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Commonwealth of Pennsylvania
Department of Environmental Protection

Processes Controlling Urban Air Pollution in the Northeast: Summer 2002

Investigations Conducted by a Consortium of University Researchers

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LIST OF ACRONYMS AND ABBREVIATIONS

AMS	Air Management Services (Philadelphia Laboratory)
API	Advanced Pollution Instrumentation
DEP	Department of Environmental Protection
DIAL	DIfferential Absorption Lidar
CAMMS	Continuous Ambient Mass Monitoring System
GCMS	Gas Chromatograph & Mass Spectrometer (combined instruments)
GRIB	GRid In Binary - Standard for data grid fields
HYSPLIT	HYbrid Single-Particle Lagrangian Integrated Trajectory
IC	Ion Chromatography
LAPS	Lidar Atmospheric Profile Sensor
LLJ	Low Level Jet
MANE-VU	Mid-Atlantic/Northeast Visibility Union
MARAMA	Mid-Atlantic Regional Air Management Association
Meos-eta	Mesoscale model that uses the coordinate "eta" as a normalized pressure base
MU	Millersville University
MM5	Mesoscale Model (version) 5
NWS	National Weather Service
NCEP	National Centers for Environmental Prediction
NESCAUM	NorthEast States for Coordinated Air Use Management
NE-OPS	NorthEast Oxidant and Particle Study
Nd:YAG	Neodymium doped into Yttrium Aluminum Garnet material used for laser rod
NARSTO	North American Research Strategy for Tropospheric Ozone
OC/EC/BC	Organic Carbon - Elemental Carbon - Black Carbon
OTC	Ozone Transport Commission
PAH	Polycyclic Aromatic Hydrocarbons
PBL	Planetary Boundary Layer
PEM's	Personal Environmental Monitors
PM	Particulate Matter
$PM_{2.5}$	Particulate Matter with aerodynamic size less than 2.5 microns
PM_{10}	Particulate Matter with aerodynamic size less than 10 microns
PSU	Penn State University
RASS	Radar-Acoustic Sounding Syayem
RAMS	Real-time total Ambient Mass Sampler
RUC	Rapid Update Cycle
SCC	Sharp Cut Cyclone
SES	Sample Equilibration System (dryer for PM)
SIP's	State Implementation Plans
SOA	Secondary Organic Aerosol
SVOCs	Semi-Volatile Organic Compounds
TASS	Tethered Atmospheric Sounding System
TEOM	Tapered Element Oscillating Microbalance
TSI	TSI Incorporated - instrument company
USEPA	United States Environmental Protection Agency
UTC	Universal Time Coordinated
VSCC	Very Sharp Cut Cyclone

SUMMARY

This research continues the activities of the NEOPS university consortium to investigate air quality issues in the northeast as a follow on to the USEPA sponsored project entitled **Investigations of Factors Determining the Occurrence of Ozone and Fine Particles in Northeastern USA**. This project has been designated as **NEOPS-DEP2002** to associate with but distinguish it from the measurement program referred to as the **NARSTO-NE-OPS** project, which was carried out during 1998, 1999 and 2001 under EPA STAR Grant **R826373**. Both of these research projects have been associated with the NARSTO (North American Research Strategy for Tropospheric Ozone) Program for data archiving purposes.

The **NEOPS-DEP2002** project included a six-week summer field measurement intensive program and was carried out during the period from the last week of June through the first week of August 2002. The measurements overlapped the activity of the three PM (Particulate Matter) Supersites in the northeast region, Baltimore, Pittsburgh and New York. Our plan was to optimize the value of all of the northeast measurements during the 2002 summer by fully overlapping the period of other measurement programs in the region. The NEOPS-DEP2002 measurements included key meteorological properties, gas chemistry, and particulate physical/chemical properties. The major instruments included remote sensing radar and lidar for vertical profiling of the meteorological and air quality properties, *insitu* measurements of meteorological profiles, aerosols and ozone from surface to 300 m using an instrumented tethered balloon, and a suite of surface based instruments for measuring the concentrations of key chemical species and particulate physical/chemical properties. Also, minor/toxic species were measured using filter samples which were analyzed with high resolution GC/MS laboratory techniques. Measurements were also obtained by the University of Maryland instrumented aircraft during flybys on two days during July. The instruments used and measurements obtained are described in more detail in the following sections. The primary results provide an important data base to test developing models and extend our understanding of physical/chemical processes which control air pollution episodes. The results are being shared with other researchers through technical workshops and web based data links. The results are in the final stage of preparation and testing to make them available to the scientific community through the national NARSTO data archive. We have placed a special emphasis on coordination with the northeast Supersites in an effort to help create a regional picture of air pollution episodes. The analysis and coordination activity will continue beyond the defined dates of this project activity.

There are three primary factors which make this activity particularly valuable. First, the NE-OPS project site and team strengths have been extended to investigate air quality and develop a meteorological context for regional collaboration with the Northeast Supersites in Baltimore, New York and Pittsburgh. Second, the NE-OPS emphasis on the measurements of particulate matter and vertical profiling of airborne PM provides the key data for understanding the regional haze questions and will support the MANE-VU (Mid-Atlantic/Northeast Visibility Union) investigations of northeast regional haze. Third, the major intensives of the prior NE-OPS projects have been conducted during summers which represented the 90th percentile warm and 10th percentile dry (1999), and the 80th percentile cool and 20th percentile dry (2001) conditions for the region, therefore these investigations should extended the range of meteorological conditions. The effort here also permits an opportunity for setting new results into context with the prior NE-OPS investigations.

PART 1: BACKGROUND OF THIS INVESTIGATION

The latest developments in remote sensing techniques and *insitu* measuring instruments were brought together as part of the NARSTO-NE-OPS program to examine the problems of the urban polluted atmosphere in two intensive eight week periods during the summers of 1999 and 2001 and during a three week pilot study in 1998. The NEOPS-DEP2002 investigation extends the activities of the prior campaigns to investigate air quality issues and to provide coordination with the northeast Supersites and the MANE-VU Program during the summer season of 2002. Intensive measurements have been made during periods of summer exceedences of the ozone and fine particle concentrations in Philadelphia PA. Local and distant sources of pollutants have been investigated using an urban site with point sensors and remote sensing instruments, making aircraft measurements to determine the upwind and downwind distribution, and using the network data from other ground sites in the Northeast region. The extended summer measurement periods have provided a critical data base that describes the vertical and horizontal distribution of the ozone and fine particle concentrations, the local concentrations of chemical species and particulate matter, and the meteorological conditions. These measurements permitted investigations to interpret the contributions from local and distant sources to the urban pollution exceedences of ozone and PM_{10} as well as the new $PM_{2.5}$ standards. Important factors of entrainment and transport to and from reservoirs in the boundary layer and the lower free troposphere have been investigated.

The EPA STAR Grant R826373 NE-OPS project was initiated on 15 April 1998 and a field site was established in northeast Philadelphia, where the initial field measurements were conducted from 1 to 22 August 1998, and the major investigations were conducted in 1999 and 2001. The field measurements were given the name NE-OPS (Northeast - Oxidant and Particle Study) and associated with the NARSTO program in order to adopt the NARSTO data archiving plan, which has also been adopted for the NEOPS-DEP program. The primary objective of the measurement program during summer 1998 was to develop the facilities for operation of the field site and to compare several instruments planned for use during the measurements program. However, a major air pollution episode occurred at the end of the field program, 21-22 August 1998, that provided an excellent set of results for investigations of air pollution episode properties. The 1999 field program resulted in a rich data set that included eight periods for intensive studies associated with air pollution events, and one of these was the largest event that occurred during the past decade. The 1999 project was extremely successful and a decision was taken to delay the planned 2000 field measurements to 2001, while using the opportunity to upgrade our field site, prepare additional sensors for measurements, and prepare the data base for analysis and modeling activity. The delay to 2001 also permitted coordinated measurements with the northeast EPA Supersite activity. The fact that no measurements were made during the summer 2000 was not a loss since that summer activity was generally uninteresting. During the 2001 field measurement program, three interesting periods were identified for special studies.

The USEPA funded three Supersites in the northeast US to conduct a set of special studies that extend beyond the national regulatory networks for PM to elucidate source-receptor relationships and atmospheric processes in support of State Implementation Plans (SIPs). The guiding principles for this research are based on the insights provided in the PM Measurements Workshop Report, *Atmospheric Observations: Helping Build the Scientific Basis for Decisions*

Related to Airborne Particulate Matter (EPA/NARSTO, October 1998). The "Supersites Conceptual Plan" outlines objectives of the Supersites Program that emphasize the need for atmospheric measurements essential for understanding atmospheric transport and meteorology on regional as well as local scales. The Supersites do not contain a major emphasis on the processes of meteorology and transport, thus the NEOPS-DEP is organized to provide additional understanding of these processes. The NE-OPS activity has provided important insights into the factors and processes controlling the evolution of air pollution episodes and is a most valuable resource for continued air pollution monitoring and investigations in the Northeast Region. Three of the Supersites (Pittsburgh, Baltimore, and New York) are located in the mid-Atlantic/northeast region. Figure 1-1 shows the northeast regional area investigated by the NE-OPS project, and it indicates its proximity to the locations of the Supersites in New York and Baltimore. It is recognized that transport, mixing, and atmospheric stability play key roles in understanding source-receptor relationships, however measurements are usually limited to surface based sensors and standard meteorological variables which do not provide the required data. Some factors which the NEOPS-DEP2002 contributes to regional studies with the Supersites include understanding of the meteorological processes such as, the thermodynamic structure, atmospheric stability, transitions between daytime and nighttime mixing, and measurement of mixing depth for the distribution of $PM_{2.5}$ and chemical species. The central location of the Philadelphia site and the special capabilities of the NE-OPS instruments and investigators have been used to advantage to characterize the regional scale.

Significant variations occur within the PBL on spatial scales of the order of tens of meters, and time scales of the order of minutes. Synoptic scale analyses are not capable of resolving structure that plays a major role in the vertical exchange between the lower troposphere and PBL. Mesoscale models continue to be plagued by large divergences in solutions for the height of the PBL when initialized with surface data without knowledge of the aloft field variables. The relationships between transport on the synoptic and regional scales as determined from NCEP analyses and mixing processes on the local (sub-grid) scale have not been resolved. Uncertainties can lead to significant differences between the model solutions of the height of the stable (nocturnal) PBL and the daytime mixed layer, as well as the determination of the daytime PBL height. Knowledge of the temporal evolution of the PBL is a critical input into models of the pollutant concentrations because it establishes the mixing volume. The Baltimore and New York Supersites are separated by over 300 km. Over this distance PM and trace gas modification can be so influenced by the northeast corridor urban plumes that attempts to characterize them will fail. Philadelphia's site location, approximately midway between the Supersites (182 km from Baltimore; 118 km from New York), provides an array of surface measurement platforms that are similar to the PM Supersites and it provides significant capability for investigations of the controlling meteorological processes by adding the aloft measurement component. The location of these three sites should allow an interesting study of the air mass along the northeast corridor.

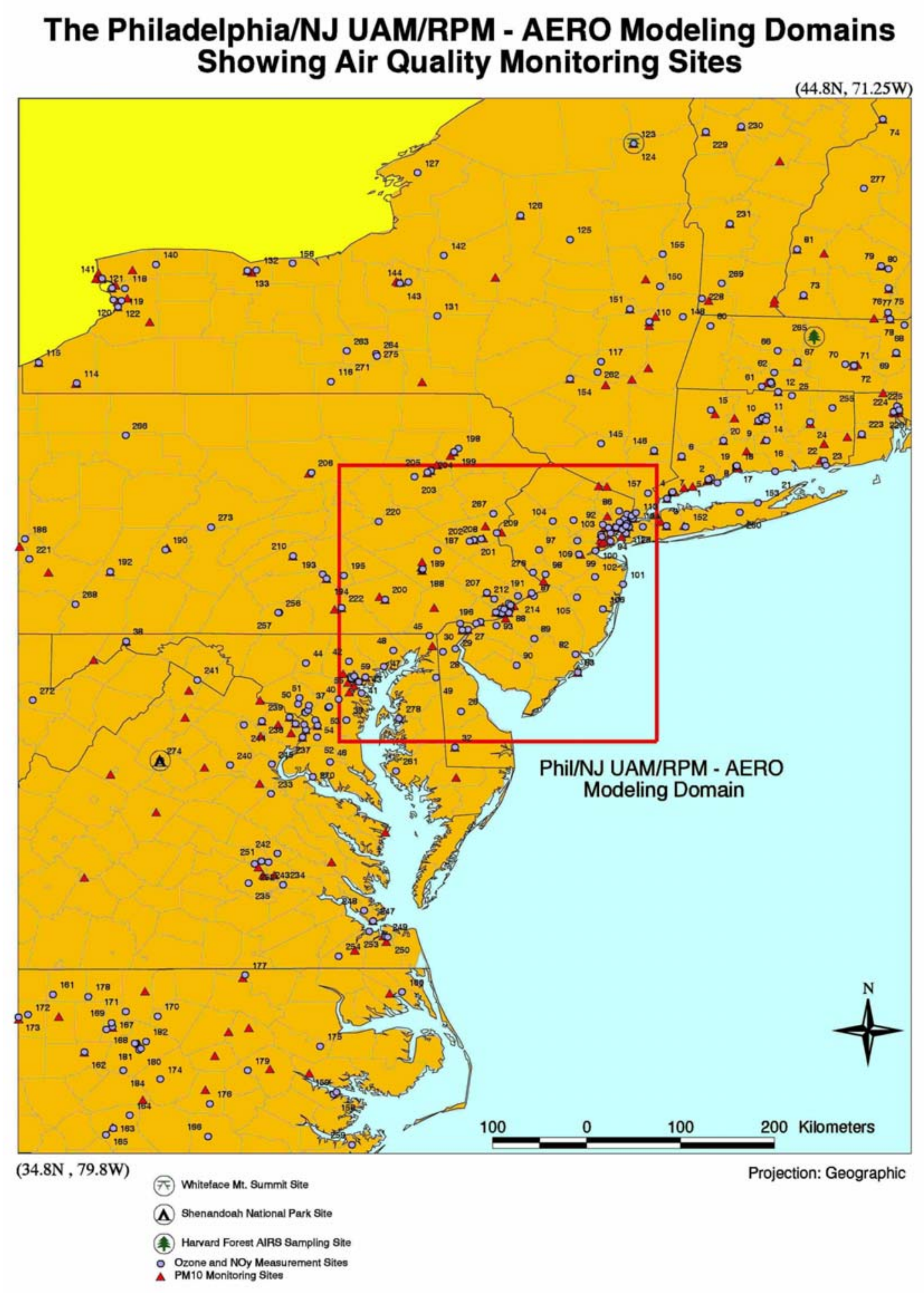

Figure 1-1. The map of the northeast region shows the regional emphasis of the NE-OPS investigation as the square centered on Philadelphia. It includes the Supersites in New York and Baltimore at its corners and the Supersite in Pittsburgh is in an important upwind location for coordinated studies.

The creation of PM Supersites in Baltimore and New York has presented a valuable opportunity to integrate aloft and surface measurements in Philadelphia, PA with those at the PM Supersites during combined field intensives. Since 1998, Philadelphia has been the site of intensive multi-institution/agency field campaigns which have focused on the processes associated with occurrence of ozone and fine particle events along the northeast corridor. Raman LIDAR, RASS (Radar-Acoustic Sounding System), tethered and free balloons, aircraft and a plethora of surface-based PM and trace gas analyzers have provided surface and aloft measurements during the NEOPS campaigns. These results are being combined with emissions inventories and numerical models to provide a detailed characterization of the local and regional conditions accompanying high ozone and fine particle events. An extensive infrastructure has been developed during these projects which involves many scientists at several universities, and close coordination with Federal and State agencies, national laboratories, regional planning organizations in the Northeast (MARAMA, OTC, NESCAUM), and the City of Philadelphia. The instruments and measurements deployed during the 1998 NEOPS pilot study (6-21 August 1998), the 9-week NEOPS field intensive (28 June – 18 August 1999), and the 2001 NEOPS (July 2001) are summarized in a recent overview (Philbrick, et. al 2002).

Table 1-1 provides a summary of the measurements conducted during the NEOPS-DEP 2002 project. This activity during the summer 2002 field intensive has led to a significant improvement in our ability to characterize the northeast corridor airshed. The NE-OPS group added a significant effort which focuses on aloft measurements during the PM Supersite summer. The opportunity to incorporate aloft measurements in Philadelphia and integrate those measurements with PM measurements in Baltimore and New York adds an important dimension to the intensives that would otherwise be lost. Moreover, the NE-OPS results from the 1998, 1999 and 2001 databases permits multi-year comparisons. The database from prior years included twelve significant air pollution episodes where either PM, ozone, or both exceeded NAAQS under a range of atmospheric conditions. The central location of Philadelphia with respect to the two PM Supersites along the northeast corridor, its influence as an up/downwind source/receptor, proximity to the coastal regions, yet more inland than either Baltimore or New York, should help elucidate important similarities and differences in the regional temporal and spatial distribution of the $PM_{2.5}$/co-pollutant complex. The results could benefit the development of SIPs, the setting of NAAQSs. The measurement program during summer 2002 was coordinated with the three northeast Supersites and with the MANE-VU project:
(a) Baltimore - John Ondov (PI) - Baltimore intensive during the month of July
(b) New York - Ken Demerjian (PI) - New York Supersite intensive measurements during July 2002
(c) Pittsburgh - Spyros Pandis (PI) - Pittsburgh Supersite intensives of several days duration through the year when pollution events occur.
(d) Regional Haze MANE-VU Project - Regional haze studies during July 2002.

The periods of special emphasis based upon the ozone and PM episodes during the summer of 2002 are shown in Figure 1-2 and are summarized in Table 1-2. The results presented in Figure 1-2 combine the Clarkson University measurements of particulate matter with the Millersville University measurements of ozone. Figure 1-3 depicts several of the instruments used to gather the measurements at the Philadelphia site during the NEOPS-DEP2002 campaign.

Table 1-1. Summary of key measurements obtained during NEOPS-DEP2002.

Trace Gases:

1. Vertical profiles of ozone and water vapor using PSU Raman Lidar
2. Suite of API analyzers and on-site calibrators to measure CO, O_3, SO_2, and NO/NO_2/NO_X by Millersville University
3. Aloft ozone concentration profiles using Millersville University's tethered atmospheric sounding system (TASS) between surface and 300 m
4. Air toxics and minor species composition of particulate matter using GC/MS laboratory analysis of filters gathered at the site and measured at laboratories of Drexel University

Particulates:

1. PSU Raman Lidar vertical profiles of optical extinction at visible and ultraviolet wavelengths
2. Millersville University tethered balloon profiles of the PM using laser diode particle nephelometers and impaction sampling on Personal Environmental Monitors (PEMs, SKC Inc.)
3. Clarkson University particulate properties using CAMMS, RAMS, Sunset Labs OC/EC, HSPH $SO_4^=$, aethalometer, and nephalometer
4. Millersville University nephelometer (TSI model 3563) total scatter and backscatter at three wavelengths
5. Particle filter samples analyzed at Drexel University using laboratory techniques for toxics and minor constituents

Meteorological Variables:

1. PSU Radar/RASS vertical profiles of wind velocity (surface to 4.5 km) and virtual temperature (surface to 2.5 km)
2. PSU Raman Lidar vertical profiles of water vapor and temperature
3. Meteorological variables (T, p, mixing ratio, wind speed and direction) as a function of height between the surface and 300 m using Millersville University's tethered sonde
4. Continuous measurements of meteorological variables recored from 10-meter tower

Real-time Regional and Synoptic Data Archive:

U.S. upper air data; U.S. surface data; Meso-eta and RUC model data; Visible and IR satellite imagery; Base reflectivity and velocity radar imagery.

Table 1-2. Special interest periods during NEOPS-DEP 2002 (29 June - 7 August 2002)

1	30Jun-4 July	1 July ozone 105 ppb, and 2 July 110 ppb
2	6-7 July	Smoke Event from fires in Canada profiled optical scatterometer on tethered balloon.
3	8-9 July	High ozone (140 ppb range) with an abrupt rise to about 145 ppb late on 8 July (8PM local), 130 ppb on 9 July
4	17-19 July	18 July ozone exceeded 100 ppb for more than 10 hours, 130 ppb on 19 July with excursions to 140 ppb
5	20 July	Sea breeze event.
6	23 July	Frontal passage and rain-out effects
7	28-29 July	Weak ozone and PM event
8	1-2 Aug	Ozone (>120 ppb) and PM Event ending with significant frontal passage
	4 Aug	130 ppb ozone

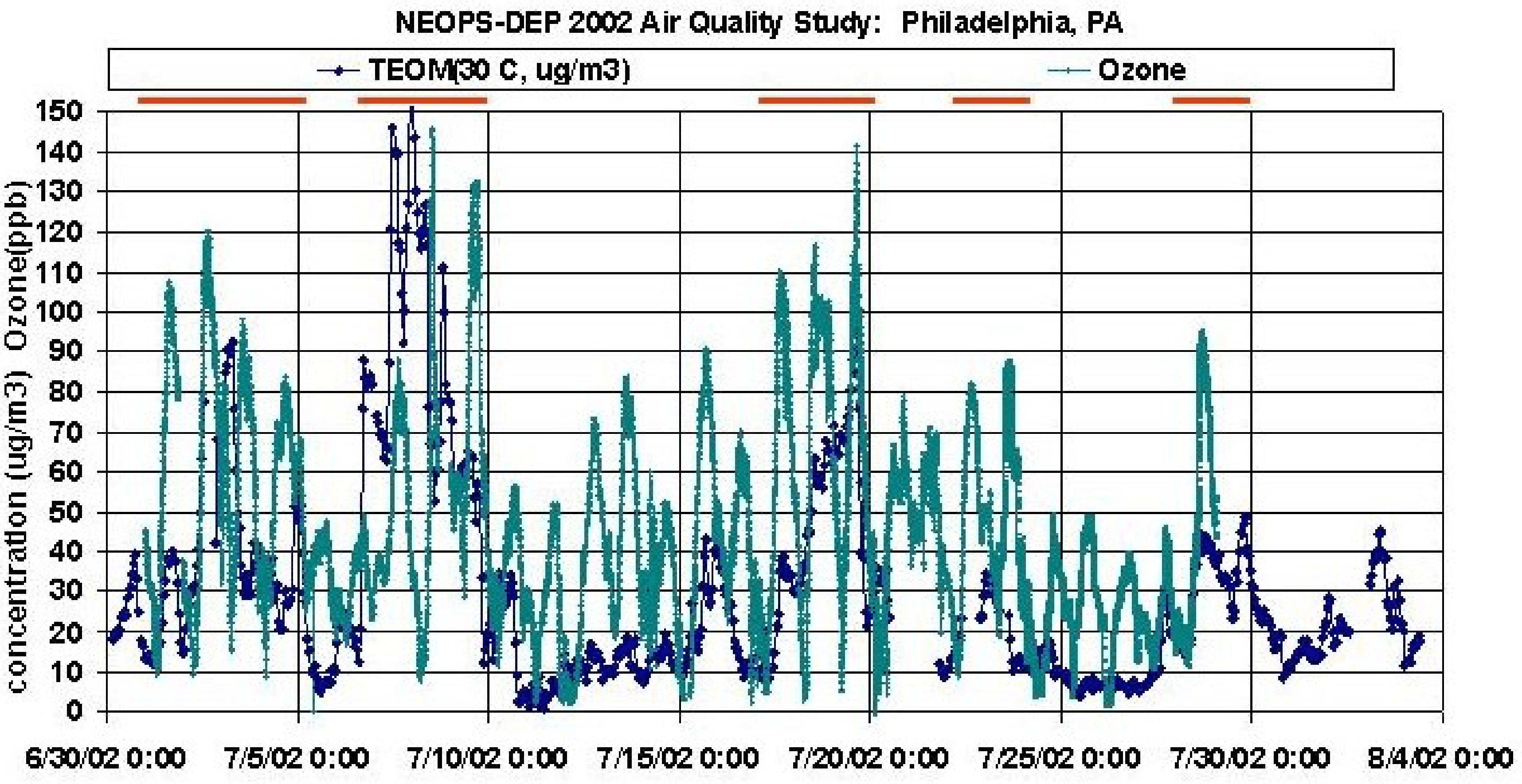

Figure 1-2. Measurements of PM2.5 (Clarkson University) and ozone (Millersville University) at the NEOPS field site in Philadelphia during the summer of 2002 show the periods of air pollution episodes.

The results in Figure 1-2 provide a useful overview of the summer 2002 conditions. The plot shows the large daily variation in the ozone concentration and identifies those periods of poor air quality. The first major episode of the 2002 summer occurred between 30 June and 4 July. Other periods of peak ozone concentration are seen to occur in 8, 10 and 19 July. Major PM events are seen to occur on 6-8 July, 18-19 July and during the period 28 July into early August. It is interesting to compare these periods because they represent the two major processes causing PM events. The first event, 30 June - 4 July, is typical of a summer ozone and PM event that can be closely tied with the transport of pollution from the westward boundary that brings the material into the regionto cause the high ozone and PM values. The second period, 6-8 July, occurs as a high PM event because of major forest fire smoke from southeastern Canada and contains a large carbon component. The PM event is followed on 8-9 July with some of the highest ozone values recorded and appears to be due the photochemical processing at elevated levels of species brought into the region from the Canadian forest fires. The third event on 18-19 July is more typical of the PM component generated by smog air chemistry and contains a large contribution from sulfate aerosol.

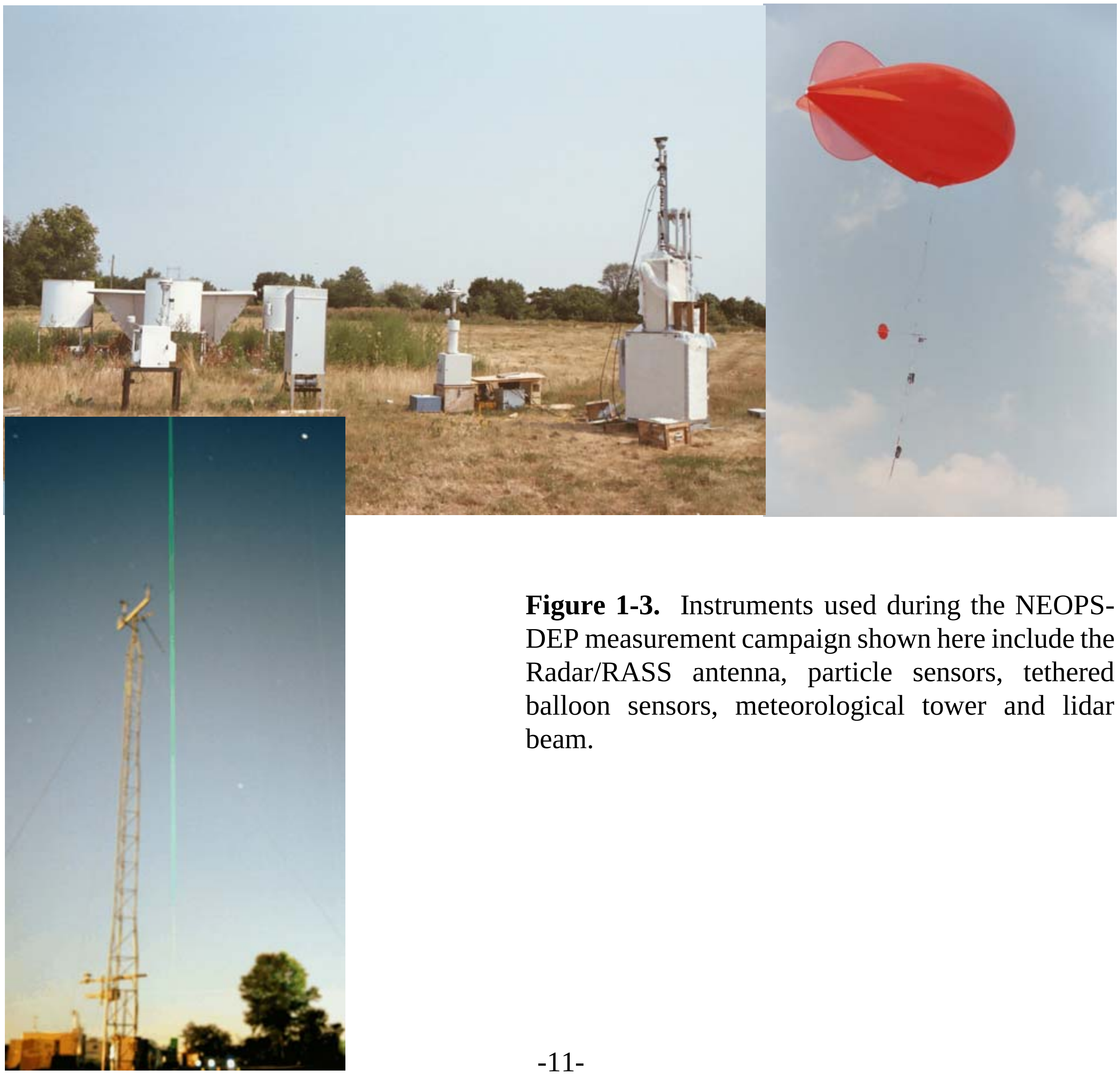

Figure 1-3. Instruments used during the NEOPS-DEP measurement campaign shown here include the Radar/RASS antenna, particle sensors, tethered balloon sensors, meteorological tower and lidar beam.

PART 2: CONTRIBUTIONS FROM PENN STATE UNIVERSITY

Remote Sensing Applications to Understanding Air Pollution Processes

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1. Project Goals

Lidar and Radar remote sensing techniques provide a special capability to measure the development and dissipation of air pollution events and provide results that contribute to our understanding of the important processes. The recent measurements have demonstrated that many of the most important processes cannot be observed from the ground based sensors, and these remote sensing techniques provide a unique view of the processes. Remote sensing techniques provide nearly continuous profiles of the key parameters that monitor the meteorological and air quality properties. A Raman Lidar, Doppler Radar and Acoustic Sounder have been used to profile the properties of the lower atmosphere. The unique Raman lidar techniques which have been developed at Penn State University (PSU) provided simultaneous profiles of the temperature, water vapor, optical extinction, and ozone. These parameters provide the key chemistry, particulate and meteorological properties needed to study air pollution episodes. Profiles of water vapor and optical extinction also define the thickness of the planetary boundary layer (PBL) and describe the vertical distribution of fine airborne particulate matter. Doppler radar is used to profile the velocity components of the wind field and describe horizontal transport and dynamics. The acoustical measurements of the speed of sound provide profiles the virtual temperature which describe the thermodynamic stability of the atmosphere. Table 2-1 summarizes the remote sensing profiles which were obtained using the LAPS Raman Lidar and the LAP-3000 Radar/RASS instruments.

Table 2-1. Remote Sensing Measurements of the LAPS lidar and the Radar-RASS instruments.

Property	**Measurement**	**Altitude**	**Time (Resolution)**
Water Vapor	660/607 Raman 294/285 Raman	Surface to 5 km Surface to 3 km	Night (1 min.) Day & Night (1 min.)
Temperature	528/530 Rot. Raman	Surface to 5 km	Night (10 to 30 min.)
Ozone	276/285 Raman/DIAL	Surface to 2 - 3 km	Day and Night (30 min.)
Optical Extinction at 530 nm	530 nm Rot. Raman	Surface to 5 km	Night (10 to 30 min.)
Optical Extinction at 607 nm	607 N_2 - 1st Stokes	Surface to 5 km	Night (10 to 30 min.)
Optical Extinction at 285 nm	285 N_2 - 1st Stokes	Surface to 3 km	Day and Night (30 min.)
Wind Speed and Direction	Doppler Velocity	Surface to 5 km	Day and Night (10 min)
Virtual Temperature	Speed of Sound	Surface to 2 km	Day and Night (1 hour)

Raman lidar techniques have proven to provide the most valuable descriptions of the evolution of air pollution events. The vibrational and rotational Raman lidar signals provide simultaneous profiles of meteorological data, ozone profiles and profiles of airborne particulate matter. The LAPS (Lidar Atmospheric Profile Sensor) is an operational prototype Raman lidar instrument, which was developed and demonstrated for the US Navy and is now used for scientific investigations. The LAPS instrument makes use of 2nd and 4th harmonic generated laser beams of a Nd:YAG laser and provides both daytime and nighttime measurements. The Raman scatter signals of vibrational states of water vapor and nitrogen provide robust profiles of the specific humidity in the lower atmosphere. The temperature profiles are measured using the ratio of rotational Raman signals at 530 and 528 nm from the 532 nm (2nd harmonic) beam of the Nd:YAG laser. In addition, the optical extinction profiles are determined from the measured gradients in each of the molecular profiles compared to the molecular scale height. We currently use the wavelengths at 284 nm (nitrogen vibrational Raman), 530 nm (rotational Raman) and 607 nm (nitrogen vibrational Raman) to determine profiles of optical extinction. The ozone profiles in the lower troposphere are measured using a DIAL (Differential Absorption Lidar) analysis of the ratio of the vibrational Raman signals for nitrogen (284 nm) and oxygen (278 nm) scattered from the 4th harmonic of the Nd:YAG. The measurements can be made both during daytime and nighttime because of the capability of the instrument to use the "solar blind" portion of the ultraviolet spectrum from the 4th harmonic of the Nd:YAG laser. The results are used to investigate the physical and chemical processes which control the evolution of air pollution episodes, and for development and testing of models of air pollution events.

The second major remote sensing activity included measurements of the wind field and the thermal structure of the lower atmosphere using a Doppler radar combined with a radio acoustic sounder (Radar/RASS). The Radar/RASS instrument is a LAP3000 manufactured by Radian International (now a part of Vaisala Corporation) which has been operated at the Philadelphia site since July 1999 by Penn State University. The instrument was obtained from EPRI with a grant from PECO and the installation was supported by MARAMA. It has the ability to measure continuously to obtain wind profiles to 4 km and virtual temperature profiles to 1.5 km. During the summer of 2002, it was operated in a mode to attempt to obtain higher time resolution results. During the first 10 minutes of each hour, it was used to measure the speed of sound to obtain virtual temperature profiles. The remaining 50 minutes in each hour was devoted to alternating 3 minute periods of 75 meter spatial resolution (0 to 2 km) and 150 meter resolution profiling (0 to 4 km).

2. Measurement Examples

The LAPS lidar instrument was transported to Philadelphia and setup at the NEOPS site in mid-June. Instrument testing was begun on 23 June and the operational phase of the activity took place between 28 June and 7 August 2002. Table 2-2 gives a summary of the periods of operation of the Raman lidar. We experienced some major hardware problems with the laser transmitter that made it impossible to collect data with the instrument between 6 and 20 July. Two service trips by engineers from the laser manufacturer were needed to finally repair the instrument. The instrument has seen much use during the past years and the laser should be serviced before a future campaign. The operating periods listed in Table 2-2 provide measurements during several very interesting and useful studies. Figure 2-1 shows lidar measurements during the early stages of the ozone/PM event on 1 July 2002. The vertical distributions of these parameters show the aloft concentrations of ozone and aerosols and the change as night approaches. Figure 2-1 shows the last six hours of the UTC day, approximately 2 PM to 8 PM local time. The transition periods between day and night are particularly interesting because these periods show the ozone stored aloft in the nighttime reservoir of the residual boundary layer.

Table 2-2. Summary of LAPS Lidar run times - 23 June – 7 August 2002 (UTC)

	Hours	Minutes		Hours	Minutes
23 June	04-06	91	24 July	00-07	380
24 June	01-02	50	25 July	09-13	214
26 June	02-03	30	26 July	07-12	306
27 June	01-02	44	27 July	00-02	71
28 June	16-18, 22-23	155	28 July	08-12, 20-23	428
29 June	00, 04-06	103	29 July	00-23	1307
30 June	00-04, 22-23	325	30 July	00-14, 18-23	1150
1 July	00-23	1296	31 July	00-23	1278
2 July	00-23	1363	1 August	00-23	1399
3 July	00-23	1407	2 August	00-23	1328
4 July	00-23	1412	3 August	00-12	749
5 July	00-02	133	4 August	20-22	61
21 July	04-06	65	5 August	01-19	1048
22 July	01-23	1281	6 August	00-23	1209
23 July	00-23	1436	7 August	00-09	512

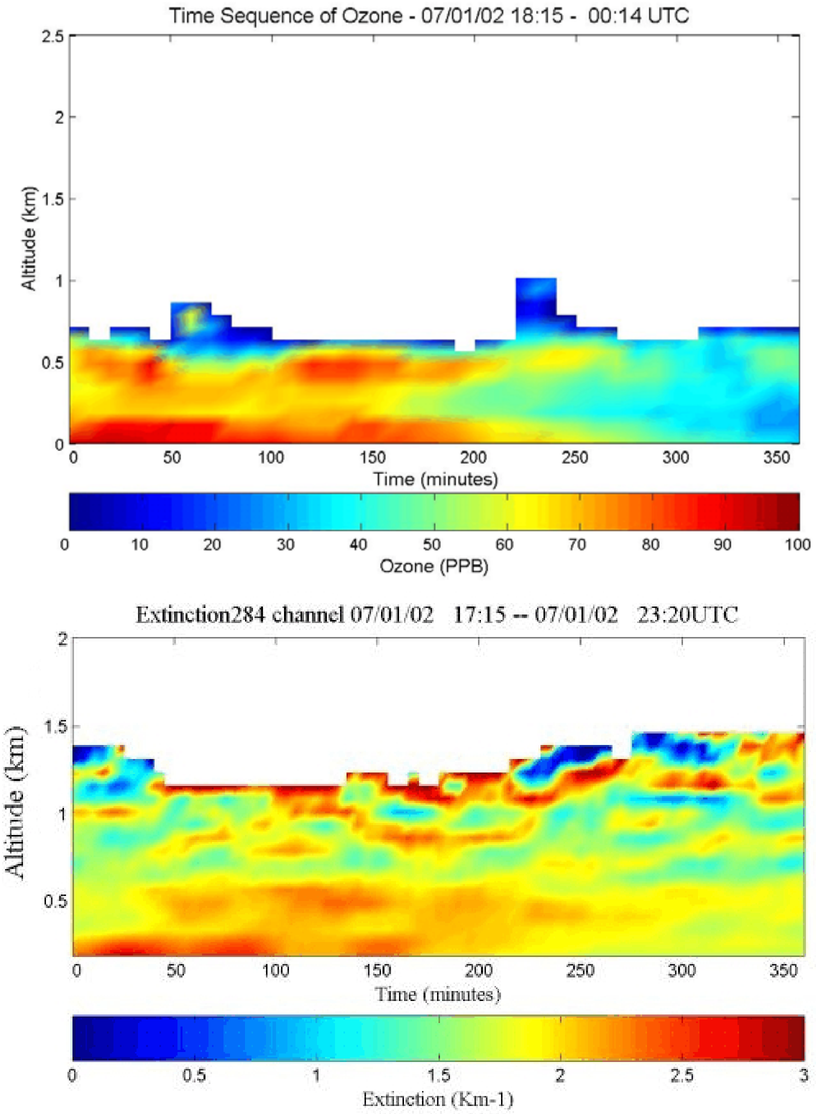


Figure 2-1. Time sequences of ozone and optical extinction (describes the distribution of $PM_{2.5}$) during the afternoon and early evening of 1 July 2002 show the transition to nighttime conditions while in the first stages of an ozone episode.

The episode began on 1 July and continued for several days. The results shown in Figure 2-2 are a continuation following after those shown in Figure 2-1. These nighttime measurements show the vertical distribution of aerosols (based upon the optical extinction at visible and ultraviolet wavelengths) and the vertical profiles of ozone. The nighttime transport of ozone and PM into the region is clearly evident in these results.

The UV extinction shows the expected response to ozone absorption in the layer at 500 meters. The visible extinction is more sensitive to the larger particles that are present between 1.0 and 1.5 km. Figure 2-2 compares the optical extinction at both visible and ultraviolet wavelengths with the ozone distribution during the first 6 hours of 2 July (8PM on 1 July to 2AM on 2 July), immediately following the measurements shown in Figure 2-1. The extinction at visible wavelengths is maximum between 1 and 1.5 km because this region corresponds to high relative humidity which leads to growth of the aerosol particle size and increases the scattering. The ultraviolet extinction has much more contribution from the process of molecular scattering, as well as from ozone absorption. The ozone results depict the nighttime reservoir of ozone above the nocturnal inversion. During this night a low level jet formed which transported ozone into the region from upstream sources.

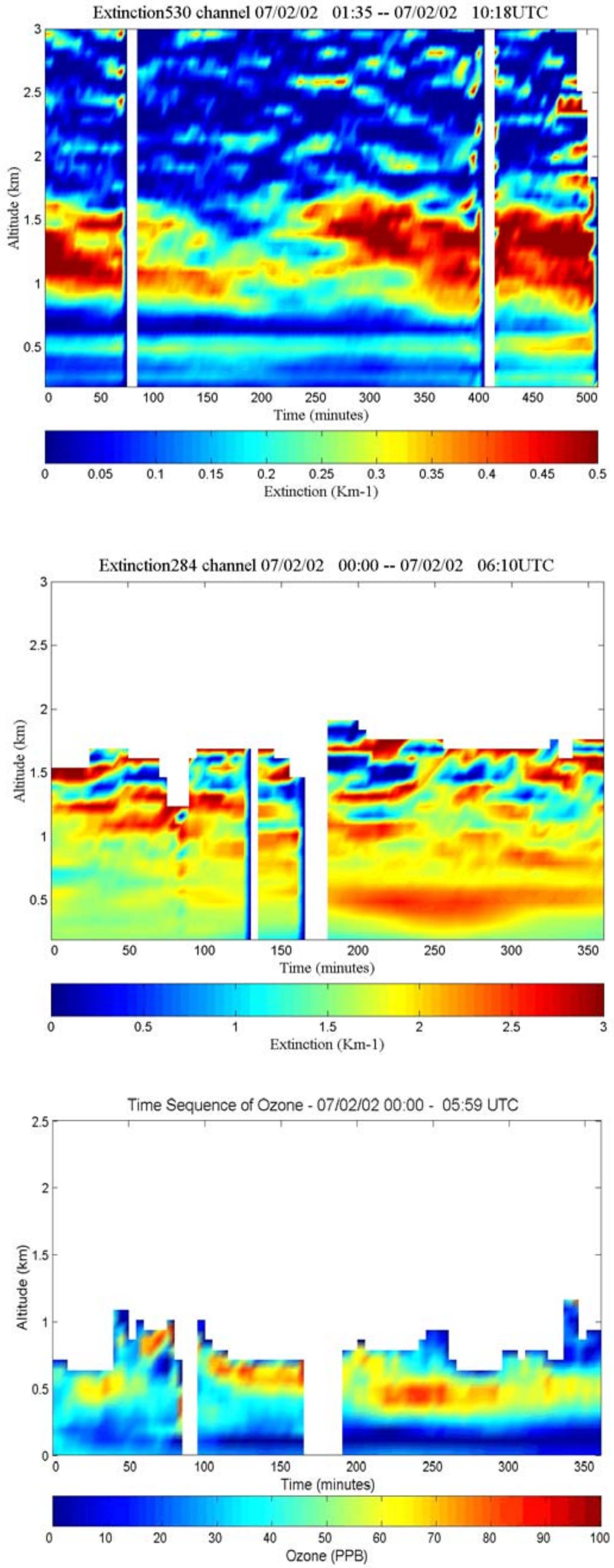


Figure 2-2. The optical extinction at visible and ultraviolet wavelengths are shown with the ozone measurements during the same night period on 2 July.

Figure 2-3 shows a longer 18-hour sequence of the ozone measurements on 2 July that extends from near sunset on 1 July through the night to 2 PM local time the following afternoon. This example shows the contribution of the nighttime residual layer as a significant storage reservoir for ozone, where it can be transported over large distances at altitudes above the nocturnal boundary layer. The reservoir contributes to the daytime ozone layer when mixing brings the material that has been transported and stored in this region to the surface.

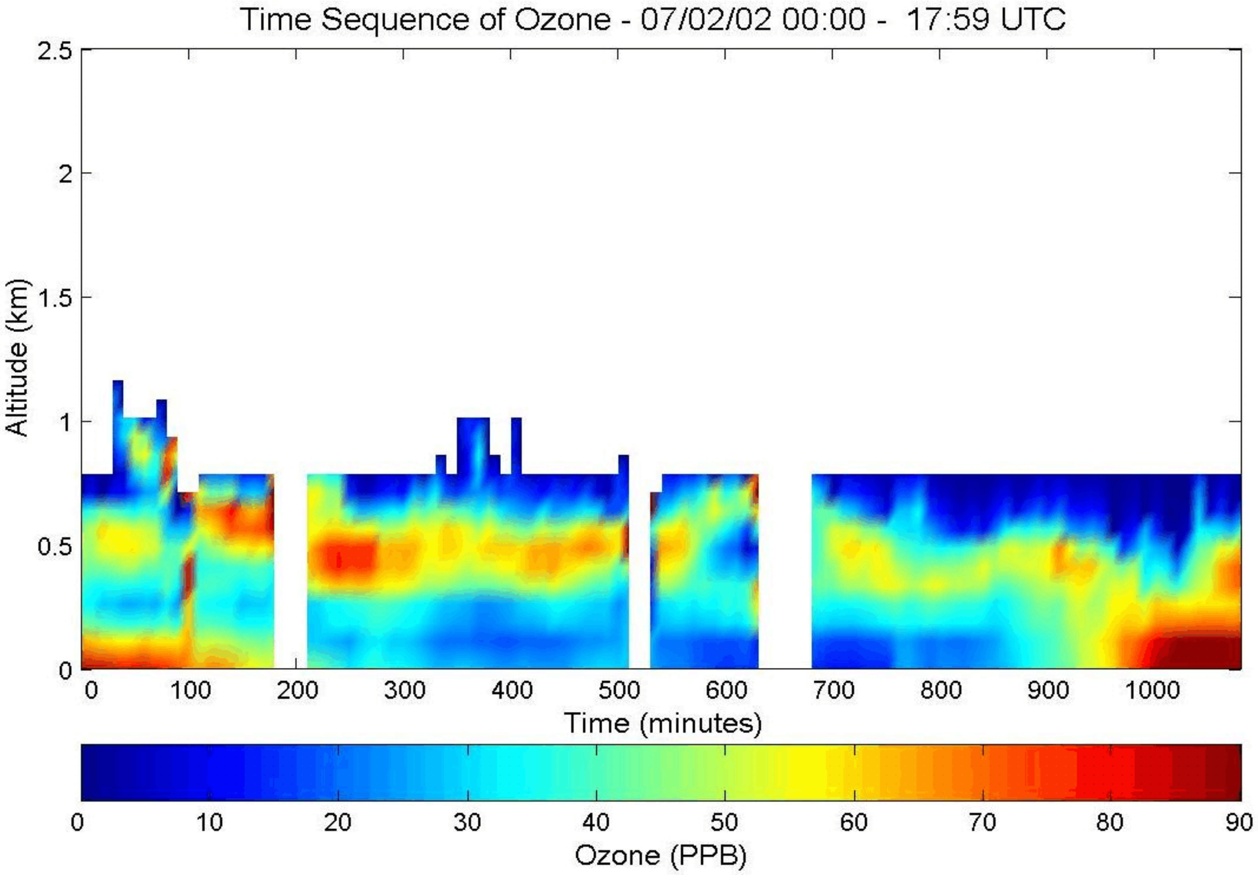


Figure 2-3. The time sequence of ozone measurements between sunset on 1 July through 2PM local time on 2 July shows the storage/transport of ozone through the night.

Most of the significant ozone episodes that have been observed in Philadelphia are associated with transport of primary and secondary sources of pollution in the region near the top of the nocturnal boundary layer. The kinematics of the transport in this region can be seen in the Doppler radar measurements of the wind field shown in Figure 2-4. The wind direction is shown with an arrow pointing the azimuth from north (vertical) through east (horizontal to right) and the magnitude is proportional to the length of the arrow and is also enhanced with a changing color scale. The early morning of 1 July shows the development of a low level jet (LLJ) which has proven to be strongly coupled with pollution episodes and is suspected to be an important contributor of the air pollution and precursor materials. At altitudes between 400 and 700 meters, the LLJ is seen to be present through this night with a maximum near 4 AM local time, and this characteristic signature is found on most nights preceding major ozone exceedences.

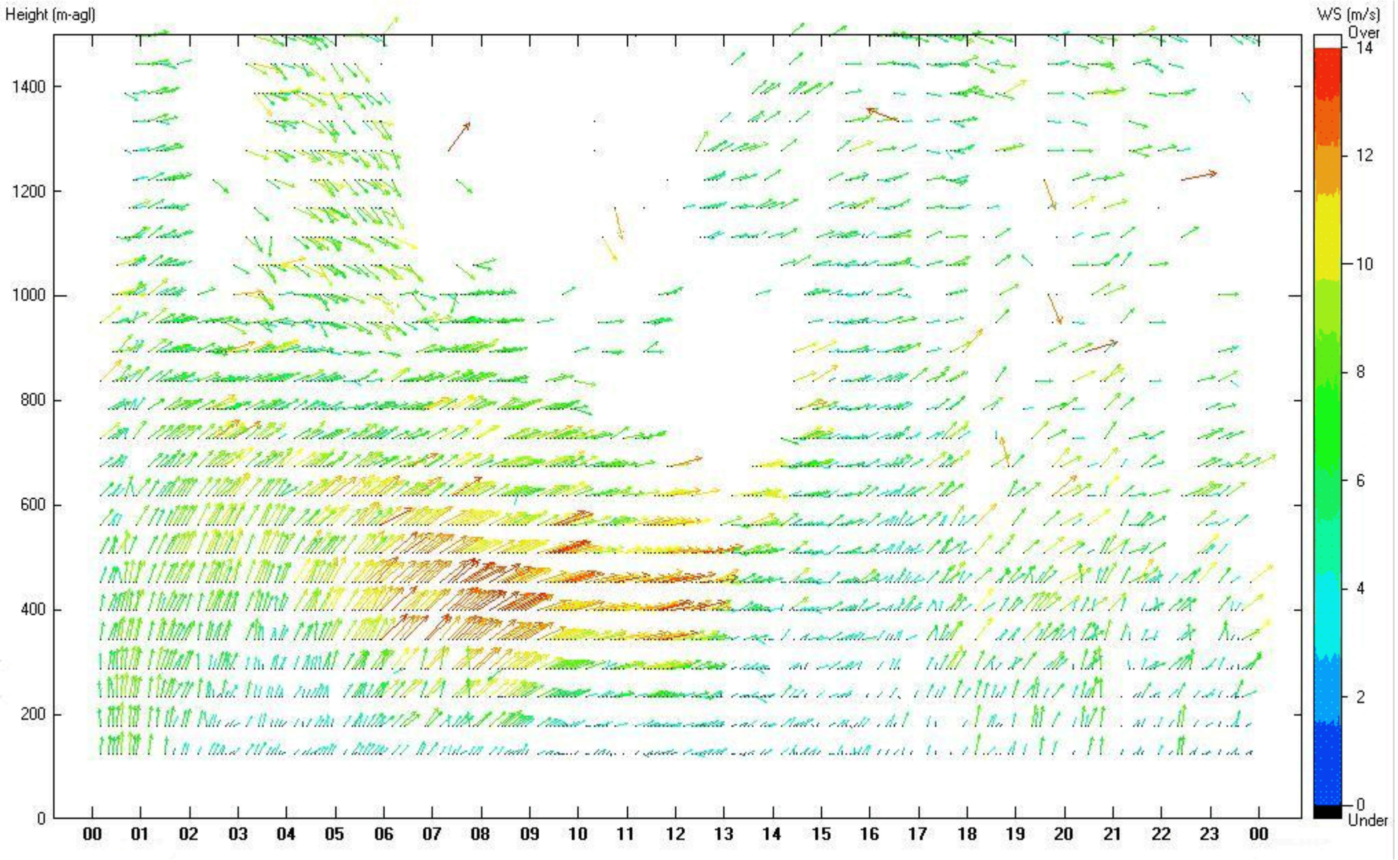


Figure 2-4. The horizontal wind field for the date of 1 July shows the development of a LLJ that contributed to the transport of pollutant materials from the south and west of Philadelphia during the night (the time scale is UTC hours).

The acoustic portion of the Radar/RASS instrument also provides an additional data set which is valuable for determining the stability of the lower atmosphere. Figure 2-5 shows the virtual temperature calculated from the speed of sound that is measured by using the Doppler radar to trace the phase progression of a sound wave through the atmosphere. The virtual temperature differs from the true temperature because of the presence of water vapor which changes the specific heat of the atmospheric gas, however this parameter is more valuable for examining the dynamic stability of the atmosphere. The gas kinetic temperature can be easily calculated using the lidar measurements of water vapor. The set hourly profiles in Figure 2-5 clearly show the development and recovery from the nocturnal temperature inversion. The development of the nighttime inversion is a key factor in the development of a stable boundary layer (positive temperature gradient) which decouples the surface friction that is normally transferred through the lower atmosphere by the action of convective turbulence. The acoustic velocity measurements are made during the first 10 minutes of each hour and the wind field is measured during the remainder of each hour. As a complement to the Radar/RASS instrument, we also maintain a 10 meter meteorological tower which provides the basic parameters, an example from those measurements for the first week of July 2002 is shown in Figure 2-6.

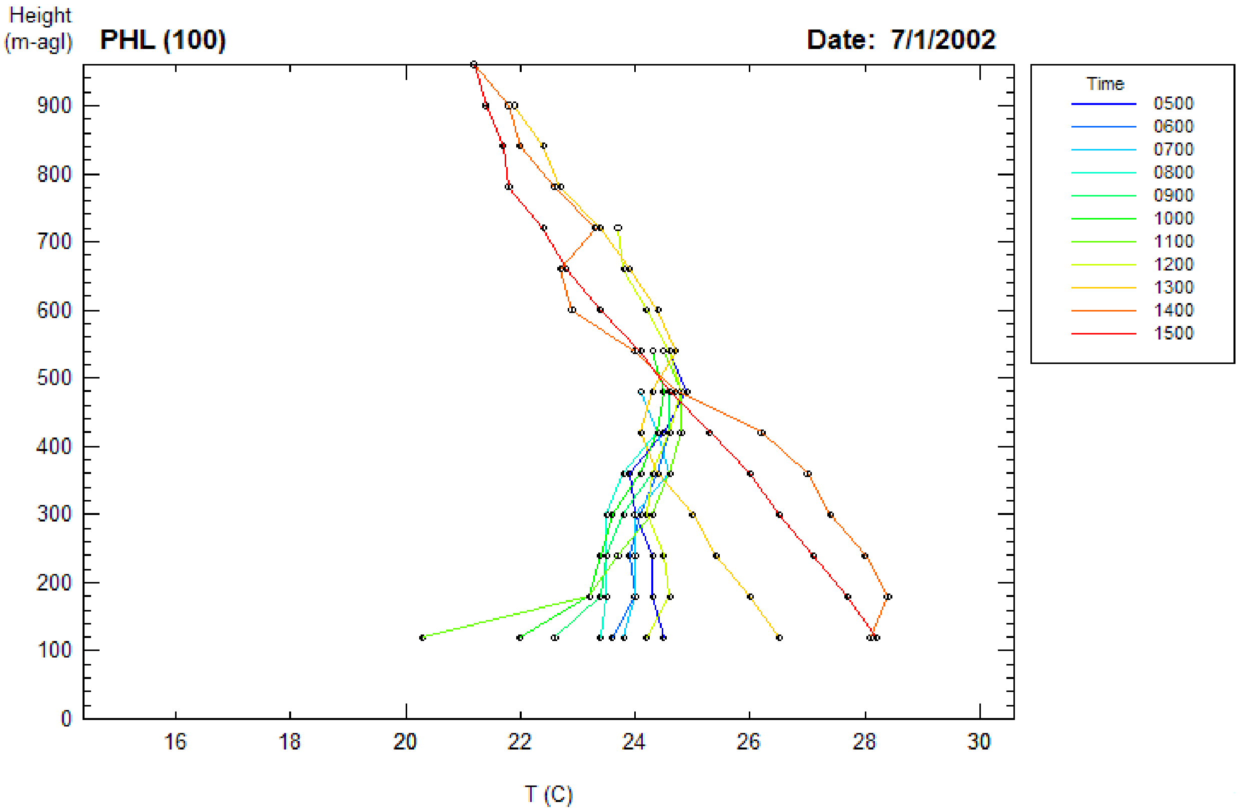


Figure 2-5. The virtual temperature measurements calculated form the measurements of the speed of sound using the Radar/RASS instrument.

3. Key Findings

The measurements and analysis performed during the Penn State University investigations have primarily focused upon the remote sensing techniques using Raman lidar, Multi-staticLidar and Radar/RASS. A major contribution of the PSU efforts is to provide a useful data set that can be used in a flexible way to test and develop atmospheric models. During 2002, the NEOPS-DEP data base included eight significant events of particular interest for investigations of air pollution episodes. The unique contributions to the program include measurements of the vertical distribution of air pollutants, ozone and particulate matter, and the vertical profiles of the meteorological properties. The Raman lidar water vapor measurements provide an excellent tracer of the short term dynamical processes and its gradients at the top of the PBL provide the best marker to study variations in the thickness of the planetary boundary layer. The growth of the daytime boundary layer, the thickness variations of the mixing region and the variation in the nighttime residual layer are best described by these profiles. The Raman lidar time sequences can be used to study the extent of the dilution volume for the pollutants injected into the surface layer, and the downward mixing of aloft layers. The variations of the PBL thickness have been found to provide one of the most critical tests for evaluation of meteorological models. The results show that high levels of ozone are frequently transported in layers above the surface and go undetected by the ground-based sensors normally used to measure ozone. The nighttime transport processes, such as the LLJ, frequently result in the layer distributions of ozone, PM and precursor materials overhead that are mixed to the ground and provide important contributions to the photochemical production of air pollution during the day.

The conclusion from these investigations is that most of the major air pollution episodes observed in the Philadelphia area are meteorologically controlled and are associated with the transport of pollutants and/or precursors from the Midwest region. During the summer 2002, as well as for previous intensives, meteorology appears to be the principal driver that ultimately determines whether or not a pollution event will occur. If the synoptic forcing is too strong, enhanced pressure gradients will inhibit the build up of trace gas concentrations by generating high winds, which serve to erode the interface between the boundary layer and the free atmosphere, and fumigate the local environment. On the other hand, if the synoptic forcing is weak, near-surface gradients create localized and regional circulations that remained largely confined to the boundary layer. Weak synoptic systems respond to this boundary layer forcing to create deep daytime convective mixed layers, shallow nocturnal boundary layers with embedded boundary layer jets, sea breeze fronts, and other convergence zones (e.g., leeside Appalachian trough) that have been observed, especially during summer 1999 and 2002, to significantly modify the trace gas concentrations at the site.

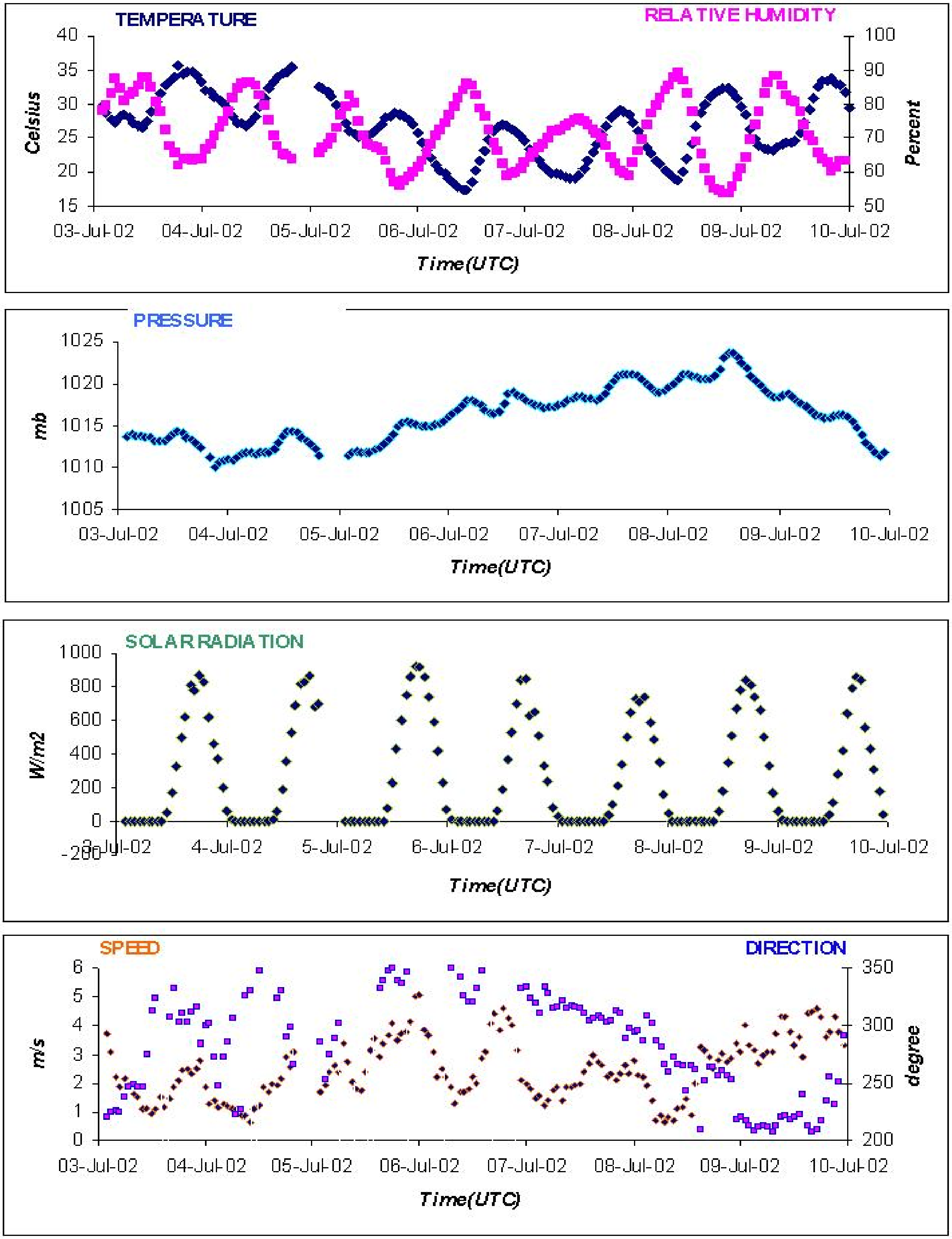


Figure 2-6. Meteorological data that was measured in the first week of July 2002, NEOPS-DEP.

PART 3: CONTRIBUTIONS FROM PENN STATE UNIVERSITY

Examination of the Regional Scale Meteorology and Development of Forecasting Tools for Air Quality

William F. Ryan
Department of Meteorology, The Pennsylvania State University

Data Collected:

1. Daily archive of critical observations and forecast information. This archive includes:
    a. NCEP surface and upper air weather charts
    b. 1200 UTC radiosonde observations and images.
    c. Hourly surface data from first order NWS stations in the region
    d. Weather discussions and forecasts from local NWS forecast offices
    e. Air quality forecasts and discussions
    f. A set of forecast images from the Eta and the PSU MM5
    g. Three times daily satellite and regional radar images.
    This archive has been posted to the NEOPS web site
2. Summary of meteorological conditions during the NEOPS-2002 IOPs. This summary is provided in the form of a web page with embedded links. This archive has been posted to the NEOPS web site.
3. Hourly analysis fields (GRIB format) from the NCEP RUC2 model for the major pollution episodes of 2002. This data is stored on CD but is available upon request.

Hypothesis R1: During the summer season, periods of high O_3 are coincident with high $PM_{2.5}$ events and this coincidence allows accurate forecasts of high $PM_{2.5}$ events.

Discussion: $PM_{2.5}$ concentrations, in the summer season in the Philadelphia area, are generally well correlated with O_3 concentrations (Figure 3-1). $PM_{2.5}$ concentrations at or just above the Code Orange threshold (40 μgm^{-3}) may occur in the absence of high O_3 concentrations but the highest $PM_{2.5}$ cases (with the exception of July 4th which introduce an artifact due to fireworks displays, and in the cases of smoke from forest fires such as the 6-7 July 2002 period) are always associated with an extended high O_3 period (Figure 3-2). While high $PM_{2.5}$ and high O_3 episodes occur in concert, the timing of the onset/termination of peak concentrations for each pollutant is often not simultaneous. From the set of cases during the 1999, 2001 and 2002 NEOPS campaigns, it appears that the onset of the most significant $PM_{2.5}$ events are accompanied by a transition to westerly transport in the boundary layer (Figure 3-3). Weather conducive to photo-chemistry, coupled with local stagnation/re-circulation can cause rapid increases in O_3 with peak concentrations reaching the Code Red range in the absence of a significant westerly transport component (e.g., August 1-4, 2002). In these conditions, $PM_{2.5}$ concentrations rise as well but are typically limited to the 30-40 μgm^{-3} range. Once the transport pattern shifts to westerly, however, $PM_{2.5}$ concentration rises rapidly. Cases exhibiting this rapid transition include July 19, 1999, July 2 and July 18, 2002. On at least one occasion (July 1-3, 1999) sustained westerly transport in a well-mixed boundary layer with strong wind leads to $PM_{2.5}$ concentrations well into the Code Orange range with little or no O_3 signal (see Tables 3.2 and 3.3 for the adopted color code assignments). For forecast concerns, it appears that our understanding of the formation of O_3 episodes will assist in forecasting $PM_{2.5}$ in association with knowledge of the wind and transport fields.

Hypothesis R2. The nocturnal low level jet acts as a conveyor of pollutants into the Philadelphia area during high $PM_{2.5}$ and O_3 events.

Discussion: The nocturnal low level jet frequently occurs in concert with O_3 pollution episodes. From mid-June to mid-August, 2002, peak 1-hour O_3 in the PHL area exceeded 100 ppbv on 19 of 21 cases where LLJs were observed. This represents two-thirds of all cases exceeding 100 ppbv during that period. As shown in Table 3-1 (from MS thesis of Verghese), the LLJ's were found to be simultaneously present at the three sites in the region where such measurements are available. The four most significant $PM_{2.5}$ events during 2002 also occurred during LLJ conditions. The association of the LLJ with pollution events does not necessarily imply causation. The weather patterns that are conducive to the formation of the coastal plain LLJ (weak synoptic scale winds, surface high pressure stationary over the region, warm temperatures) are also conducive to pollution events (Figure 3-4). However, lidar observations during 2002 showed that O_3 concentrations can be enhanced within the layer affected by the low level jet (Figures 3-5 and 3-6). Continuing research on the results from 2002 will seek to quantify this effect by determining the concentrations of O_3 and other parameters within the LLJ. (Provisional title: The Eastern Coastal Plain Low Level Jet: Identification, frequency of occurrence and influence on local and regional air quality, Ryan, W. F., R. D. Clark, S. Verghese and R. Philbrick).

Table 3-1. Table of occurrence of nocturnal low level jets during NEOPS-DEP 2002.

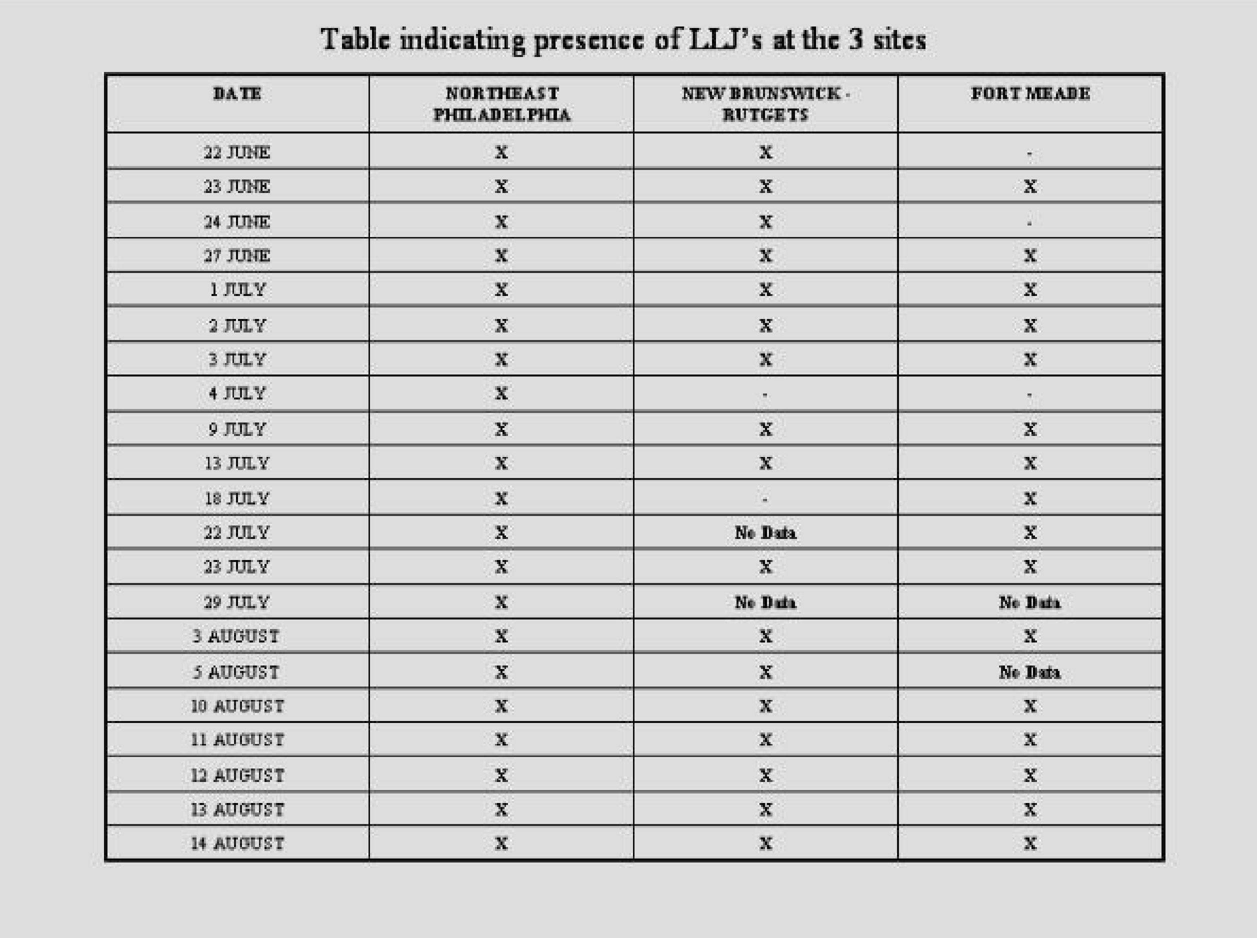


Table indicating presence of LLJ's at the 3 sites

DATE	NORTHEAST PHILADELPHIA	NEW BRUNSWICK - RUTGETS	FORT MEADE
22 JUNE	X	X	-
23 JUNE	X	X	X
24 JUNE	X	X	-
27 JUNE	X	X	X
1 JULY	X	X	X
2 JULY	X	X	X
3 JULY	X	X	X
4 JULY	X	-	-
9 JULY	X	X	X
13 JULY	X	X	X
18 JULY	X	-	X
22 JULY	X	No Data	X
23 JULY	X	X	X
29 JULY	X	No Data	No Data
3 AUGUST	X	X	X
5 AUGUST	X	X	No Data
10 AUGUST	X	X	X
11 AUGUST	X	X	X
12 AUGUST	X	X	X
13 AUGUST	X	X	X
14 AUGUST	X	X	X

A more restrictive criteria for LLJ's has been proposed which appears to better define the location and character of the jet is the thesis of Verghese (2003). Because the LLJ core is typically only a couple of hundred of meters thick and residing in the residual layer at the top of the nocturnal inversion, models have difficulty simulating detailed its characteristics. Many model sensitivity experiments have been run that reasonably simulate the general features of the LLJ, such as the characteristic inertial oscillation, the timing of the LLJ, and its height AGL. However the maximum speed and timing of the speed maximum are only approximately modeled. Unfortunately, these details are too often a manifestation of the choice of the boundary layer parameters and the choice of the vertical and horizontal grid resolution. The model treatment of the diffusion of energy and momentum in both the vertical and horizontal planes depends greatly on the parameterization. The result depends on how it handles the second and third order terms in the momentum or TKE equations. In the shallow shear zones above and below the layer of maximum winds, second order terms can dominate the transfer of momentum away from the jet core. These inherently non-linear effects have not been adequately captured by numerical mesoscale models. As a consequence, the LLJ is simulated with too broad a layer for the maximum winds, or with speeds that do not agree with those observed. If the BL parameterization results in lesser wind speeds, then the Coriolis force affecting the inertial oscillation and the ageostrophic wind components are weaker. The reverse occurs with stronger wind speeds. This condition will affect the assumptions made about LLJ transport, as well as the timing and concentration of the mixing process on the morning following a LLJ episode, and ultimately the prediction of trace gas concentration the following day. Moreover, the horizontal extent of the simulated LLJ has not been verified by observation.

The coastal low level jet (LLJ) has not been systematically studied to date. It is only with the onset of the radar profilers that we can routinely observe the jet at discrete locations. Along the I-95 Corridor, the LLJ is observed as a nocturnal phenomenon, persisting for 6-8 hours, limited to the 200-800 m vertical layer with peak winds on the order of 10-15 ms^{-1}. The profiler network, however, is inadequate to determine the full regional extent of the jet. Dynamical considerations suggest that this feature is limited to the coastal plain but the westward extension of the jet is still unknown. Previous observations from Arendtsville in southeastern PA during the NARSTO campaigns in 1995 and 1996 observed the LLJ at least as far west as that location. Based on limited results from the 2003 season, the higher resolution numerical weather prediction models from NCEP (at 12 km resolution) appear to capture some of the LLJ features.

The key findings of the NEOPS study are that the LLJ is frequently associated with periods of high O_3 and $PM_{2.5}$ and, *most importantly*, that the air mass transported by the jet is laden with O_3, precursors and fine particles. Because the full horizontal extent of the area affected by the LLJ is unknown, the source of chemical species within the jet is not exactly known. However, the primary wind direction within the jet is southwestward, with a slow turning to the west during the early morning hours. For PHL, this suggests that the source of the air within the jet is intra-regional in nature and likely from locations south of PHL and west of the I-95 Corridor.

It is important to note that the LLJ is an intermittent phenomenon that is embedded within a larger synoptic scale flow pattern. As has been known for several years, the characteristic synoptic scale transport pattern (on the scale of days, from the surface through the depth of the well mixed layer) during high O_3 events in the mid-Atlantic is west to east. This synoptic scale flow accounts for the increase in regional scale O_3 that accompanies Code Red episodes in the PHL area. The LLJ is embedded within the synoptic scale flow along the coastal plain at levels from 200-800 m and for a portion of the overnight hours. As a result, while the synoptic scale flow from west to east sets the regional load, the LLJ appears to be a mechanism for transporting "dirty" air within the region.

Aircraft studies and longer term observations from the elevated O_3 monitors at Shenandoah NP have shown that, during multi-day O_3 episodes in the mid-Atlantic, the regional scale O_3 concentrations are on the order of 80-100 ppbv or more. These results are corroborated by the NEOPS study with the additional of high resolution observations of the elevated plume of polluted air actually entering the PHL area. In addition, the NEOPS results show that enhanced summer season $PM_{2.5}$ concentrations are also associated with a similar transport pattern. The results from the 1999-2002 campaigns show that while local emissions in a relatively stagnant air mass can cause $PM_{2.5}$ concentrations to reach the 40 μgm^{-3} range (Code Orange for $PM_{2.5}$), excursions into higher concentrations require the additional regional component. Meteorological analysis during the NEOPS campaigns show that the increased $PM_{2.5}$ concentrations during these event follow the transition to westerly transport sources.

Meteorological Analysis:

The details of the meteorological analysis of the events is maintained on the project web site and by William F. Ryan, The Pennsylvania State University Department of Meteorology, wfr1@psu.edu at http://www.atmos.umd.edu/~forecaster/summary_2002.htm

Table 3-2. Explanation of Ozone Color Code Assignment

Color Code	Ozone Concentration (ppbv)
green	0 - 60
light yellow	61 - 79
dark yellow	80 - 99
light orange	100-110
dark orange	111-124
red	125+

Table 3-3. Explanation of PM Color Code Assignment

Color Code	PM Concentration ($\mu g/m^3$)
Green	0 - 15.4
Yellow	15.5 - 40.4
Orange	40.5 - 65.4
Red	65.5 - 150.4
Purple	>150.5

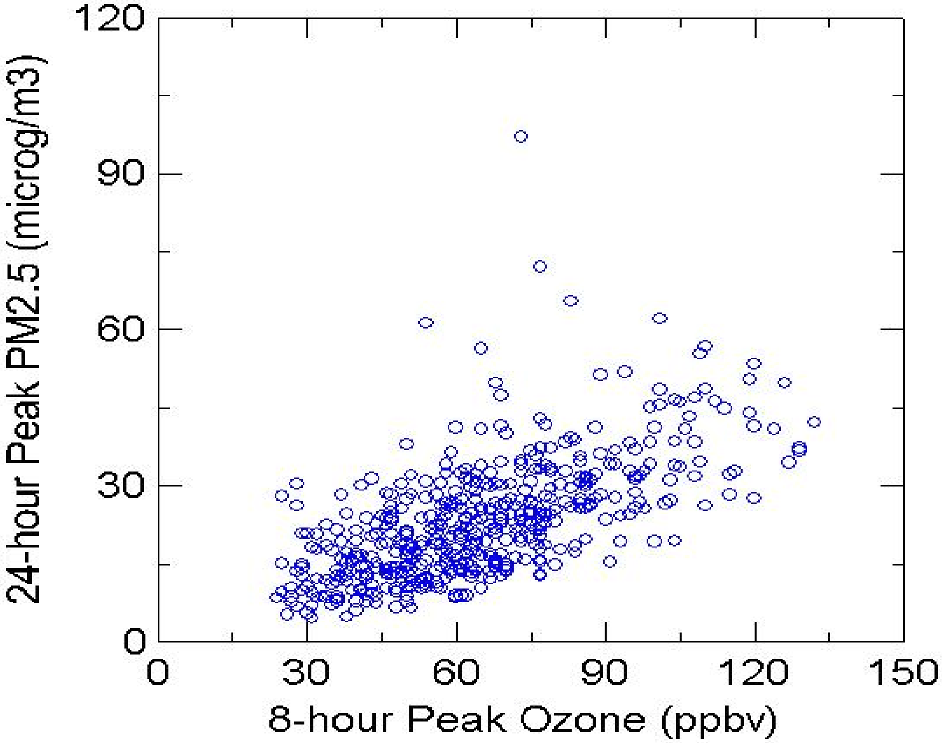


Figure 3-1. Peak 8-hour O_3 for the Philadelphia non-attainment area and peak 24-hour PM2.5 concentrations for the Washington DC – Philadelphia Corridor. $PM_{2.5}$ concentrations are from the state operated FRM monitors.

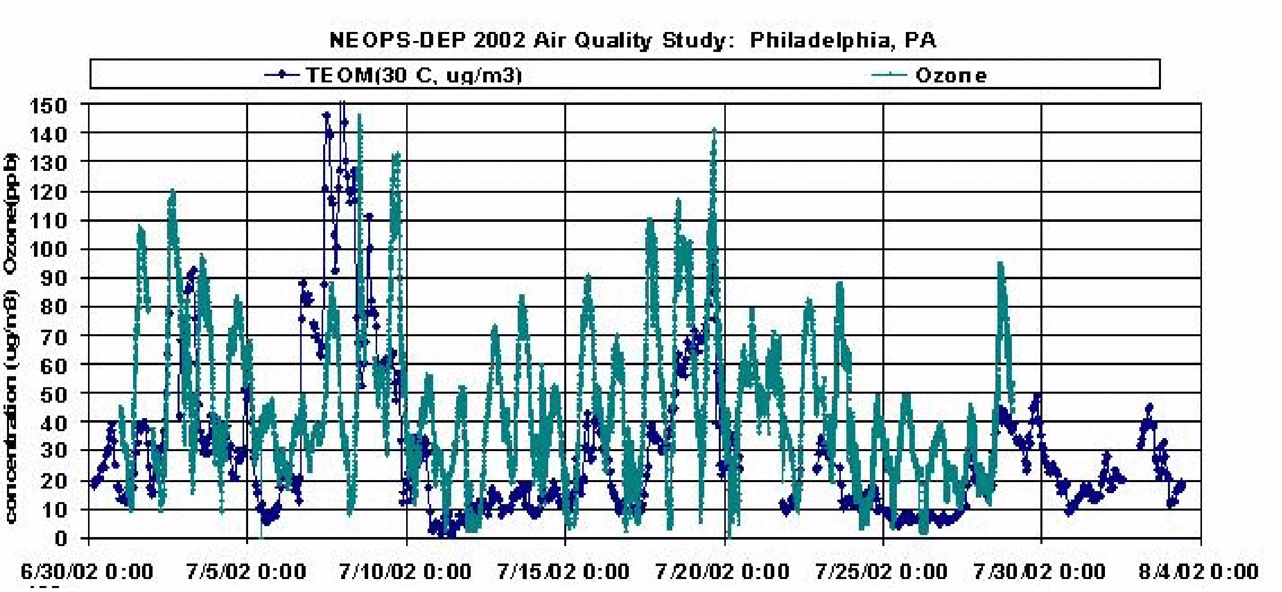


Figure 3-2. Ozone concentrations and 24-hour running mean $PM_{2.5}$ for the NEOPS-DEP2002 campaign at the Baxter Water Treatment Center in North Philadelphia (Phillip Hopke, Clarkson University and Richard Clark, Millersville University).

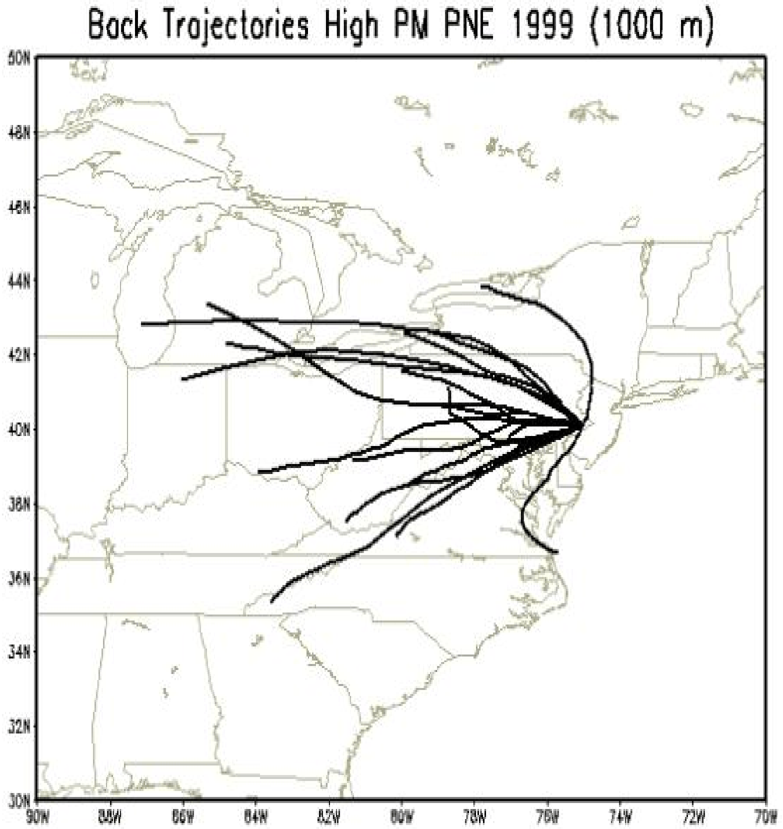


Figure 3-3. HYSPLIT back trajectories from NOAA (http://www.arl.noaa.gov/ready/hysplit4.html) during the highest $PM_{2.5}$ cases observed during the 1999 NEOPS campaign. Back trajectories initiate at the NEOPS site in Philadelphia at 1000 m agl and are run for 24 hours. Meteorological data is provided by the Eta Data Assimilation System (EDAS).

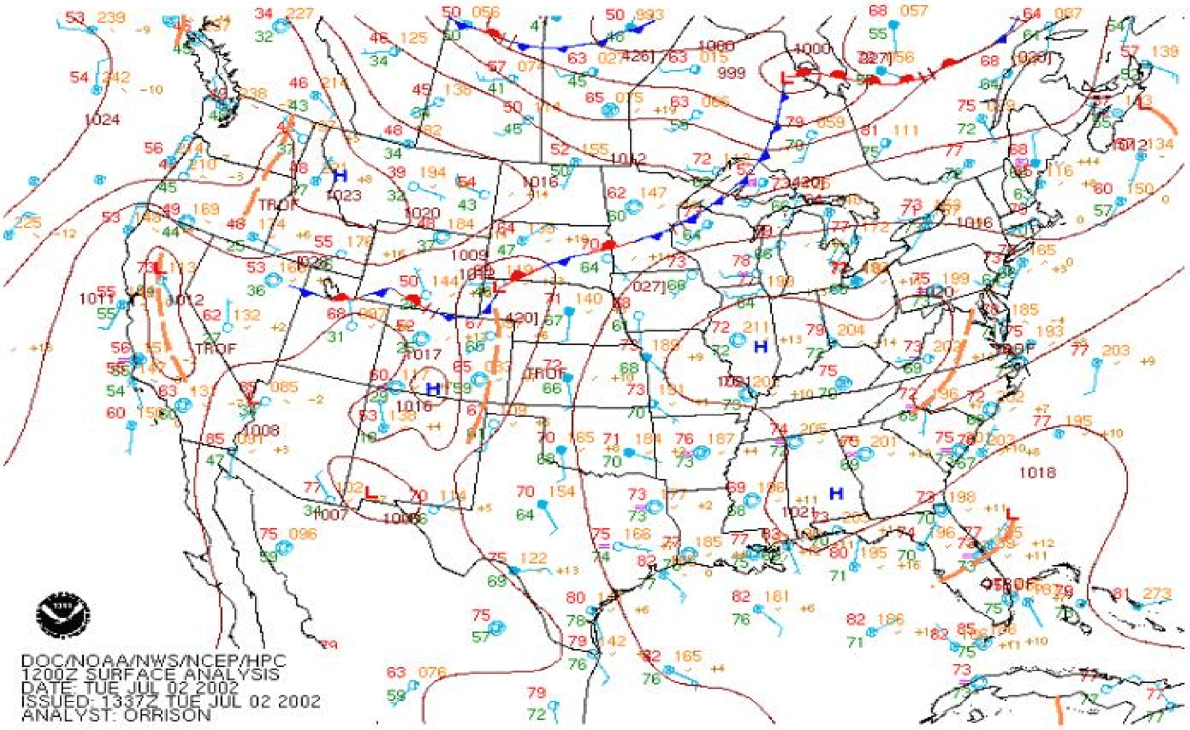


Figure 3-4. NCEP surface weather analysis for 1200 UTC on July 2, 2002.

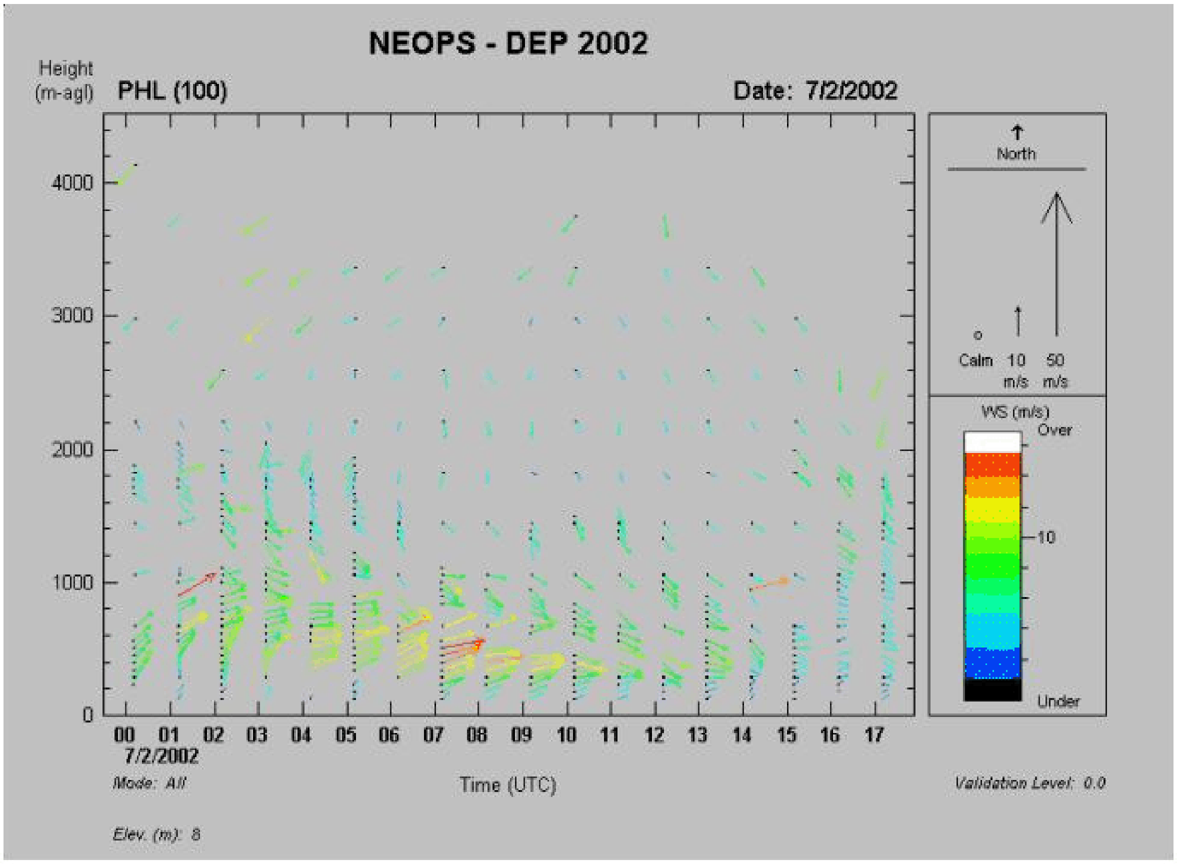


Figure 3-5. Wind profiler time series from the NEOPS Baxter site, July 2, 2002. The low level jet is seen during the hours from ~ 0000-1300 UTC with a maximum near 0700 UTC.

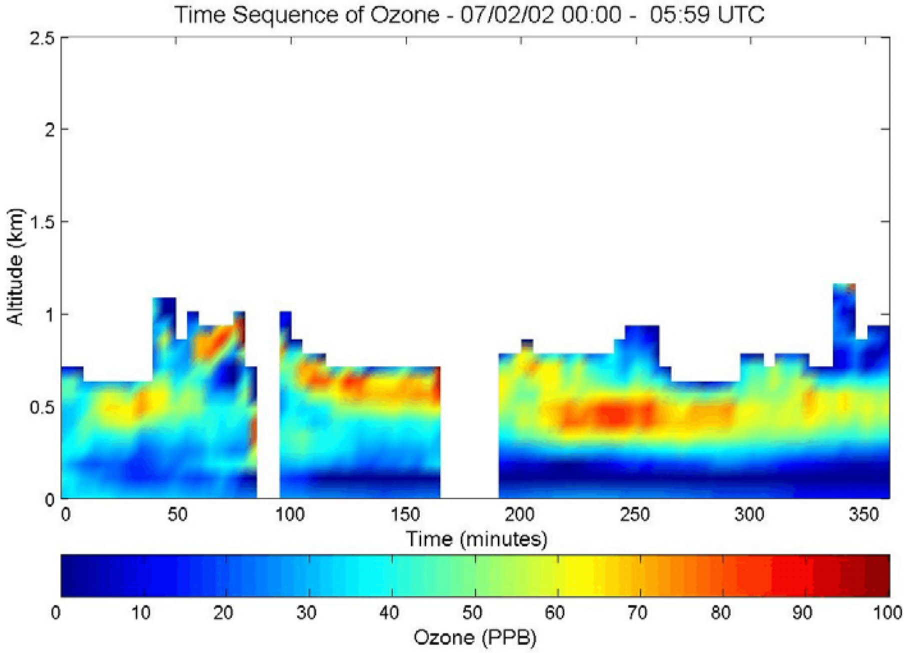


Figure 3-6. Lidar measurements of ozone on 2 July 2002 show the variation of ozone aloft during the night when it is carried into the region by transport that is augmented by the LLJ.

PART 4: CONTRIBUTIONS FROM MILLERSVILLE UNIVERSITY

Boundary Layer Meteorology Influences on Air Quality

Richard D. Clark
Department of Earth Sciences, Millersville University

1. Project Objectives

Millersville University's participation in NE-OPS-DEP includes intensive field measurements obtained from 29 June through 2 August 2002. In compliance with the Statements of Work submitted to Pennsylvania State University (PSU) under this contact, Millersville University (MU) provided a tethered balloon system, which was used to document the vertical and temporal variations in meteorological variables, ozone concentration, fine particle mass in the lower atmospheric boundary layer between the surface and 300 m AGL. In addition, MU provided surface measurements of meteorological variables, ozone concentration, and fine particle concentration (nephelometric technique), conducted a full suite of calibrations of all instruments, and provided a benchmark for inter-comparisons with the PSU Raman Lidar and Clarkson University measurements. The suite of surface instrumentation included a three-wavelength TSI nephelometer for total- and back-scattering coefficients, and API analyzers for measurement of CO, O_3, SO_2, and $NO/NO_2/NO_X$, and a laser-diode scatterometer for ground-truthing the PM measurements onboard the tethersonde system. MU also provided a complete set of back trajectories with which to study transport into the Philadelphia area. MU maintained 24/7 operations during several episodes.

The primary objective of NE-OPS-DEP was to continue the core activity begun in 1998 under NARSTO-NE-OPS to investigate the factors leading to high ozone, PM, and haze along the Northeast corridor. This activity was particularly valuable in 2002 because it was coordinated with intensive field operations at the Northeast Supersites in Baltimore, New York, and Pittsburgh and MANE-VU. Moreover, this study examined an additional summer of air pollution episodes, which are being used to broaden the database and help to put observed differences between the summers of 1999, 2001, and 2002 into context.

2. Summary of Key Measurements

Millersville University (MU) provided instruments and platforms to obtain the following key measurements in summer 2002:

Trace Gases:

1. MU deployed Advanced Pollution Instrumentation (API) analyzers and a complete suite of calibrators to measure CO, O_3, SO_2, and $NO/NO_2/NO_X$.
2. Aloft O_3 concentrations were obtained using the MU tethered atmospheric sounding system (TASS) to altitudes of 300 m AGL.

Particulates:

1. MU profiled PM between the surface and 300 m using an optical scattering instrument suspended on the 9 m^3 balloon.
2. MU deployed a three-wavelength nephelometer (TSI model 3563) to measure the total and back scatter coefficients at three wavelengths as a proxy for particle concentration and an intercomparison with the PSU Raman Lidar extinction coefficient measurements.
3. Integrated dry mass PM fine was obtained at the surface using Personal Environmental

Monitors (PEMs, SKC Inc.) This was part of an internal effort to try to speciate PM fine using dual-polarized microscopy.

Meteorological Variables:

Meteorological variables (ambient temperature, pressure, water vapor mixing ratio, wind speed and wind direction) were obtained as a function of height (300 m AGL) and time using the TASS.

Real-Time Regional and Synoptic Data Archive:

1. MU provided the real-time and archived data for the project, which included U.S. upper air data at 00 and 12 UTC; U.S. hourly surface station data; Initialization and forecast fields for both the Meso-Eta and RUC model data; Base reflectivity and velocity data from the Fort Dix WSR-88D radar; Visible and IR satellite imagery.
2. Derived back-trajectories at 500, 2000, and 5000m using the HYSPLIT processor.

3. Key Activities of Millersville University

MU provided a research team (PI-Clark plus four student research assistants), a mobile atmospheric/environmental lab, a tethered balloon sounding system, which included a full suite of instruments and sensors for aloft measurements, surface-based instruments to measure meteorological variables, trace gas concentrations, PM concentrations by proxy, and total and back scatter coefficients for the period from 29 June through 2 August at the Northeast Philadelphia Baxter Site (N 40° 03', W 75° 00'). The period was selected to run concurrently with the PM Supersite intensives in Baltimore, New York, and Pittsburgh, and MANE-VU in the Northeast.

Over the five-week period, MU obtained a total of 562 vertical profiles of the lower atmospheric boundary layer between the surface and 300 m using the TASS. Figure 4-1 shows the daily distribution of these profiles. Each profile consists of a record of temperature, pressure, derived altitude, relative humidity, derived specific humidity, wind speed, wind direction, ozone concentration, and PM concentration derived from measurements of scattering. The profiles were obtained with a temporal resolution of about 30 minutes, and a vertical (spatial) resolution of about 3 meters in altitude; an example of a typical vertical profile in shown in Figure 4-2. During episodes the TASS was operated continuously, daytime and nighttime, to capture the full evolution of the lower boundary layer. While the field project was underway, MU was archiving 00 UTC and 12 UTC upper air data, hourly surface station observations, Meso-Eta and RUC model initializations and forecasts fields, radar and satellite imagery, and back trajectories for the project duration. These data were used to put the Philadelphia measurements into a regional and synoptic context for a better understanding of the contributions from extended transport and source-receptor relationships. In addition, Meso-Eta model initial fields were downloaded on site and used with an application (Bufkit) to nowcasting and project forecasts. These archives are available to all investigators.

In addition to the aloft measurements, MU provided a suite of surface instruments to record one-minute averages of trace gases (CO, O_3, SO_2, and $NO/NO_2/NO_X$), and total and back scatter coefficients at three wavelengths (Figures 4-3 and 4-4) from 29 June through 6 August 2002. These measurements were used to provide a record of daily trace gas concentrations at the Baxter site, as well as to compare regional concentrations with DEP monitoring sites and to support the operations of the PSU and Clarkson groups.

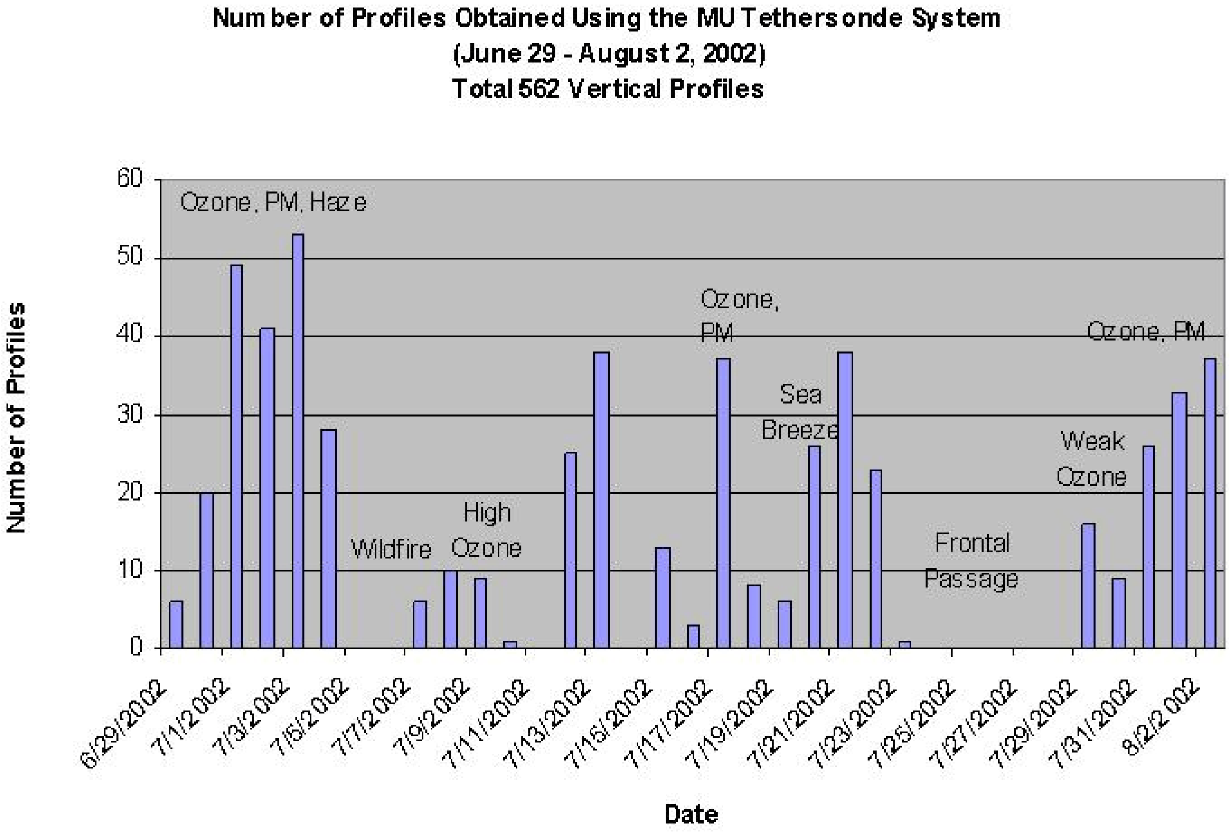


Figure 4-1. The number of vertical profiles performed per day using the MU-TASS

4. Key Findings and Conclusions

Table 4-1 summarizes the episodes documented during the summer NEOPS-DEP2002 field project. For each of these episodes, aloft and surface measurements obtained by MU were used to characterize the lower boundary layer. The event codes have been explained previously in Tables 3-2 and 3-3.

The typical mid-Atlantic daytime condition in summer in the absence of strong synoptic forcing is one of near-surface pressure gradients being established by differential heating generated by the land-water discontinuities, and enhanced by the slopes along the piedmont in the lee of the Appalachian Mountains. This boundary layer forcing produces significant baroclinicity in the lower troposphere that diminishes with height. The resulting pressure field is oriented parallel to and between the mountains and the coastline with a pressure gradient force vector directed toward the northwest, and a resulting southerly to southwesterly geostrophic wind decreasing with height (i.e. the thermal wind reverses and diminishes with height). Under these weak synoptic conditions, mixed layers can develop to thicknesses as much as 2 km (more typically around 1.5 km), sea breeze convergence zones strengthen and encroach inland, low level wind maxima establish around sunset and evolve overnight, and the Appalachian leeside trough intensifies by day and subsides at night. Under weak synoptic conditions the entire mid-Atlantic region, including the I-95 corridor, is strongly influenced by undulating local and regional (mesoscale) circulations.

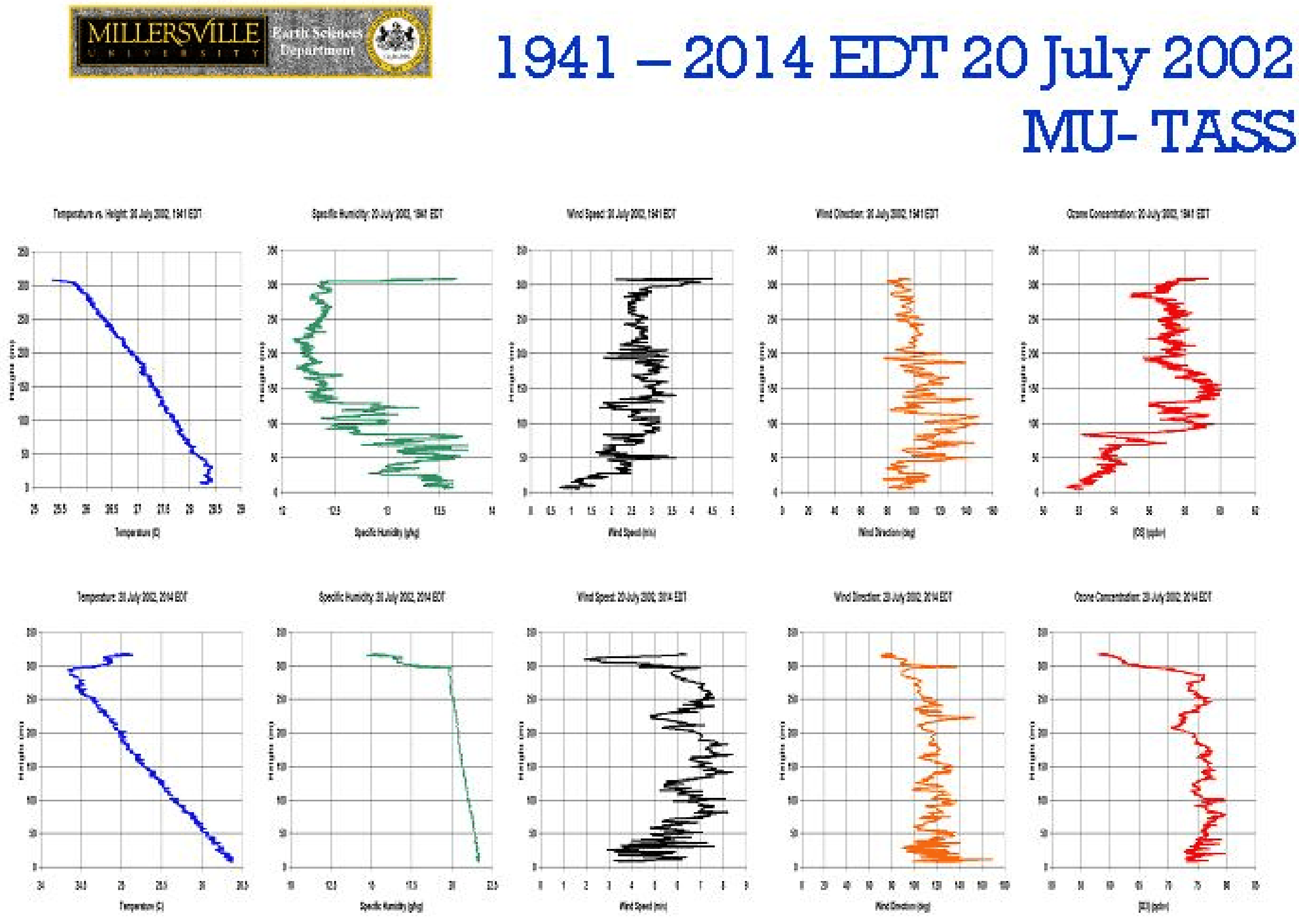

1941 – 2014 EDT 20 July 2002
MU- TASS

Figure 4-2. Example of measurements taken with sensors onboard the MU-TASS

20 July 2002
Surface Trace Gases

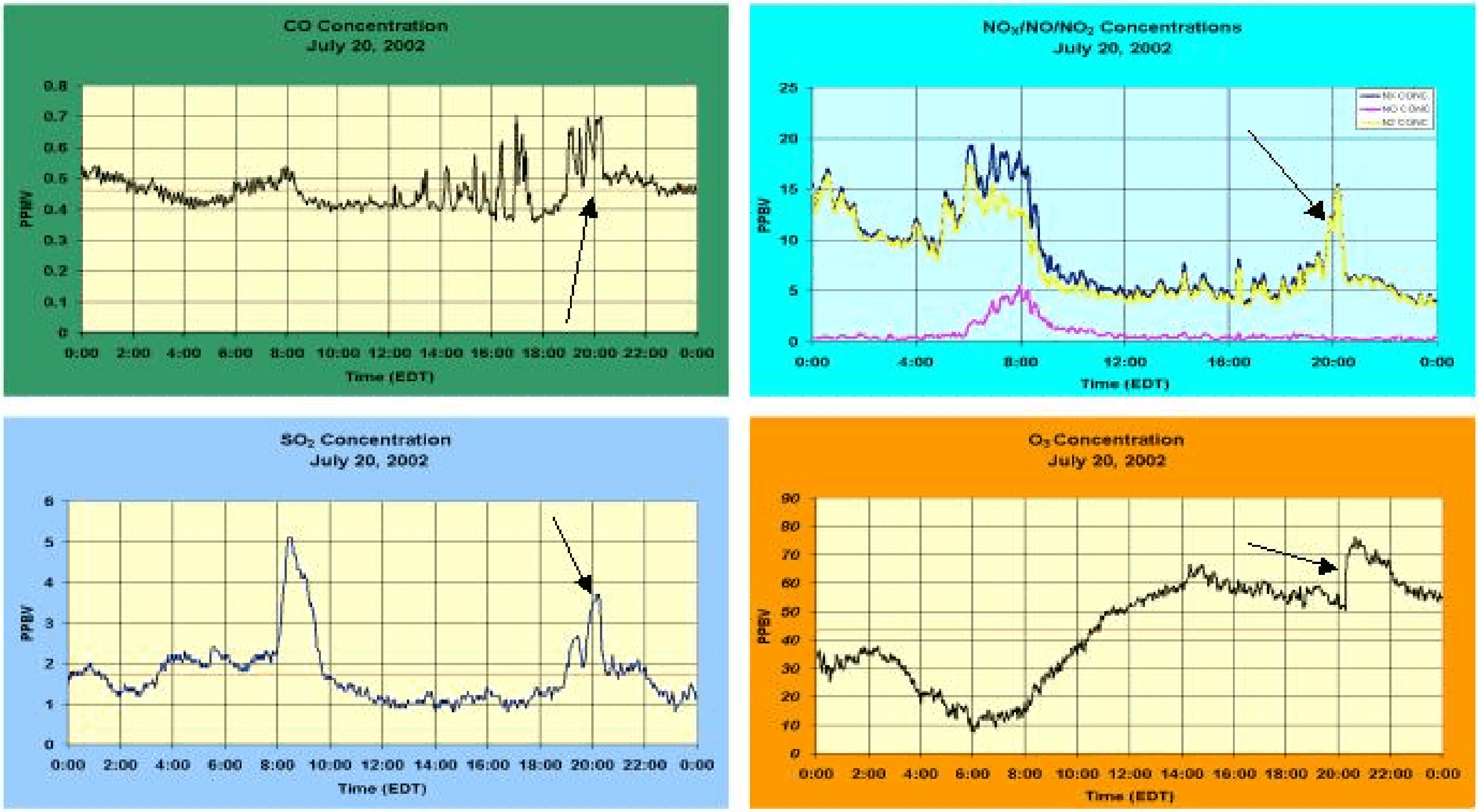


Figure 4-3. Examples of one-minute averages of trace gases measured by MU API Analyzers.

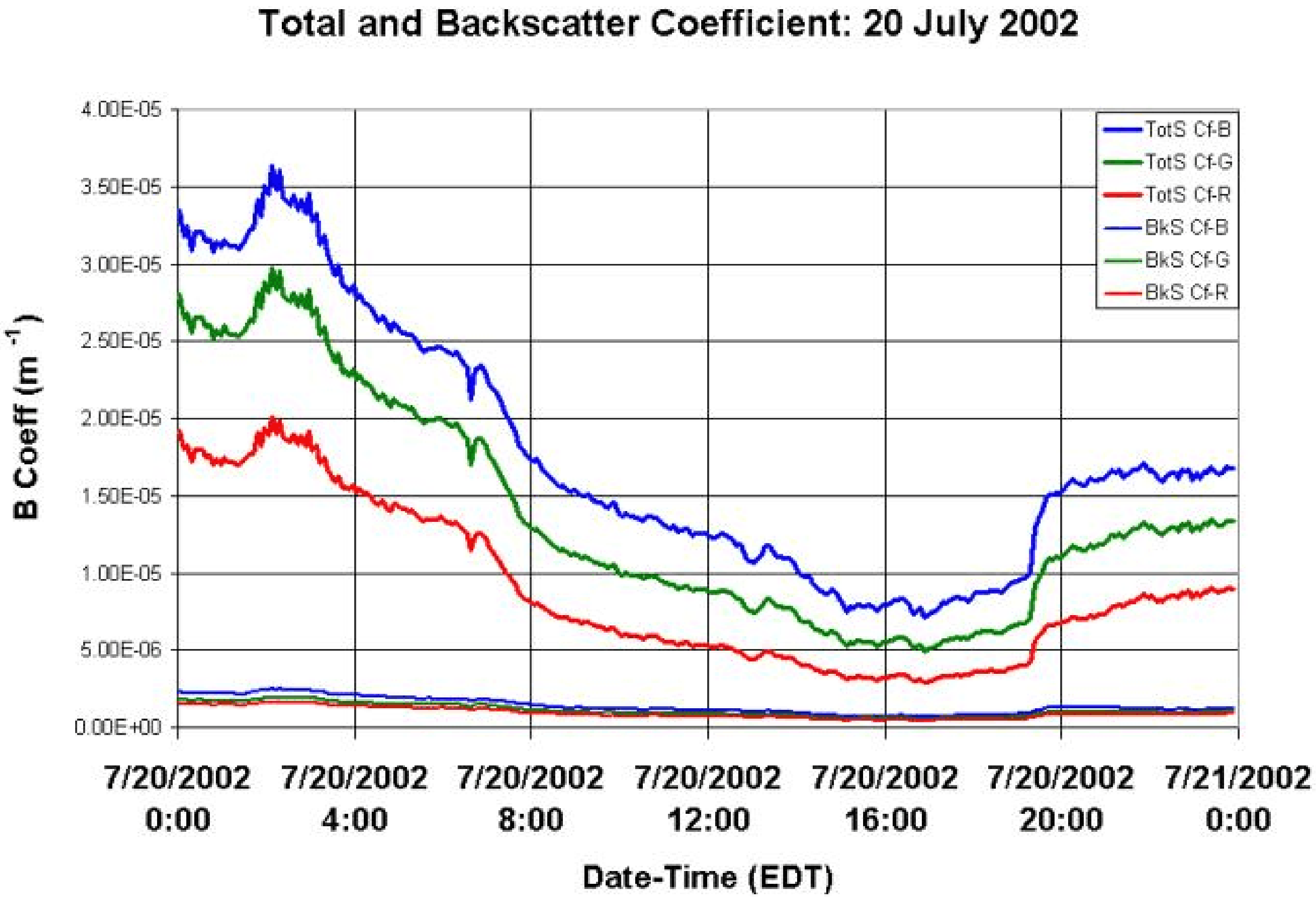
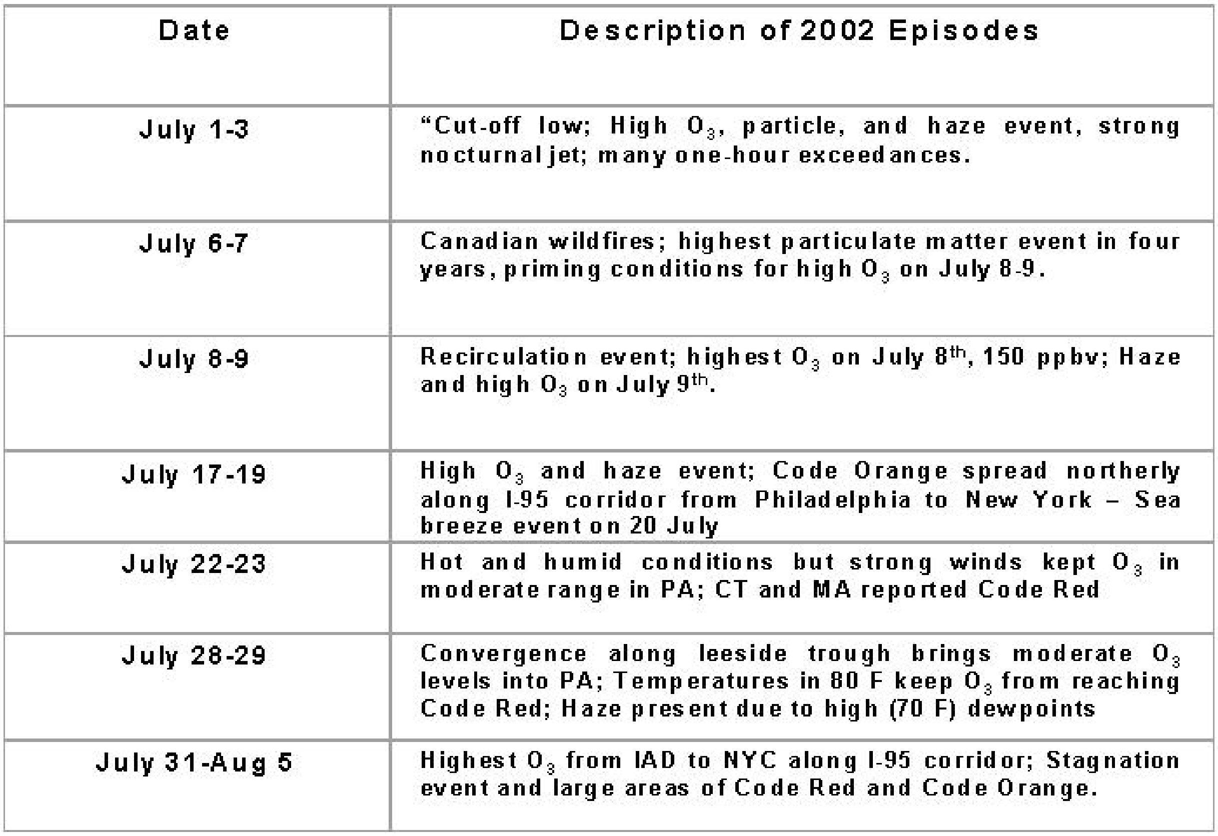


Figure 4-4. Example of one-minute averages of scatter coefficients obtained with the MU TSI Nephelometer.

Table 4-1. Summary of the 2002 Episodes



Date	Description of 2002 Episodes
July 1-3	"Cut-off low; High O_3, particle, and haze event, strong nocturnal jet; many one-hour exceedances.
July 6-7	Canadian wildfires; highest particulate matter event in four years, priming conditions for high O_3 on July 8-9.
July 8-9	Recirculation event; highest O_3 on July 8th, 150 ppbv; Haze and high O_3 on July 9th.
July 17-19	High O_3 and haze event; Code Orange spread northerly along I-95 corridor from Philadelphia to New York – Sea breeze event on 20 July
July 22-23	Hot and humid conditions but strong winds kept O_3 in moderate range in PA; CT and MA reported Code Red
July 28-29	Convergence along leeside trough brings moderate O_3 levels into PA; Temperatures in 80 F keep O_3 from reaching Code Red; Haze present due to high (70 F) dewpoints
July 31-Aug 5	Highest O_3 from IAD to NYC along I-95 corridor; Stagnation event and large areas of Code Red and Code Orange.

The influence of the sea breeze convergence zone on the air chemistry at the Philadelphia site was documented on three occasions in 2002. During the passage of a sea breeze front, ozone concentrations will generally decrease rapidly, often by a factor of two, while PM "wet" concentrations increase due to the activation of sub-micron aerosols to sizes that can be detected by laser-diode scatterometers in the moist air mass. Sea breezes are typically fumigation events, and their timing and subgrid-scale characteristics are still poorly modeled. Millersville University captured several strong sea breeze frontal passages in 1999 and 2002. Each was distinct from the other, and the consequences, were very difficult to predict even a short time before passage. While most sea breezes are considered beneficial to air quality in that they reduce the trace gas concentrations by replacing polluted urban air with cleaner maritime air, on one occasion (see Figs. 4-2 to 4-4 and note arrow at 2000 EDT), the sea breeze resulted in an increase in trace gas concentrations at the site. Analysis showed this event to be caused by a slight change in wind direction from ENE to ESE, but this was enough to modify the transport of air from a fetch along north-central NJ where the air was cleaner, to air being brought in from the Atlantic coastal region, where on this hot Saturday in July, the traffic due to weekend visits to the NJ and DE shores appears to be responsible for the deterioration in the quality of this air mass. The total change in wind direction was only about 20°, which resulted in a 2-fold increase in SO_2, 3-fold increase in NO_X, and a 50% increase in O_3 concentrations. More typical of the sea breeze front would be a decrease in these trace gas concentrations by similar amounts, accompanying 90° shifts in wind direction from southerly to easterly.

Another recurring feature of the summertime mesoscale environment along the northeast corridor is the nocturnal LLJ. Nocturnal low-level jets (LLJ) are known to transport significant quantities of precursors, pollutants, and particulates great distances, and contribute to increases in trace gas and particulate concentrations in areas where the local production may not have otherwise yielded exceedances. The tethersonde systems in conjunction with the lidar and wind profiler measurements provided a detailed characterization of the transport and subsequent mixing processes that were associated with LLJs. While there remain many uncertainties regarding the horizontal extent of the LLJ, delineation of the vertical structure based on the NE-OPS field experiment shows that the LLJ forms under clear sky conditions in the presence of a quasi-stationary anticyclone, which allows for a maximal amount of differential heating between the coast regions and the Appalachian leeside. LLJs forming over the mid-Atlantic are generally confined to a layer between 400-800 meters AGL, where they reside on top of the nocturnal inversion within the remnants of the previous day's convective mixed layer (residual layer). Within this "residual" layer, winds have been observed by the Philadelphia profiler to reach speeds approaching 15 m/s. Northeast LLJs, like their better-known Great Plains counterparts, are boundary-layer-forced low-level wind maxima, and as such, exhibit the distinctive inertial oscillation cause by the action of Coriolis force on the ageostrophic wind component. This characteristic rotation of the wind field is important to air chemistry because of its ability to change the trajectories of air parcels reaching the site from upstream locations. This is a persistent feature of the LLJ that is easily resolved in the EPA HYSPLIT back trajectories as well as in the wind profiler data obtained at the site. Both data sets are included as part of the NEOPS-DEP2002 database.

Under typical summertime conditions where the mid-Atlantic region is under the influence of the subtropical Bermuda High and the upper level dynamics are weak, i.e., nearly barotropic, a southerly to southwesterly LLJ will develop around sunset concurrent with the development of the surface nocturnal inversion and the cessation of turbulence. Over the nighttime period, the LLJ can transport a significant quantity of polluted air from Baltimore-Washington DC urban plumes north to northeastward along the I-95 corridor. By 0100-0400 local time, the wind field has undergone an inertial rotation to become more westerly such that upstream trajectories indicate the transport of ozone and precursors that are more characteristic of the western boundary. Measurements of water vapor content using the PSU lidar shows that this air is much drier than air originating from the south, partly because it is continental air, and partly because westerly flow will result in downsloping on the leeside of the Appalachians, where air can dry out during adiabatic descent (compression). Other findings associated with LLJ phenomena are the "bursting" events that occur in the early morning hours that result from mechanical (dynamical) instabilities in the shear zones below the layer of maximum winds. These bursting events vertically mix ozone to the surface even in the presence of thermal stability causing increases in ozone concentrations on the order of 20-30 ppbv in the absence of local production and solar insolation.

The rapid onset of mixing and the concurrent rapid rise in ozone was observed in a number of cases in both 1999 and 2002. Transport appears as a significant contributor to the high surface level ozone concentrations. The PSU lidar indicates as much as 80 ppbv ozone can be confined to the residual layer during nighttime periods, wind profiler measurements at the NEOPS site place the LLJ within the residual layer, and tethered balloon measurements document a very rapid mixing between the surface and the residual layer in the morning hours just after sunrise. Based on these episodic measurement periods, the conceptual model that follows suggests that as much as 30-50% of the surface level ozone could have been transported over the site by the LLJ and mixed down to the surface the following morning. The observed increase in ozone concentrations is too large to be accounted for on the basis of NO_X reactions alone (Kleinman). Moreover, in every case where > 100 ppbv ozone concentrations were observed, a LLJ was embedded in the nocturnal BL. The static stability of the nocturnal inversion prevents ozone from mixing to the surface at night, except during periodic "bursting events" that can occur when vertical wind shear brings creates short-lived pockets of mechanical instability and turbulence. Observations of surface ozone and its precursors reveal a sudden increase in ozone at times when production should be nonexistent (0200 – 0400 EDT), and an attendant increase in the ambient temperature as warmer air mixes down. These bursts signal the release of mechanical instability in the shear zone below the layer of maximum winds.

Combined measurements from the PSU lidar, wind profiler/RASS, and tethered balloon system provide a robust characterization of the effects of local and regional circulations on the trace gas and particulate matter concentrations at the Philadelphia site. These observations provide critical input for model validations attempting to simulate boundary layer growth and decay and the all-important transition periods, especially during the rapid development of the daytime mixed layer because of its relationship to the forecasts of ozone and $PM_{2.5}$. Numerous model validation experiments have been carried out using an initialization that leads to the development of a nocturnal jet. In fact, because of its conceptually straightforward dynamics relative to more complex meteorological phenomena, including the fact that the phase change of the aerosol can be ignored, observations of LLJs have been used to validate models such as the Penn State/NCAR MM5 and its predecessors since the early 1970s. MM5 has been a useful tool in predicting and diagnosing important features of LLJ, but still fail to resolve the details of momentum transport via turbulent fluxes and fall short of capturing the timing and intensity of the maximum winds. Moreover, between the paucity of aloft observations of the nocturnal wind field over the northeast, partly due to the sparseness of a suitable 915 MHz profiler network for these types of studies, and also because models can only approximately simulate the complex flows that are influenced by the convoluted terrain in the Appalachian leeside, the horizontal extent of the LLJ remains an area for study. The next generation mesoscale model, the Weather Research and Forecasting (WRF) modeling system, will soon replace the MM5 with improved physics and better parameterization schemes. WRF is currently undergoing testing by at a number of institutions, including Millersville University, and may be our best vehicle to predict features of the LLJ that are important to air quality.

Regardless of the modeling system, our understanding of the LLJ and other subgrid scale phenomena such as the sea breeze front, which can have a dramatic affect air quality in the northeast, will always be subject to the model resolution and the appropriateness of the BL parameterization to the problem at hand. Most important is the ability of the numerical system to handle the diffusion of momentum in stratified layers where shear is the dominant turbulence production mechanism, and to capture the timing and extent of the daytime mixed layer development. Recognizing that these are problems endemic to any modeling system, it would be advisable to begin to develop ensemble modeling of the LLJ and other local and regional circulations as is done in operational forecasting, allowing for an estimation of the quantitative uncertainty based on the ensemble. With models capable of being run on high-end and relatively low cost PCs, it would be prudent to consider establishing a WRF forecast for the region with partners from institutions running WRF.

PART 5: CONTRIBUTIONS FROM CLARKSON UNIVERSITY

Measurements of Real-Time $PM_{2.5}$ Mass, Sulfate, and Carbonaceous Aerosols

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Chemical species in $PM_{2.5}$ were measured in Philadelphia, Pennsylvania during July 2 to August 2, 2002. Continuous or semi-continuous concentrations of $PM_{2.5}$, organic carbon (OC), elemental carbon(EC), black carbon(BC), and sulfate were measured. Quartz filter samples were analyzed for filter-based OC/EC and sulfate. Sulfate concentrations were determined using a high-time resolution sulfate analyzer and ion chromatography (IC). BC concentrations were analyzed using a two-wavelength Aethalometer. Continuous $PM_{2.5}$ mass concentrations were obtained every ten minutes by using a 30^{o}C Tapered Element Oscillating Microbalance (TEOM) (Rupprecht and Patashnick, Albany, New York) with a sample equilibration system (SES) dryer. The 1400a TEOM was configured with a PM_{10} head, a $PM_{2.5}$ sharp cut cyclone (SCC), a sample equilibration system (SES) dryer, and a tapered element oscillating microbalance, which directly measures particle mass collected on a filter by drawing ambient air through a filter at a constant flow rate, while continuously weighing the filter and calculating rolling ten-minute smoothed mass concentrations. The SES is designed to reduce the possibility of PM mass concentrations being overestimated due to the moisture affinity of some types of particles. Also, the SES allows the mass collected on the filter to equilibrate more rapidly than when in the presence of high humidity levels. Thus, the TEOM monitor operating at 30°C reduces the loss of semi-volatile organic compounds (SVOCs) in $PM_{2.5}$.

Carbonaceous materials in $PM_{2.5}$ were measured by using three analyzers, a semi-continuous OC/EC field instrument (Sunset Laboratory, Forest Grove, Oregon, USA), a thermal-optical OC/EC laboratory instrument (Sunset Laboratory, Forest Grove, Oregon, USA), and a two-wave-length Aethalometer (Magee Scientific, Berkeley, California, USA). The semi-continuous OC/EC field instrument is based on the National Institute for Occupational Safety and Health (NIOSH) Method 5040. The light transmittance monitored by the laser beam through filters was used for determining a split point that elemental carbon formed by pyrolysis from the elemental carbon that was originally in the sample. To reduce uncertainties due to low concentration of elemental carbon, samples for the field OC/EC instrument were collected for 105 minutes and were analyzed for 15 minutes every two hours. The FID response of the Sunset lab OCEC instrument was calibrated with micropipette deposits on sample filters of sucrose solution after every third analysis to reduce the variability.

High time resolution black carbon (BC) concentrations were measured by using a two-wavelength Aethalometer (AE-20, Magee Scientific, Berkeley, California, USA) during the measurement periods. Aerosol BC was measured using the Aethalometer with the optical attenuation method since BC can strongly absorb light over a broad region of the near infrared (λ = 880 nm), and BC mass was obtained by determining the attenuation of light transmitted through a sample filter. The specific attenuation coefficient (σ) is a critical parameter to convert attenuation measurements to BC mass concentrations and manufacturer's value is 16.6 m^2 g^{-1}. The two-wavelength Aethalometer has another wavelength beam (λ = 370 nm) to identify the presence of certain organic compounds such as polycyclic aromatic hydrocarbons (PAH) which strongly absorb UV wavelengths.

Five-minute averaged continuous sulfate concentrations were measured using a continuous sulfate analyzer originally designed by Harvard School of Public Health (HSPH) and built at Clarkson University. The continuous sulfate analyzer consists of three main parts, a sample pretreatment system to segregate $PM_{2.5}$ using a VSCC, and then a sodium carbonate coated denuder is used to remove positive and negative interferences such as SO_2, and the NOx is removed using a carbon monolith. A heated stainless steel tube which reduces the particulate sulfate to SO_2 was operated at around 700 °C. The converted SO_2 gas was introduced into an SO_2 analyzer (43C-TLS, Thermo Environmental Instruments Inc, Franklin, Massachusetts, USA). To quantify background concentrations, a zero purge system periodically supplied particle free air to the furnace and the readings were used to determine the background concentration at that time.

1. *Continuous and semi-continuous $PM_{2.5}$ measurement and analysis*

The variations of $PM_{2.5}$, semi-continuous OC/EC, and continuous sulfate concentrations measured in Philadelphia are shown in Figure 5-1. Note that the periods corresponding to a malfunction of the continuous sulfate analyzer from July 2-5 and the unusual Canadian forest fire episode observed in Philadelphia during July 6-9, 2002 were excluded from Figure 5-1. In Philadelphia, the highest $PM_{2.5}$ was observed around 3 PM on July 19 with a mean of 93 µg m^{-3}, see Figure 5-1. Several high peaks, which were strongly correlated with higher sulfate concentrations, have been associated with severe summer haze, when the maximum sulfate concentration (52 µg m^{-3}) and the highest $PM_{2.5}$ concentrations were observed. The haze episodes corresponded to periods when the $PM_{2.5}$ aerosol in Philadelphia contains an increased average mass fraction of sulfate. In contrast to the sulfate results, there was no significant correlation between OC and haze episodes. The higher OC levels with a mean of 10 µg m^{-3} were observed on July 17 and 18 while the highest EC occurred at 7 a.m. July 17 with a mean of 2.3 µg m^{-3}. However, the residuals between the total $PM_{2.5}$ and the sum of three chemical species increased during the haze associated with high $PM_{2.5}$ mass concentrations at the site. The differences probably indicate that the organic mass (OM), obtained by multiplying the measured OC concentrations by the typical value of 1.4, significantly increased during the haze episode. These results are consistent with the presence of increased concentrations of secondary organic aerosols (SOA).

The daily average measurements mass concentrations and standard errors of $PM_{2.5}$, semi-continuous carbonaceous species, BC, and continuous sulfate concentrations measured in Philadelphia are presented in Table 5-1. OC accounted for 21% of the mass concentration of $PM_{2.5}$ while sulfate accounted for 37 %, which is primarily due to the frequent haze episodes in Philadelphia. During the most severe haze period July 17 to July 19, 2002, sulfate concentrations ranged from 5 to 32 µg m^{-3} with a mean of 20 µg m^{-3}. By comparison, the mean sulfate concentration during the study period, excepting this large haze episode, ranged from 2 to 16 µg m^{-3} with a mean of 7 µg m^{-3}, which is only 35% of the mean concentration during the haze episode. In Philadelphia, sulfate was most dominant chemical component, among the four measured species, in the $PM_{2.5}$.

The average EC concentrations were relatively very low and only accounted for less than 2% of the $PM_{2.5}$ mass concentration. The concentrations of Aethalometer BC using manufacturer absorption efficient, 16.6 m^2 g^{-1} ranged from 0.1 to 3.1 µg m^{-3}. The highest peak of BC was observed at 3 AM July 17 when $PM_{2.5}$ was only 14 µg m^{-3}. During the haze episodes BC values were only weakly correlated with $PM_{2.5}$ or sulfate values.

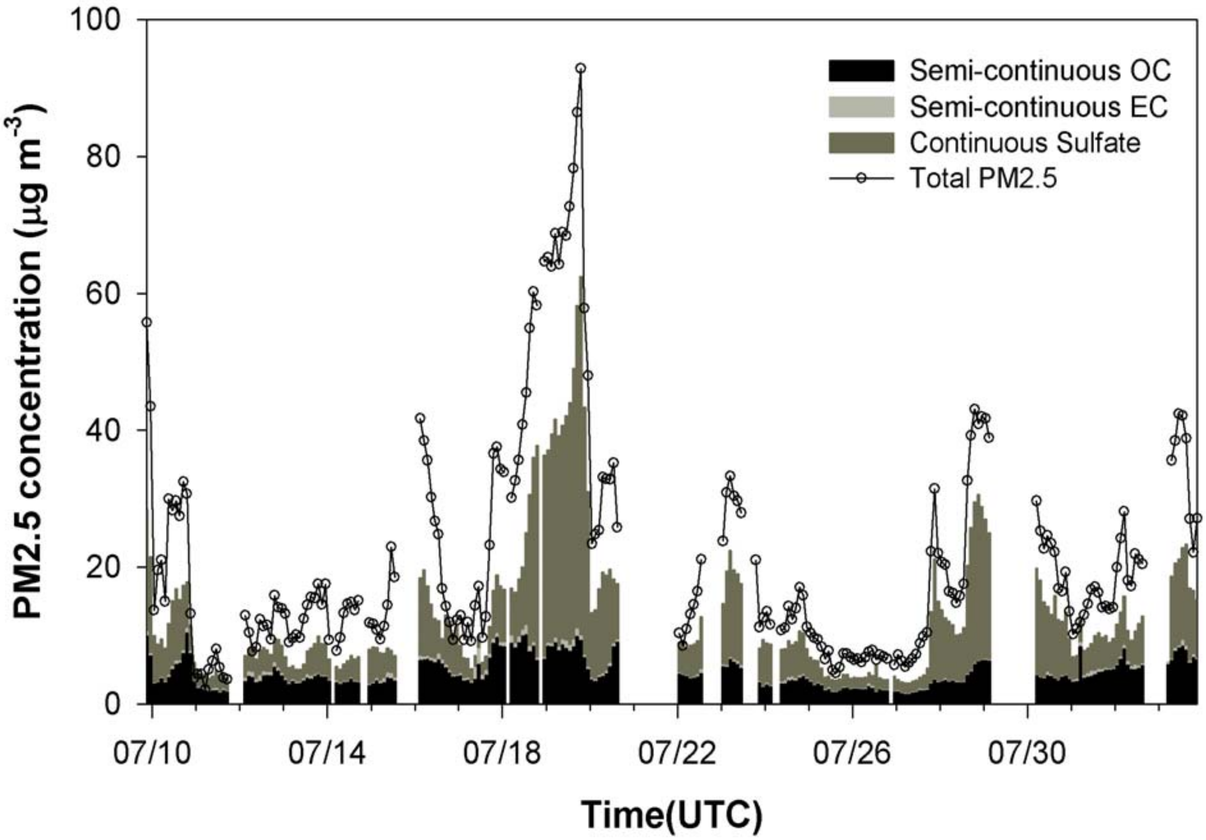

Figure 5-1. Two-hourly variations of the chemical compositions of PM2.5 measured in Philadelphia, PA during the summer of 2002.

Table 5-1. Statistical values of total $PM_{2.5}$, semi-continuous carbonaceous $PM_{2.5}$, continuous sulfate concentrations in Philadelphia, PA.

Measurement period	**7/10 - 8/2/2002**
$PM_{2.5}$ (μg m $^{-3}$)	22.1 ± 1.0
OC (μg m^{-3})	4.7 ± 0.1
EC (μg m^{-3})	0.3 ± 0.02
BC (μg m^{-3})	0.6 ± 0.03
Sulfate (μg m^{-3})	8.1 ± 0.6
Valid sample number	238

2. *Variations of carbonaceous compound concentrations.*

Diurnal variations of OC and EC are shown in Figure 5-2. Although EC concentrations were relatively lower than OC, the observed pattern clearly supports the conclusion that EC concentrations were strongly correlated with morning rush-hour period between 7 AM and 9 AM local time. The morning peak is due to motor vehicle emissions accumulated within the thin morning boundary layer (typically 300-500 m), which results in a smaller mixing volume, and during generally calm conditions, which limit horizontal transport and diffusion. The evening rush-hour peaks between 5 PM and 7 PM local time were relatively weak. It is likely that particulate matter is more highly dispersed during that time of day since mixing layer height in summer is typically maximum (2-3 km) from 3 PM to 5 PM local time. In contrast to EC, there was no clear pattern of OC concentrations as a function of time of day. It is expected that sources of OC are less related to traffic sources, and are linked with a variety of stationary sources and with processes of formation of secondary organic aerosol(SOA) during the afternoon.

Diurnal variations of BC obtained during weekdays and weekends are shown in Figure 5-3. The peak values were observed during the morning rush-hour with the highest concentration near 6 AM local time on weekdays. There was no significant diurnal variation of BC during weekends. The variations of BC are strongly correlated with motor vehicles and the mixing volume of the morning boundary layer, similar to the EC concentration variations. The mean BC during weekdays ranged from 0.1 to 2.4 µg m^{-3} and the mean was a factor of about 3 times higher than the mean BC during weekends.

3. *Comparison of $PM_{2.5}$ mass and chemical species*

Correlations between $PM_{2.5}$ mass concentrations measured using a 30°C TEOM with SES, filter-based sulfate, semi-continuous carbonaceous compounds, and an Aethalometer for BC are summarized in Table 5-2. Each two hour integrated carbonaceous aerosol concentration and one hour average Aethalometer BC were compared with $PM_{2.5}$ during the same period. Also, the sulfate concentrations were compared with the $PM_{2.5}$ as twenty four-hour integrated averages during the study period (thus many fewer pairs in Table 5-2). Results of a major Canadian forest fire aerosol episode from July 6 to 9 were excluded because unusual values were observed. Table 5-2 shows that TC and OC concentrations were better correlated with $PM_{2.5}$ mass concentrations ($r^2 = 0.62$, slope = 0.1) than were the EC concentrations. Aethalometer BC concentrations were only poorly correlated with the $PM_{2.5}$ mass concentrations. The best correlation was found between $PM_{2.5}$ mass and filter-based sulfate concentrations ($r^2 = 0.96$). The correlations between real-time $PM_{2.5}$ mass concentrations and continuous sulfate concentrations are shown in Figure 5-4 ($r^2 = 0.88$). These results further demonstrate that the formation of sulfate from photochemical reactions of SO_2 cause the dramatic increases of $PM_{2.5}$ mass in the region.

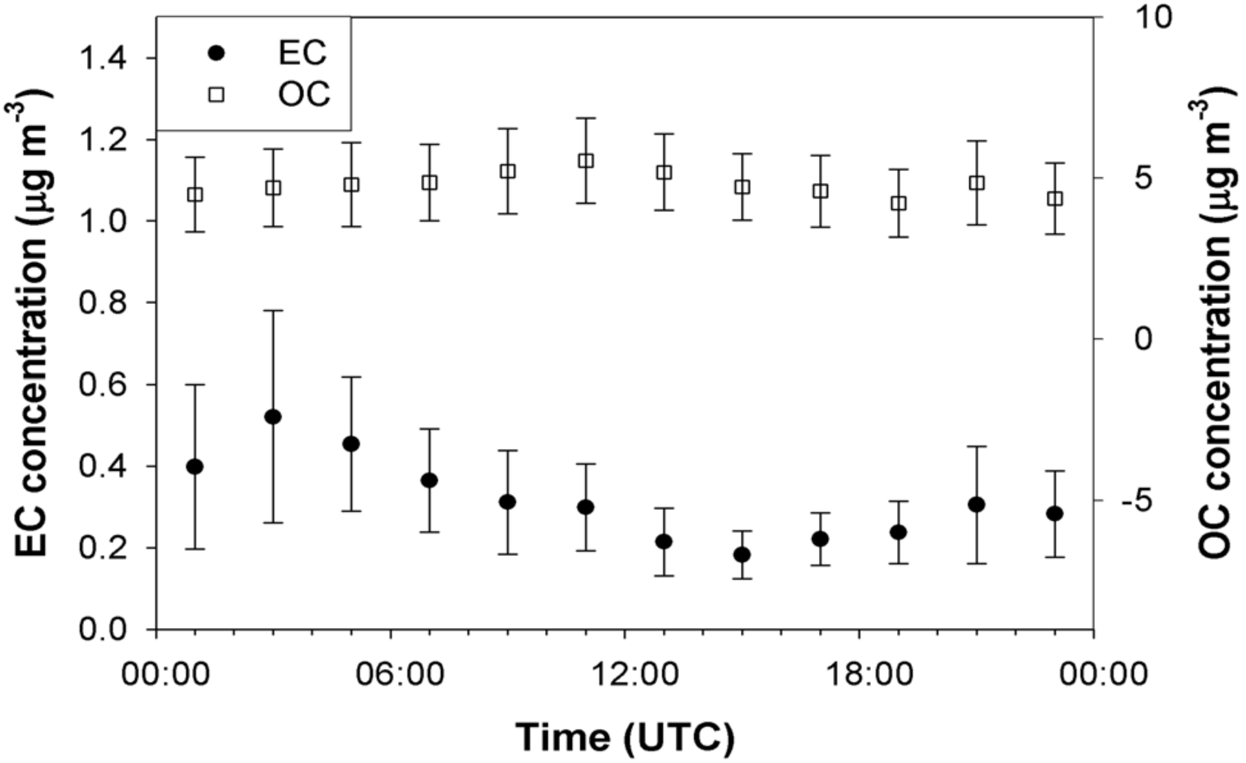

Figure 5-2. Temporal variations of semi-continuous OC and EC measured in Philadelphia, PA during the summer of 2002.

Table 5-2. Statistical summary of correlation between $PM_{2.5}$ mass and semi-continuous OC, EC, Aethalometer BC, and filter-based sulfate measurements in Philadelphia, PA.

		Slope (±SE) + intercept(± SE)	**Correlation (r^2)**	**Number of Pairs**
$PM_{2.5}$	**TC**	0.11(±0.01)+ 2.63(±0.15)	0.62	238
	OC	0.10(±0.01)+ 2.43(±0.14)	0.63	238
	EC	0.01(±0.00)+ 0.20(± 0.03)	0.13	238
	BC	0.02(±0.00)+ 0.27(±0.02)	0.36	519
	SO_4^{2-}	0.51(±0.03)- 2.49(±0.69)	0.96	24

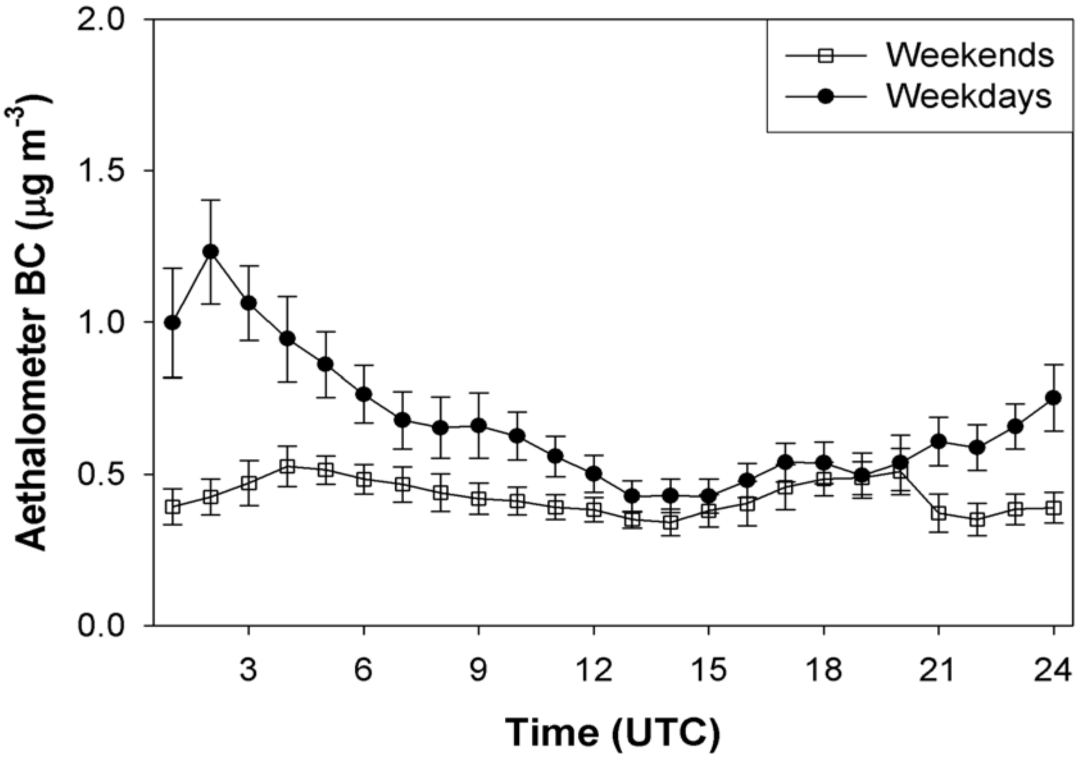

Figure 5-3. Diurnal variations of black carbon (BC) measured using a two-wavelength Aethalometer in Philadelphia, PA during the measurement period July 10 to August 2, 2002.

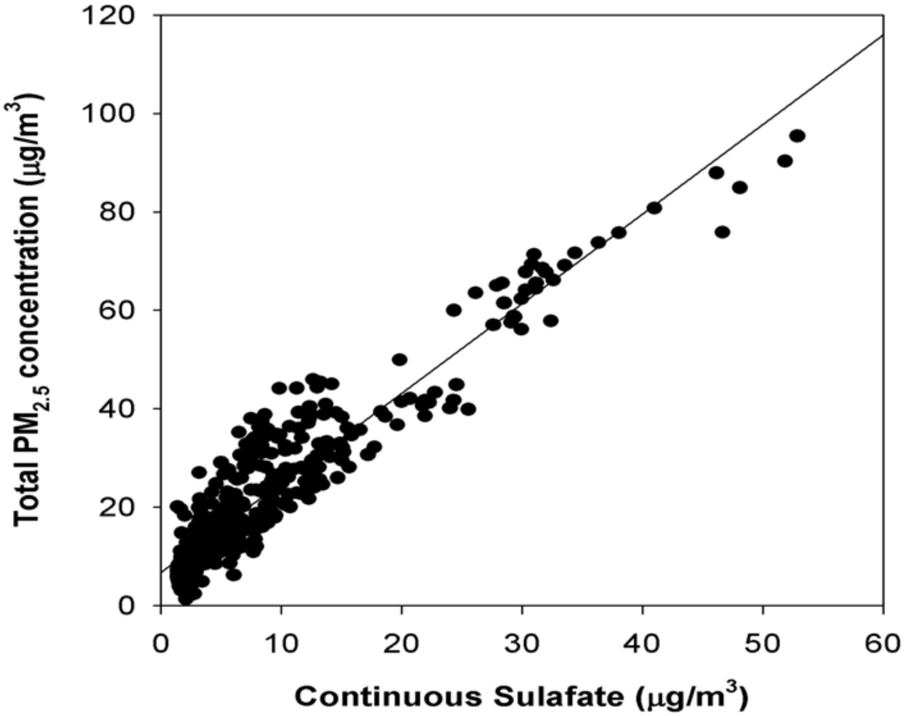

Figure 5-4. Correlation between real-time $PM_{2.5}$ concentrations and sulfate concentrations measured using a continuous sulfate analyzer.

4. *Influence of Canadian forest fire*

A Canadian forest fire started on July 2 and severe smoke was transported to the monitoring site in Philadelphia during the period from July 6 to July 9, 2002. Table 5-3 shows statistical summary of real-time $PM_{2.5}$ mass and carbonaceous species measured in Philadelphia during the Canadian forest fire episode. $PM_{2.5}$ concentrations ranged from 12 to 164 µg m^{-3} with a mean of 79.8 µg $^{-3}$. The highest $PM_{2.5}$ mass concentration was observed around midnight on July 7, 2002 (local time). The mean $PM_{2.5}$ value during the forest fire was approximately 4 times higher than the mean during the rest of the measurement period July 1 to August 2. The highest OC and EC concentrations were observed around midnight July 7 and around 9 AM on July 8, respectively. Compared with the normal ambient conditions, the OC and EC increased dramatically by factors of 7 and 9, respectively. On average, the $OC/PM_{2.5}$ ratio for the forest episode was 0.38 while the $EC/PM_{2.5}$ ratio was 0.028. The TC fraction of $PM_{2.5}$ mass showed a 10% increase with a mean ratio of 0.42. For the Aethalometer BC, the $BC/PM_{2.5}$ ratio was 0.029 and the mean concentration was approximately 4 times higher than the mean observed during normal days. The highest concentration of BC was observed on the morning of July 7 with a value near 8.0 µg m^{-3}.

In addition, EC and Aethalometer BC tended to be poorly correlated with $PM_{2.5}$, whereas OC showed a strong correlation ($r^2 = 0.95$). Note that average correlation coefficient between $PM_{2.5}$ and OC measured during normal days was 0.63. During the fire event, it has been found that the correlation coefficient of Aethalometer BC ($r^2 = 0.14$) was significantly lower than the coefficient of EC ($r^2 = 0.58$). It suggests that OC was more likely to be transported from the Canadian forest fire site, and Aethalometer BC tended to be poorly correlated with EC during the fire event.

There were two severe haze episodes, July 1 to 4 and July 17 to 19. The correlation between Philadelphia measurements of semi-continuous EC and Aethalometer BC (BC_A) during the two severe haze events is compared with measurements during the Canadian forest fire episode in Figure 5-5. During the haze event days, the slope of EC versus Aethalometer BC is 3.69 ± 035 with a high correlation ($r^2 = 0.66$). The BC_A concentrations were typically larger than EC concentrations. However, during the forest fire event, the correlation between EC and BC_A dramatically changed. On the afternoon of July 7, the slope changed from 3.07 to 0.35 while the correlation coefficient decreased slightly ($r^2 = 0.59$). The dramatic change of the proportionality between semi-continuous EC and Aethalometer BC during the Canadian forest fire shows clearly that a change occurred in the attenuation coefficient that was due to the different origin and properties of the BC aerosols.

As previously described, the AE-20 Aethalometer measurers at two-wavelengths, 880 nm and 370 nm, to provide the near UV wavelength for identifying the presence of UV absorbing organic compounds (BC_{UV}), such as polycyclic aromatic hydrocarbons (PAH). The presence of such compounds can be detected even if the values of components measured using this second wavelength cannot be quantified as mass concentrations. The levels of BC_{UV} were typically less than or similar to the BC_A concentrations during the normal measurement periods. However, as shown in the Figure 5-6, the UV absorbing organic compound concentration increased significantly to become much larger than BC_A concentrations during the fire episode period. It can be anticipated that the one of the most abundant UV absorbing organic species were PAHs since burning of wood emits this species along with various other hydrocarbons. Thus, the instrument does respond to UV absorbing species and provides information that the mixture of sources of black carbon have changed.

Table 5-3. Statistical summary of real-time $PM_{2.5}$, semi-continuous OC and EC, continuous Aethalometer BC in Philadelphia during the Canadian forest fire, July 6 to July 9, 2002.

	$PM_{2.5}$ (μg m^{-3})	**Organic Carbon (μg m^{-3})**	**Elemental Carbon (μg m^{-3})**	**Black Carbon (μg m^{-3})**
Mean	79.8	30.6	2.9	2.3
Standard Deviation	36.2	16.2	1.6	1.5
Standard Error	4.0	2.5	0.2	0.2
Minimum	12.0	3.1	0.1	0.3
Maximum	164.0	67.1	6.2	8.0
Valid number	82	41	41	82

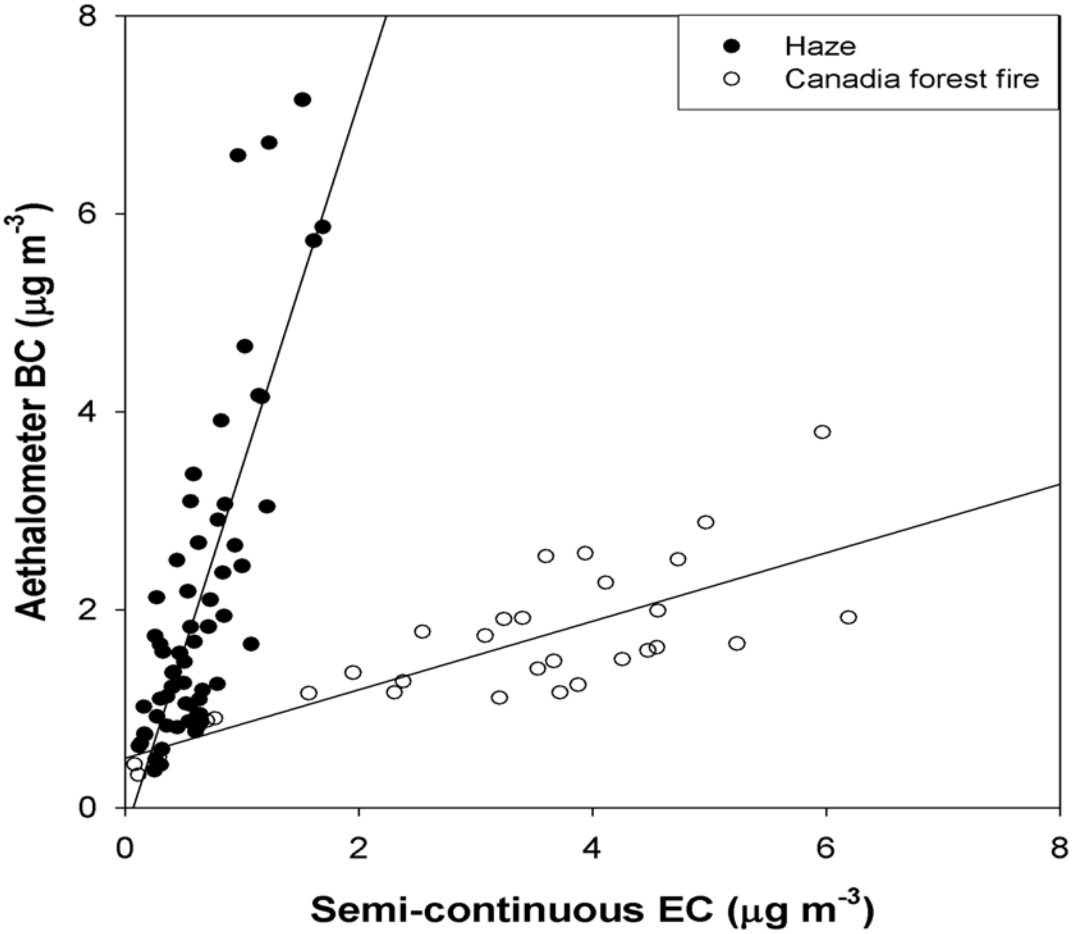

Figure 5-5. Correlation between black carbon measured using the Aethalometer and elemental carbon measured the Sunset lab OC/EC analyzer during the severe haze episodes and the Canadian forest fire episode in Philadelphia, PA.

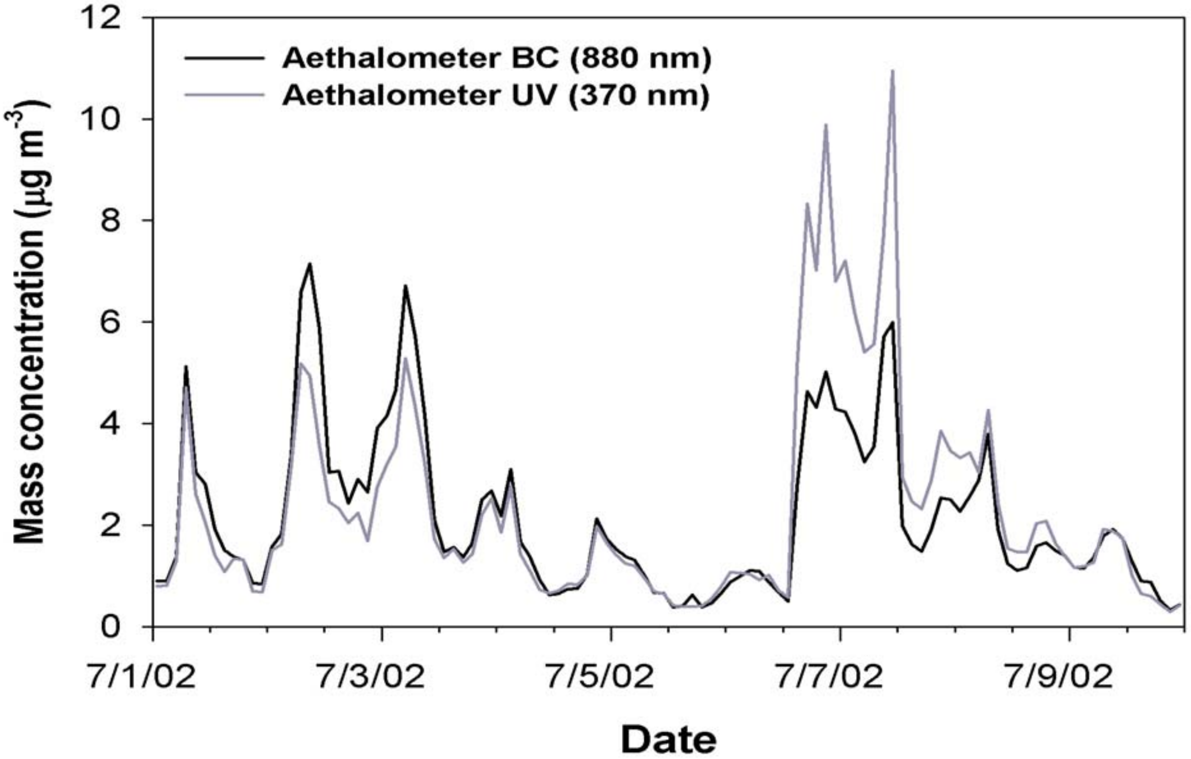

Figure 5-6. Black carbon measured at 880 nm compared with measurement at 370 nm shows the additional signal due to ultraviolet absorbing organic matter during the Canadian forest fires.

5. *Comparison of daily filter-based samples*

Daily variations of quartz filter-based concentrations of OC, EC, and sulfate and the twenty four-hour average $PM_{2.5}$ mass concentrations measured using the 30 °C TEOM with SES are shown in Figure 5-7. In contrast to the semi-continuous measurement result, the filter-based sulfate concentrations collected during July 2 to 5 and the filter-based OC and EC obtained in Philadelphia during the Canadian forest fire period, July 6 to July 9, 2002 were included in the result.

OC, EC and sulfate in Philadelphia accounted for 55 %, 8 %, and 25 % of the $PM_{2.5}$ concentration. As shown in the bottom of Figure 5-7, the highest 24-hour average $PM_{2.5}$ was observed on July 7 with a mean of 107.3 µg m^{-3} and the average $PM_{2.5}$ during the two days, July 7 and 8 exceeded the twenty-four hour average $PM_{2.5}$ standard, 65 µg m^{-3}. In addition, during the severe haze episode on July 19, the sulfate concentrations dramatically increased from 22% to 51% of $PM_{2.5}$ mass. Furthermore, OC concentrations dramatically increased during the Canadian forest fire, and the high mass fraction of OC in Philadelphia was influenced by the forest fire episode. The ratio of sums of three species, OC, EC, and sulfate to $PM_{2.5}$ mass concentrations ranged from 0.65 to 1.70 with a mean of 0.99. The sum tends to exceed to the $PM_{2.5}$ when $PM_{2.5}$ concentration was relatively low. The excess mass above $PM_{2.5}$ concentrations measured using the 30^{o}C TEOM with SES was probably influenced by the positive interference of SVOCs. The particulate organic mass should be included to obtain actual species contribution to $PM_{2.5}$ mass concentration, and it can be estimated by multiplying the mass of OC by a factor of 1.2 ~ 2.1. The remainder of the $PM_{2.5}$ mass, when compared with the sum of three measured components, is likely to be nitrate and crustal material.

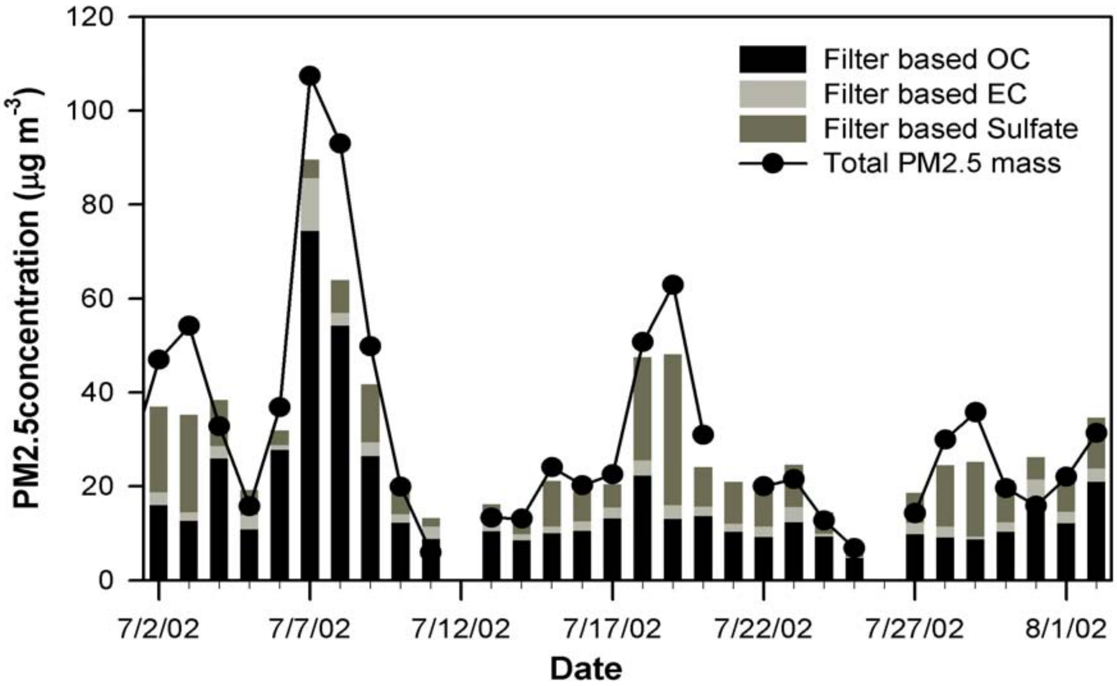

Figure 5-7. Temporal variations of filter-based measurements of organic carbon (OC), elemental carbon (EC), sulfate and daily averaged $PM_{2.5}$ mass concentrations in Philadelphia, PA.

6. *Potential Source Contribution Function Analysis*

Potential Source Contribution Function (PSCF) analysis combines particle data with air parcel back trajectories to identify potential source areas and the preferred pathways that give rise to the observed high particle concentrations [Zeng, Y, and Hopke, P.K., Atmospheric Environment, **1989**, *23*, 1499-1509; Cheng, M.D., Hopke, P.K., Zeng, Y., J. Geophys. Res.-Atmosphere **1993**, *98*, 16839-16849]. Five day back trajectories arriving twelve times in a day at 500 m above the ground level were calculated using the NOAA HYSPLIT model [Draxler, R.R. and G.D. Hess, 1998, An Overview of the Hysplit_4 Modeling System for Trajectories, Dispersion, and Deposition, Aust. Met. Mag., 47, 295-308]. The vertically mixed model starting at 500 m above the ground level was used to calculate the five-day backward trajectories arriving at the mid-point of the two-hour integration period..

Using the particle data consisting of $PM_{2.5}$, b_{scat}, OC, EC, and sulfate described in the prior section, PSCF analyses were performed based on the average values as a criterion for the measured particle parameters. This procedure has been described in a number of prior publications [e.g., Cheng, M.-D., Hopke, P.K., Barrie, L.; Rippe, A., Olson, M., Landsberger, S., *Environ. Sci. Technol.* **1993**, *27*, 2063-2071; Hopke, P.K., Barrie, L.A., Li, S.-M., Cheng, M.-D., Li, C., Xie, Y., J. Geophys. Res., **1995**, *100*, 16595-16603] and the details of the calculation are omitted here, for more information see Polissar et al. [*Environ. Sci. Technol.* **2001**, *35*, 4214-4226]. Air parcel back trajectories are related to the composition of collected material by matching the time of arrival of each trajectory at the receptor site to the sampling time interval. The PSCF value for a single grid cell is calculated by counting the trajectory segment endpoints that terminate within that grid cell. The movement of an air parcel is described as segment end points of coordinates in terms of latitude and longitude.

Five-day backward trajectories starting at the height of 500 m above the ground level were computed every hour producing 120 endpoints per sample. The geophysical region covered by the trajectories was divided into 2664 grid cells of 1° × 1° latitude and longitude so that there are approximately 42051 end points / 2664 cells or 16 trajectory end points per cell in average. In PSCF analysis, it is likely that the small values of n_{ij} produce high PSCF values with high uncertainties. In order to minimize this artifact, an weight function $W(n_{ij})$ was applied when the number of the end points per a particular cell was less than about three times the average values of the end points per cell [Polissar *et al.*, 2001].

$$W(n_{ij}) = \begin{cases} 1.0 & 48 < n_{ij} \\ 0.7 & 5 < n_{ij} \leq 48 \\ 0.4 & 2 < n_{ij} \leq 5 \\ 0.2 & 2 \leq n_{ij} \end{cases}$$

Results

The PSCF results are displayed in the form of maps of the area of interest on which the PSCF values are displayed in terms of a color scale, see Figures 5-8 through 5-12. The PSCF map for sulfate (Figure 5-8) shows influence of Midwestern coal-fired power plants in Ohio River Valley. Areas of peak influence are located in the western end of the river valley in southern Indiana and Illinois and northern Kentucky. This area of peak influence is about the same distance from Philadelphia as the upper Ohio River Valley, areas are from Underhill, VT where they were found to have high influence [Polissar, A.V., Hopke, P.K., Poirot, R.L., *Environ. Sci. Technol.* **2001**, 35, 4604-4621]. Such behavior suggests that there are competitive processes between the chemical conversion of $SO_2 \rightarrow SO_4$ resulting in particle formation and dispersion and deposition of sulfur in transit. The area of potential influence includes the area around southern Lake Michigan and across northern Illinois.

Figure 5-9 shows that $PM_{2.5}$ has a similar pattern with more trailing of the area of influence into the Gulf of Mexico. This additional area may represent the increased influence of humidity on $PM_{2.5}$ mass. In the summer, it is unlikely that the nafion drier is fully drying the particles [Stanier, C., Khlystov, A.Y., Chan, W.R., Mandiro, M., Pandis, S.N., *Aerosol Sci. Technol.* 2003, in press]. The conversion of $SO_2 \rightarrow SO_4$ results in the formation of NH_4HSO_4 that is difficult to dewater. There is also a small area of high potential to the east of the southern end of Hudson’s Bay. This area will be discussed subsequently along with the OC and EC maps.

The PSCF map for B_{scat} in Figure 5-10 shows an even greater influence of the Gulf of Mexico potentially indicating an even greater effect of humidity on the measurements. There is no area in the vicinity of Hudson’s Bay corresponding to the area in that appears in the $PM_{2.5}$ map. OC and EC (see Figures 5-11 and 5-12) have the largest areas in the region to the east of Hudson’s Bay. Beginning on July 2, there was a large boreal forest fire in this area. A cold front brought this material down into the mid-Atlantic region beginning on July 6. Its influence lasted from July 6 to 10 and the PSCF analysis clearly identified the fire’s location. The lack of data during this interval may be responsible for the lack of an apparent area in the b_{scat} map.

In addition to the fire location, there are other small high potential areas such as Pittsburgh, Toledo to Michigan City, central Illinois, St. Louis and northeastern Missouri to southwestern Iowa. The urban areas are expected to be OC and EC source areas. The nature of the areas in central Illinois, Missouri and Iowa are uncertain. There were additional areas in western Quebec and in Ontario near Lake Huron that could be additional fire zones. This area also appears in the $PM_{2.5}$ map.

These results support the utility of the PSCF method. In this application, the location of the Quebec fire area was clearly identified correctly. This result lends support to the likely validity of the identification of the areas for the other sources.

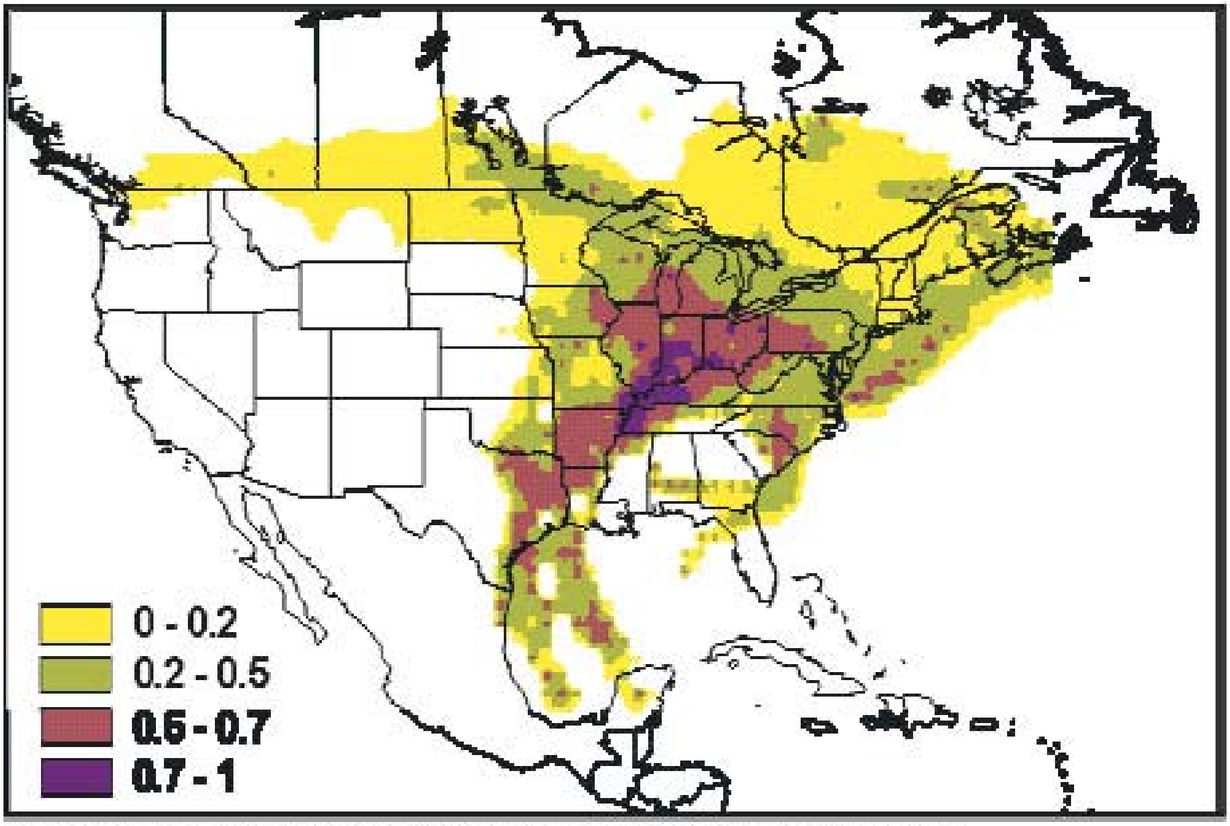

Figure 5-8. Potential Source Contribution Function (PSCF) plot for sulfate

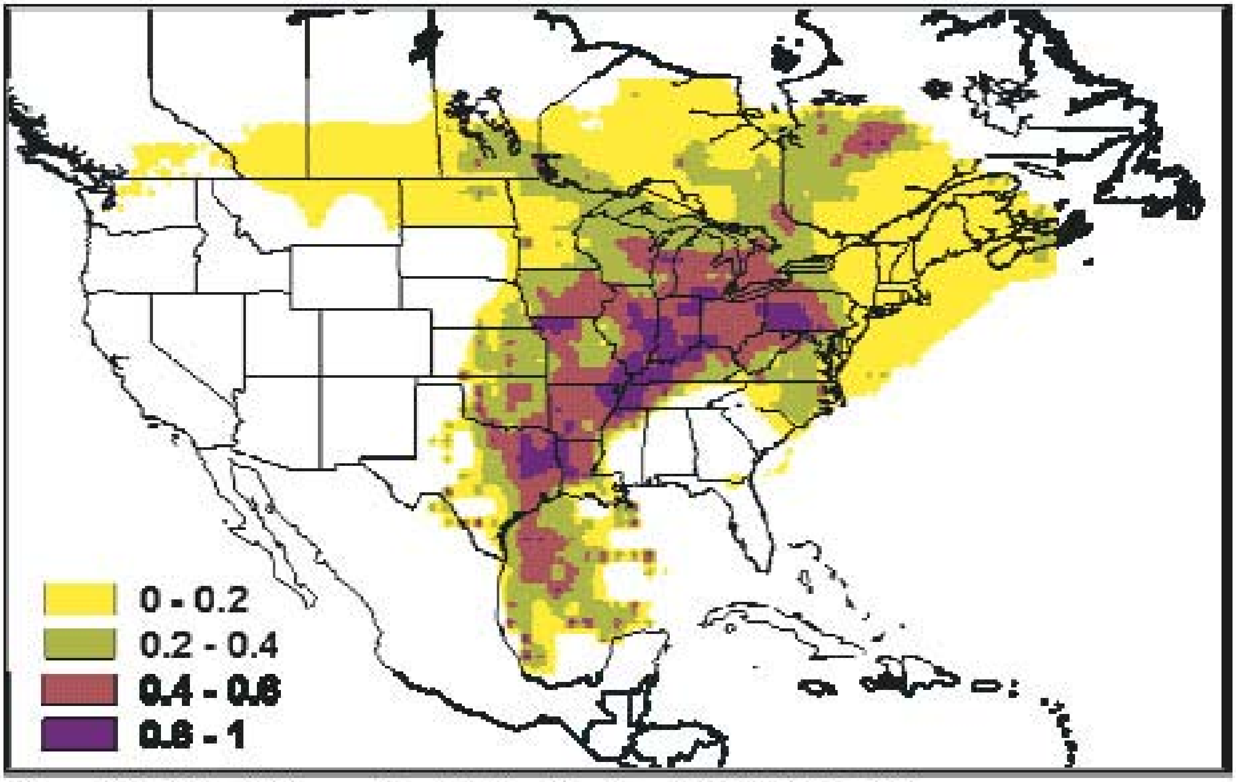

Figure 5-9. Potential Source Contribution Function (PSCF) plot for $PM_{2.5}$

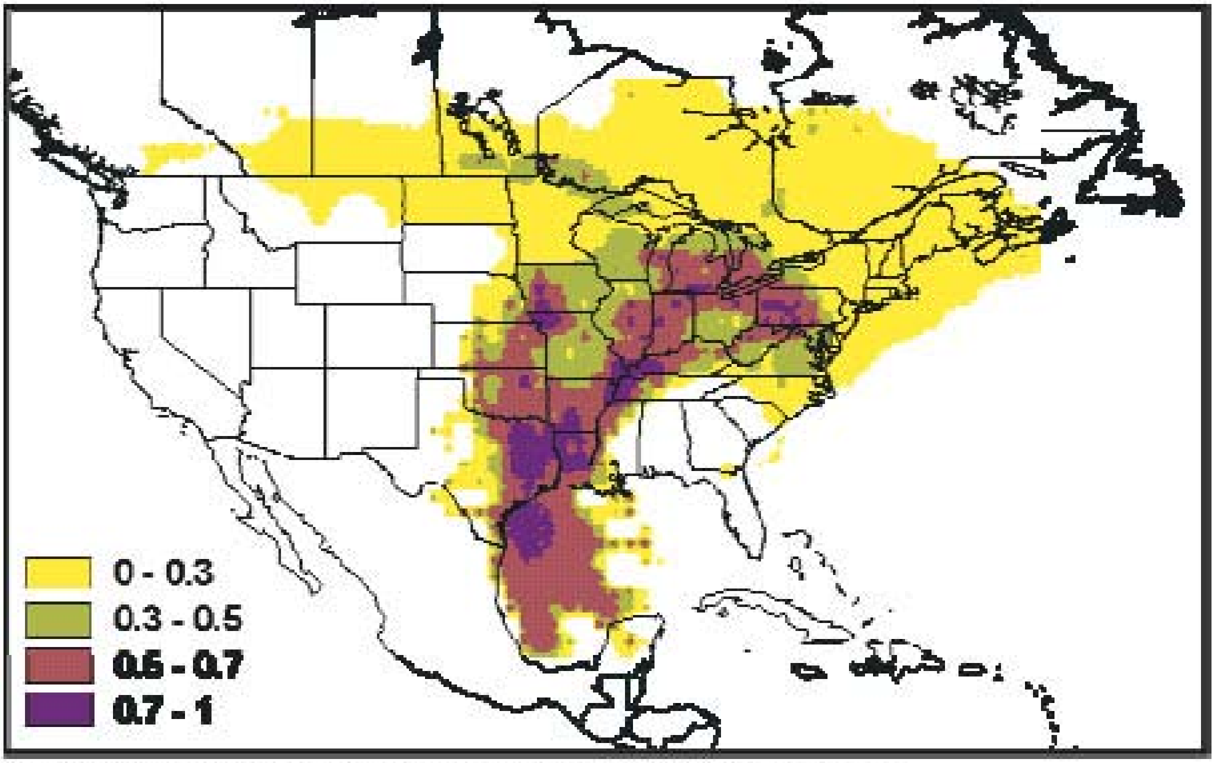

Figure 5-10. Potential Source Contribution Function (PSCF) plot for B_{scat}

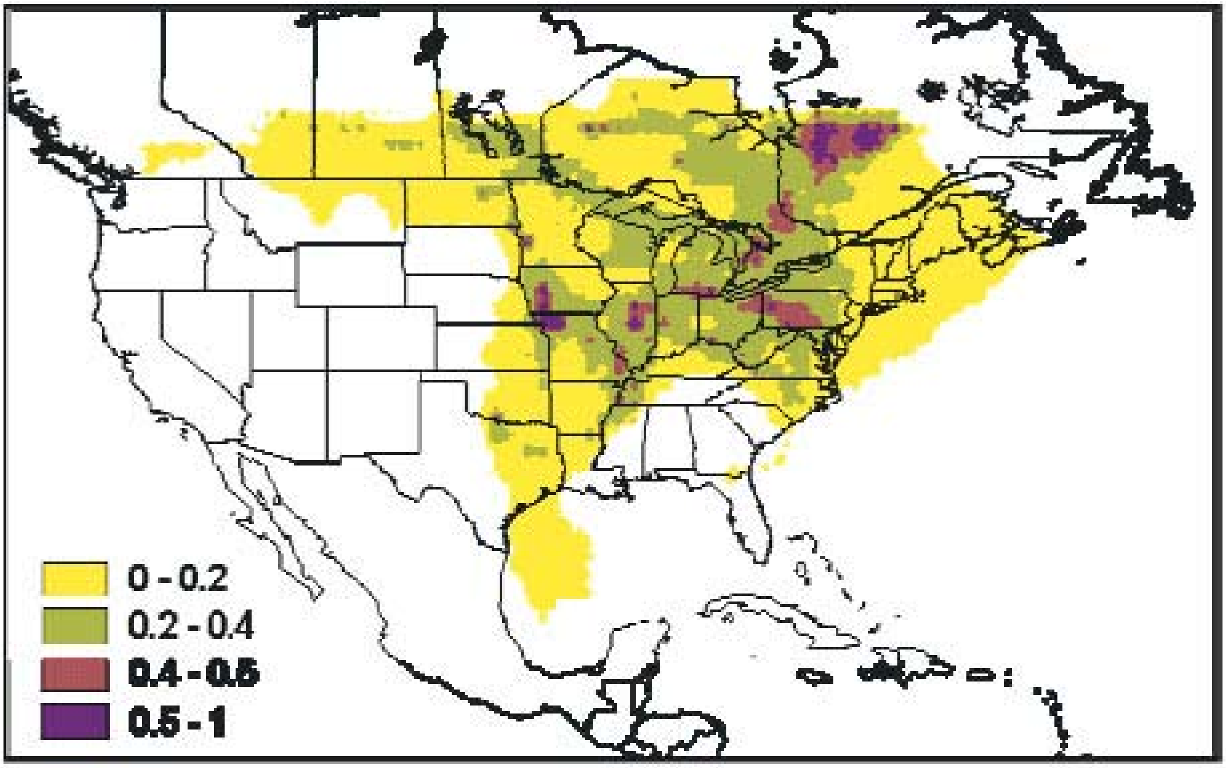

Figure 5-11. Potential Source Contribution Function (PSCF) plot for OC

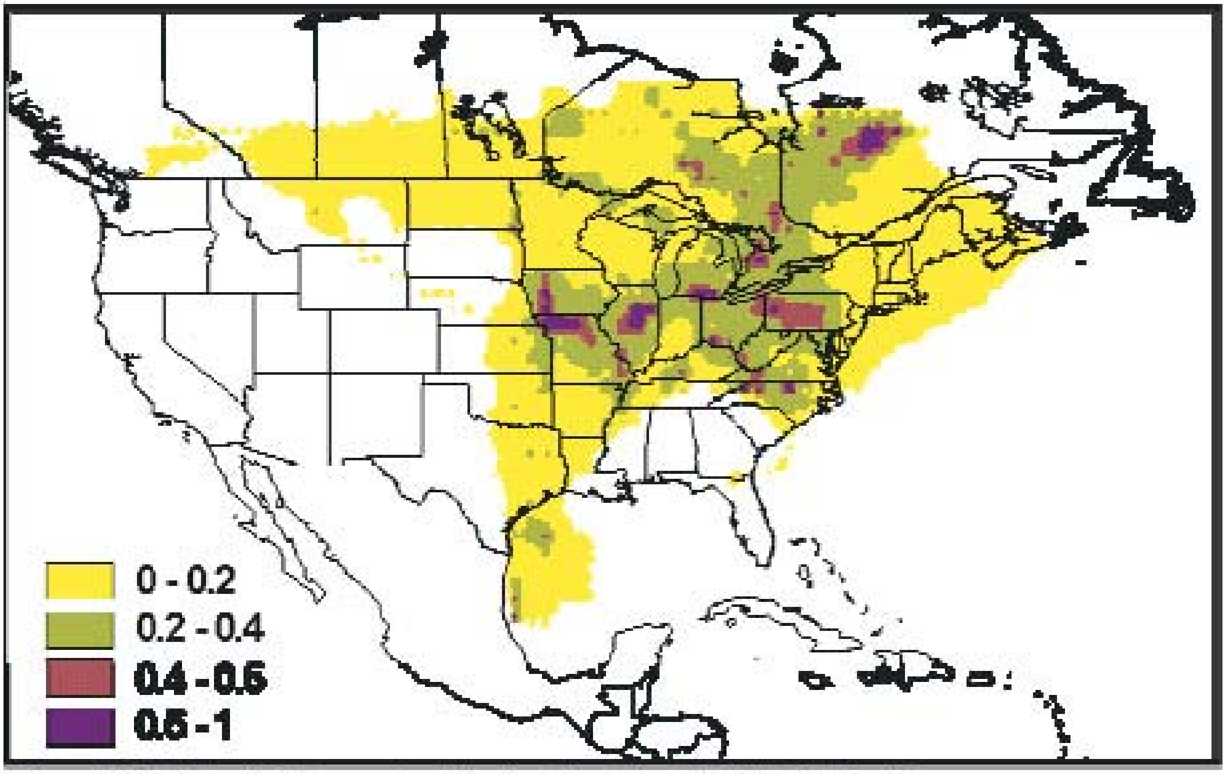

Figure 5-12. Potential Source Contribution Function (PSCF) plot for EC

PART 6: CONTRIBUTIONS FROM DREXEL UNIVERSITY

Investigation of PM Sources Based Upon Laboratory Analysis of Particulate Matter Composition

Steve McDow*
Department of Chemistry, Drexel University

Measurements of specific organic compounds by gas chromatography-mass spectrometry (GCMS) were used to compare the relative contributions of primary (directly emitted) and secondary (photochemically generated) sources of particulate organic matter. Organic composition during air pollution events was compared to organic composition on other days, and chemical composition was also compared between different air pollution events. Chemical composition was also used to assess the relative contribution of anthropogenic and biogenically generated organic matter.

It is not possible to account for more than a small percentage of the particulate organic matter using GCMS because the bulk of the organic mass cannot be resolved chromatographically. However, much of the unresolved mass is often chemically similar to resolved compounds, so it is possible to get a sense of the chemical characteristics of the organic fraction by analyzing for selected compounds. Two classes of compounds were analyzed in this study. Dicarboxylic acids are formed photochemically through a variety of atmospheric reactions. Although they can also be emitted by automobile exhaust, our results suggest that they are present at extremely high concentrations during ozone events when other automobile exhaust indicators remain at more typical concentrations. This suggests that automobile exhaust contributions due to primary particulate emissions are of minor importance during air pollution episodes. However, this does not rule out a significant contribution from secondary formation of particulate matter during transport after emission of volatile organic precursors in automobile exhaust. Alkanes are heavy hydrocarbons that originate primarily from automobile exhaust or epicuticular wax from plants. The biogenic alkanes have formulas that contain an odd number of carbon atoms, while motor vehicle exhaust contains roughly equal amounts of odd and even numbers of carbon atoms. In addition the specific pattern of alkane concentrations (i.e., the ratio of odd to even-numbered alkanes) provides information about the relative importance of biogenic and anthropogenic primary sources. The relative amount of dicarboxylic acids and alkanes can provide a rough estimate of the relative importance of primary and secondary sources of organic particulate matter.

Figure 6-1 shows the concentration of total dicarboxylic acids through the course of the study. Dicarboxylic acid concentrations are generally below 1 $\mu g/m^3$ except during the three well-defined ozone episodes of July 1-3, July 7-9, and July 17-19. Dicarboxylic acid concentrations clearly follow the same pattern as ozone concentration, as indicated by Figure 6-2. Figure 6-2 shows that ozone peaks on the same day as dicarboxylic acids during the July 1-3 and July 17-19 episodes, and one day later during the July 7 to 9 episode.

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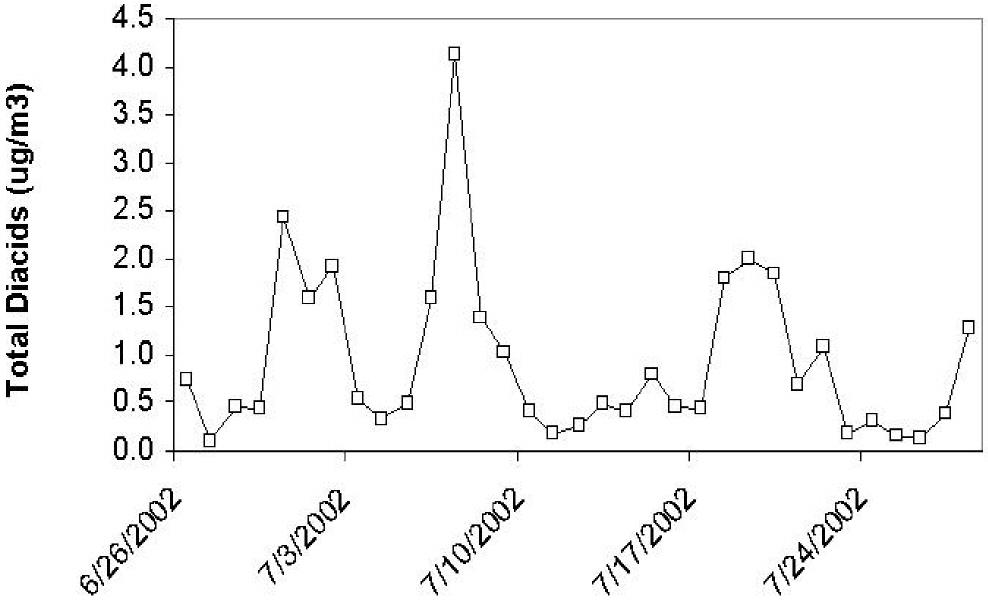

Figure 6-1. Total dicarboxylic acid concentrations

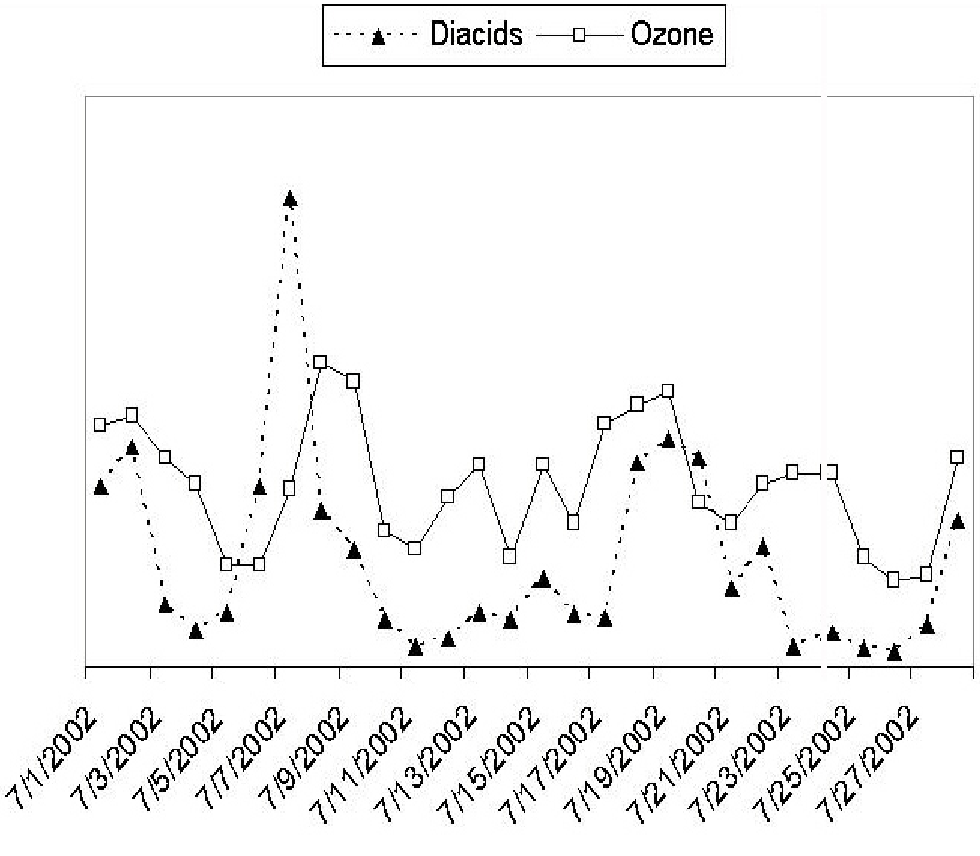

Figure 6-2. Comparison of relative changes in diacid and ozone concentrations

Figure 6-3 shows the concentrations of total alkanes through the course of the study. Concentrations are reasonably constant for most of the study, but are elevated during the period from July 3 to July 6, and reach a dramatic maximum in the forest fire plume on July 7. Figure 6-4 compares relative concentrations of alkanes and dicarboxylic acids through the study period.

If alkanes are considered representative of primary emissions and dicarboxylic acids are considered an indicator of secondary formation, the results indicate a relatively constant level of primary emissions throughout the study period, with concentrations rarely changing by more than a factor of two from day to day except during the forest fire plume. In contrast, dicarboxylic acid concentrations exhibit much more variability, increasing by up to a factor of five or more during the ozone episodes of July 1-3 and July 17-19. The same trend is exhibited in Figure 6-5, which shows the ratio of total dicarboxylic acid concentration to total alkane concentration. The data indicate that a greater proportion of particulate organic matter is secondary in nature during the July 1-3 and July 17-19 episodes, but that in spite of the extremely high dicarboxylic acid concentrations observed in the forest fire plume, there is little difference in the ratio during this episode. From the total dicarboxylic acid data, it is not clear whether this is because the dicarboxylic acids arise from primary sources or whether elevated levels of secondary organic aerosol are roughly equally matched by primary organic pollutants associated with the plume. It is also evident that there is considerable variation in the ratio between episodes, suggesting that secondary organic material may fluctuate more than primary emissions from day to day.

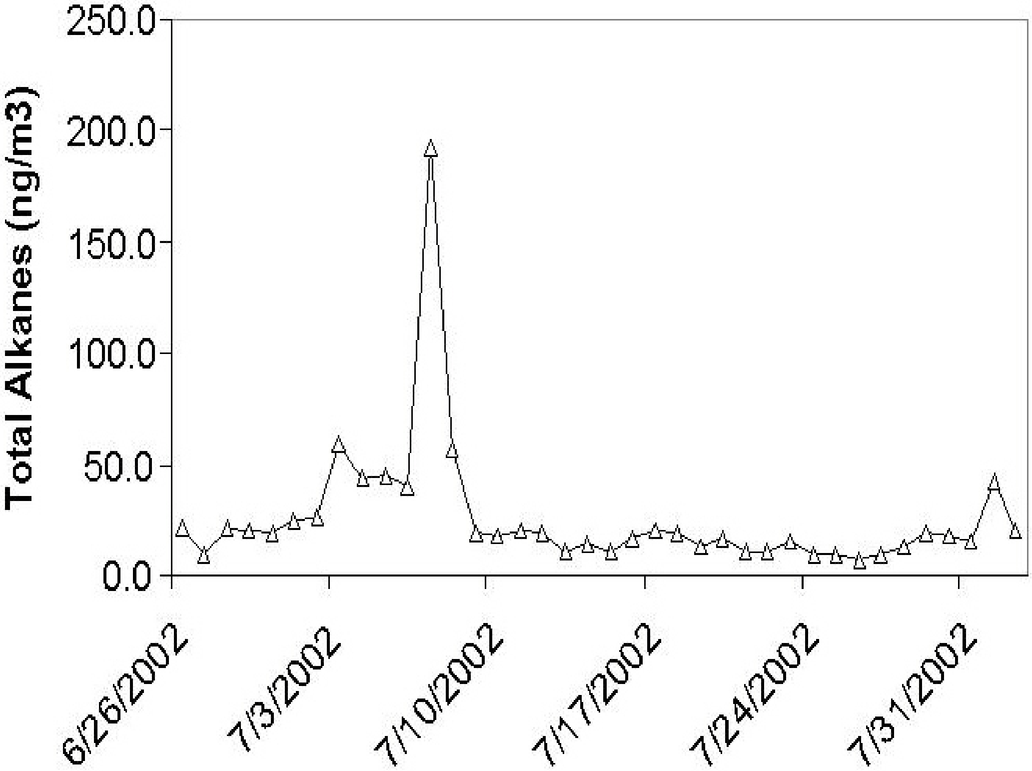

Figure 6-3. Total alkane concentrations

Figures 6(a) and 6(b) describe the relationship between representative dicarboxylic acids, succinic acid and phthalic acid, with ozone concentration. A moderate trend is observed with substantial scatter.

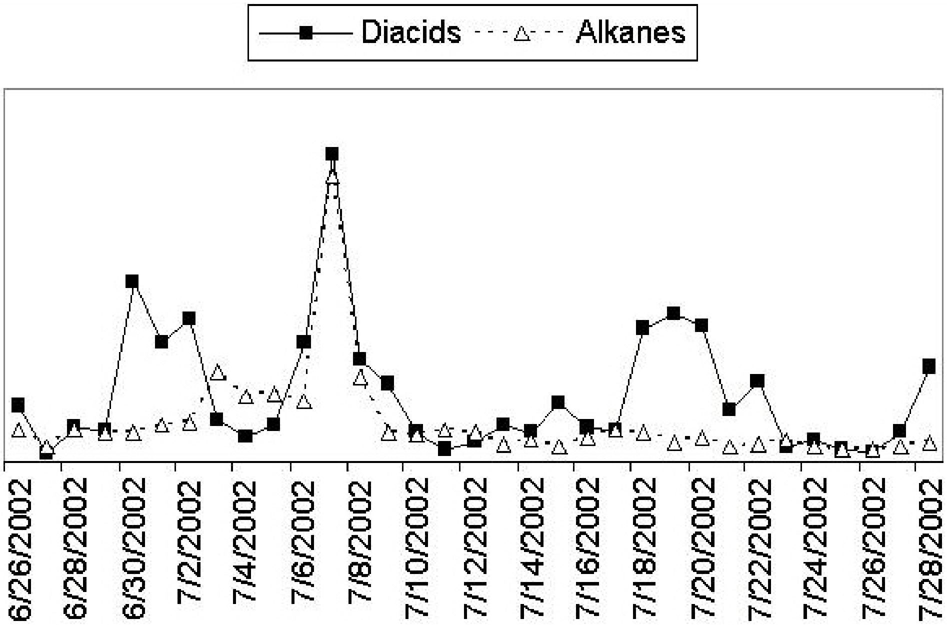

Figure 6-4. Comparison of relative changes in dicarboxylic acid and alkane concentrations

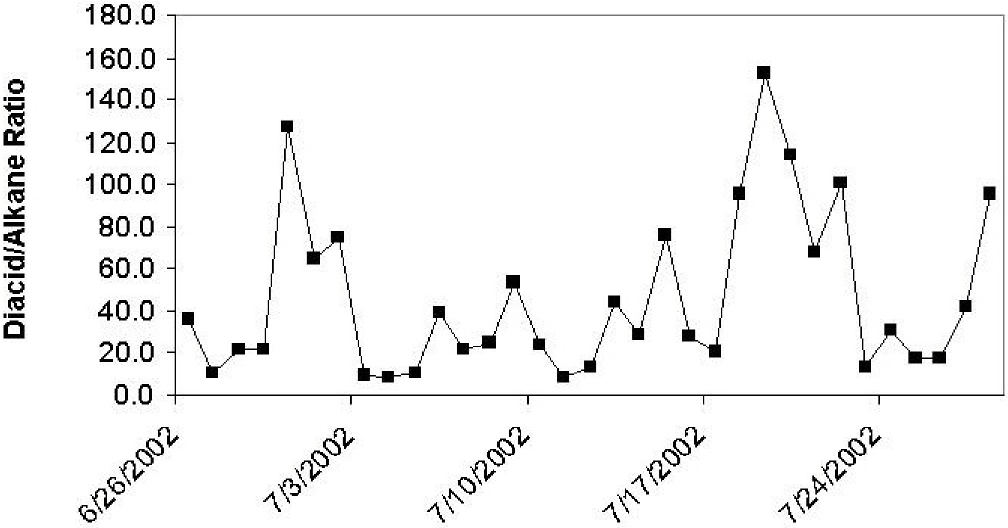

Figure 6-5. Ratio of total dicarboxylic acid concentration to total alkane concentration.

Figure 6-7 shows the differences in distribution of individual dicarboxylic acids between the three events. The highest concentrations of all species were generally observed during the forest fire episode on July 7. However, there are some striking differences in the patterns of different dicarboxylic acids. Malonic, succinic, glutaric and phthalic acids are only slightly higher on July 7 than during the other two episodes, and malic acid is even lower on July 7 than on July 2. In contrast, adipic, suberic, and azelaic acids are several times higher on July 7 than during the other episodes. Azelaic acid is a photochemical product of biogenic emissions, produced when naturally occurring oleic acid reacts. It is noteworthy that it is much higher relative to the other dicarboxylic acids on July 7 than during the other episodes, and the results suggest it may be possible to distinguish between biogenic and anthropogenic precursors of secondary organic aerosols. However, oleic acid is also used in cooking and a forest fire plume may not be representative of general biogenic emissions.

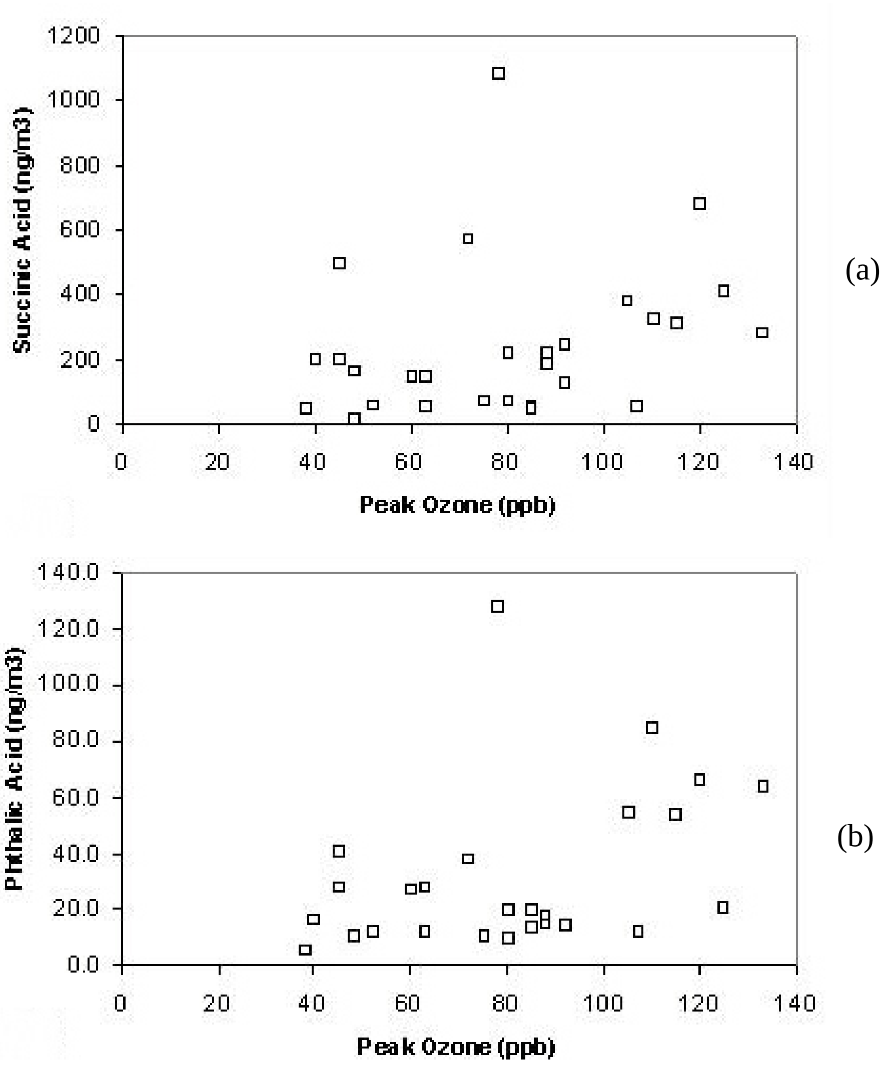

Figure 6-6. Variations with ozone for
(a) succinic acid, and
(b) phthalic acid

Dicarboxylic acid concentrations were compared to wind direction to consider the question of whether secondary organic aerosol or its precursors could be transported from outside the region. For example, air from the southwest follows the urban northeast corridor, while air from the northwest is likely to encounter significant biogenic precursors as it passes over extensive forests. Wind direction is based on afternoon wind trajectories from 1800 UTC (2 PM local). There were very few days with wind from the northeast or southeast, so these are combined. On most days wind was from the northwest quadrant, and this has been divided into north-northwest and west-northwest. As shown in Figure 6-8, the lowest concentrations of succinic and phthalic acid are observed for wind from the east, which generally indicates a marine origin. The highest concentrations are observed for wind from the north-northwest. Since this includes days when the sampling site was in the forest fire plume, Figure 6-9 is provided with the forest fire plume excluded. The maximum for this wind direction is preserved for phthalic acid, but succinic acid varies little with wind direction except for air of marine origin, when the forest fire plume is excluded. It is clear that a southwesterly wind direction is no more favorable for secondary organic aerosol formation than other winds originating over land.

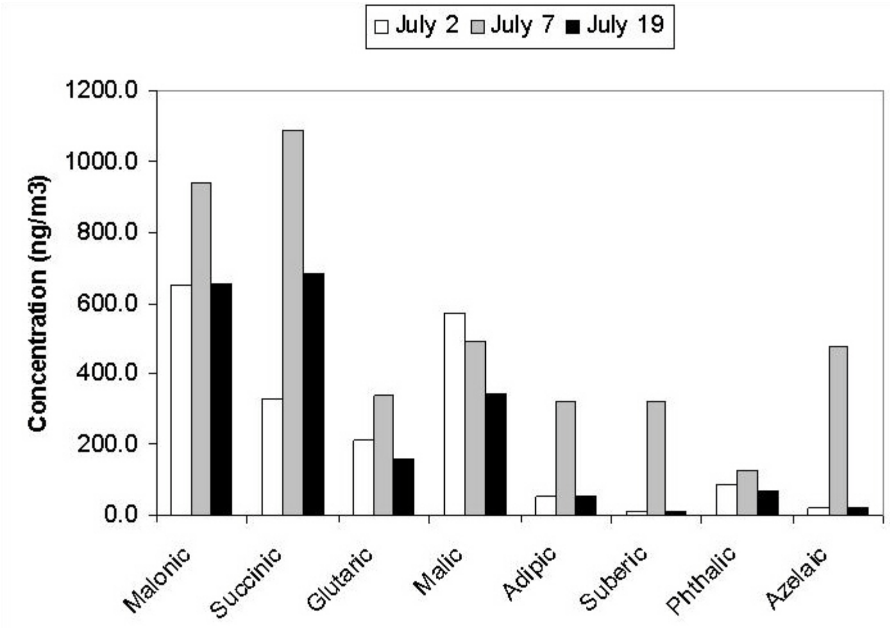

Figure 6-7. Variation of dicarboxylic acid concentrations in different events

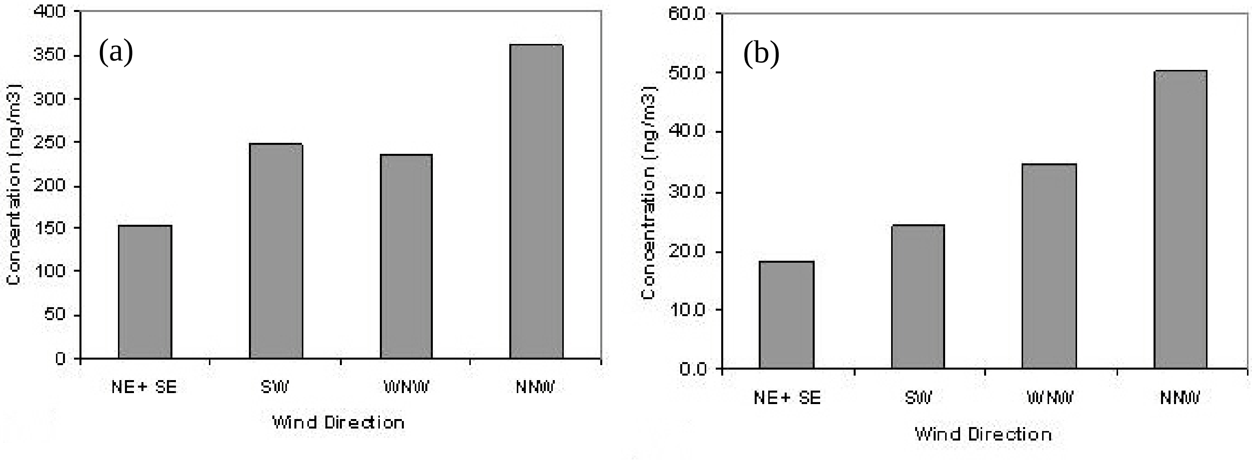

Figure 6-8. Variation of concentration with wind direction *including* forest fire episode for (a) succinic acid and (b) phthalic acid.

Figure 6-10 shows how the ratio of alkanes with an odd number of carbon atoms to those with an even number of carbon atoms varied during the study. Anthropogenic sources are generally automotive and the odd and even alkanes are emitted in roughly equal amounts. Biogenic sources emit exclusively alkanes with an odd number of carbons and they make up a substantial portion of leaf and other plant waxes. These are continually sloughed off and can make up a significant portion of the particulate hydrocarbons in rural and remote areas. An odd/even ratio of 1 to 2 indicates primarily anthropogenic emissions. A ratio above 2 indicates a substantial biogenic contribution. As indicated in Figure 6-10, the ratio fluctuated considerably during the study. It was often below 2 but also frequently as high as 3 or more, indicating that both plant wax and anthropogenic sources impacted the sampling site. Of particular interest are the high ratios observed in the forest fire plume July 7-9, which is consistent with the presence of biogenic plant-derived aerosol. Also the high value of July 2 is coincident with a high ozone level, suggesting a possible biogenic contribution to ozone precursors. The ratio is relatively low during the July 17-19 episode.

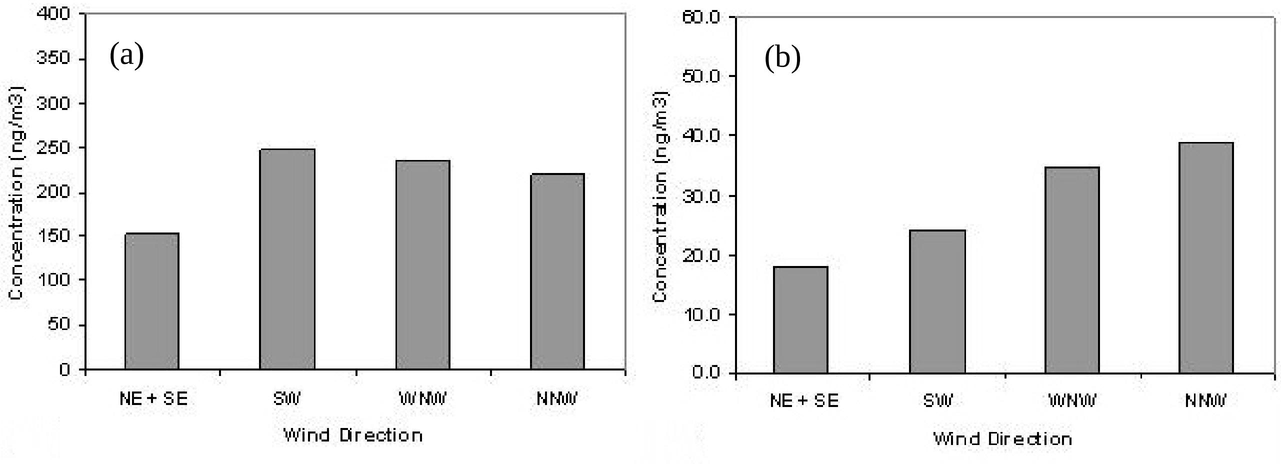

Figure 6-9. Variation of concentration with wind direction *excluding* forest fire episode for (a) succinic acid and (b) phthalic acid

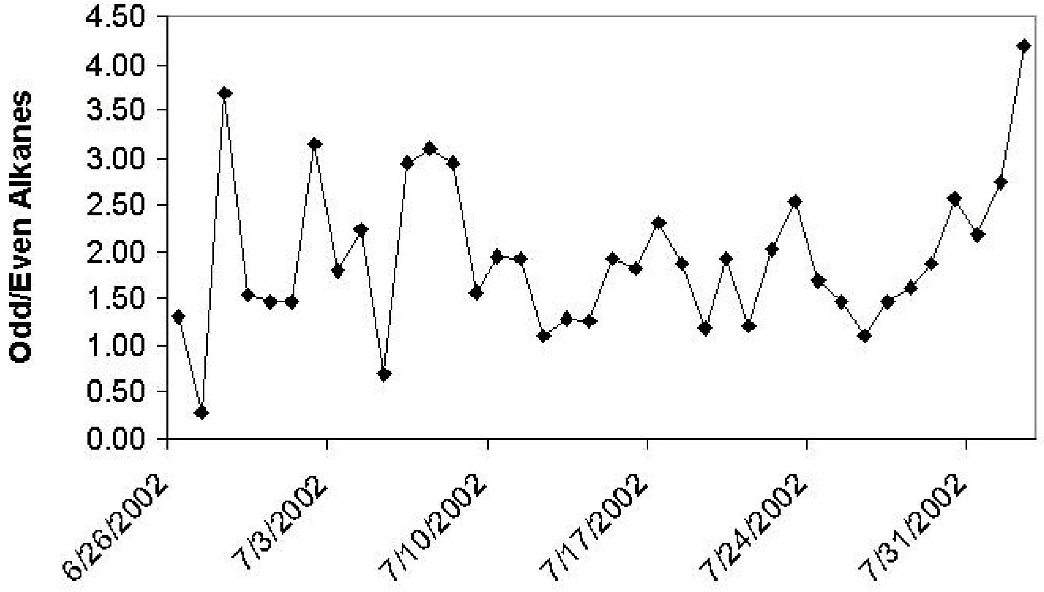

Figure 6-10. Odd carbon / even carbon alkane ratio

Total alkane concentration appeared to be more strongly dependent on wind direction than total dicarboxylic acid concentration, indicating a potentially stronger influence of wind direction on primary than secondary organics. Figure 6-11 shows considerably higher alkane concentrations when the wind is from the northwest than from the southwest, even after the forest fire plume is excluded. This is likely due to transport of primary biogenic aerosol from leaf wax and other materials. Figure 6-12 illustrates this by showing that the odd to even alkane ratio is also higher when the wind is from the northwest. When the forest fire plume is excluded an odd/even alkane ratio of greater than 2 is only observed for wind from the west-northwest.

Wind from this direction is likely to have maximum exposure to forested areas. Figure 6-13 shows that even alkane concentrations are also greater for wind from the northwest, especially the north-northwest. The even alkanes are most likely from automobile emissions, and could result from greater exposure to I-95 traffic, but if this is the case, it is not clear why lower concentrations are observed for winds from the southwest. In any case, primary organic aerosol emissions appear to be both biogenic and anthropogenic, and in both cases, their highest concentrations are associated with a northwest wind.

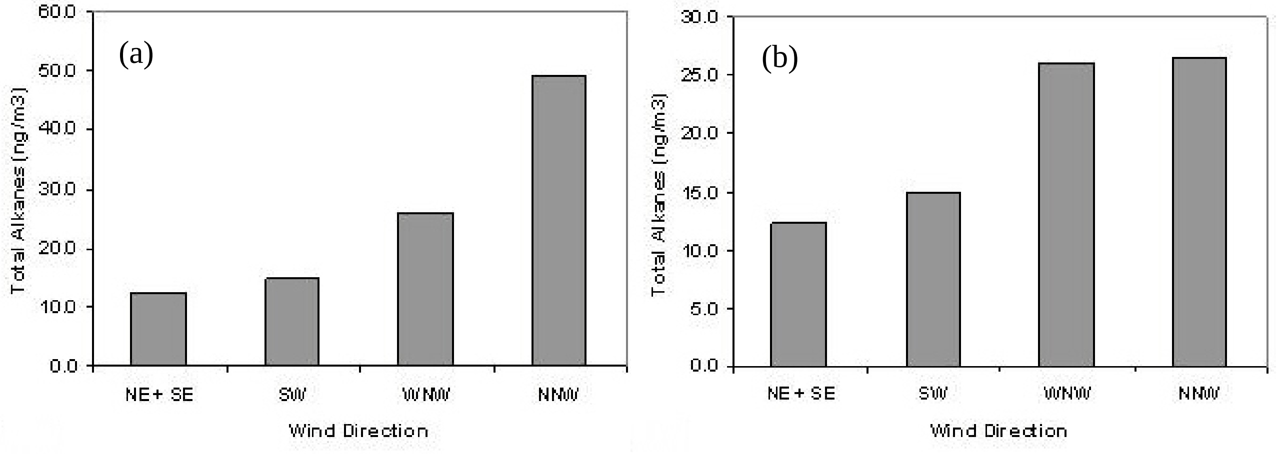

Figure 6-11. Total alkane concentration versus wind direction with (a) forest fire included, (b) forest fire excluded.

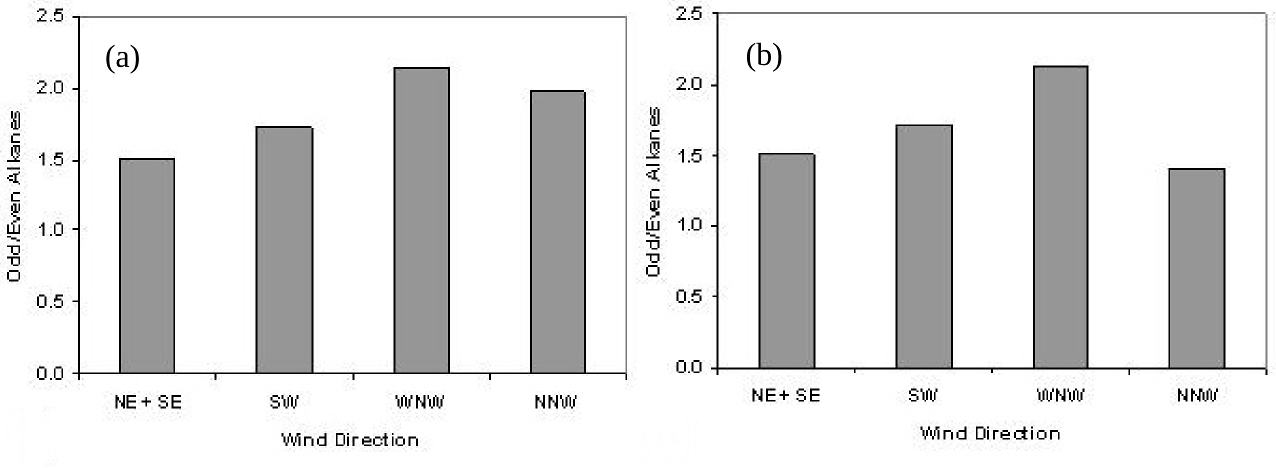

Figure 6-12. Odd/Even alkane ratio versus wind direction with (a) forest fire included, (b) forest fire excluded.

To test whether the dicarboxylic acids could also be due to automobile exhaust, two representative dicarboxylic acids were plotted against even alkane concentrations. The results are shown in Figure 6-14. The trends are similar in strength to the trends exhibited by each of these compounds with ozone. Phthalic acid is somewhat more strongly associated with ozone, while succinic acid is somewhat more strongly associated with even alkanes, but the differences are very small. This suggests that between air pollution episodes a substantial amount of the dicarboxylic acids could be from automobile exhaust, limiting their use as a tracer of secondary organic aerosols on more typical days.

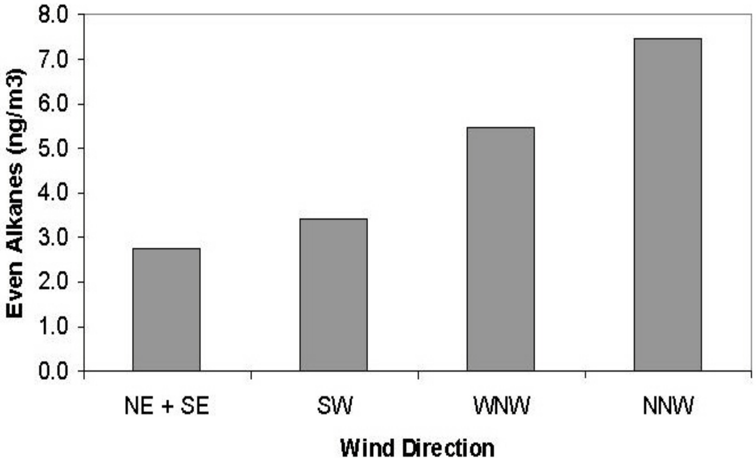

Figure 6-13. Even alkanes versus wind direction

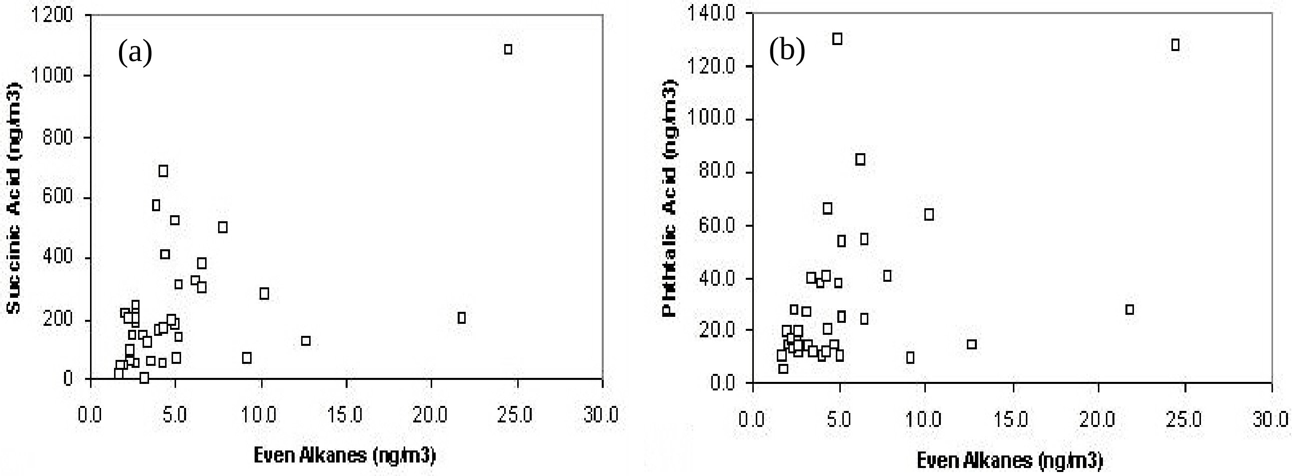

Figure 6-14. Variations in the even alkanes are compared with variations in the acids, (a) succinic acid, and (b) phthalic acid.

The following conclusions can be drawn from the analysis of these results:

1. Summer organic aerosol in Philadelphia consists of a relatively constant level of primary organic particulate matter, punctuated by extreme episodes of high levels of secondary organic aerosol during ozone events.

2. A significant fraction of particulate organic matter during ozone episodes is accounted for by dicarboxylic acids, which exceeded 1 $\mu g/m^3$ in all three episodes.

3. Primary organic particulate matter is both biogenic and anthropogenic in nature, with the relative importance fluctuating from day to day.

4. Primary organic matter is possibly associated more strongly with northwest winds, with little difference observed for secondary organic particulate matter, except both exhibit lower concentrations in air of marine origin.

5. While secondary aerosol formation events may be responsible for dramatic increases in particulate organic carbon, the relatively constant contribution of primary sources could make a greater contribution to annual average particulate levels, and more research is needed to sort out the relative contributions of anthropogenic and biogenic sources.

PART 7: PROJECT SUMMARY

The measurements of the NEOPS-DEP2002 campaign were completed less than one year ago and thus the efforts on the interpretation of the results are expected to continue for some time. During the period since the campaign was completed, several publications and presentations have made use of the results, and those are listed at the end of this part of the report. The prior sections of this report have indicated the types of measurements conducted and presented examples of results. Rather than trying to make a complete summary of the activities here, several of the papers listed below are appended to provide a better perspective of how the results are being used, and indicate the expected directions for the further studies. Several of the papers are available as .PDF files on the NEOPS-DEP directory under the PSU web site http://lidar1.ee.psu.edu/. A primary near term goal is to complete the data archiving so that it will be available for future use for analysis, and for use in development and testing of models. The process of archiving all of the data on the NARSTO national archive is underway.

1. Questions and Hypotheses Examined

A Data Workshop on the NEOPS-DEP2002 project was conducted at Penn State University on 2-3 December 2002 and a Science Workshop was conducted 12-13 May 2003. During these workshops, the results were studied and hypotheses examined to learn from the measurements and decide how best to analyze the data. The following list of questions and hypotheses were considered:

1. Are all of the major northeast air pollution events coupled with transport from the midwest?
2. Are the increases of the PAH's associated with the fire aerosols principally responsible for the changes of absorptivity (optical density)?
3. Are high ozone pollution episodes consistent with high PM events? What forecasting parameters work well? Can you deduce high ozone levels from high PM events?
4. Do all sulfate events have associated PM events? When are the $PM_{2.5}$ peaks, do they correspond to higher ozone levels? How often does high ozone occur without a PM increase? Why?
5. Can we separate <u>regional sulfates</u> from <u>local sulfates</u>? What are the sources?
6. What is the climatology of the nocturnal Low Level Jet with respect to the chemistry and meteorology? Is the LLJ a source of material or just an indicator of the meteorological pattern?
7. How is the ambient aerosol size, number and optical density related to PM (also use the data from 2001, 1999)?
8. What is the extent to which boundary layer depth parameters define pollutant mixing volume characteristics?
9. What are the relative contributions of active chemistry compared to dynamical changes during an air pollution episode?
10. Can the ETA model be verified using the tethersonde, lidar, radar and RASS data?
11. How does the uniqueness of the Philadelphia region affect air pollution (specifically ozone)? (Sea breeze, Low Level Jets, Factories, Power Generation, Traffic Patterns, Appalachian Mountains)

Several of these questions are described and answered, at least partially, in prior sections of this report, and others are being addressed in work that is underway. The researchers will continue to analyze and interpret the results, and report their investigations relative to these and other related questions. One of the major outcomes from the NEOPS investigations is the demonstration of the fact that the critical processes can only be understood when the vertical profiles are examined. The meteorological properties are the most important factors in controlling the degree to which the emissions from power generation, industrial processes, and transportation are concentrated within a region. The regional transport of pollutants, the storage and transport aloft, and the vertical mixing of the boundary layer are key factors, and these are only properly characterized with observations by continuous remote sensing techniques. The combination of the lidar, tethered sonde, radar, and RASS during the NEOPS-DEP2002 program have provided valuable insights into the transport processes that control the evolution of air pollution episodes.

2. Meteorological Analysis

The meteorological conditions over the northeast region which have controlled the air pollution episodes during the NEOPS-DEP 2002 project are summarized by Bill Ryan and available on the web sites:

http://www.atmos.umd.edu/~forecaster/summary_2002.htm

http://lidar1.ee.psu.edu/

The episodes that have been analyzed which correspond with NEOPS-DEP2002 intensive measurement periods are:

July 1-3
July 7-9: Canadian Wildfires
July 17-19
NEOPS IOP July 22-23
NEOPS IOP July 28-29
July 31-August 5

3. Summary of the 2002 Conditions

A few selected results are summarized here to provide an overview of information which helps to characterize the 2002 summer, and that is valuable for understanding the relationships to other years. Figure 7-1 shows a summary of the ozone and particulate matter during the month of July 2002. These measurements were made with instruments at the NEOPS site in northeast Philadelphia, the ozone measurements by Millersville University (Richard Clark) and the particle measurements by Clarkson University (Philip Hopke). Figure 7-1 shows the comparison of ozone and particulate concentrations. The time sequence of the variations in $PM_{2.5}$, EC, OC, BC, total carbon and sulfate are compared with the ozone during the month of July 2002 in this figure. Better resolution plots of the comparisons of $PM_{2.5}$, sulfate and OC with ozone are shown in Figures 7-2 through 7-4. These figures indicate the range of events and conditions observed during the 2002 summer campaign.

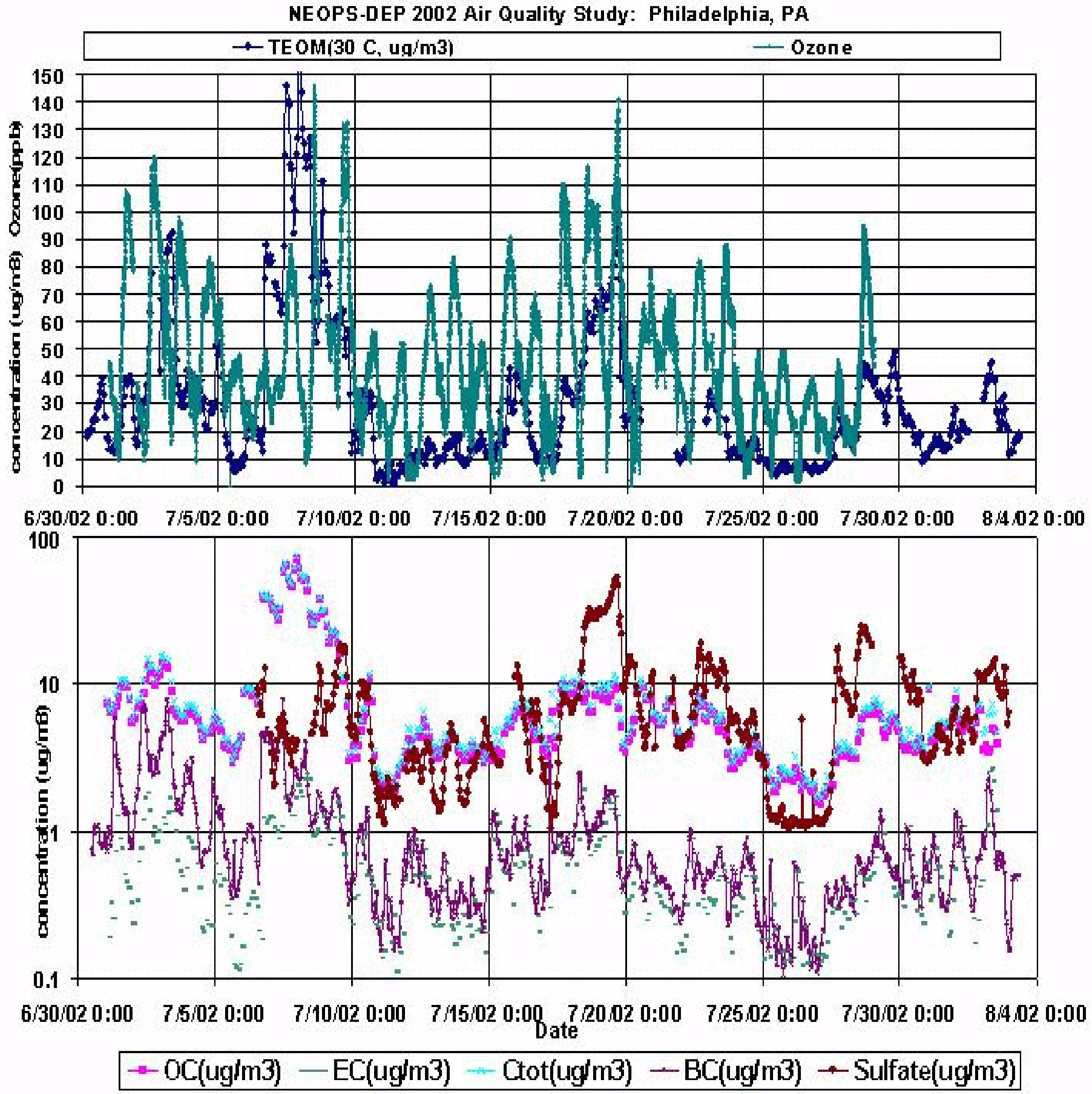

Figure 7-1. Measurements of particulate properties by Clarkson University and ozone measurements from Millersville University are combined to show the variations that occurred during the NEOPS-DEP 2002 campaign at the Philadelphia site.

Figures 7-1 through 7-4 provide a general overview of the conditions that existed during the summer of 2002. The goal of the NEOPS program has been to bring together the best and most up-to-date techniques to measure the detailed chemistry, aerosol properties, profiles of ozone, profiles of aerosols, and meteorological conditions to archive an improved understanding of the physical and chemical processes that govern air pollution. Our purpose is to understand the meteorological influences upon the evolution and distribution of ozone and fine particle concentrations during air pollution episodes and to find the proper context of regional scale factors. The measurements of vertical profiles of the important properties obtained using lidar, radar, tethersondes and aircraft spirals clearly shows the incursion of processed precursor materials from an aloft layer, which are transported into the region, and then mixed downward to the surface by the daytime convective boundary layer. The transported material appears to be important in the initiation of an ozone and particulate matter pollution events during several investigations. Vertical profiles of the ozone, aerosol extinction, water vapor and other meteorological parameters provide the important results to understand the evolution of air pollution episodes. Time sequence profiles clearly show the advection of aloft layers of polluted air into the region followed by entrainment into the daytime convective mixed layer and subsequent transport to the surface. Time sequences of ozone and aerosol (PM) profiles obtained during the NE-OPS project studies between the surface and 3 km altitude show the importance of the surface layer (first 100 meters) and PBL dynamics in determining the actual pollution hazard for the regional population. Hazardous levels of ozone are frequently observed existing above the surface layer. The intensity of vertical transport, and presence of surface layer gases that can destroy ozone, can make significant differences in the level of human exposure. Examination of several episodes demonstrates that the local surface exposure depends upon the development of convective activity, wind-shear driven transport, and presence of surface gaseous species. The results show the importance of measuring the vertical structure to understand the processes governing air pollution. The results from these measurement programs are being submitted to the national archive (NARSTO archive) so that the larger community of modelers and researchers will have access to this valuable data set.

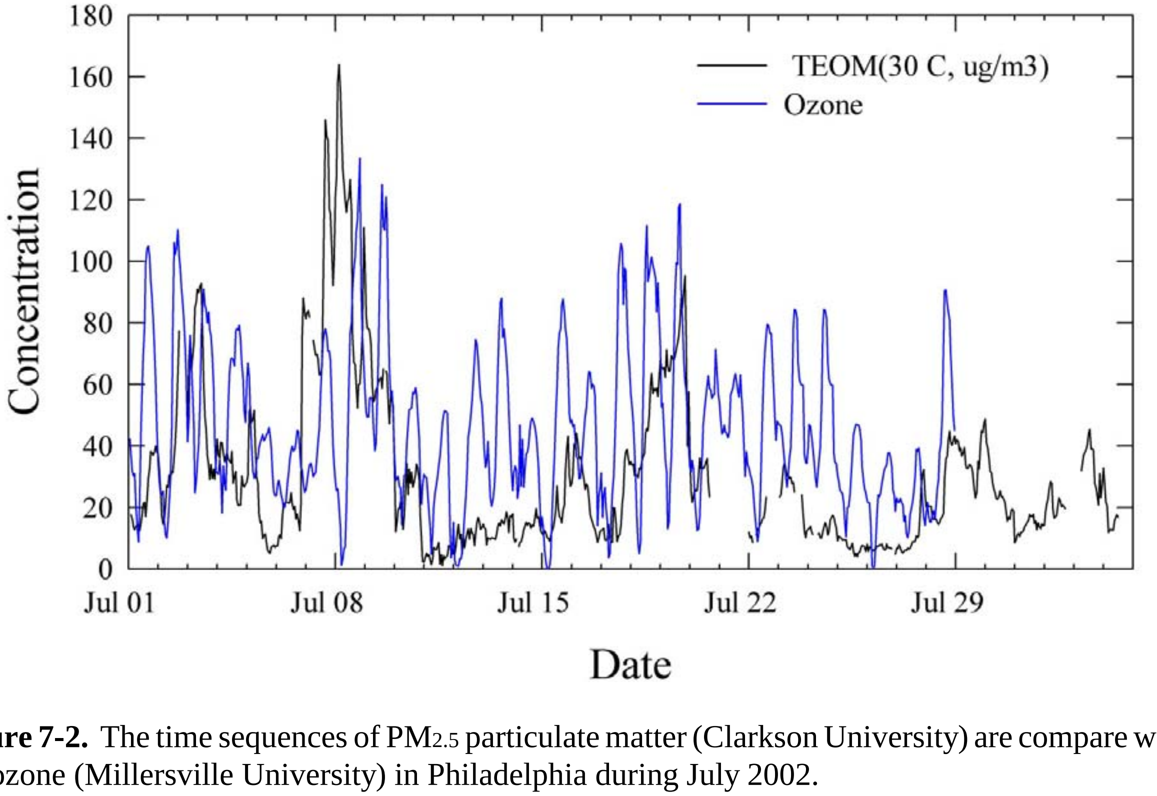

Figure 7-2. The time sequences of PM2.5 particulate matter (Clarkson University) are compare with the ozone (Millersville University) in Philadelphia during July 2002.

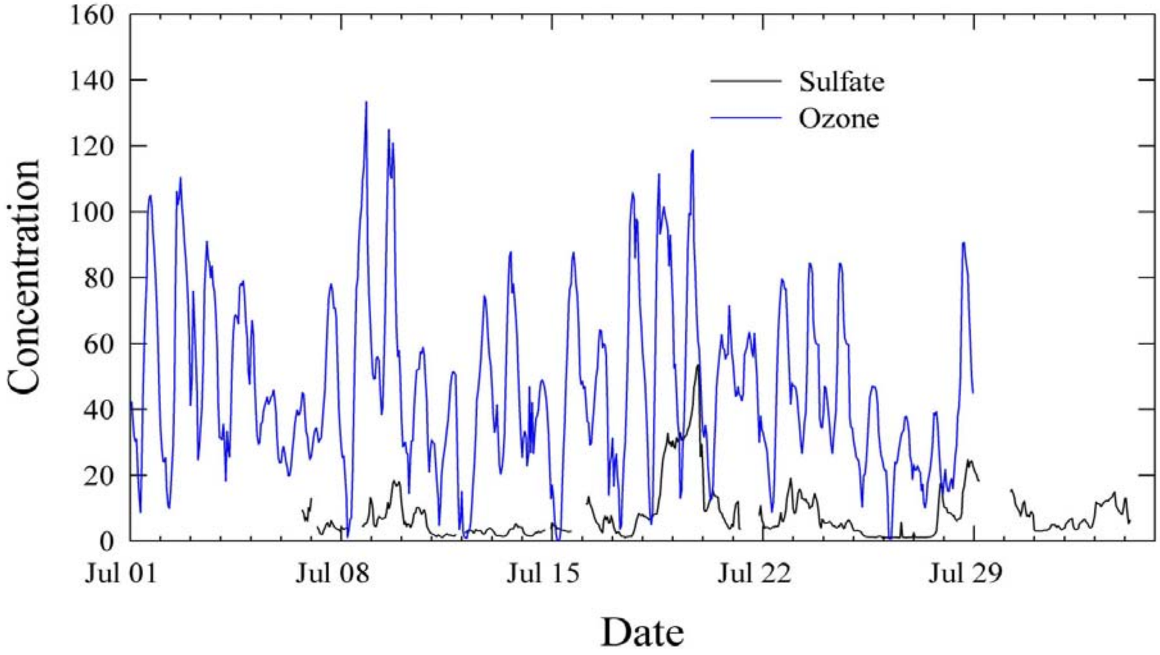

Figure 7-3. The sulfate concentrations (Clarkson University) are compared with the ozone (Millersville University) during the NEOPS-DEP 2002 campaign in Philadelphia during July 2002.

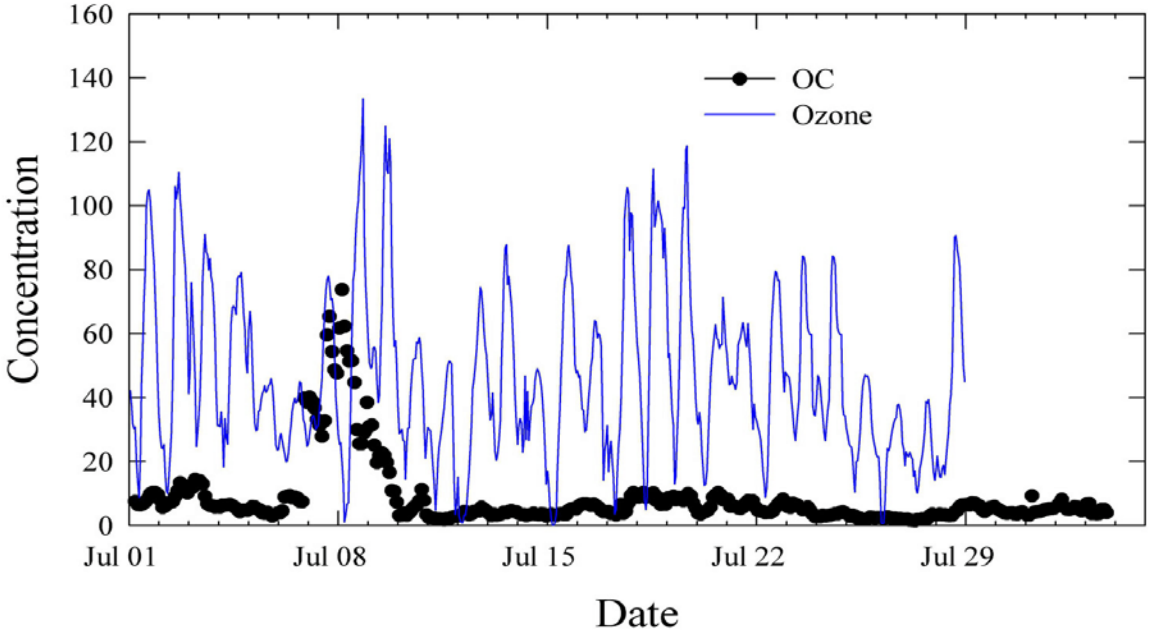

Figure 7-4. Comparison of the OC measurement (Clarkson University) with the ozone time sequence (Millersville University) shows the period of high OC when the smoke from Canadian forest fire reached the site, and the following ozone enhancement.

4. Archiving of the NEOPS-DEP2002 Data

The efforts to complete the data archive of the summer 2002 data with the NARSTO national archive are well underway and should be completed within the next few months. The data is also being made available to other researchers on request at the project web site:

http://www.lidar1.ee.psu.edu

5. Publications and Presentations

Most of the work for preparation of interpretation and publication of the results is still ahead because this report is being drafted only nine months after the measurement campaign. The following list highlights the reports on the results that have occurred to date, several other papers and reports are in preparation.

Publications

Clark, R. D., "Using GEMPAK/GARP in undergraduate research," *Bull. Amer. Meteor. Soc.* **83**, 178-180, 2002.

Philbrick, C. Russell, "Application of Raman Lidar Advancements in Meteorology and Air Quality Monitoring," in Remote Sensing of the Atmosphere, Environment, and Space, SPIE , 4893-11, 2003.

Li, Guankun, and C. Russell Philbrick, "Lidar Measurements of Airborne Particulate Matter," in Remote Sensing of the Atmosphere, Environment, and Space, SPIE , 4893-15, 2003.

Philbrick, C. R., W.F. Ryan, R.D. Clark and B.G. Doddridge, "Advances in Understanding Urban Air Pollution from the NARSTO-NE-OPS Program," Proceedings of the American Meteorological Society 5th Conference on Atmospheric Chemistry, 6.1, 2003.

Ryan, W.F., C.R. Philbrick and R.D. Clark, "Summary of the Meteorological Conditions During the NEOPS July 2002 Intensive Observing Period," Proceedings of the American Meteorological Society 5th Conference on Atmospheric Chemistry, 6.2, 2003.

Collier, Jason P., S. Unni, S.J. Verghese, A. Willitsford, C.R. Philbrick, R.D. Clark, and B.G. Doddridge, "Raman Lidar Measurements of Tropospheric Ozone," Proceedings of the American Meteorological Society 5th Conference on Atmospheric Chemistry, 6.3, 2003.

Clark, Richard D., C.-H. Jeong and C.R. Philbrick, "The Influence of Canadian Wildfires on Air Quality in Philadelphia during NE-OPS DEP," Proceedings of the American Meteorological Society 5th Conference on Atmospheric Chemistry, 6.4, 2003.

Clark, Richard D., W.F. Ryan and C.R. Philbrick, "Modification of Surface and Boundary Layer Meteorology and Chemistry by Seabreeze Incursions during NE-OPS," Proceedings of the American Meteorological Society 5th Conference on Atmospheric Chemistry, 6.6, 2003.

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Willitsford, Adam, J.P. Collier, S. Unni, S.J. Verghese, C.R. Philbrick, D. O'Donnell, E. Hohman, D. Unruh, R. Walker, Jr., and R.D. Clark, "Development of an Air Pollution Episode During the NEOPS-DEP 2002 Investigation," Proceedings of the American Meteorological Society 5th Conference on Atmospheric Chemistry, 6.9, 2003.

Verghese, Sachin J., S.N. Kizhakkemadam,, A. Willitsford, J.P. Collier, S. Unni, and C.R. Philbrick, "Characterization of Nocturnal Jets over Philadelphia During Air Pollution Episodes Using Radar/RASS and Raman Lidar," Proceedings of the American Meteorological Society 5th Conference on Atmospheric Chemistry, 6.10, 2003.

Philbrick, C. Russell, "Remote Sensing of Atmospheric Properties Using Lidar," Proceedings of the International Symposium on Spectral Sensing Research (ISSSR), 34 (16 pages) 2003.

Jeong, Cheol-Heon, Doh-Won Lee, Eugene Kim, and Philip K Hopke, "Measurement of Real-time PM2.5 Mass, Sulfate, and Carbonaceous Aerosols at the Multiple Monitoring Sites," (submitted to Atmos Envir, 2003).

Jeong, Cheol-Heon, Philip K Hopke, Eugene Kim, and Doh-Won Lee,"The Comparison Between Thermal Optical Transmittance Elemental Carbon and Aethalometer Black Carbon Measured at Multiple Monitoring Sites," (submitted to Atmos Envir, 2003).

Begum, Bilkis Ara, Eugene Kim, Cheol-Heon Jeong, Doh-Won Lee, and Philip K Hopke, "Identification of Source Regions for Atmospheric Particles Measured in Philadelphia, Pennsylvania," (submitted to Envir, Sci. and Tech. 2003).

Theses

Kizhakkemadam, Sriram: Estimation of Boundary Layer Depth From Raman Lidar Using 2-D Spatial Filters, Master of Science Thesis in Department of Electrical Engineering at Penn State University, December 2002.

Verghese, Sachin J.: Characterization of Low-Level Jets and Their Influence on Air Pollution Using Raman Lidar and Wind Profiling Radar/RASS, Master of Science Thesis in Department of Electrical Engineering at Penn State University, August 2003.

Unni, Sameer: Measurement and Analysis of Optical Extinction Properties, Master of Science Thesis in the Department of Electrical Engineering at Penn State University, December 2003.

Presentations

Philbrick, C. Russell: "Application of Raman Lidar Advancements in Meteorology and Air Quality Monitoring," Invited Presentation for the Third Asia-Pacific Symposium on Remote Sensing of the Atmosphere, Environment, and Space, Hangzhou, China (November 2002)

Li, Guankun, and C. Russell Philbrick: "Lidar Measurements of Airborne Particulate Matter," Third Asia-Pacific Symposium on Remote Sensing of the Atmosphere, Environment, and Space, Hangzhou, China (November 2002)

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Ryan, W.F., C.R. Philbrick and R.D. Clark: “Summary of the Meteorological Conditions During the NEOPS July 2002 Intensive Observing Period,” American Meteorological Society 5th Conference on Atmospheric Chemistry, Long Beach CA (2003)

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Clark, Richard D., C.-H. Jeong and C.R. Philbrick: “The Influence of Canadian Wildfires on Air Quality in Philadelphia during NE-OPS DEP, American Meteorological Society 5th Conference on Atmospheric Chemistry, Long Beach CA (2003)

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Willitsford, Adam, J.P. Collier, S. Unni, S.J. Verghese, C.R. Philbrick, D. O’Donnell, E. Hohman, D. Unruh, R. Walker, Jr., and R.D. Clark: “Development of an Air Pollution Episode During the NEOPS-DEP 2002 Investigation,” American Meteorological Society 5th Conference on Atmospheric Chemistry, Long Beach CA (2003)

Verghese, Sachin J., S.N. Kizhakkemadam,, A. Willitsford, J.P. Collier, S. Unni, and C.R. Philbrick: “Characterization of Nocturnal Jets over Philadelphia During Air Pollution Episodes Using Radar/RASS and Raman Lidar,” American Meteorological Society 5th Conference on Atmospheric Chemistry, Long Beach CA (2003)

Clark, R. D., R. Walker Jr., D. O’Donnell, E. Hohman, and D. Unruh, 2003: “Low level jets over the mid-Atlantic region during NE-OPS 1999-2002,” American Meteorological Society 5th Conference on Atmospheric Chemistry, Long Beach CA (2003)

Clark, R. D., “The influence of local and regional circulations on the particle and trace gas concentrations in the Northeast during NARSTO-NE-OPS,” University of Alabama-Huntsville (March 2003)

Jeong, Cheol-Heon, Doh-Won Lee, Eugene Kim, Philip K Hopke: “Measurement of Real-Time PM2.5 Mass and Fine Chemical Compositions at Northeast Philadelphia,” 2003 AAAR Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health, Pittsburgh, PA (April 2003)

Jeong, Cheol-Heon, Doh-Won Lee, Eugene Kim, Philip K Hopke: “ Influence of a Canadian Forest Fire on Measurements of Carbonaceous Compounds in Fine Particulate Matter in July 2002 in Philadelphia,” 2003 AAAR Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health, Pittsburgh, PA (April 2003)

Jeong, Cheol-Heon, Doh-Won Lee, Eugene Kim, Philip K Hopke, Robert Gelein: “The Comparison Between Thermal Optical Transmittance Elemental Carbon and Aethalometer Black Carbon Measured at Multiple Monitoring Sites,” 2003 AAAR Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM, Pittsburgh, PA (April 2003)

Philbrick, C. Russell, "Applications of Lidar Techniques to Describe Atmospheric Optical Properties," Invited Presentation for the SPIE AeroSense Photonics for Defense and Security, Orlando FL (April 2003)

Philbrick, C. Russell: "Remote Sensing of Atmospheric Properties," Invited Presentation for the International Symposium on Spectral Sensing Research, Santa Barbara CA (June 2003)

Philbrick, C. Russell, William F. Ryan, Richard D. Clark, Philip K. Hopke and Stephen R. McDow: "Processes Controlling Urban Air Pollution in the Northeast: Summer 2002," Invited Presentation for the MARAMA MANE-VU Workshop, Windsor-Locks CT (June 2003)

Philbrick, C. Russell: "Results from the Northeast Oxidant and Particle Studies (NE-OPS)" MARAMA Regional Air Quality, Asheville NC (August 2003)

6. Summary of Key Findings

The measurements obtained during the summer of 2002 in the NEOPS-DEP program have added significantly to our understanding of the air pollution episodes. When considered together with our results from the prior NARSTO-NEOPS investigations in 1999 and 2001, we can begin to draw several conclusions about the summer air pollution episodes in the Philadelphia and infer conditions in the regional area. The statements which can be made to generally describe our current knowledge are:

(1) All of the major summer air pollution episodes that we have observed in the Philadelphia area included a major contribution transported from distant sources. From the set of cases during the 1999, 2001 and 2002 NEOPS campaigns, it appears that the onset of the most significant $PM_{2.5}$ events are accompanied by a transition to westerly transport in the boundary layer.

(2) The major factor that controls the magnitude and timing, the development and dissipation, of the air pollution episodes is the regional scale meteorology. The major episodes would not develop without the factors which accumulate the chemical pollutants and allow photochemical processing to generate the ozone and PM components. Weather conducive to photo-chemistry, coupled with local stagnation/re-circulation can cause rapid increases in O_3 with peak concentrations reaching the Code Red range in the absence of a significant westerly transport component (e.g., August 1-4, 2002). In these conditions, $PM_{2.5}$ concentrations rise as well but are typically limited to the 30-40 μgm^{-3} range.

(3) NEOPS-DEP2002 contributes to regional studies, coordinated with the Supersites, to include an emphasis on understanding of the meteorological processes such as, the thermodynamic structure, atmospheric stability, transitions between daytime and nighttime mixing, and measurement of mixing depth for the distribution of $PM_{2.5}$ and chemical species. Knowledge of the temporal evolution of the PBL is a critical input into models of the pollutant concentrations because it establishes the mixing volume.

(4) Remote sensing and vertical profiling techniques are critical for understanding the processes governing air pollution episodes. The Raman lidar water vapor measurements provide an excellent tracer of the short term dynamical processes, and the specific humidity gradients at the top of the PBL provide the best marker to study variations in the thickness of the planetary boundary layer.

The variations of the PBL thickness have been found to provide one of the most critical tests for evaluation of meteorological models.

(5) High levels of ozone are found to be frequently trapped and transported in layers above the surface, undetected by the ground-based sensors that are normally used for measurements. Horizontal and vertical nighttime transport processes, such as the LLJ's and dynamical bursting events, are frequent contributors of chemical species, particulate matter and precursors for photochemical formation during the major episodes. The nocturnal low level jet frequently occurs in concert with O_3 pollution episodes. From mid-June to mid-August, 2002, peak 1-hour O_3 in the PHL area exceeded 100 ppbv on 19 of 21 cases where LLJs were observed. This represents two-thirds of all cases exceeding 100 ppbv during that period. Intra-regional transport of air parcels over distances of 200 to 400 km occur in a LLJ during a night, however these air pollution episodes occur during periods of large scale stagnation in the region, thus the effective transport of materials by LLJ's becomes even more important on these days.

(6) Specific meteorological conditions are important in catalyzing the region for development of major air pollution episodes. If the synoptic forcing is too strong, enhanced pressure gradients will inhibit the build up of trace gas concentrations by generating high winds, which serve to erode the interface between the boundary layer and the free atmosphere, and fumigate the local environment. On the other hand, if the synoptic forcing is weak, near-surface gradients create localized and regional circulations that remained largely confined to the boundary layer. Weak synoptic systems respond to this boundary layer forcing to create deep daytime convective mixed layers, shallow nocturnal boundary layers with embedded boundary layer jets, sea breeze fronts, and other convergence zones (e.g., leeside Appalachian trough) that have been observed, especially during summer 1999 and 2002, to significantly modify the trace gas concentrations at the site.

(7) Tethered balloon and lidar measurements suggest a very rapid down mixing of species from the residual boundary layer during the early morning hours. The rapid increase observed in ozone concentrations is too large to be accounted for on the basis of NOx reactions (Kleinman) alone. Moreover, in every case where > 100 ppbv ozone concentrations were observed, a LLJ was present during the evening and early morning hours. The nocturnal inversion prevents ozone trapped in the residual layer from being lost at the surface, and makes it available for horizontal transport by the LLJ, followed by vertical transport to the surface by bursting events and daytime convection.

(8) The data set that has been gathered in the NEOPS-DEP provides the type of results needed to test the next generation models, for example the Weather Research and Forecast System (WRF model), which is currently undergoing significant testing. Millersville University is using the WRF in an operational mode, and testing it in a research mode. The NEOPS data are expected to play an important role in activities to develop and validate air quality models.

(9) Dicarboxylic acids are formed photochemically through a variety of atmospheric reactions and can also be emitted by automobile exhaust. Our results show that they are present at extremely high concentrations during ozone events when other automobile exhaust indicators remain at more typical concentrations, suggesting that contributions from secondary formation process are important. Alkanes are heavy hydrocarbons originating primarily from automobile exhaust or epicuticular wax

from plants. Since biogenic alkanes have formulas that contain an odd number of carbon atoms, while motor vehicle exhaust contains roughly equal amounts of odd and even numbers of carbon atoms, the results show the relative contributions of biogenic and anthropogenic primary sources.

10. Summer organic aerosols in Philadelphia consists of a relatively constant level of primary organic particulate matter, punctuated by extreme episodes with high levels of secondary organic aerosol during ozone events. Primary organic particulate matter is both biogenic and anthropogenic in nature, with the relative importance fluctuating from day to day, and possibly associated more strongly with northwest winds. Secondary aerosol formation events may be responsible for dramatic increases in particulate organic carbon, while the relatively constant contribution of primary sources could make a greater contribution to annual average particulate levels. More research is needed to sort out the relative contributions of anthropogenic and biogenic sources.

7. Acknowledgments

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