

**Development of a Regional Site for Special Purpose  
Measurements of Fine Particulate Mass and Composition**  
("Supersite" Development)

Final Report

Prepared for EPRI and DOE's National Energy Technology Laboratory

By

Roger L. Tanner and Staff of the  
Air, Land, and Water Sciences Department  
Tennessee Valley Authority  
Muscle Shoals, AL 35662

July 22, 2002

## I. INTRODUCTION

Following the development of the 1996 National Ambient Air Quality Standard (NAAQS) for particulate matter, which included both an annual and a 24-h standard for fine particles (aerodynamic diameter  $\leq 2.5 \mu\text{m}$ ), criticism was directed at the proposed implementation of the standard due to the lack of  $\text{PM}_{2.5}$  and composition data. To remedy this deficiency, EPA developed a 3-tiered monitoring strategy which included deployment of 1000+  $\text{PM}_{2.5}$  mass monitors, a lesser number (150-200) of monitoring sites where chemical speciation of aerosol samples would be obtained. A handful of enhanced monitoring sites (a.k.a. "Supersites") throughout the U.S. would develop new measurement approaches, compare them to existing systems, and generally study the processes by which  $\text{PM}_{2.5}$  mass concentrations and chemical composition develop. EPA was aided in designing these networks by a National Academy of Sciences committee which has reviewed both the strategies and the progress toward those strategies which are being made by EPA (NRC, 1998, 2001).

One of the most important issues in the mid-south region in which TVA operates is the composition of  $\text{PM}_{2.5}$  mass, and the degree to which the emissions of sulfur and nitrogen oxides from TVA's power plants contribute to fine particulate matter ( $\text{PM}_{2.5}$ ) and regional haze. TVA staff recognized the need for enhanced monitoring of the mass and chemical composition of fine particles in the Tennessee Valley, and set up a  $\text{PM}_{2.5}$  mass network and made measurements of  $\text{PM}_{2.5}$  composition, beginning in 1997 in response to this need. Staff have reported the chemically speciated data thus obtained for the Valley in several recent publications (Tanner and Parkhurst, 2000, 2001; Tanner et al., 2002).

TVA staff further believed that that the establishment of regional "Supersites" by other Federal agencies would assist EPA in evaluating methodologies for the characterization of  $\text{PM}_{2.5}$  and its sources, and in developing the most cost-effective mitigation strategies for fine particulate matter. Coincident with the establishment of fine particle measurement networks, EPA was also developing regional haze regulations for Class I areas including the Great Smoky Mountains National Park (GSMNP) in the TVA region. Thus, the development of a fully equipped monitoring site in or near GSMNP, the largest Class I area in the southeast, and also within the sphere of influence of major urban areas and major point sources of sulfur and nitrogen oxides, was proposed to provide a unique platform for methods testing and special purpose monitoring. The proposed monitoring site would also generate an extremely valuable data set for evaluating the precision and accuracy of mass data from EPA's extensive network, for improving models to identify sources of  $\text{PM}_{2.5}$ , and for developing improved control strategies.

With these considerations in mind, and with support from EPRI, the Department of Energy (NETL), and TVA internal sources, TVA staff established an enhanced monitoring site in 1999 at Look Rock, TN, just west of the GSMNP and collocated with the IMPROVE network site operated by the National Park Service (NPS). This "background" site was established and located to provide a contrast to EPA "Supersite" and speciation networks which have an urban orientation. The approach was also consistent with the urban/rural site plan of the SEARCH network operated by EPRI and the Southern Company in the region between the Tennessee Valley and the Gulf Coast. This report summarizes the results of the TVA Supersite Study conducted at Look Rock and other satellite sites over several intensive sampling periods between October, 1999 and August, 2001.

## **II. DESCRIPTION OF EXPERIMENTAL STUDIES**

### ***A. Site Description.***

The enhanced monitoring site operated by TVA at Look Rock consisted of an 8'X12' shed on a cement platform, over which was constructed a 12'X12' wooden platform with 3' shelves around the outside (see Figure 1). Federal Reference Method (FRM) PM<sub>2.5</sub> samplers were placed on the shelves. Other particulate instruments such as the PC-BOSS (see description below) were placed on the floor of the platform or inside the shelter, with the inlets protruding 1-2m above the surface of the platform (e.g., TEOM, Aethalometer, ORNL particle sizing instruments). Gaseous instruments were located in the shelter with inlets placed at the top of a 10-m fold-down tower. The tower also contained instruments for continuous recording of wind speed and direction and solar radiation. Ambient temperature and humidity were recorded using sensors associated with the TEOM instrument.

### ***B. Sampling Protocols.***

Several intensive sampling campaigns were conducted for 3 to 5-week periods between October, 1999 and July-August, 2001 as part of the Supersite program. The instruments operated by TVA at the site during those periods are shown in Table 1. In addition to the TVA instrumentation, the NPS IMPROVE site (see Figure 2) operated the IMPROVE particulate sampler in its normal Wednesday-Saturday, 24-h schedule, as well as operating an ozone monitor and a nephelometer (Optek "open-door" model) continuously during these intensive sampling periods. Beginning in the summer of 2000, NPS has operated the newer version of the IMPROVE module on an every-third-day basis.



Figure 1. TVA Enhanced Monitoring Site at Look Rock



Figure 2. Look Rock IMPROVE Station Operated by NPS

**Table 1. TVA Supersite Sampling Periods for 1999-2000**

| Sampled Species  | Sampling Method                      | Data Recovery          |
|--|--------------------------------------|------------------------|
| <b>Sampling Period: Fall, October 12-26, 1999</b>                                      |                                      |                        |
| Mass, Composition  | FRM-Teflon                           | 75%                    |
| Composition incl. OC/EC  | FRM-Quartz                           | 82%                    |
| Mass and Composition incl.. SVOC   | PC-BOSS (Original Design)            | 80-96% <sup>§</sup>    |
| Ozone  | UV Absorption                        | >95%                   |
| NO/NO <sub>2</sub> /NO <sub>y</sub>  | Chemiluminescence                    | >90%                   |
| SO <sub>2</sub>  | Pulsed Fluorescence                  | >95%                   |
| CO   | NDIR                                 | >90%                   |
| Continuous mass  | TEOM (dryer A)                       | >95% <sup>#</sup>      |
| Wind speed and direction, T, RH, Solar Radiation                                       | Standard met package                 | >95%                   |
| <b>Sampling Period: Spring, Apr. 24-May 12, 2000 (Additions or Modifications Only)</b> |                                      |                        |
| Mass and Composition incl.. SVOC   | PC-BOSS (Modified Design)            | 60-98%                 |
| SO <sub>2</sub>  | High-sensitivity Pulsed Fluorescence | >95%                   |
| C14 of Organic aerosols  | PM <sub>10</sub> HiVol               | 80%                    |
| <b>Sampling Period: Summer, Aug. 16-Sep. 9, 2000 (Additions or Modifications Only)</b> |                                      |                        |
| Particle size distributions  | ORNL SMDS*                           | Partial                |
| C14 of Organic aerosols  | TSP HiVol                            | 90%                    |
| <b>Sampling Period: Summer, June 30-Aug. 14, 2001 (Add/Mods Only)</b>                  |                                      | <b>Time Resolution</b> |
| Particle size distributions  | ORNL SMDS (upgrade)*                 | 30 min                 |
| <sup>14</sup> C of Organic aerosols  | PM <sub>10</sub> HiVol               | 24 h                   |
| Elemental (black) carbon   | Aethalometer                         | 5 min ave.             |
| Continuous mass  | R&P TEOM (dryer B)                   | 5 min ave.             |
| Continuous sulfate   | Harvard/TVA                          | 10 min ave.            |
| Continuous sulfate   | R&P 8400S                            | sample/10 min          |

<sup>§</sup> Accuracy compromised by instrument performance.

<sup>#</sup> Accuracy and time resolution compromised by instrument performance.

\* Data obtained by M.-D. Cheng of Oak Ridge National Laboratory.

### C. Description of Instrumentation.

1. *PC-BOSS*. The PC-BOSS used in this study is TVA's version of the Particle Concentrator-BYU Organic Sampling System (PC-BOSS, Pang et al., 1997, 2001; Ding et al., 2002), a chemical speciation sampler designed to collect and quantify the semi-volatile portion of ambient aerosols (largely organic species and particulate nitrate). It does so by sampling a large flow (typically 80-150 Lpm) through a cyclone inlet designed to exclude coarse particles. Air flow then passes through a virtual impactor called a particle concentrator designed to divert most of the flow (referred to as the major flow) and essentially all of the ultrafine particles (< ca. 0.1 μm in aerodynamic diameter), while collecting the accumulation mode particles in the "minor flow" on a pair of filter packs, which are then analyzed. The gases in the minor flow, including most

VOCs, are removed with very high efficiency by passing through a parallel-plate denuder which contains activated carbon.

There were several differences between the BYU and TVA BOSS systems as they were first deployed in the Atlanta Supersite intercomparison study. Additional upgrades were also made in the TVA PC-BOSS system during its several deployments at the Look Rock "Supersite". These differences and upgrades are described below:

- ◆ The TVA system used an inlet flow of about 100 Lpm (monitored continuously with 10 min averages recorded by the data logging system during each sampling period), as compared to 150 Lpm for BYU.

- ◆ Unlike the BYU system, a side stream flow was not used. Instead, a quartz filter was used to collect particles from the major flow, which was monitored continuously by a mass flow meter. Sulfate concentrations were determined by IC in filter extracts prepared after filter punches had been analyzed for OC/EC by DRI using the TOR method (Chow et al., 1994). These concentrations were used to estimate the fraction of mass which was not collected in the minor flow stream. (Of course, the OC value from analysis of this filter is **not** free of positive OC artifact from absorption of gaseous VOC, as is the value from the minor flow quartz filter.)

- ◆ The lower size cut of the particle concentrator was calculated to be in the range of 0.10 to 0.15  $\mu\text{m}$  for the lower flow rates used.

- ◆ The denuder flow in the TVA PC-BOSS was controlled by downstream mass flow controllers at  $30.0 \pm 0.2$  Lpm, 15 Lpm in each of the two filter packs collecting particles in the minor flow stream. During the 2001 field studies, these flows were reduced to 12.0 Lpm through each filter pack; this was done to ensure constant, controlled flow at the higher altitude (~825 m MSL) of the Look Rock site.

- ◆ For the quartz/CIF filter pack in the minor flow stream, sulfate and nitrate were determined by IC and ammonium was determined by indophenol colorimetry. Organic and elemental carbon were determined on the quartz filter prior to extraction by DRI using the TOR method; semi-volatile organic compounds (SVOCs) in the ambient aerosols were determined on the CIF filter by BYU with the TPV method (Tang et al., 1994).

- ◆ For the Teflon/nylon filter pack in the minor flow stream of the TVA PC-BOSS, mass was determined gravimetrically, sulfate and nitrate were determined by IC, and ammonium was determined by indophenol colorimetry; nylon filters were extracted with IC eluent and nitrate determined in the extract by IC.

Serious leakage problems were noted in the initial application of the TVA PC-BOSS system at Look Rock. This led to the modified PC-BOSS system to that shown in Figure 3,

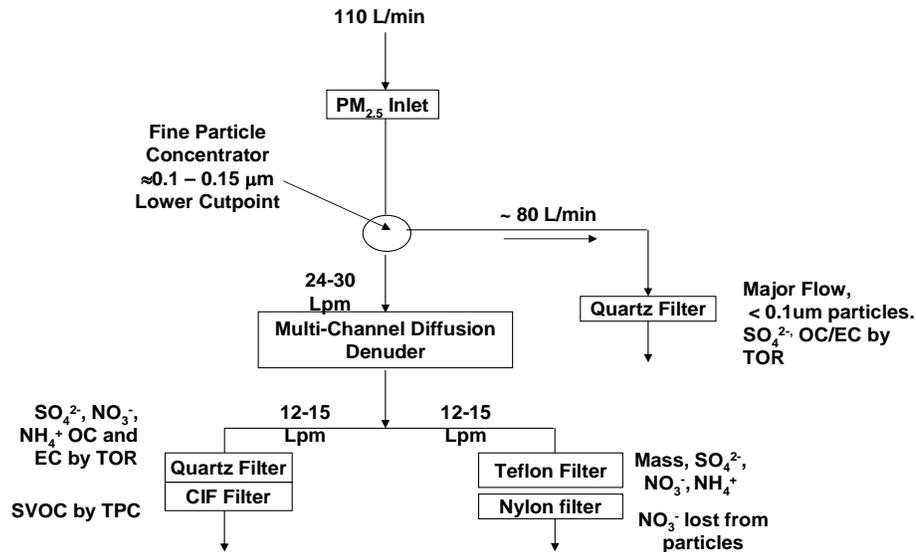


Figure 3. Schematic of the TVA PC-BOSS System

which is the present configuration. Data logging functions are now conducted using a Campbell Model 21x system which is located on the platform in a water proof suitcase. The suitcase also contains the solenoid valves which monitor the flow. The data logging program allows for automated switching of valves for preset sampling interval. Current status of the valves, flows, etc. are also accessible by remote access using a modem attached to the data logger. A complete set of operating procedures has been developed for the PC-BOSS system as used at Look Rock, incorporating all of the upgrades.

2. *TEOM*. A EPA-certified TEOM instrument with a 2.5  $\mu\text{m}$  cyclone inlet and humidity control was used to perform 5-minute averaging fine particle mass concentration measurements using its own dedicated sampling line. The cyclone is of the older design, and has not been replaced with the newer, so-called "sharp-cut" cyclone. This TEOM was initially operated at 30°C with a non-commercial Nafion dryer for humidity control. Air was pumped at reduced pressure through a tube external to a flexible Nafion tube which was the same ID as the TEOM sample flow, providing the water vapor gradient to reduce the humidity of the incoming sample air by about 30% below ambient. Due to the fragility and potential for (non-detectable) leaks in this experimental setup, it was replaced in late calendar 2000 by R&P's commercial drying system (a.k.a, the sample equilibration system, SES). This system operates on the same principle of

recycling sample and by-pass air downstream of the flow controllers and at lowered pressure external to a Nafion tube through which the incoming air passes. This TEOM instrument, equipped with a 2.5 $\mu$ m cyclone inlet and humidity control was used to perform 5-minute averaging fine particle mass concentration measurements using its own dedicated sampling line.

3. *Aethalometer*. This instrument continuously measures the attenuation of a beam of light transmitted through a filter while the filter is continuously collecting a sample of particulate matter. Using an appropriate value for the specific attenuation of the filter + particulate sample, the increase in attenuation from one sampling period to the next can be related to the black carbon concentration collected during that period (usually of the order of 5 min). The instrument (hardware and software) thus operates by:

- ◆ quantitatively collecting the aerosol sample at high efficiency using a fiber-reinforced quartz filter in the form of an advanceable tape;
- ◆ accurately measuring the optical attenuation of the collected aerosol deposit;
- ◆ calculating the increase in the BC component of the aerosol deposit and relating it to the BC concentration;
- ◆ displaying and recording this data along with the necessary instrument control and diagnostic data.

This instrument was operated at Look Rock for four month-long periods in 2001, one of which coincided with the Summer 2001 intensive sampling period. The inlet air sample consisted of a portion of the bypass flow of the TEOM instrument. Problems were observed with the instrument during field periods, which were traced to particulate intrusions into the light path and to a problem with the filter advance mechanism. We also noted that the precaution of minimizing the vibration (from pumps and/or other vibrating equipment) must be adhered to rigorously to enable operation with the required precision.

#### 4. *HiVol sampling for $^{14}C$ measurements of organic aerosols.*

Samples were taken for 24-h periods using a conventional high volume sampler with a PM10 inlet for sampling periods in April-May, 2000, July-August, 2001, and October-November, 2001. Due to equipment problems, sampling done in August-September, 2000, was conducted with a portable Staplex high volume sampler without a size-selective inlet, hence the samples from that period approximate total suspended particulate (TSP) samples. Samples were collected on 8x10-in (20x25 cm) tissue quartz filters, removed from the sampler within 24 hr of collection, and stored at -20°C until analysis.

Portions of the 20x25 cm filters were submitted for analysis by staff of Woods Hole Oceanographic Institute's (WHOI) National Ocean Sciences Accelerator Mass Spectrometry

(NOSAMS) facility, using a procedure in which the organic aerosol is combusted to CO<sub>2</sub> to quantify the amount of carbon, the <sup>13</sup>C/<sup>12</sup>C ratio is measured, then the CO<sub>2</sub> is converted to an iron/graphite pellet and analyzed for <sup>14</sup>C by accelerator mass spectrometry (ref). Portions of the filters are also analyzed for organic and elemental carbon by the DRI TOR technique.

5. *Gas-Phase Instruments (Level II)*. Individual 1/4" OD Teflon sampling lines are used to deliver sample air containing NO/NO<sub>2</sub> and NO<sub>y</sub> to their respective monitors housed inside the trailer. The NO and NO<sub>2</sub> was sampled through a common sampling line that was split to pass either through a photolytic cell or directly into a TEII 42S instrument which had its converter removed. The converter from the TEII 42S NO<sub>y</sub> instrument was placed outdoors in the inlet box at a height of 10 m above ground, and operated at 350°C. A dedicated sample line extended from the converter to the second TEII 42S to obtain NO<sub>y</sub> measurements. Teflon lines were installed to allow introduction of a standard gas mixture, calibrant gases from a standard addition system, or zero air at the sample intakes. These sample lines were used during span and zero procedures and during calibration.

The site was equipped with a TEII Model 111 Zero Air generating system and a modified TEII 146 Dynamic Gas Calibrator. The TEII 146 was modified to allow gas addition method span checks for the NO, NO<sub>2</sub>, and NO<sub>y</sub> gas monitors using individual cylinders of NO, NO<sub>2</sub>, and n-propyl nitrate (NPN) gas standards. The NO<sub>y</sub> converter efficiency was checked daily by the gas addition of NPN and weekly by gas addition of HNO<sub>3</sub>. Calibrations are conducted at the start and end of the study, or more frequently if instrument performance requires calibration. Calibrations were conducted on the NO<sub>x</sub>-NO<sub>y</sub> analyzers using an ESE-built gas dilution system that was modified by TVA and integrated to a TEII 146 Dynamic Gas Calibrator using NIST traceable gas cylinders of NO. NO<sub>2</sub>/air from an EPA Protocol gas cylinder supplied by Scott Specialty Gas was used to determine the photolytic cell's conversion efficiency for NO<sub>2</sub>. The catalytic converter on the NO<sub>y</sub> measurement systems was checked using NPN gas standards from Scott-Marrin. Calibrations were conducted through the sampling inlets using gas substitution methods, consisting of a zero reading and 4 upscale points with 3 points in the ambient measurement range.

This same general procedure was used to provide zero and calibration gases by the gas substitution method through the inlet lines for the ozone (UV absorption method), SO<sub>2</sub> (pulsed fluorescence method) and CO (NDIR method) instruments.

6. *Continuous Sulfate Instruments*. Two techniques for continuous, short-time-resolution determination of particulate sulfate were compared at the Supersite during the July-August, 2001 sampling campaign. One was the Aerosol Dynamics, Inc. (ADI) method for sulfate, using the instrument commercialized by R&P as their Model 8400S (Stolzenburg and Hering, 2000; Hering

and Kirby, 2001). In this method, fine-mode aerosol containing sulfate is collected at high humidity on a platinum strip for several minutes. A low-voltage, high current discharge is then applied to the strip, converting most of the sulfate to SO<sub>2</sub> which is released and quantified by a pulsed fluorescence SO<sub>2</sub> analyzer. One reading for sulfate is obtained every 10 or 15 min by the analyzer, using aqueous standards applied to the Pt strip to calibrate the instrument system. These standards contained dissolved organics (oxalic acid) in amounts designed to alleviate problems of low (ca. 70%) conversion of sulfate to SO<sub>2</sub> which are observed if pure ammonium sulfate standards are used. An R&P Model 8400S instrument was deployed at Look Rock, and the required vendor training conducted on site.

A second technique, devised by G. Allen and Harvard School of Public Health (HSPH) staff (Allen et al., 2001), and constructed and operated by TVA under a no-fee arrangement with HSPH, consisted of the following: sample air, after passing through a 2.5- $\mu$ m cyclone, is denuded of SO<sub>2</sub> by a URG annular denuder, then passes through a heated SS tube (TEII Model 350) at about 800°C, which converts the sulfate in the sample air to SO<sub>2</sub>. This SO<sub>2</sub> is continuously measured using a TEII Model 43C-trace level pulsed fluorescence analyzer. Zeroing is accomplished by passing ambient air through a particulate filter prior to the SO<sub>2</sub> denuder for 5-10 min/sampling hour. The TEII 43C is calibrated with the "Level II" calibration system (see above). For the summer, 2001, sampling campaign, no direct calibration of the system with known concentration of aerosol sulfate was conducted, and the efficiency of conversion of aerosol sulfate to SO<sub>2</sub> in this system is not accurately known.

### **III. RESULTS AND DISCUSSION**

We now discuss the results from work conducted in the Supersite project in terms of several areas of interest. One is instrument development work in two major areas: sampling techniques developed to obtain chemical composition data, and deployment and operation of continuous instruments for particle mass and composition. The second area is the specific evaluation of the potential of the FRM sampler to under-measure the organic fraction of fine mass, using the particle concentrator-BOSS system as a potentially artifact-free chemical speciation sampler for fine particles. The third area is an evaluation of the use of integrated FRM and PC-BOSS sampling (the former throughout the year and the latter during intensive campaigns at Look Rock) to determine seasonal variations in composition, and (with the help of internal co-funding) to compare these seasonal variations with those observed at other urban and rural sampling sites in the region. Lastly, we will discuss the results obtained from continuous particle mass and composition (black carbon, sulfate) measurements at the Look Rock site. Focus is on

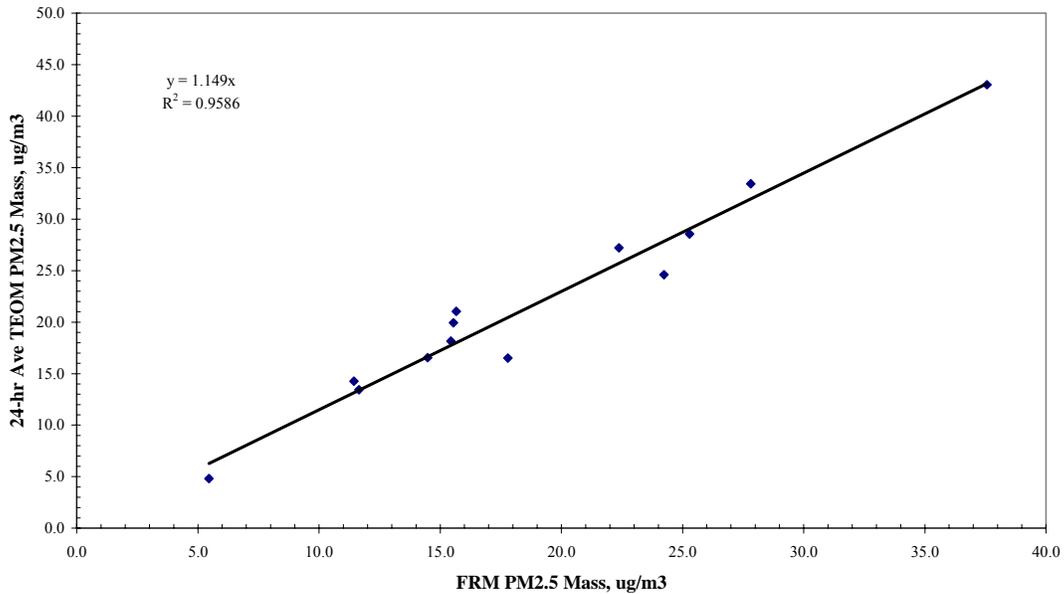
how to use these continuous measurement techniques for both process studies, and to evaluate the extent to which they can be used for source identification and to obtain accurate exposure assessments in rural areas of the region than possible with 24h (i.e., FRM) sampling.

### ***A. Instrument Development***

Several instrument systems which are important in characterizing PM<sub>2.5</sub> mass and chemical composition in the region have been developed and/or deployed during this project:

- ◆ The Level II system of trace gas measurements utilizing through-the inlet-calibration was used for all campaigns after Fall, 1999. This system was developed for SOS field studies in 1994-95, and is described in the Experimental section.
- ◆ The evolution of the TEOM system is described in more detail in the Experimental section. Prior to the installation of the commercial SES humidity control system, the time resolution of the mass measurements was no better than about 1 h due to the cycling of the mass readings. This is caused by the moisture uptake and release from the TEOM filter, its collected particles, and perhaps other internal components as well. The accuracy of the TEOM data taken prior to the summer, 2000, campaign are questionable. For the summer, 2000, campaign the 24-h averaged TEOM PM<sub>2.5</sub> mass data are well correlated with, but biased low compared to collocated FRM and IMPROVE PM<sub>2.5</sub> mass concentrations by about 20%. For the summer, 2001, campaign, with the commercial SES attached, the correlation is very good (see Figure 4), but the TEOM is biased high by about 15% over this sampling period. In conclusion, there remain problems with the accuracy of the TEOM for other than warm seasons when using the SES system, but overall it appears to give reliable PM<sub>2.5</sub> mass data with time averaging of 15 min or less which are well correlated with 24-h averaged FRM masses. In terms of future improvement, there are new approaches to continuous fine mass measurements being commercialized—the Harvard-Andersen pressure differential approach, reportedly a new  $\beta$ -gauge-based instrument from BGI, and a dual-pathway, unfiltered-filtered configuration for the TEOM to "fix" the volatilization from the filter problem. However, none of these innovations were available for use in this project.
- ◆ The development of the two continuous sulfate measurement systems used in the summer, 2001, intensive have been described above. The HSPH/TVA continuous sulfate system appears to give results comparable to the integrated FRM. However, the conversion efficiency of the heated tube has not yet been well characterized when used in the 800-850 °C range, the heated tube has a very limited lifetime and is expensive. It does give continuous readings and requires

**Figure 4. 24-Hr Average TEOM Mass vs. FRM Mass  
Look Rock, July-Aug, 2001**



less than 10 min of zeroing each hour. In our hands, the R&P Model 8400S ran with a tolerably low operator time. However, the instrument we received reported sulfate levels only 60-80% of the integrated FRM sulfate results on Teflon or quartz filters, even when using the calibration factor for conversion efficiency. This factor is derived from directly applied, oxalic acid-containing aqueous standards, and was about 71% during the summer, 2001 field measurements at Look Rock. During later tests in our on-site sampling trailer at Muscle Shoals, we tracked down 2 major manufacturing defects in the instrument we received. When these defects were replaced and/or corrected, the performance of the 8400S system was comparable in precision and accuracy to the HSPH/TVA system.

The other major instrument development in this project was the optimization of the TV PC-BOSS sampler, which is described in detail in the Experimental section, and conclusions concerning its field use are described in the next section.

### ***B. Semi-Volatiles Issues***

TVA staff were concerned at the time the PM<sub>2.5</sub> NAAQS was proposed about how precise and accurate the proposed Federal Reference Method for PM<sub>2.5</sub> mass was since it would be used to evaluate both the level of human exposure to fine particles and the effectiveness of any controls which might be placed on sources of fine particles and their precursors. Fine particles

collected from urban and rural sites contain significant quantities of material, including  $\text{NH}_4\text{NO}_3$  and semi-volatile organics, which can be lost during and after sample collection on a filter. This volatilization can result in significant under-sampling of these particulate species, leading to inaccuracies in measurements of semi-volatile species are needed to properly apportion the sources of fine particles. As a result, TVA began the development and application of a denuder-based sampling method which would collect and characterize both non-volatile and volatile constituents of fine particulate matter. Our initial collaboration with BYU and the HSPH developers of the "particle concentrator" led to a scoping field study (July, 1997), from which we concluded:

- ◆ Organic aerosol constituents were a significant portion of the total measured fine particle mass at a rural site in TN during summer, based on measurements in July, 1997.
- ◆ The semi-volatile fraction of organic aerosol fine mass was variable but averaged about 1/3, with the semi-volatile fraction being significantly higher at night. This counterintuitive result suggests that daytime conversion of semi-volatiles to less volatile organic particulate matter may be important.
- ◆ Agreement of sulfate concentrations between quartz and Teflon channels of TVA's PC-BOSS, and of mass and sulfate concentrations between duplicate PC-BOSS samplers and between PC-BOSS and annular denuder samplers was not as good as might reasonably be expected. No procedural errors in sampling or analysis have been identified which would explain these differences, hence some re-design of the apparatus was needed.

The remaining, significant problems in field applications of the PC-BOSS apparatus in field environments required an upgrading of the system to improve flow control and simplify the data acquisition. This upgrade was deployed in the SOS Nashville 99 study, during the Atlanta Supersite intercomparison, and at the Look Rock site, all in the summer and fall of 1999. The TVA PC-BOSS operated during the entire Atlanta Supersite experiment and obtained mass and composition, with data recovery averaging 91% (range: 83-97%). Average mass observed by the PC-BOSS was  $25.7 \mu\text{g}/\text{m}^3$ , with about 49% of the aerosol mass being ammonium sulfate and about 36% being non-volatile organic carbon (NVOC). Volatilizable organic aerosol constituents from the quartz filter media denuded of gaseous organics averaged  $35 \pm 16\%$  of the NVOC, and the % was about the same during the 12-h daytime sampling periods as at night. The fractions of fine mass and chemical species in the major flow stream (< about  $0.1 \mu\text{m}$  aerodynamic diameter) were larger than anticipated based on the nominal size-cut of the concentrator. A re-designed instrument with improved control of flows through the filters and simplified data logging procedures, was used in three subsequent field sampling campaigns at the Look Rock Supersite.

### C. *Integrated Sampling*

1. *Look Rock PM<sub>2.5</sub> composition results compared to other sites.* A chemically speciated data set was obtained from collocated FRM sampling with Teflon and quartz filters in the TN Valley during all 4 seasons during 2001, operated simultaneously at an urban site in Chattanooga, a rural site in Lawrence County, TN, as well as at the “background” Supersite location at Look Rock.

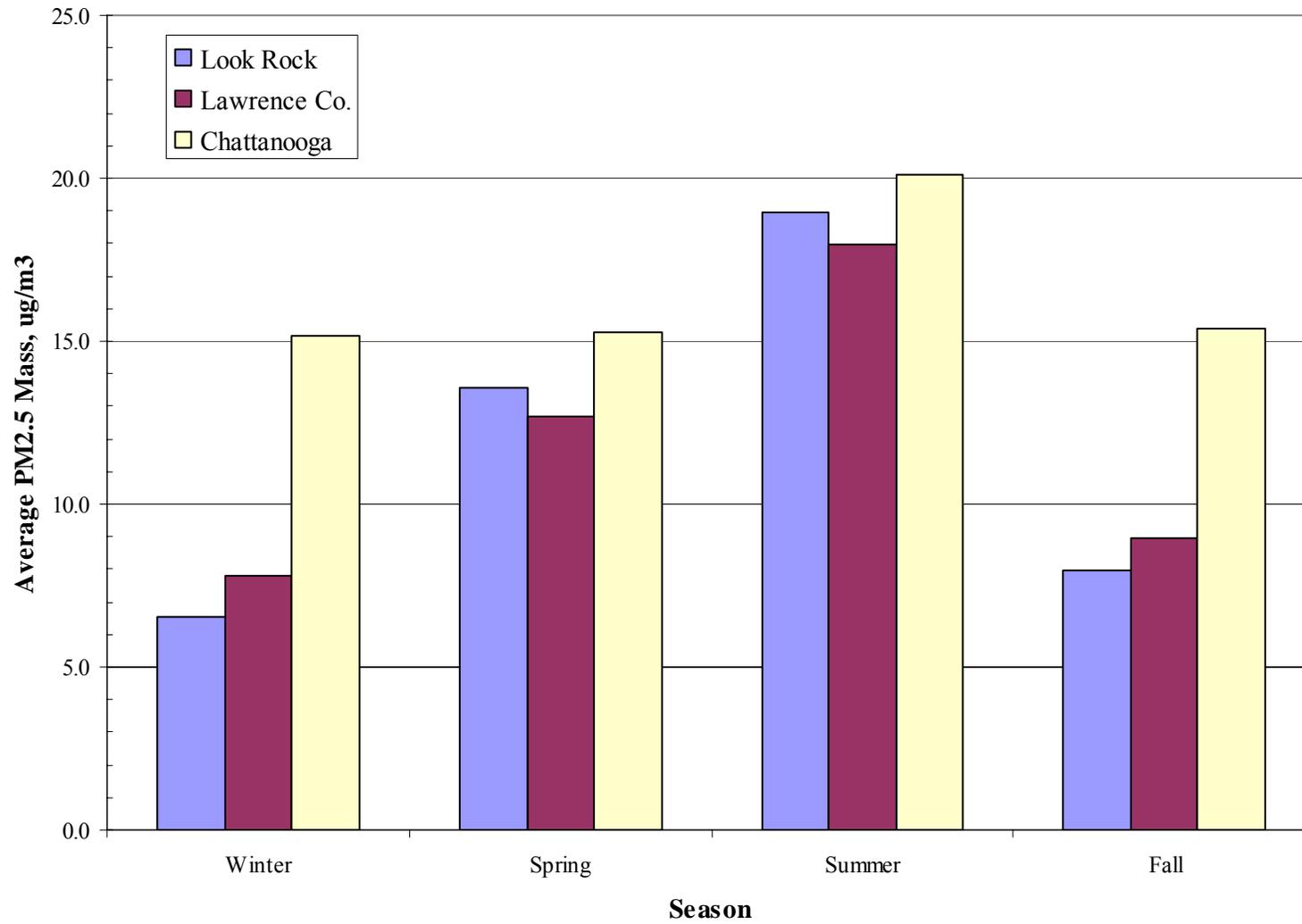
In presenting the composition results by site and season (see Figure 5), we follow a convention of presenting the major constituents as follows: nitrate as ammonium nitrate (this is valid for fine particulate matter, although not always so for PM<sub>coarse</sub> or PM<sub>10</sub>); sulfate as ammonium sulfates, based on actual measurements of aerosol ammonium and correcting for that portion of ammonium associated with nitrate; organic aerosol as organic carbon by the thermo-optical reflectance (TOR) method multiplied by the commonly used 1.4 factor to account for other elements (H, N, S, etc.) present in organic aerosol (but see discussion below); elemental carbon as directly measured by TOR; trace elements/metals by XRF calculated as their predominant oxides; "other", defined as the remainder of FRM-measured mass not accounted for as sulfates, nitrates, organics, EC or trace elements.

At the Look Rock Supersite, mass levels for one-month periods of every-third-day sampling varied from 6.4 µg/m<sup>3</sup> in winter to 19.0 µg/m<sup>3</sup> during the summer period with an all-sample average of about 12 µg/m<sup>3</sup>. Sulfate was the largest component of mass, but significant ammonium nitrate was found only during the winter period. Particulate organic carbon was a major component of fine mass (26-41 %, average 33%) throughout the entire year.

Mass concentrations at the rural Lawrence county site were generally higher than the Look Rock site (except they were about the same in summer). The all-sample "annual" average at this site was 12.9 µg/m<sup>3</sup>, still below the annual PM<sub>2.5</sub> NAAQS. Sulfate and organic mass fractions were the largest fractions of mass throughout the year, and again nitrate levels were negligible except in the winter sampling period.

At the urban site, mass levels averaged from 15 µg/m<sup>3</sup> in winter to 20 µg/m<sup>3</sup> in the summer, with the largest component over all seasons being organic C, and with significant ammonium nitrate levels only in winter. There were small but significantly greater elemental carbon levels at the urban site than at either the rural or background sites; this trend was especially noticeable in the winter period. Over all sites, results show a consistent pattern with highest contributions to fine mass from organic carbon and sulfates, and relatively higher carbonaceous levels in urban vs. rural and background sites.

**Figure 5. Average PM2.5 Mass by Season, 2001**



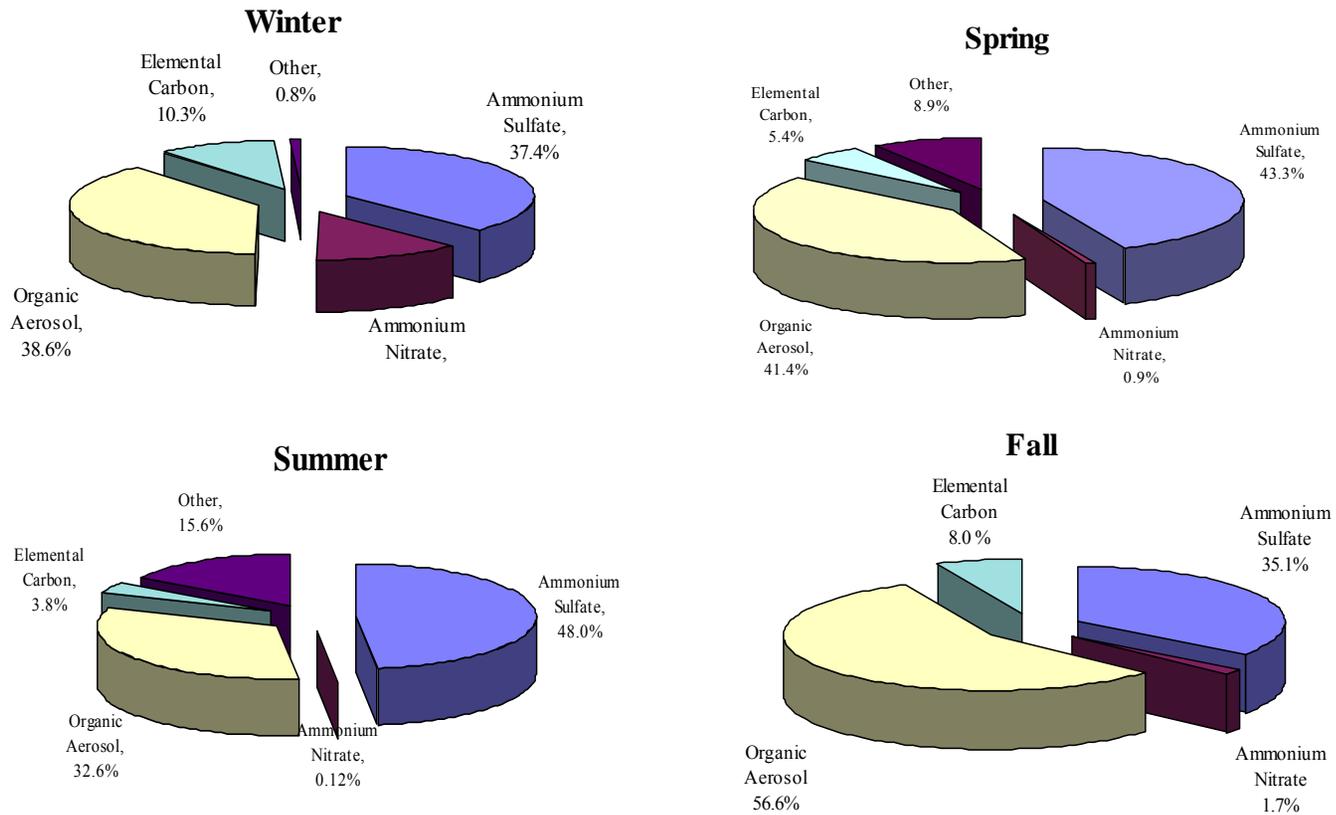
2. *PM<sub>2.5</sub> chemical composition at Look Rock.* Chemical composition data for Look Rock during the four seasons of 2001 are shown in Figure 6. In general, contributions to PM<sub>2.5</sub> mass from sulfates are highest only at the background site or in the summer season. No significant levels of particulate nitrate were found at any of the sites except in the winter season. These trends are quite consistent with other mass data obtained by EPA in the Southeastern U.S. and mass and composition data obtained by the SEARCH network (Jansen, 2002). Only moderate year-to-year differences are found in the chemical composition of PM<sub>2.5</sub> mass at Look Rock, as shown in Figure 6 comparing data from the 2000 and 2001 summer intensives.

3. *Source implications from <sup>14</sup>C measurements.* Significant portions of PM<sub>2.5</sub> mass consists of organic and elemental carbonaceous material. In the southeastern United States typically 1/3 of the FRM-measured fine mass consists of organic carbon and, in urban areas, of the order of 10% consists of elemental carbon. The organic portion of this carbonaceous is a complex mixture of primary compounds and secondary materials formed in situ from primary emissions, both deriving from a variety of sources which are dynamically changing in time and space. Source characterization has been hampered by this complexity, and further constrained by lack of knowledge of secondary formations processes and the cost of using source specific tracers. One underutilized way of addressing these shortcomings is through the measurement of the <sup>14</sup>C content of organic aerosol particles.

Based on the two-source model, organic aerosol carbon may consist of "modern" or recently formed carbonaceous material in equilibrium with current concentrations of atmospheric <sup>14</sup>CO<sub>2</sub> which has formed from the interaction of cosmic rays with atmospheric nitrogen. The second source of aerosol carbon is derived from fossil carbon whose age greatly exceeds the half-life of <sup>14</sup>C (ca. 5800 y) hence contains essentially no <sup>14</sup>C. By measuring the <sup>14</sup>C content of ambient aerosols, along with the <sup>13</sup>C/<sup>12</sup>C isotopic ratio to correct for fractionation processes, the fraction of modern carbon ( $f_m$ ) in aerosol samples can be determined, and the fraction derived from fossil fuel combustion determined as  $1-f_m$ .

Measurements have now been made of the <sup>14</sup>C content of PM<sub>10</sub> samples collected at TVA's enhanced monitoring facility at Look Rock, TN, during three seasons: spring of 2000, summers of 2000 and 2001, and fall, 2001. Results, calculated as the fraction of modern carbon, are reported in Tables 2 and 3 for all four of these periods. Variable fossil carbon fractions ( $1-f_m$ ) were observed during the spring, 2000, season (Table 2), decreasing from about 45% in mid-April to about 10% in mid-May in about the same time frame as the leaves of the predominantly

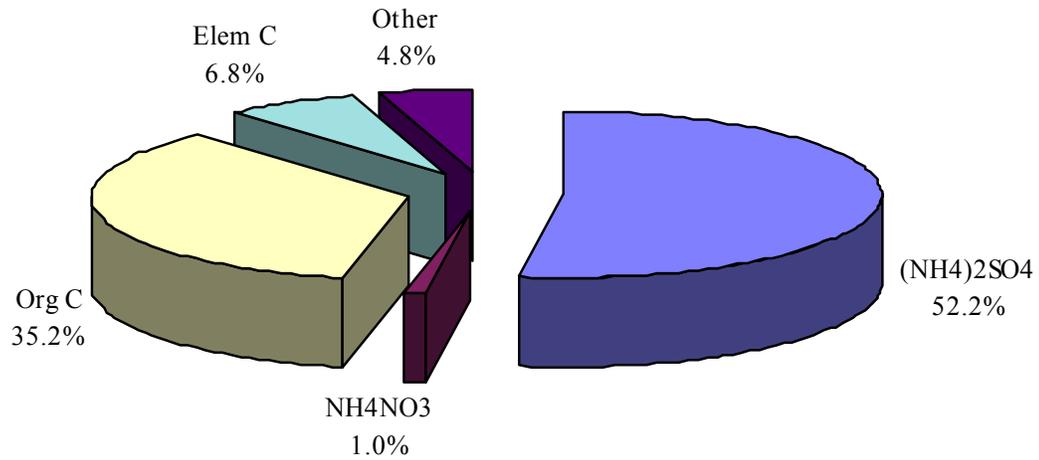
**Figure 6. Look Rock Aerosol Composition, 2001**



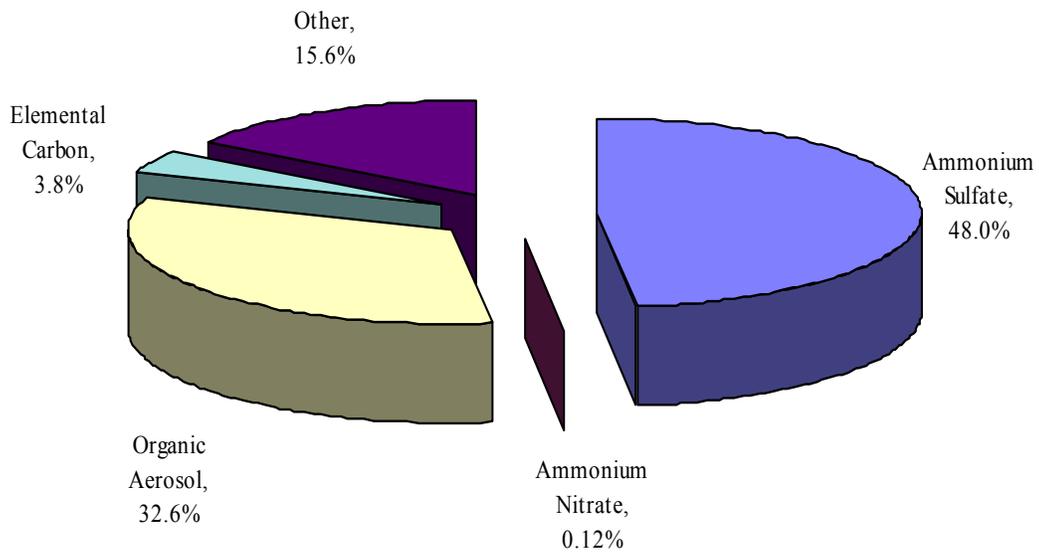
# Figure 7

## Average Chemical Composition of Fine Particles at Look Rock

Summer, 2000: Average Mass Concentration = 17.1 ug/m<sup>3</sup>



Summer, 2001: Average Mass Concentration = 19.0 ug/m<sup>3</sup>



**Table 2. Look Rock FRM Chemical Composition Data  
with Fraction of Modern Carbon, 2000**

| <i>Date</i>         | <i>PM<sub>2.5</sub> Mass,<br/>μg/m<sup>3</sup></i> | <i>Sulfate,<br/>μg/m<sup>3</sup></i> | <i>TOR OC*1.4,<br/>ug/m3</i> | <i>Fraction of<br/>Modern Carbon</i> |
|---------------------|--|--------------------------------------|------------------------------|--------------------------------------|
| <i>Spring, 2000</i> |  |                                      |                              |                                      |
| 4/26/00             | 6.86   | 3.2 <sup>a</sup>                     | 2.1                          | <b>0.597<sup>b</sup></b>             |
| 4/28/00             | 13.22  | 5.7                                  | 4.0                          | <b>0.592</b>                         |
| 5/02/00             | 19.46  | 7.62                                 | 6.50                         | <b>0.822</b>                         |
| 5/04/00             | 14.35  | 6.38                                 | 4.58                         | <b>0.774</b>                         |
| 5/06/00             | 18.12  | 7.19                                 | 5.53                         | <b>0.798</b>                         |
| 5/08/00             | 16.90  | 6.39                                 | 5.37                         | <b>0.912</b>                         |
| 5/10/00             | 9.08   | 3.39                                 | 2.62                         | <b>0.914</b>                         |
| <i>Summer, 2000</i> |  |                                      |                              |                                      |
| 8/26/00             | 17.34  | 8.0                                  | 4.92                         | <b>0.389</b>                         |
| 8/28/00             | 14.30  | 6.9                                  | 5.06                         | <b>0.435</b>                         |
| 8/30/00             | 13.55  | 4.7                                  | 4.20                         | <b>0.464</b>                         |
| 9/01/00             | 15.72  | 7.3                                  | 4.41                         | <b>0.378</b>                         |
| 9/03/00             | 12.46  | 6.6                                  | 4.02                         | <b>0.406</b>                         |
| 9/05/00             | 19.22  | 11.0                                 | 1.52                         | <b>0.434</b>                         |
| 9/07/00             | 4.75   | 1.9                                  | 2.59                         | <b>0.274</b>                         |

<sup>a</sup>data in italics estimated from PC-BOSS data;

<sup>b</sup>fraction of modern carbon from PM10 HiVol samples.

mixed deciduous forest surrounding the sampling site emerged. Relatively constant fractions of 60±10% fossil carbon were observed during the late summer period (mid-August to early September, see Table 2) in 2000. This occurred during a period in which the fine mass and organic carbon concentrations were generally decreasing from >20 μg/m<sup>3</sup> to levels near the annual average of about 12 μg/m<sup>3</sup>.

Data for the summer, 2001, period, which included the entire month of July, showed a different pattern (Table 3), with the fraction of fossil carbon varying from 12 to 27 %. This sampling period exhibited widely varying fine mass concentrations from <10 to as high as 40 μg/m<sup>3</sup> (based on TEOM continuous monitoring of PM<sub>2.5</sub> mass). The reasons for this wide variation in fraction of fossil carbon from season to season and summer to summer are not yet clear.

**Table 3. Look Rock FRM Chemical Composition Data  
with Fraction of Modern Carbon, 2001**

| <i>Date</i> | <i>PM2.5 Mass,<br/>µg/m<sup>3</sup></i> | <i>Sulfate,<br/>µg/m<sup>3</sup></i> | <i>TOR OC*1.4,<br/>ug/m<sup>3</sup></i> | <i>Fraction of<br/>Modern Carbon</i> |
|-------------|---|--------------------------------------|---|--------------------------------------|
|             |   | Summer, 2001                         |   |                                      |
| 7/3/01      | 17.94                                   | 6.30                                 | 6.35                                    | <b>0.823</b>                         |
| 7/6/01      | 11.36                                   | 4.94                                 | 4.23                                    | <b>0.758</b>                         |
| 7/9/01      | 14.40                                   | 5.13                                 | 5.61                                    | <b>0.882</b>                         |
| 7/12/01     | 17.61                                   | 6.00                                 | 7.26                                    | <b>0.801</b>                         |
| 7/15/01     | Est. 18.                                | 6.58                                 | 6.16                                    | <b>0.728</b>                         |
| 7/18/01     | 37.49                                   | 15.38                                | 9.42                                    | <b>0.860</b>                         |
| 7/24/01     | 15.36                                   | 6.17                                 | 5.97                                    | <b>0.855</b>                         |
| 7/27/01     | 11.57                                   | 3.37                                 | 4.72                                    | <b>0.828</b>                         |
| 7/30/01     | 15.69                                   | 7.91                                 | 3.86                                    | <b>0.798</b>                         |
|             |   | Fall, 2001                           |   |                                      |
| 10/10/2001  | 4.71                                    | 1.86                                 | 3.22                                    | <b>0.619</b>                         |
| 10/19/2001  | 9.96                                    | 3.32                                 | 5.50                                    | <b>0.681</b>                         |
| 10/22/2001  | 16.54                                   | 5.89                                 | 7.55                                    | <b>0.740</b>                         |
| 10/25/2001  | 2.58                                    | 1.24                                 | 1.72                                    | <b>0.751</b>                         |
| 10/28/2001  | 6.58                                    | 1.89                                 | 2.95                                    | <b>0.782</b>                         |
| 11/03/2001  | 9.92                                    | 3.05                                 | 6.38                                    | <b>0.757</b>                         |
| 11/06/2001  | 9.37                                    | 1.51                                 | 6.52                                    | <b>0.822</b>                         |

<sup>a</sup>data in italics estimated from PC-BOSS data;

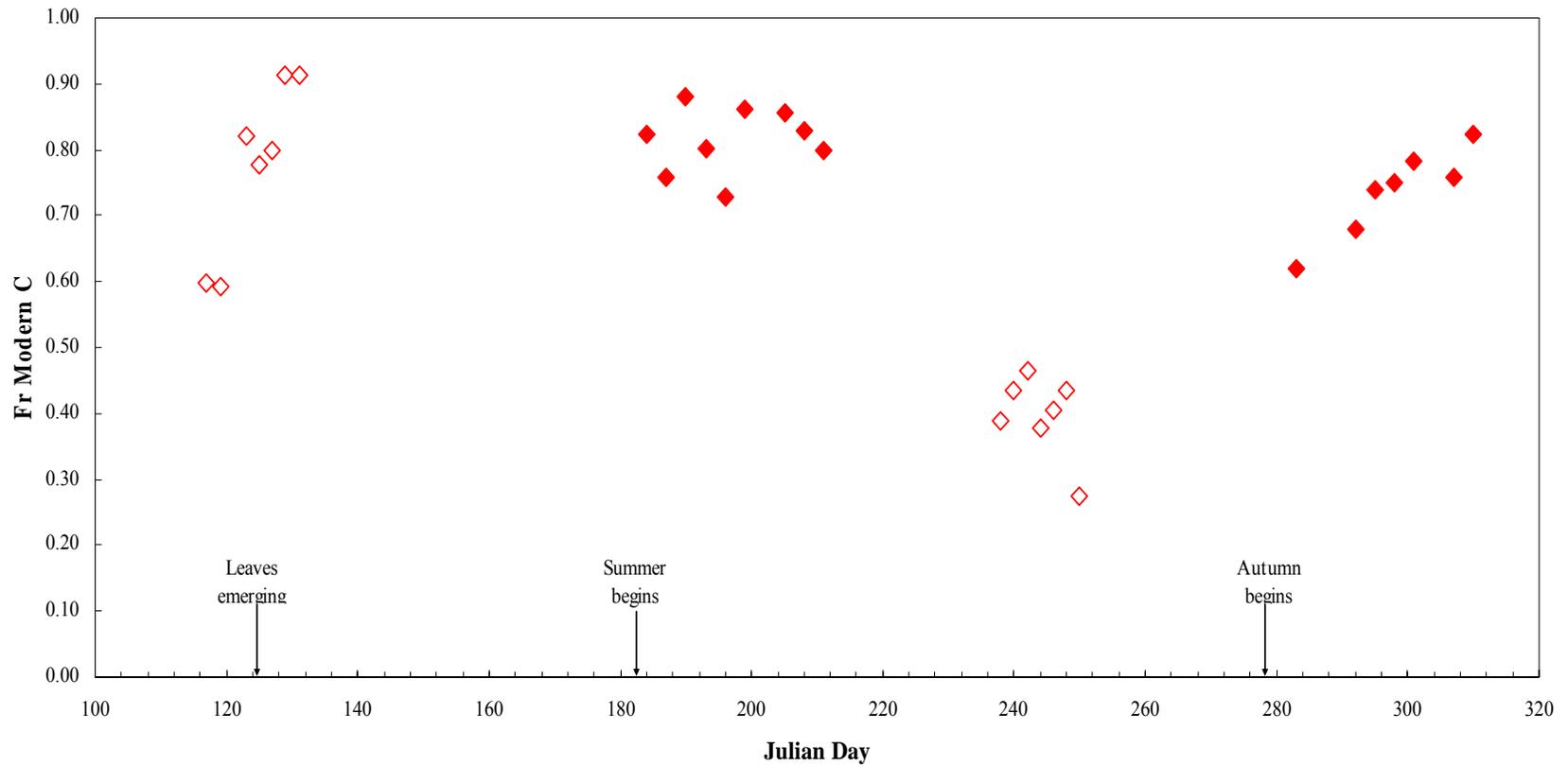
<sup>b</sup>fraction of modern carbon from PM10 HiVol samples.

Finally, data acquired in the late October-early November, 2001, period are shown in Table 3. The observed fractions of fossil carbon varied from 18-38%, with a general trend of decreasing fossil carbon for this October-November period, paralleling the senescence and drop-off of leaves in the surrounding forest. A summary of all of our "fraction of modern carbon" data by Julian day is shown in Figure 5. We note that the relation of observed fractions of fossil carbon to controllable anthropogenic organic carbon sources is complex. Products of fossil fuel combustion, largely from mobile sources (gasoline- and diesel-powered vehicles), clearly comprise in the large part the fossil-derived organic carbon in ambient aerosols. There is a major

**Figure 8**

**Fraction of Modern Carbon by Julian Day**

Open diamonds: 2000; Filled diamonds: 2001



contribution to the "modern" organic carbon from natural emissions of trees and other plant life which are converted by photochemical oxidation to non-volatile, secondary organic products, as well as some contributions from resuspended plant detritus. However, there are also contributions to "modern" aerosol organic carbon from wood-burning and combustion of agricultural wastes, and these are anthropogenically derived and thus potentially controllable sources. Wood burning contributions to "modern" carbon is complicated by the residual radiocarbon derived from thermonuclear bomb tests in the mid-twentieth century, since combusted wood can be several decades old. Large seasonal variations in these sources are also expected. Even with these complexities in interpreting fraction of fossil carbon data, we suggest that the observed fractions of modern carbon are lower limits to the fraction of fine organic carbon in atmospheric aerosols which could be targeted for emissions reductions. Since organic carbon fractions of fine mass average  $\frac{1}{3}$  or more of the  $PM_{2.5}$  mass, organic carbon aerosols are a legitimate target for any necessary future control strategies.

#### ***D. Continuous Particle and Gas Measurements.***

Several continuous measurements techniques have been used at Look Rock since the last major intensive measurement study, SEAVS, in 1995. The NPS has measured ozone concentrations by the Federal Reference Method and light scattering using an Optek "open door" nephelometer on a continuous basis at the site since 1984 and 1993, respectively. At a nearby tower, NPS has also deployed a digital camera aimed at selected vistas and designed to display (through transmittal to the GSMNP website) visibility conditions at the park every 15-min, with one picture per day from the camera also archived for future use.

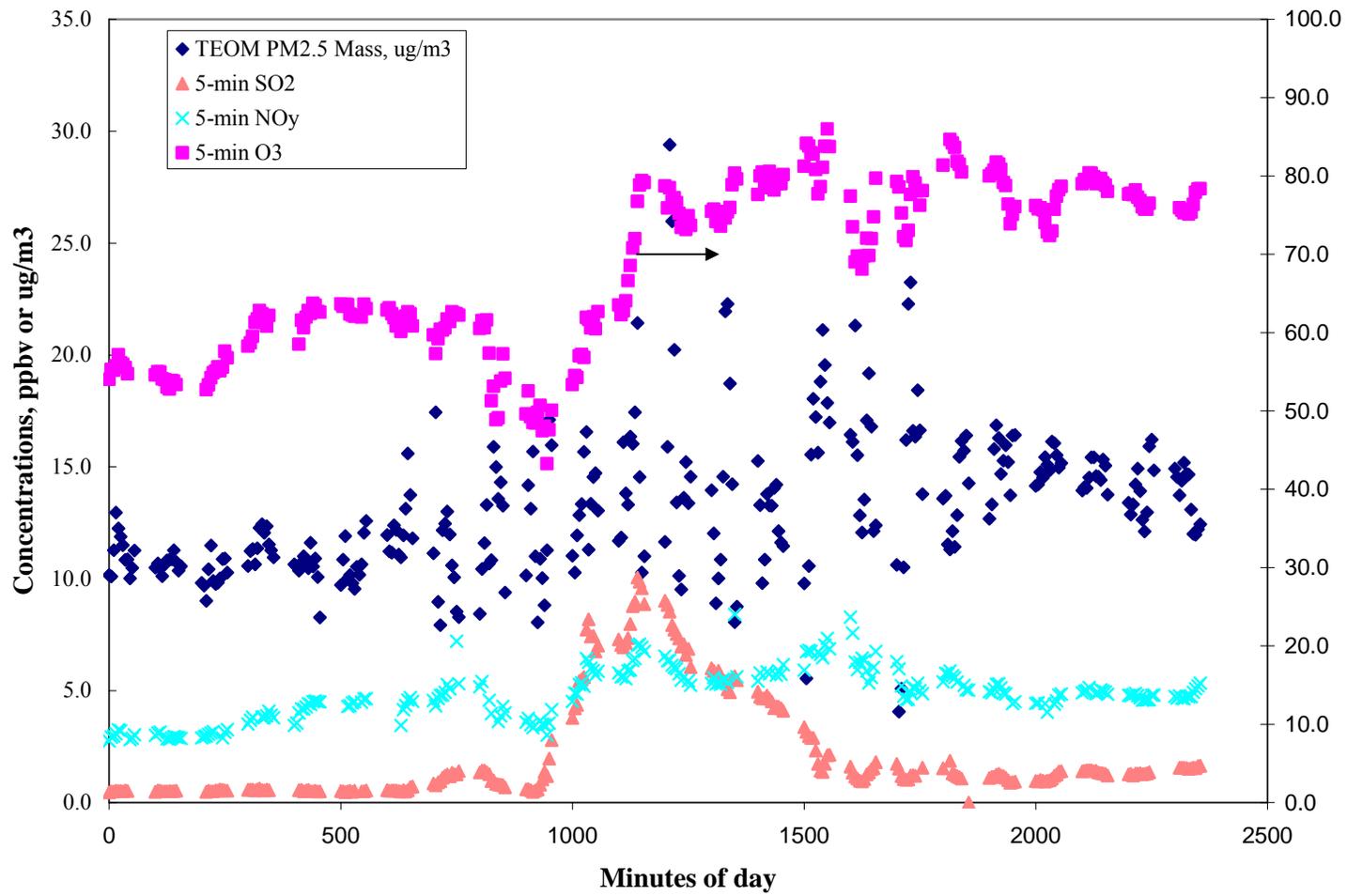
For the campaign periods shown in Table 1, TVA has deployed additional instrumentation at the site. This included measurements of  $SO_2$  by the pulse fluorescence technique, CO by the NDIR technique, ozone (identical to the NPS instrument), nitrogen oxides (NO,  $NO_2$ , and  $NO_y$ ) using chemiluminescence instruments (2), and fine particle mass by the TEOM instrument with a 2.5- $\mu m$  cyclone inlet, beginning in October, 1999. Air entering the TEOM was dried using a Nafion dryer (see above) and operated at 30°C. During the summer campaigns of 2000 and 2001, particle size measurements were made at the site by M.D. Cheng of Oak Ridge National Laboratory using scanning differential mobility analyzers (2 in tandem). Beginning in January, 2001, (during the adjunct 3-site composition studies) a 2-channel aethalometer was deployed at Look Rock for the measurement of black carbon (estimate of elemental carbon, EC). Finally, during the summer, 2001, campaign, two continuous sulfate analyzers were deployed at the Look Rock site, one the commercially available R&P 8400S instrument based on the

collection and flash volatilization approach developed by Hering et al. (1998), and the second a continuous thermal evolution system development by Allen et al. (2001), and constructed under license with the Harvard School of Public Health (referred to hereafter as the TVA/HSPH instrument).

The campaigns conducted in this project have served as a test bed for the development of continuous instruments under rigorous field conditions. The body of data have been analyzed in at least a preliminary fashion to determine how it can be used to elucidate the relationships between sources of fine particles and their gaseous precursors at this site. We were particularly interested in pursuing whether persistent correlations could be developed from which contributions from local, nearby urban area, sub-regional (Tennessee Valley) and regional sources of particles and their gaseous precursors could be differentiated. This has proven extremely difficult, in part because of the complications of terrain features on transport to this ridge-top site. As a result, much of the analysis we have intended to do of short term variability in fine mass and its chemical constituents at the Look Rock site is still in progress. We give two examples of sampling days in which gaseous and particulate matter concentrations have been analyzed over periods of one hour or less. We also attach as Appendix I a manuscript (Cheng and Tanner, accepted for publication in *Atmospheric Environment*, 2002) describing an analysis of the particulate size distributions and composition and their relationships to the gaseous concentrations at the Look Rock site.

The first example is taken from the summer, 2000, campaign, and shows the variability observed in gaseous and particulate fine mass concentrations on 23 August, 2000 (Figure 9abc). As the morning boundary layer builds past the ridge-top level (between 0900 and 1000), the wind shifts from down-slope to upslope (S to NW) and decreases (Fig. 9c). Simultaneously, there is a large increase in  $\text{SO}_2$  and  $\text{NO}_y$  as valley air reaches the site. There is a modest increase in the TEOM mass, but it remains quite variable in the afternoon, an effect we do not think is due to problems with the instrumentation. Although there was no precipitation on this date, there were episodes of cloudiness around 1230 hr and especially between 1430 and 1530 hours (Fig. 9b). This correlated to temporary increases in wind speed and a weakening of upslope flow. Although there were some variations in  $\text{NO}_y$  and ozone later in the day, the complexity of the wind flow and the cloud cover variability precluded any rigorous assignment of sources. About 2 hours after the maximum in  $\text{SO}_2$  and  $\text{NO}_y$  concentrations, a large burst of 10-100 nm particles was observed with the SDMS (Cheng and Tanner, 2002), but again, without chemical speciation of the nanoparticles, it could not be determined which sources (urban, point sources, or biogenic emissions) were responsible for the peaks in nanoparticle numbers.

**Figure 9a. Trace Gases and TEOM Fine Mass**  
**Look Rock, 8/23/00**



**Figure 9b**

30-min Total Sky Radiation at Look Rock, TN

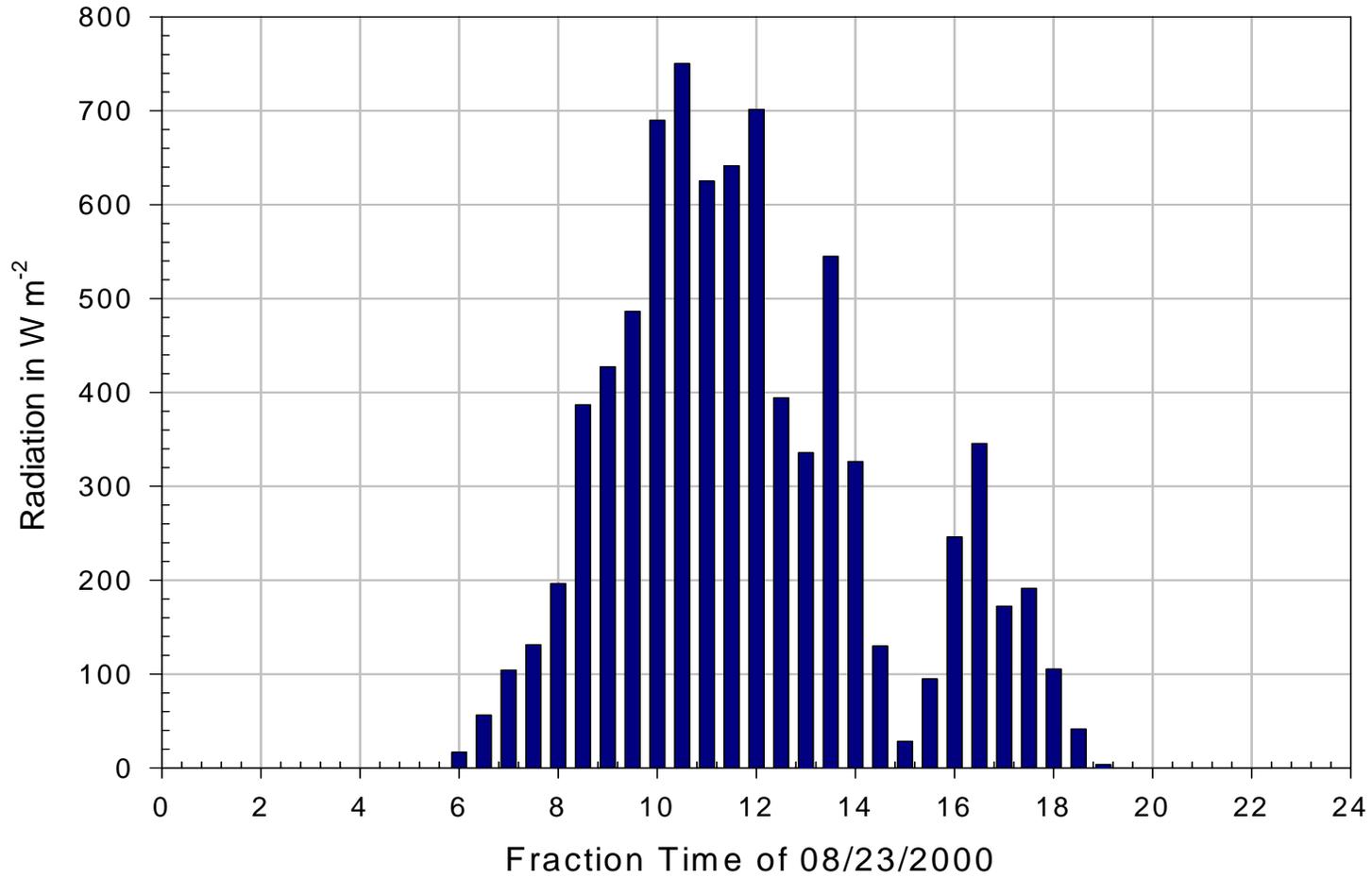
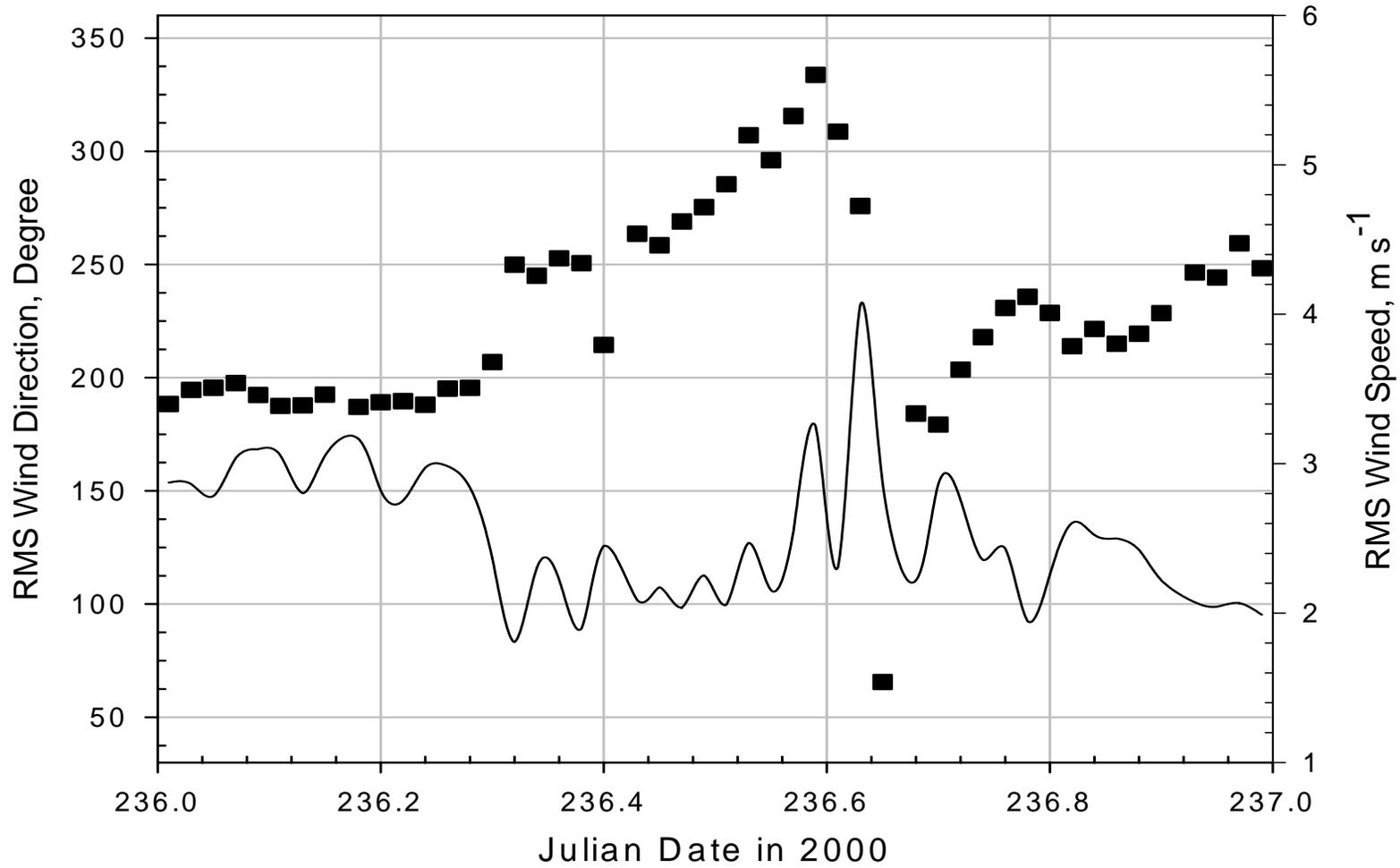


Figure 9c. Wind Speed and Direction at Look Rock  
August 23, 2000

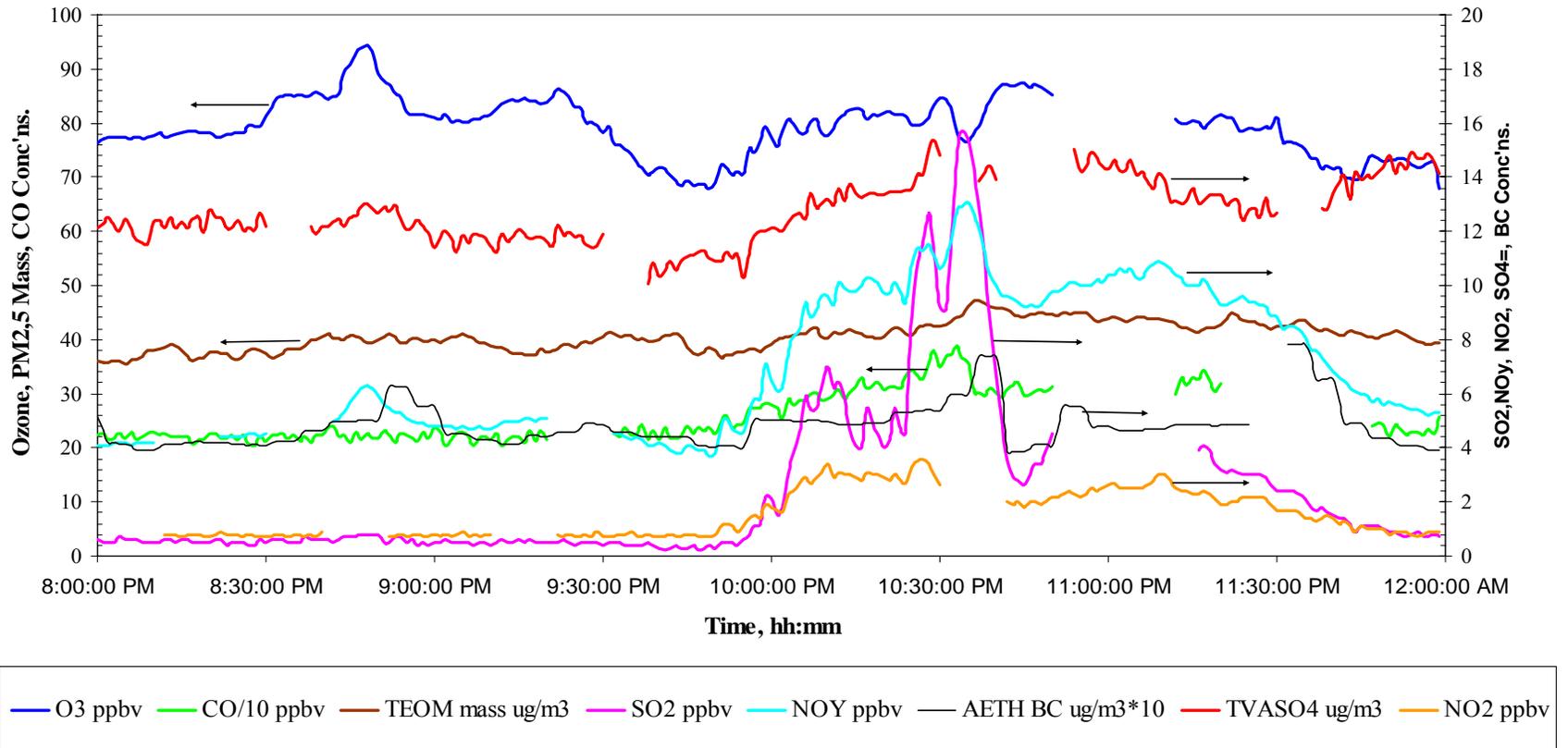


The second example is taken from a period during the evening of July 21, 2001 (2000-2400 hr, see Figure 10). In this case we display concentrations for a suite of gaseous species—Ozone, CO, SO<sub>2</sub>, NO<sub>y</sub> and NO<sub>2</sub>—and several aerosol metrics—TEOM fine mass, aethalometer black carbon, and sulfate (HSPH/TVA instrument)—during a period of light northerly winds. Based on the wind speed and direction, observed peaks in pollutants could have originated from area and point sources in the greater Knoxville area, with emission release times in the 1200-1500 time period when the boundary layer was fully developed and well above the elevation of Look Rock. Since the peaks occurred over a few hours, they of course would not be noticed in 24-hr mass or chemically speciated data.

Particularly noteworthy is the fact that the background mass and sulfate levels are relatively high (about 38 and 13 µg/m<sup>3</sup>, respectively) and the increases due to Knoxville area emissions are detectable but small. Contrast this to the results for gaseous species SO<sub>2</sub>, NO<sub>y</sub>, NO<sub>2</sub>, and even CO, where the changes above background are much more significant. Relative increases in black carbon and ozone levels are intermediate. Note also that the NO<sub>x</sub> plume from the mixture of urban and point sources is quite mature, with chemical ages exceeding 0.7. We conclude from this data that the ozone production from Knoxville area sources of precursors was essentially completed during its several-hour transport to Look Rock. In contrast, only a small portion of the SO<sub>2</sub> emissions from the Knoxville area have been converted to sulfates, as indicated by both the relative molar increase in sulfate and the increase in TEOM fine mass. This is consistent with the rates of formation of ozone and secondary sulfate under summertime conditions, from which it can be concluded that the spatial footprint for formation of secondary sulfates from SO<sub>2</sub> is much larger than the footprint for ozone formation from NO<sub>x</sub> and VOC precursors.

Much additional analysis of the data from the Supersite remains to be done, but it is clear that a principal limitation of the Look Rock site is its ridge-top location. This location makes the identification of sources of particulate matter arriving at the site very difficult due to the upslope-down slope wind circulation, and the presence of a well-mixed boundary layer at the elevation of the site during daytime hours which collapses to below the site at night. Even with these difficulties, we have identified circumstances in which transport to the site from the Knoxville area can cause elevated levels of continuously monitored gaseous and particulate species. Thus far, these elevated "plumes" have relative increases in primary and secondary species which are consistent with known atmospheric chemical processes.

**Figure 10.**  
**Continuous Gas and Particle Data**  
**Look Rock, 2000-2400 hr, 7/22/01**



## References

- Allen, G.A., D. Harrison, and P. Koutrakis (2001). A new method for continuous measurement of sulfate in the ambient atmosphere, presented at the 20<sup>th</sup> Annual Conference, American Association for Aerosol Research, Portland, OR, October.
- Cheng, M.-D. and R.L. Tanner (2002). Characterization of ultrafine and fine particles at a site near the Great Smoky Mountains National Park, *Atmos. Environ.*, accepted.
- Chow, J.C.; Watson, J.G.; Pritchett, L.C.; Pierson, W.R.; Frazier, C.A.; Purcell, R.G. (1993) *Atmos. Environ.* **27A**, 1185-1201.
- Ding, Y., Y. Pang, and D.J. Eatough (2002) A high volume diffusion sampler for the routine monitoring of fine particulate matter: I. Design and optimization of the PC-BOSS, *Aerosol Sci. Technol.*, in press.
- Hering, S. and B. Kirby (2001). "Standard Operating procedure for the Routine Operation of the R&P 8400S Ambient Particulate Sulfate Monitor", June 4 draft.
- Jansen, J.J. (2002). "SEARCH: The PM<sub>2.5</sub> NAAQS and Particulate Matter Composition", presented at the NETL Conference on PM<sub>2.5</sub> & Electric Power Generation: Recent Findings and Implications, Pittsburgh, PA, April 9-10.
- Pang, Y., Y. Ding, K. Warner, D.J. Eatough, N.L. Eatough, and R.L. Tanner (1997). A BOSS for routine sampling for semi-volatile fine particulate material. **In:** Proceedings of a Specialty Conference on "Visual Air Quality: Aerosols and Global Radiation Balance", Air and Waste Management Assoc., Pittsburgh, Vol. I, pp.302-309.
- Pang, Y., Y. Ren, F. Obeidi, R. Hastings, D.J. Eatough, and W.E. Wilson (2001) Semi-volatile species in PM<sub>2.5</sub>: Comparison of integrated and continuous samplers for PM<sub>2.5</sub>, *J. Air Waste Manage. Assoc.* **51**, 25-36.
- Sioutas, C., P. Koutrakis, and B.A. Olson (1994). Development and evaluation of a low cutpoint virtual impactor, *Aerosol Sci. Technol.* **21**, 223-235.
- Stolzenburg, M.R. and S.V. Hering (2000). A new method for the automated measurement of atmospheric fine particle nitrate, *Environ. Sci. Technol.* **34**, 907-914.
- Tang, H., E.A. Lewis, D.J. Eatough, R.M. Burton, R.J. Farber (1994) Determination of the particle size distribution and chemical composition of semi-volatile organic compound in atmospheric fine particles, *Atmos. Environ.* **28**, 937-947.

**Acknowledgement**

Work to obtain the data set from 3 stations during all seasons was funded through the Supersite project, supplemented by additional internal funding from TVA. Funding for analysis of samples from the Chattanooga and Lawrence County sites was provided by DOE; site operation and mass measurements of the Lawrence County Teflon FRM samples were provided by the Tennessee Department of Environmental Protection, since this site is part of Tennessee's contribution to EPA's national PM<sub>2.5</sub> mass network. Assistance in sampling at the Chattanooga site was provided by Kathy Jones and her staff at the Chattanooga-Hamilton Count Air Pollution Control Bureau.