor to convert the difference of the two channels from the Aethalometer™ into WSPM was then applied to the data obtained at the satellite sites. Running the Unmix model on the data obtained at several of the satellite sites was possible for the sites that had a comprehensive selection of parameters currently in operation. This was used to compare the results from the core site; however, the core site provided the most robust analysis, given the time-resolved speciation data and the high sensitivity of the trace gas measurements. Comparisons of these results against more traditional measures of wood smoke indicators (i.e., PAHs) were also made.

Aethalometer™ Data Processing

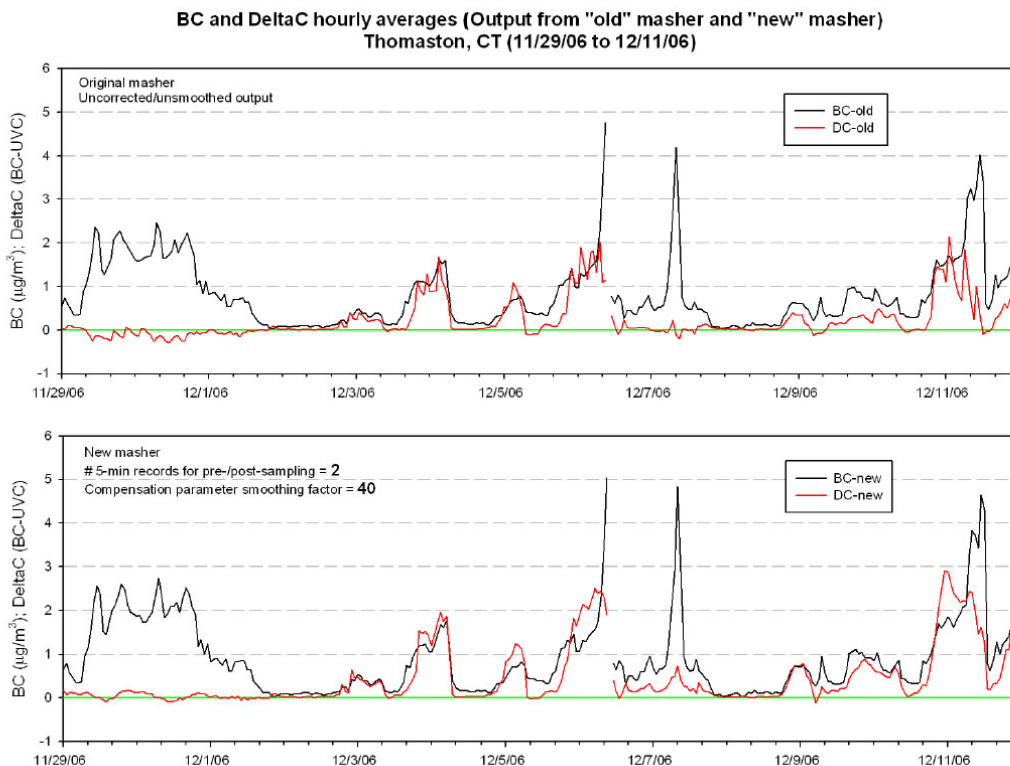
The Magee Scientific Aethalometer™ is the widely used method to measure atmospheric BC on a near-real time basis. The Aethalometer™ measures optical attenuation on a quartz fiber tape. It has been shown that BC measurements typically decrease with increased spot loading – a saturation effect that is a function of spot loading.^{12,13} The Aethalometer™ DataMasher is a post-processing software package used to validate 1-min and 5-min Aethalometer™ data and create valid one-hour averages. Earlier versions of the DataMasher did not compensate for the filter saturation effect. This study funded the development of an enhanced version of the DataMasher that applies a correction to the raw Aethalometer™ data to compensate for the filter saturation effects. All Aethalometer™ data in this study was post-processed with the newly developed DataMasher with saturation effect correction capabilities.

Although results from the original Aethalometer™ DataMasher vs. the newer DataMasher with saturation effect correction were reasonably comparable as demonstrated in Figure 2, there is an enhanced response in both the BC and UVC channels and there's essentially a zeroing-out of the Delta-C channel. In the earlier version of the DataMasher, where the saturation matrix effects were not compensated for, Delta-C routinely fell below zero in the warmer weather months with the presence of little or no WSPM.

¹²Virkkula, Aki, *et al.* **2007**. A Simple Procedure for Correcting Loading Effects of Aethalometer™ Data. *J. of Air & Waste Management Assoc.* **(57)** 1214-1222.

¹³Turner, Jay R., Hansen, Anthony D. and Allen, George A. Paper No. 37. "Methodologies to Compensate for Optical Saturation and Scattering in Aethalometer™ Black Carbon Measurements." Symposium on Air Quality Measurement Methods and Technology, San Francisco, CA, April 30 – May 2, 2007.

Figure 2: BC and Delta-C hourly averages post-processed with DataMasher with and without filter saturation effect correction.



Modeling Methods

Source apportionment was determined with Unmix modeling, an EPA approved software. Unmix takes a given set of pollutants and the corresponding concentrations and determines the amount of sources, the source compositions and the source contributions to the given sample set.^{14,15,16} For detailed procedures on data formatting, estimating source profiles, etc., for the Unmix modeling software, see the EPA Unmix 6.0 Fundamentals and User Guide.⁹

For the purposes of this study, Unmix modeling was conducted for four of the monitoring sites; Thomaston, East Hartford and New Haven sites in Connecticut, as well as, the Springfield site in Massachusetts. WSPM monitoring was also conducted at Danbury, Cornwall and Mansfield; however the modeling was not run due

¹⁴ Henry, R.C. **1997**. History and Fundamentals of Multivariate Air Quality Receptor Models. *Chemometrics Intelligent Laboratory Systems* (37) 37-42.

¹⁵ Environmental Protection Agency. R&D. **2007**. EPA UNMIX 6.0 Fundamentals and User Guide. EPA/600/R-07/089

¹⁶ Christensen, William F., Schauer, James J. and Lingwall, Jeff W. **2006**. Iterated Confirmatory Factor Analysis for Pollution Source Apportionment. *Environmetrics* (17) 663–681.

to a lack of gaseous and/or particulate data. For the purpose of assessing the contribution of WSPM to total $PM_{2.5}$ concentrations, it was concluded that the four data sets modeled would be sufficient.

The Springfield, MA data set did not include volatile concentrations, thus only four sources were considered. The three Connecticut data sets included gaseous concentrations (NO , NO_x , NO_2 and SO_2), particulate concentrations (volatile and non-volatile) and the three Aethalometer Channels (BC, UVC and Delta-C), allowing for the potential of five sources (only if present).

Several modeling runs were conducted on the Thomaston dataset to assess the entire study period, as well as, individual quarters to determine any seasonality to the modeling results. Single modeling runs were conducted for the East Hartford, New Haven and Springfield sites that covered data obtained for the duration of the study period.

The Unmix source composition results showed that defining pollutants were evident in each resulting source, hence chemical markers were evident. A combination of the Unmix source composition (chemical markers), time series of source strength, and source strength dependency on wind direction was used for determining the source type. Then using the following chemical markers; Delta-C as the chemical marker for wood smoke, SO_2 as the marker for oil combustion, Volatile PM as the marker for non-local industrial sources, NO as the marker for fresh combustion and NO_2 as the marker for aged combustion; factors could be developed for each source type to determine a particular sources $PM_{2.5}$ portion.

Summary of Results

This section summarizes the results obtained in this study. First, the modeling results and scaling factor determinations are addressed. Then an overall summary by site along with monthly averages are presented. The analysis then focuses on more resolute sampling periods, estimating the contribution of WSPM when elevated 24-hour and hourly $PM_{2.5}$ levels were observed, along with binning that information into different temperature categories. Finally, both winter and summer wood smoke driven events are looked at to determine the contribution of WSPM during these events and the impact on both the ozone and $PM_{2.5}$ measurements.

- **Modeling Results Summary**

Unmix Modeling was conducted for the Thomaston, East Hartford, New Haven and Springfield, MA sites. Table 2 shows the scaling factors determined for all the modeling runs. The scaling factor is defined as the number that Delta-C must be multiplied by to calculate WSPM concentrations. As shown in Table 2, the scaling factors were reasonably consistent for most modeling runs, (with the exception of the New Haven individual quarter runs). The lowest scaling factor, a 2.7 estimated at Thomaston for 1st quarter 2008, is suspect based on inconsistent volatile PM measurements from the FDMS 8500 unit which affected the modeling results. This quarter was not included in the determination of the universal, study-wide scaling factor that was used to scale the Delta-C WS signal to WSPM concentrations at all sites. The scaling factor for Thomaston for the five-quarter (4th quarter 2006 through 4th quarter 2007) model run, which included the volatile channel, was 5.0. The scaling factors for the individual one-quarter modeling runs of 2006-2008

winter periods were 8.2, 8.4, 6.9 and 6. It was determined that not including the volatile PM channel was appropriate for running the Unmix model. In addition it was also determined that the New Haven model runs were not representative scaling factors for wood smoke. The large variety of PM_{2.5} sources and the minimal contribution of wood smoke indicator (Delta C) created an artificially high wood smoke scaling factor. Thus a more reliable site to base a wood smoke scaling factor would be that which wood smoke is a larger contributor to the whole PM_{2.5}, such as Thomaston. Therefore the universal, study-wide scaling factor was determined to be 7.8, was estimated by taking the average of the scaling factors from the three valid winter one-quarter modeling runs at Thomaston (1st quarter of 2008 was excluded as it was determined unreliable due to suspect 8500 FDMS volatile PM data). For consistency across the study period and for all analysis conducted relative to this project, all Delta-C observations were scaled up to WSPM concentrations using the universal, study-wide scaling factor of 7.8.

Table 2: Scaling Factors Determined from Unmix Modeling; Delta-C*Scaling Factor = WSPM (µg/m³)

Site	Time Period	Scaling Factor With Volatiles	Scaling Factor Without Volatiles
Thomaston	Universal, Study-wide Scaling Factor based on average of Thomaston individual quarterly model runs from: Qtr 4, 2006 through Qtr 4, 2007	6.30	7.80
	Qtr 4, 2006 through Qtr 4, 2007	5.0	N/A
	Qtr 4, 2006	6.0	8.2
	Qtr 1, 2007	7.8	8.4
	Qtr 2, 2007	5.1	N/A
	Qtr 3, 2007	6.4	N/A
	Qtr 4, 2007	6.2	6.9
	Qtr 1, 2008	2.7	6.1
East Hartford	Qtr 4, 2006 through Qtr 1, 2008	6.4	N/A
New Haven	Qtr 4, 2006 through Qtr 1, 2008	4.8	N/A
	Qtr 4 2006	N/A	24.0 ¹⁷
	Qtr 1 2007	N/A	22.7 ¹⁷
	Qtr 4 2007	N/A	6.9
	Qtr 1 2008	N/A	10.5 ¹⁷
Springfield, MA	Qtr 4, 2006 through Qtr 1, 2008	N/A	8.8

¹⁷ The New Haven model runs were not representative scaling factors for wood smoke. The large variety of PM_{2.5} sources and the minimal contribution of wood smoke indicator (Delta C) created an artificially high wood smoke scaling factor.

• Overall by Site Summary

The overall annual average of the contribution of WSPM to $PM_{2.5}$ was determined by taking the average of the weighted monthly averages depending on the availability of valid averages for a given month. For instance, if January 2007 and January 2008 monthly averages were available for a given site, then the average of these two months were taken to represent January. If only August 2007 was available for a given site, then that average alone was taken to represent August. Once the 12 monthly averages established, then an annual average was taken for each site. These results are shown in Table 3. Data utilized to determine annual averages was primarily from the September 2006 through April 2008 time period; however, when monthly averages at the East Hartford McAuliffe Park site were not available due to inadequate data capture, data obtained from January 2006 through August 2006 was substituted.

Annual $PM_{2.5}$ concentrations were determined by transforming continuous $PM_{2.5}$ data to be “FRM-like” based on regressions performed on $PM_{2.5}$ FRM and continuous $PM_{2.5}$ measurements obtained at each site for the study period. This allowed $PM_{2.5}$ FRM-like values to be established for each hour of each day for the entire study period to give a complete assessment of $PM_{2.5}$ measurements and fill in the holes created from one-in-three day $PM_{2.5}$ FRM sampling.

The annual average contribution of WSPM ranged from 1.7% of the total $PM_{2.5}$ measured at the New Haven site up to 17.3% at Thomaston. The average annual WSPM contribution at the Cornwall Mohawk Mountain site, elevation 1,656 ft., was 5.0 % of the total $PM_{2.5}$ concentrations observed. The remaining three Connecticut sites, Danbury, East Hartford and Mansfield, were at 11.6%, 12.3% and 11.9%, respectively. The average annual WSPM contribution at the Springfield, MA site was 10.8% of the total $PM_{2.5}$ measurements

Table 3: Annual Averages for $PM_{2.5}$, WSPM and Contribution of WSPM to Total $PM_{2.5}$

Site	Overall Annual Average		
	$PM_{2.5}$ ($\mu\text{g}/\text{m}^3$)	WSPM ($\mu\text{g}/\text{m}^3$)	Contribution of WSPM to Total $PM_{2.5}$
Cornwall (Mohawk Mountain)	8.0	0.32	5.0 %
Danbury	11.7	1.10	11.6%
East Hartford	10.7	1.06	12.3%
Mansfield	10.0*	0.96	11.9%
New Haven	11.6	0.16	1.7 %
Thomaston	9.7	1.36	17.3%
Springfield, MA	10.6	0.92	10.8%

*No $PM_{2.5}$ sampling at Mansfield; substituted everyday $PM_{2.5}$ values from East Hartford McAuliffe Park to estimate WSPM contributions at Mansfield site for the period of September 2006 through March 2008.

• **Monthly Averages of WSPM Contribution**

Monthly average WSPM contributions to $PM_{2.5}$ were determined by averaging all valid hourly FRM-like $PM_{2.5}$ and WSPM values. Figure 3 is a time-series graph of the monthly WSPM contributions for each site from January 2006 through April 2008. As expected, the WSPM contribution is strongly correlated with the time of year. The colder, winter months WSPM contributions are much greater than what is observed during the warmer, summer months. For all sites, maximum monthly average WSPM contributions in the winter ranged from 10.8 to 41.3%, while maximum monthly summertime averages ranged from zero to 6.1%. Figure 4 presents the same weighted monthly averages that were used to determine the annual average contribution to WSPM to total $PM_{2.5}$ percentages in Table 3. Also on the Figure 4 time series graph, are the average monthly temperatures by site in degrees Fahrenheit ($^{\circ}F$) on the secondary y-axis. Again, the strong correlation to season/monthly temperature is apparent in Figure 4.

Figure 3: Monthly average WSPM contribution to total $PM_{2.5}$ concentrations

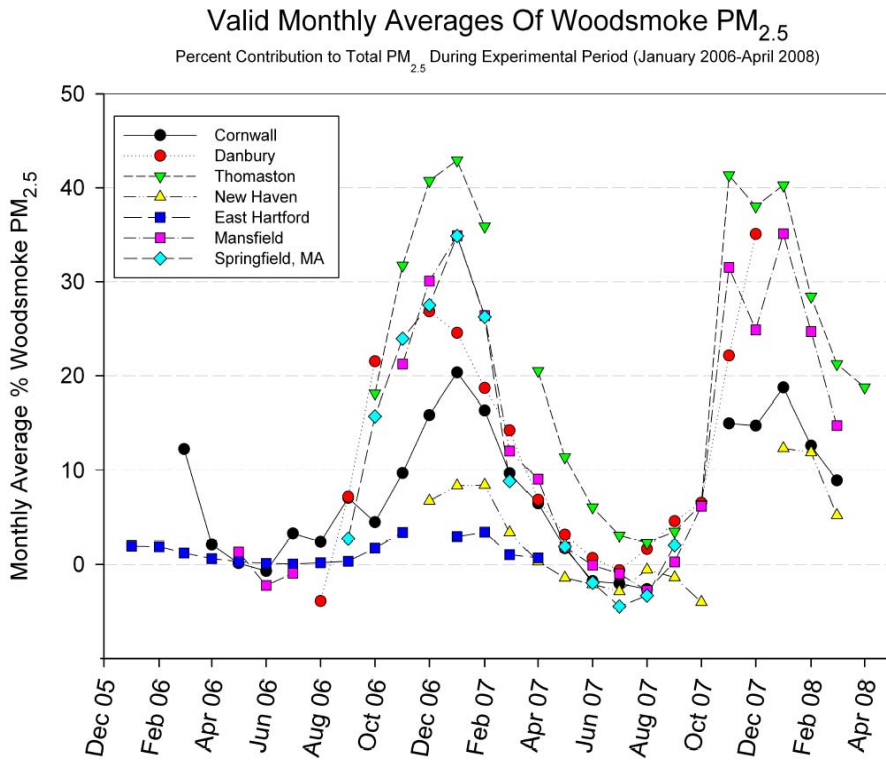
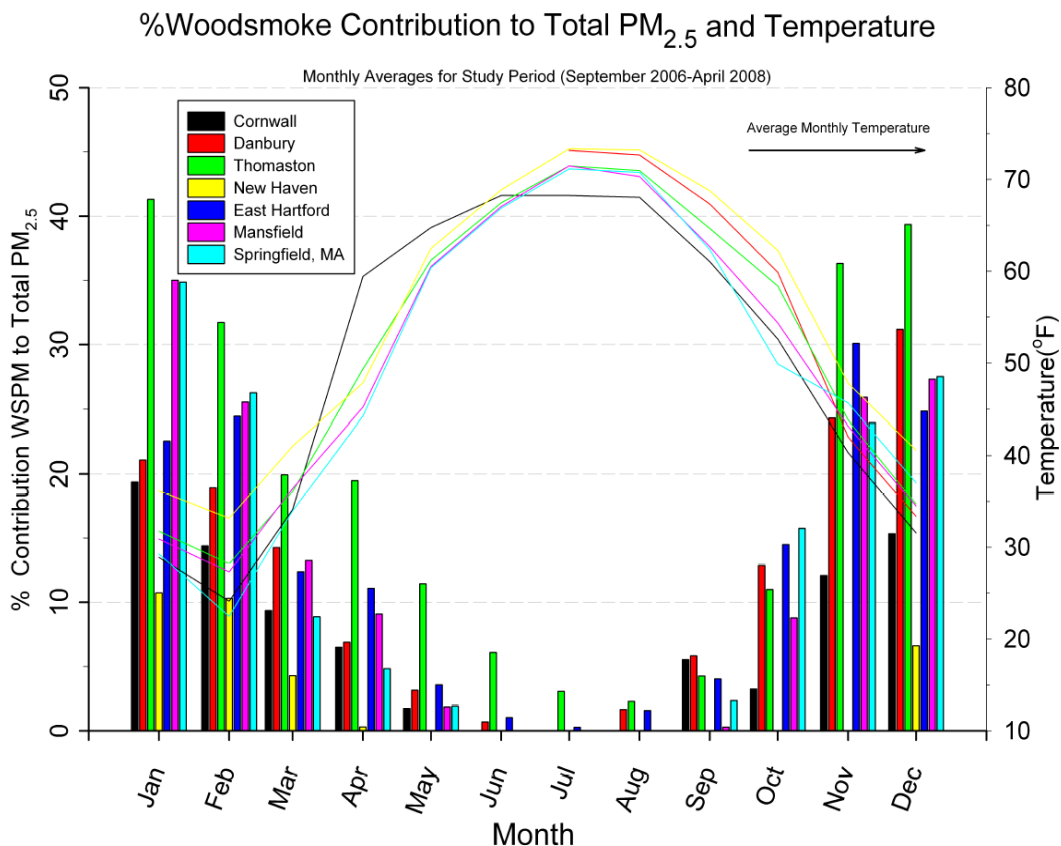


Figure 4: Monthly average WSPM contributions and temperatures by site



- **PM_{2.5} daily averages > 15 µg/m³; PM_{2.5} hourly averages > 30 µg/m³**

Fine particulate data was binned to look at WSPM contributions when PM_{2.5} concentrations were elevated. In addition to separating by PM_{2.5} concentrations, average ambient temperature measurements were also utilized to assess overall WSPM contributions. Table 4 shows the breakdown by site when the 24-hr PM_{2.5} concentration was greater than 15 µg/m³ and separated for when the daily average ambient temperature was less than and greater than 45°F. For the five sites in Table 4, the average WSPM contribution to PM_{2.5} was 23.9% when the 24-hr PM_{2.5} concentration was greater than 15 µg/m³ and the 24-hr average ambient temperature measurement was less than 45°F. Conversely, when the 24-hr PM_{2.5} concentration was greater than 15 µg/m³ and the 24-hr average ambient temperature measurement was greater than 45°F, the average WSPM contribution to PM_{2.5} was only 4.2%. Figure 5 also illustrates the differences for the two temperature categories at the five sites.

Table 4 also shows the breakdown by site when the hourly PM_{2.5} concentration was greater than 30 µg/m³ and separated for when the daily average ambient temperature was less than 32°F, less than 45°F and greater than 45°F. For the five sites in Table 4, the average WSPM contribution to PM_{2.5} was 30.9% when the hourly PM_{2.5} concentration was greater than 30 µg/m³ and the hourly average ambient temperature measurement was less than 32°F. When the hourly ambient temperature was less than 45°F and the hourly

PM_{2.5} concentration was greater than 30 µg/m³, the WSPM contribution dropped to 22.8%. When the hourly PM_{2.5} concentration was greater than 30 µg/m³ and the hourly average ambient temperature was greater than 45°F, the average WSPM contribution to PM_{2.5} was only 1.7%. Figure 6 also illustrates the differences for these three temperature categories at the five sites.

Table 4: WSPM Contribution to Total PM_{2.5} by Temperature Category for elevated hourly and 24-hour PM_{2.5} concentrations

Site	24-hr PM _{2.5} FRM > 15 µg/m ³ Contribution of WSPM to Total PM _{2.5}		1-hr PM _{2.5} FRM-like > 30 µg/m ³ Contribution of WSPM to Total PM _{2.5}		
	< 45° F	> 45° F	< 32° F	< 45° F	> 45° F
Cornwall (Mohawk Mountain)	13.5 %	2.4 %	0.9 %	0.5 %	0.6 %
Danbury	30.0 %	10.0 %	56.8 %	45.1 %	2.6 %
New Haven	8.9 %	0.9 %	25.4 %	15.5 %	0.9 %
Springfield, MA	28.8 %	2.2 %	50.0 %	34.9 %	0.9 %
Thomaston	38.0 %	5.5 %	48.4 %	17.8 %	3.5 %

Figure 5: WSPM Contribution to Total PM_{2.5} by Temperature Category for elevated 24-hr PM_{2.5} concentrations

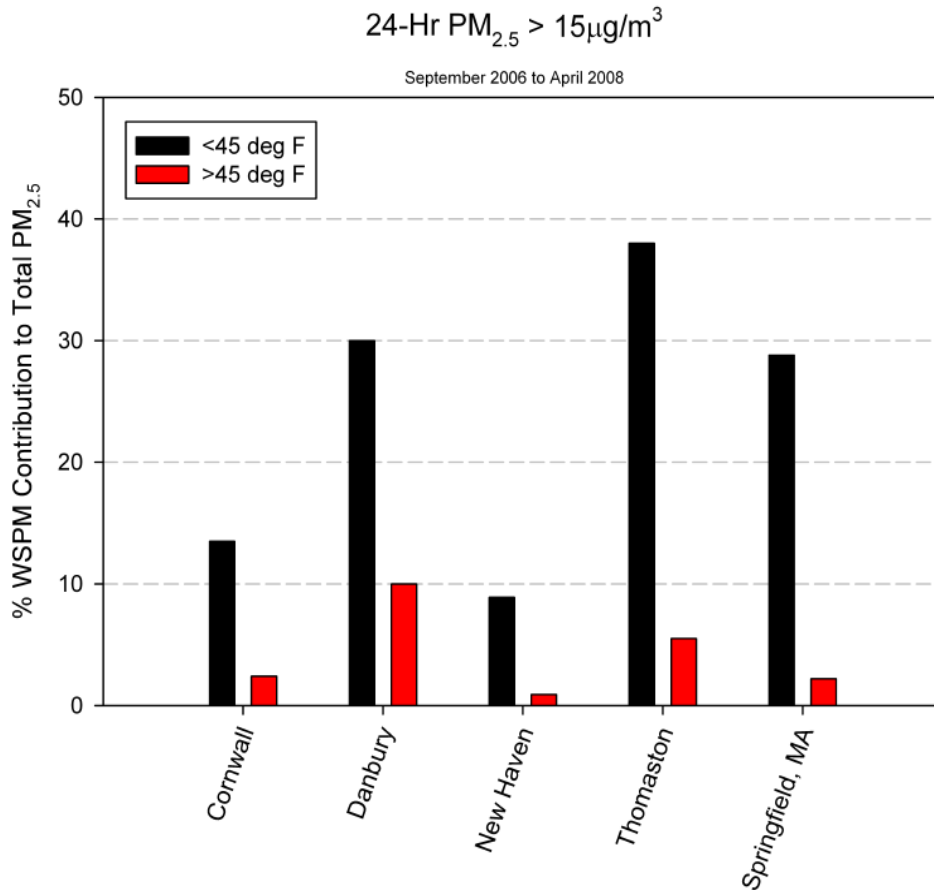
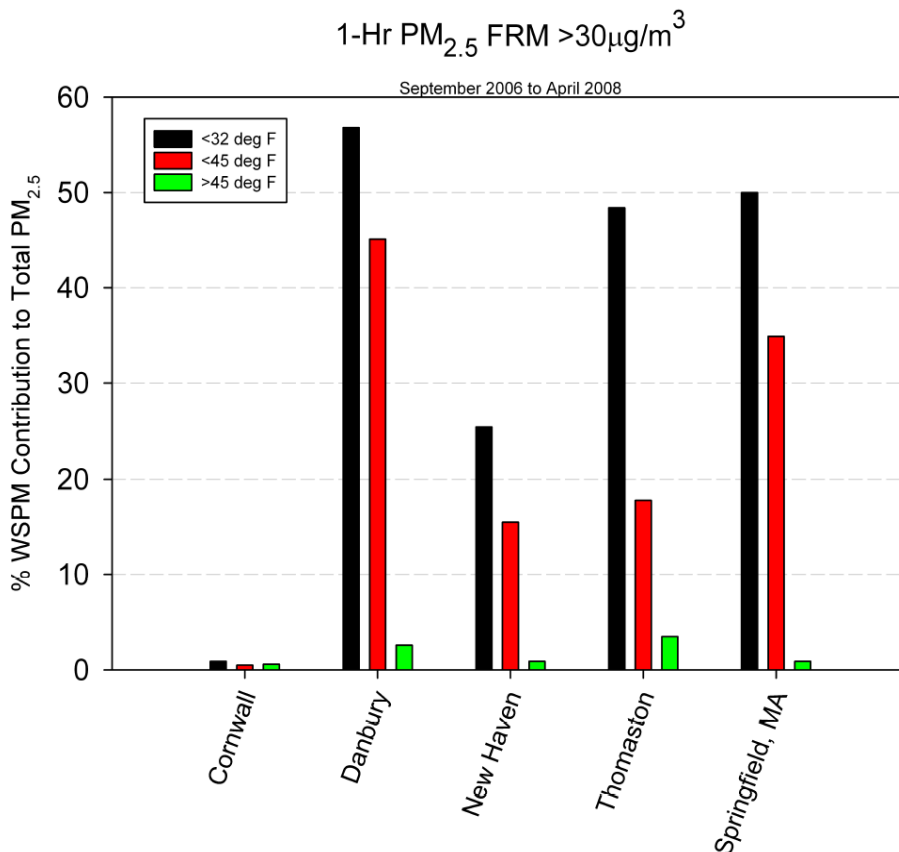


Figure 6: WSPM Contribution to Total PM_{2.5} by Temperature Category for elevated hourly PM_{2.5} concentrations



• **Wood Smoke Events**

A typical winter season will have a greater WSPM contribution in periods of temperatures at or below 45°F as noted in Figures 5 and 6. In addition to displaying a temperature correlation, the magnitude and period of peak contribution is dependent on atmospheric stability. As one would expect with a local source, stable inversion conditions tend to enhance and elongate periods of high WSPM. The degree of overall contribution varies as weather systems move into and out of the area. During these periods of atmospheric stability, especially areas that are prone to air stagnation, such as valley locations, local wood burning sources can significantly contribute to ambient PM_{2.5} concentrations.

An example of these wintertime inversion events is shown in Figure 7. Although there are several inversion-type events illustrated in Figure 7, the event on December 6, 2006 was most pronounced with hourly PM_{2.5} concentrations approaching 50 µg/m³ and WSPM concentrations well over 10 µg/m³. PAH levels also following the same trend as the PM_{2.5} and WSPM concentrations. PM_{2.5}, WSPM and PAH concentrations built up through the evening of December 5th and the early morning hours of December 6th as winds speeds were less than 1 m/s and ambient temperatures steadily dropped. Approximately mid-morning of December 6th, as ambient temperatures rose and wind speed increased, the inversion lifted and all air pollutant

concentrations decreased significantly with PAH and WSPM levels approaching zero and PM_{2.5} concentrations approaching 5 µg/m³. Figure 8 focuses in on the December 5th to December 6th wood smoke event.

The diurnal pattern of WSPM influences is common in the winter. Figure 9 illustrates the higher concentration of WSPM during the early morning and evening hours and significantly lower WSPM levels from mid-morning to late afternoon. This is partly due to inversion-like meteorological conditions common during the colder, winter months, but also corresponds to when wood burning actually occurs, with very little wood-burning conducted during the work-day hours and then increased burning during the traditional at-home evening hours. As atmospheric stability increases throughout the night, WSPM levels build up until the inversion lifts – usually mid-morning. Figure 9 is a composite of all hourly WSPM concentration averages, spread and 95th percentiles at the Thomaston site from two winter periods (December 1, 2006 through March 31, 2007 and December 1, 2007 through March 31, 2008).

Figure 7: Classic Winter Inversion Event – Thomaston, CT; Nov. 29, 2006 through Dec. 11, 2006

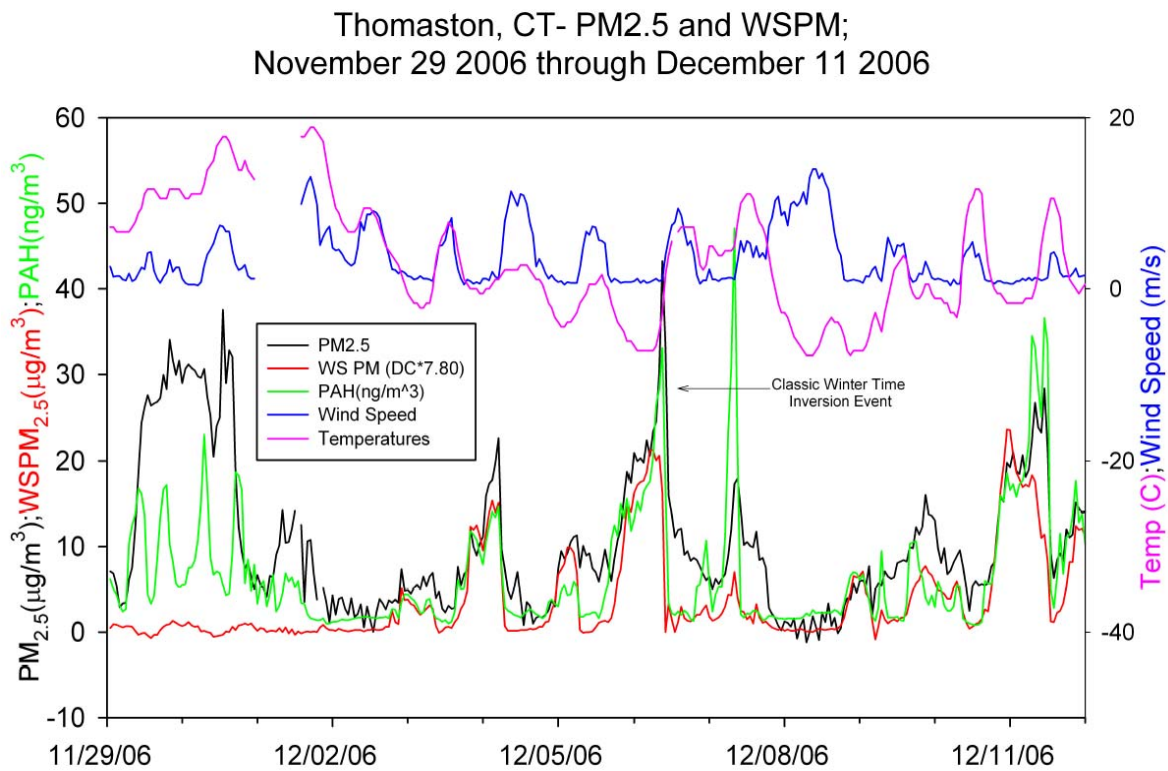


Figure 8: Classic Winter Inversion Event – Thomaston, CT; Dec. 4, 2006 through Dec. 6, 2006

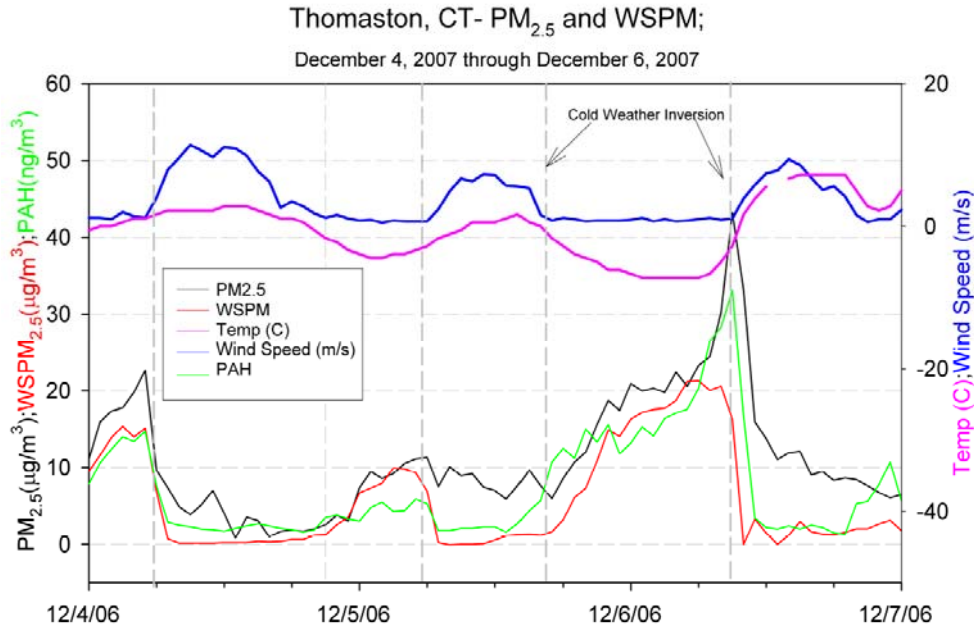
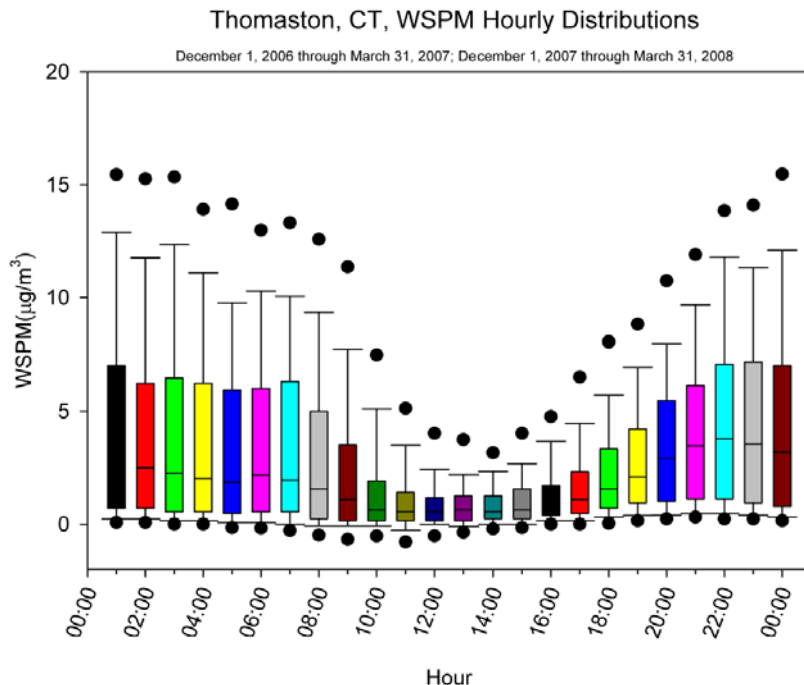


Figure 9: WSPM Average Hourly Concentrations at Thomaston, CT; Dec. 1, 2006 through Mar. 31, 2007; Dec. 1, 2007 through Mar. 31, 2008.



In addition to the evaluation of WSPM contributions to typical wintertime inversion events, analysis conducted in this study was also used to identify possible forest fire transport events. On May 25, 2007 the entire state observed elevated ozone and $PM_{2.5}$ levels (See Figure 10). In fact, this event was seen on a regional scale with high ozone and $PM_{2.5}$ throughout New England (See Figure 11). Together this suggested a large scale transport event which was further validated by Figure 12, which displays the back trajectories and corresponding satellite images of the days preceding the pollutant spike. Wildfire smoke plumes can be seen emerging from the areas indicated as the air mass' origination by the NOAA Hysplit model.

Although it seems apparent that the source of these pollutant spikes is wood smoke, the WSPM concentrations, although elevated during this period, did not necessarily correlate with the times that other pollutants were elevated (See Figure 13). This in combination with the large spikes in PAHs, ozone and $PM_{2.5}$, PAHs and secondary pollutants, can be attributed to the magnitude of the source, weather patterns and reaction time allotted for the initial plume. Recent findings have noted that primary wood smoke pollutants (those that would be detected on the Aethalometer™ UV channel) are oxidized through ozonolysis and ultra-violet reactions when in the atmosphere for an extended period of time.^{18,19,20} The oxidation of these primary organic pollutants result in secondary organic pollutants which are no longer detectable in the UV spectrum.

¹⁸ Jimenez, J.L., *et al.* **2009**. Evolution of Organic Aerosols in the Atmosphere. *Science* **(326)** 1525-1529.

¹⁹ Ward, Tony and Lange, Todd. **2010**. The Impact of Wood Smoke on Ambient $PM_{2.5}$ in the Northern Rocky Mountain Valley Communities. *Environmental Pollution*. **(158)** 723-729.

²⁰ Zhang, Xuan, Chen, Zhongming, Wang, Hongli, He, Shuzhong and Daoming, Haug. **2009**. An Important Pathway for Ozonolysis of Alpha-Pinene and Beta-Pinene in Aqueous Phase and its Atmospheric Implications. *Atmospheric Environment*. **(43)** 4465-4471.

So, although the Delta-C measurement provides a consistent indicator of wood smoke for local wood burning sources, it is much less reliable for wood smoke that has undergone significant transport, particularly when exposed to UV radiation.

Figure 10: Hourly Ozone and PM_{2.5} Concentrations; May 2007

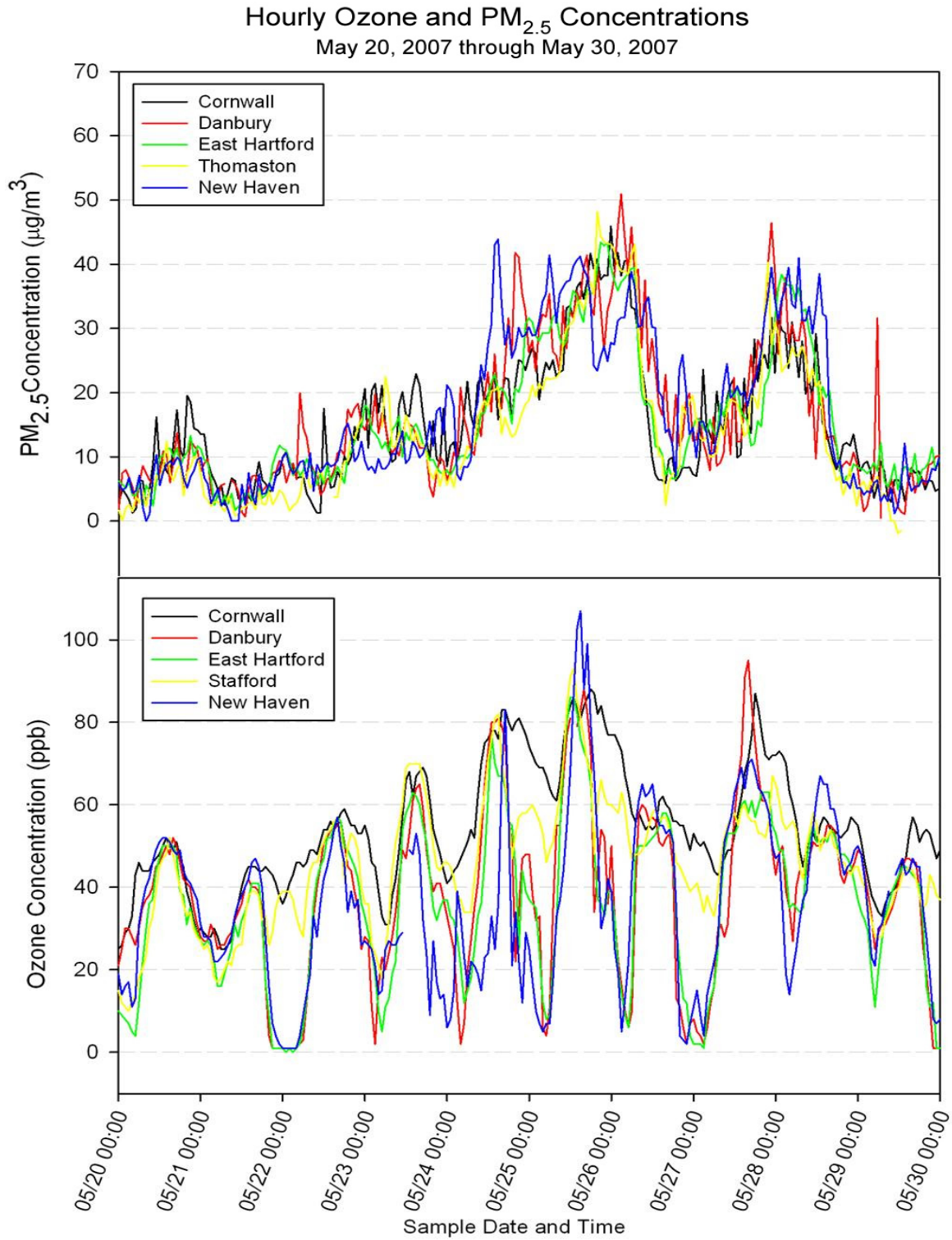


Figure 11: 24-hour Average $PM_{2.5}$ Concentrations; May 25, 2007

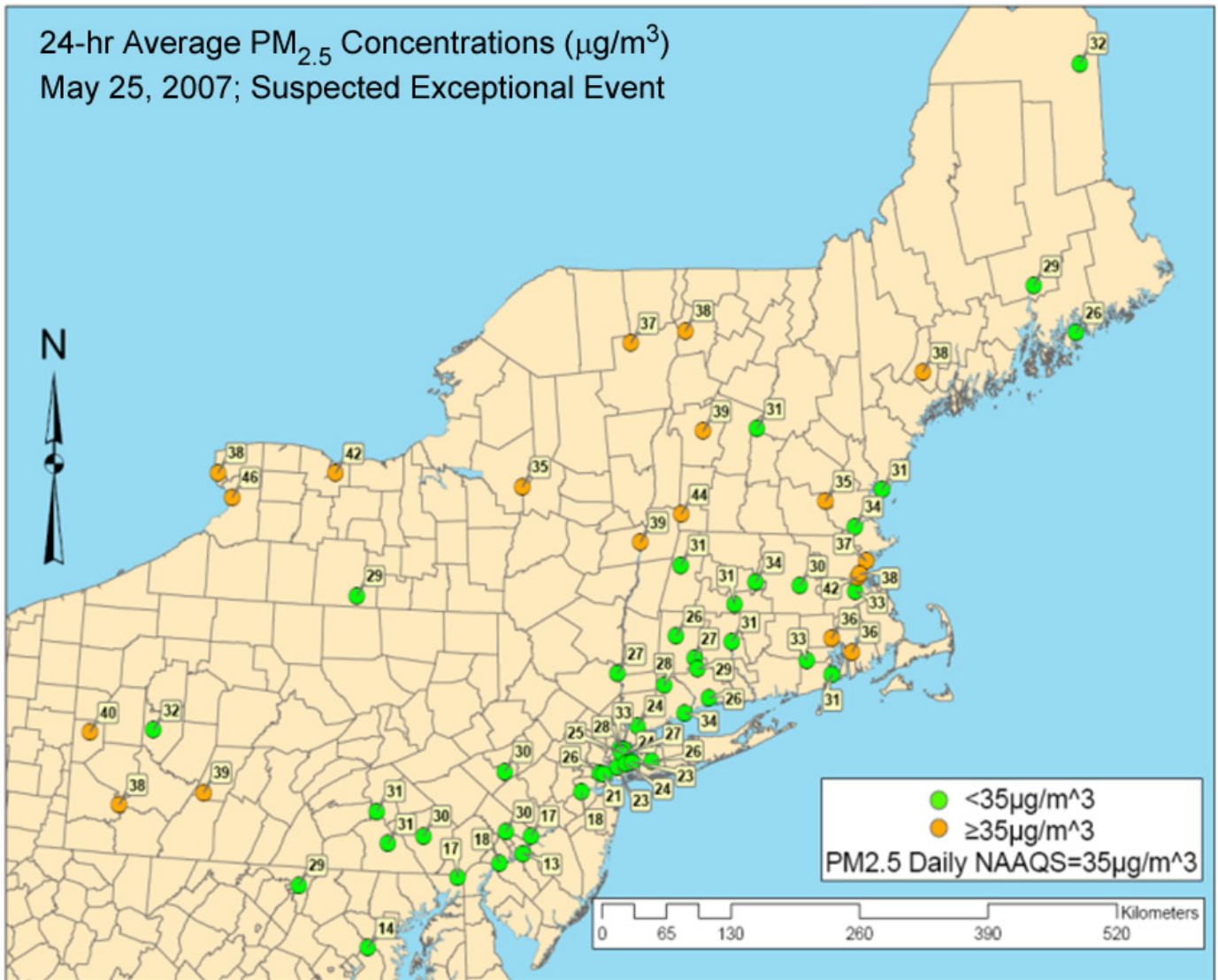


Figure 12: NOAA Hysplit Model and Satellite Images of Wildfire Event; May 25, 2007

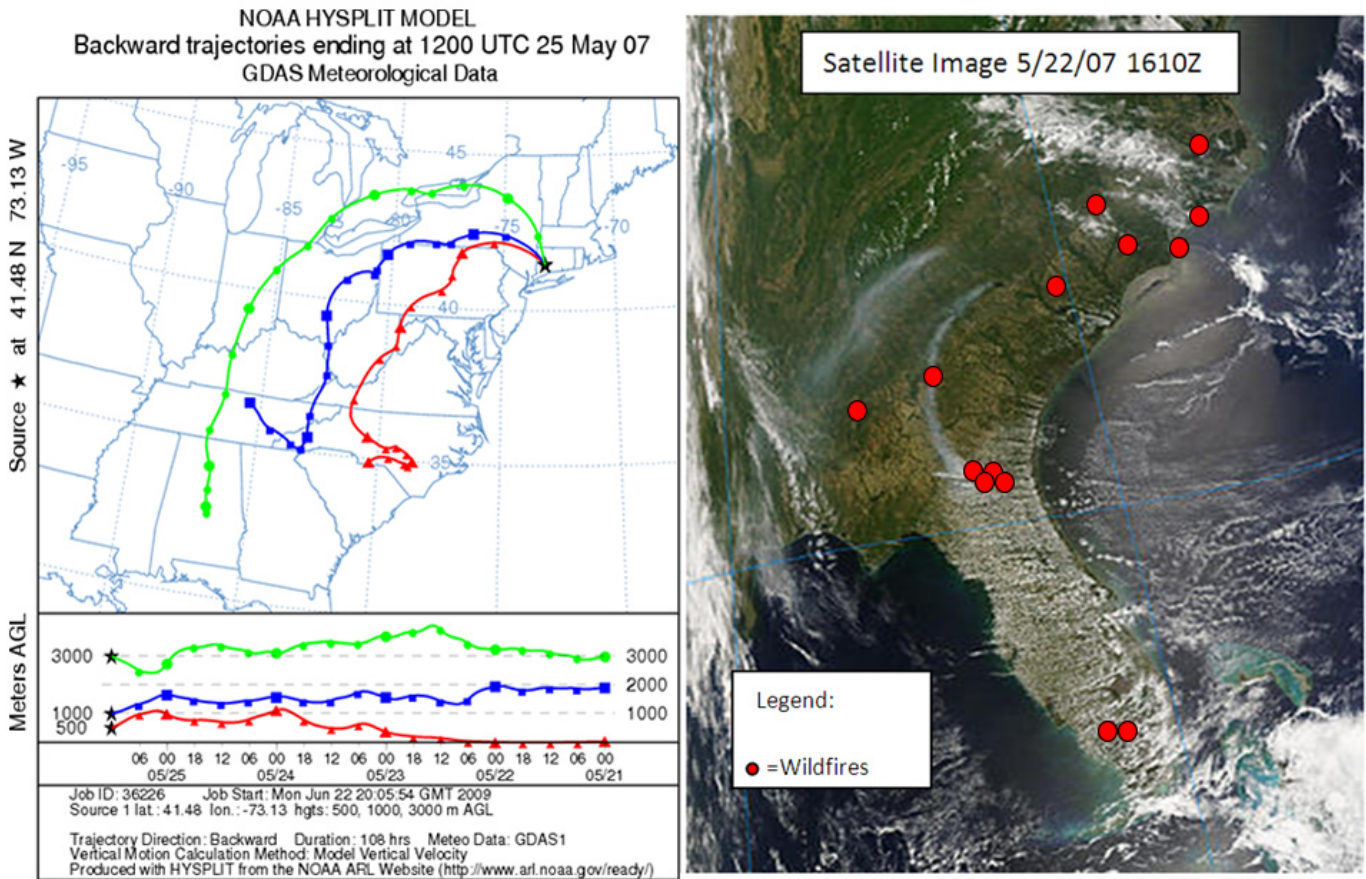
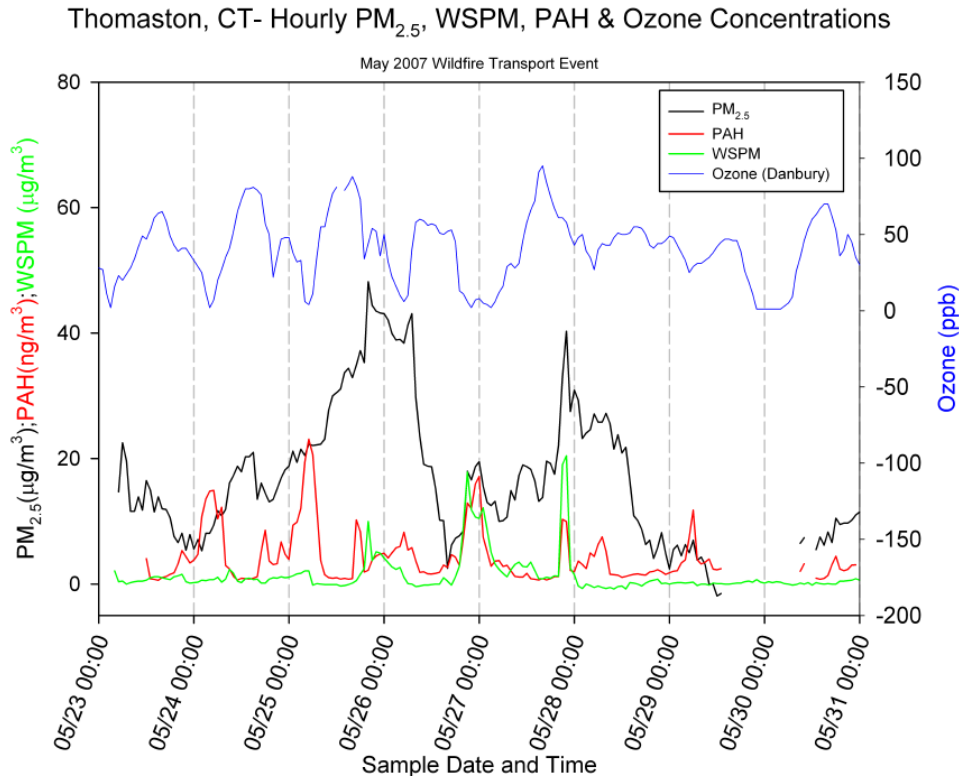


Figure 13: PM_{2.5}, WSPM, PAH and Ozone Hourly Concentrations; Thomaston, CT – May 2007 Wildfire Event



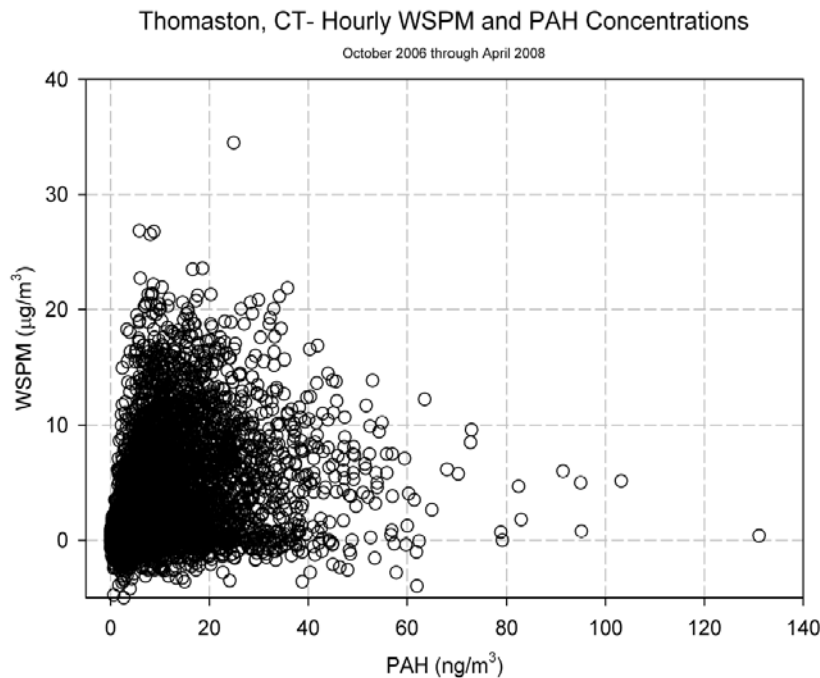
- **Delta-C vs. PAH**

Traditionally, PAH measurements have been used as an indicator of the presence of wood smoke. In this study, although PAH concentrations did follow WSPM concentrations when WSPM levels were elevated, there were many occasions when PAH levels were elevated and Delta-C was not. This could indicate the presence of transport wood smoke; when wood smoke is transported over long distances the primary organic compounds have been oxidized and thereby not detectable by the Aethalometer™ UV-C channel, as described in the section above.

Also note Figure 7; this figure also displays instances where PAH and WSPM (calculated from Delta-C) track with each other and instances where they do not. During December 4, 2006 through December 6, 2006 PM_{2.5}, WSPM and PAHs are all elevated during inversion conditions and then all drop off significantly once the inversion lifts and atmospheric mixing occurs. Several days earlier, November 29-30, 2006, PM_{2.5} and PAH measurements are elevated while WSPM is near zero. Given the fact that ambient temperatures are near 70°F, it is probable that the elevated PM_{2.5} and PAH concentrations are not from local wood burning sources. Mobile sources are known to drive ambient PAH concentrations, a New England based study estimated mobile sources to account for ~76-84% of the PAH concentrations observed and wood smoke to

account for 13-16% of the PAH concentrations.²¹ Figure 14 is a scatterplot of all hourly WSPM (as derived from the Delta-C) and PAH measurements collected at the Thomaston site during the study period, note the poor correlation. Figure 15 displays the BC as a function of PAH concentrations during the summer month of August 2007. August 2007 is a period in which one would not expect wood smoke, thus the primary driver of PAH would likely be mobile sources. BC being another known mobile source²² would then be expected to correlate with the PAH concentrations, figure 15 displays this correlation which is stronger than figure 14, as would be expected.

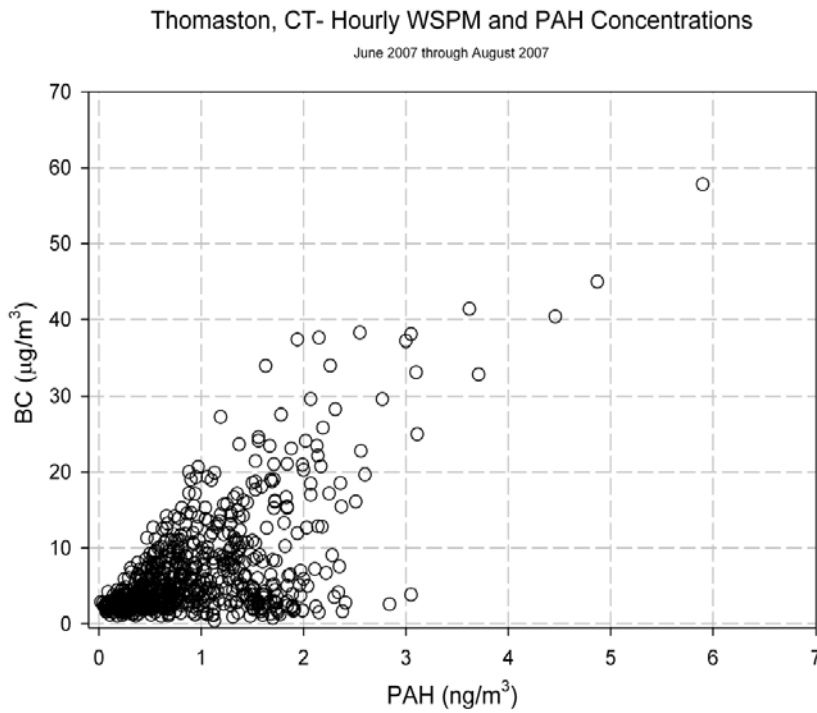
Figure 14: WSPM and PAH Hourly Concentrations; Thomaston, CT – October 2006 through April 2008



²¹ Golomb D., Barry Fisher, P. Varanusupakul, M. Koleda and T. Rooney. **2001**. "Atmospheric Deposition of Polycyclic Aromatic Hydrocarbons Near New England Coastal Waters." *Atmospheric Environment*. **(35)** 36. 6245-6258

²² NREL, **2004**. "Mobile Source Black Carbon Emissions." *Black Carbon and Climate Change Technical Workshop San Diego, CA*.

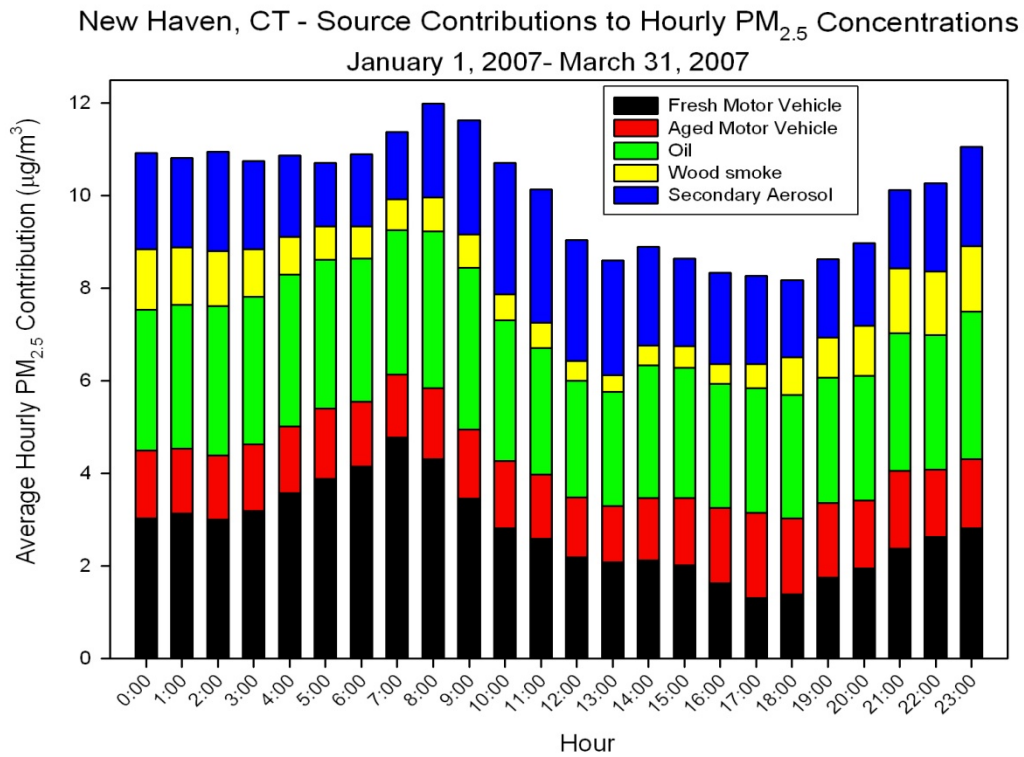
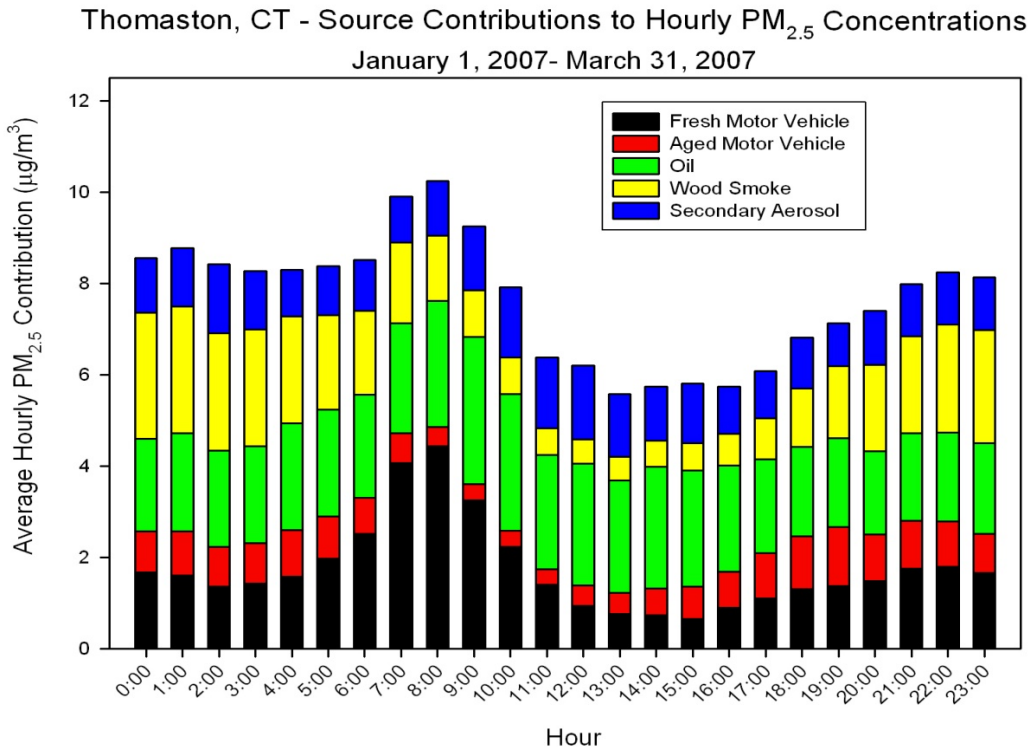
Figure 15: BC and PAH Hourly Concentrations; Thomaston, CT –August 2007



- **Modeled Source Contributions**

In addition to utilizing Unmix modeling results to determine Delta-C scaling factors and in turn approximate WSPM contributions to total PM_{2.5}, the modeling also provides highly time resolved information on fresh and aged motor vehicle, oil burning and secondary aerosol sources. Figure 16 illustrates the source contributions to hourly PM_{2.5} concentrations for the Thomaston and New Haven sites for the period of January 1, 2007 through March 31, 2007. This shows the average source contributions to total PM_{2.5} from each source for each hour and demonstrates how the value of this highly time resolved data set and modeling results. Patterns that emerge include the morning rush-hour peak for mobile sources, the steady contribution from oil-burning sources and decrease in the wood burning sources during the traditional work-day hours.

Figure 16: Source Contributions; Thomaston & New Haven, CT; January 1, 2007 to March 31, 2007



Conclusions

This project has built on previous work that identifies the Delta-C measurement from a 2-wavelength Aethalometer™ to be a specific indicator of wood smoke. Through modeling, a scaling factor was determined to convert the wood smoke indicator signal into WSPM concentrations. Although there was some variability between scaling factors derived from different sites or different seasons at the same site, they were consistent enough to apply a study-wide scaling factor of 7.8 to achieve a reasonable approximation of WSPM concentrations to determine WSPM contributions to total PM_{2.5} measurements.

With WSPM concentrations determined for each site at an hourly time resolution, analysis was conducted to evaluate the impact of WSPM on an annual and monthly basis, as well as, when daily and hourly PM_{2.5} concentrations were elevated and categorized in various temperature bins. Although the annual average WSPM contributions to PM_{2.5} (1.7 to 17.3% for all sites) did not approach the 38% estimate of PM_{2.5} emissions in Connecticut from wood burning sources from 2002 MARAMA emission estimates, WSPM was shown to contribute significantly to total PM_{2.5} during the colder, winter months, particularly when the meteorological conditions were conducive to atmospheric stability and wintertime inversions. The maximum monthly average of WSPM contributions to PM_{2.5} levels was 41.3% with maximum daily and hourly contributions approaching 74.3% and 100%, respectively.

Potential future efforts related to this work could include fully evaluating the modeling results for all sources. The source apportionment modeling not only provided valuable information related to wood smoke source profiles, but the modeling also quantified contributions from other sources such as fresh and aged mobile sources, home heating oil and secondary aerosols with hourly time resolution. Understanding the contributions of these sources and the diurnal and seasonal patterns can greatly enhance the ability to develop control strategies to address these sources, as well as, determine the effectiveness of both current and future mitigation efforts.

Another area that warrants additional investigation is determining an adequate marker or indicator to quantify, or at least qualify, wood smoke that is transported regionally. Due to photochemical reactions, it does appear that the optical characteristics of the wood smoke are altered enough to render absorption measurements at 370 nm to be ineffective.