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Ambient fine particulate concentrations and chemical composition at two sampling sites in metropolitan Pittsburgh: a 2001 intensive summer study

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Abstract

The concentration and chemical composition of ambient fine particulate material ($PM_{2.5}$) is reported for two sampling sites in the Pittsburgh, Pennsylvania metropolitan area: the Department of Energy, National Energy Technology Laboratory (NETL) PM study site south of the city center, and the Carnegie Mellon Pittsburgh Air Quality Study (PAQS) site 5 km east of central Pittsburgh established with funding by the EPA Supersites Program and by DOE-NETL. Data from these sampling sites were characterized by one to three-day episodes with $PM_{2.5}$ concentrations (constructed from the sum of the chemical components) exceeding $40.0 \, \mu g \, m^{-3}$. The episodes were dominated by high concentrations of ammonium sulfate. The fine particle concentrations were compared with meteorological data from surface weather maps and a Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT model), with back-trajectories estimated over 24 h. High $PM_{2.5}$ concentrations were associated with transition from a high pressure to a low pressure regime in advance of an approaching frontal system indicating long-range transport of pollutants. In contrast, fine particulate organic material appeared to be dominated by nearby sources. Distinct differences were observed in the diurnal variations in concentration between the two sites. The NETL site showed clear maximum concentrations of semi-volatile organic material (SVOM) during midday, and minimum concentrations of nonvolatile organic compounds in the afternoon. In contrast, the Carnegie Mellon PAQS site showed an absence of diurnal variation in SVOM, but still with minimum concentrations of nonvolatile organic compounds in the afternoon and evening. Neither site showed significant diurnal variation in ammonium sulfate.
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1. Introduction

Fine particulate matter is a ubiquitous component of the atmosphere, and has become a persistent and pervasive environmental problem that imposes significant health risks (Schwartz, 2001; Pope, 2000) and economic costs (Hughes and Lovei, 1999) on society. In 1997, the United States Environmental Protection

Agency (EPA) revised the National Ambient Air Quality Standards for fine particulate matter ($PM_{2.5}$), establishing a 24-h average concentration limit of $65 \, \mu g \, m^{-3}$, and an annual average concentration of $15 \, \mu g \, m^{-3}$. Achieving these standards will require strategies for modeling and monitoring airborne concentrations so that appropriate emission reductions can be achieved. This demands an understanding of the factors responsible for current airborne particle levels.

In July 2001, researchers from several universities, research laboratories, and government agencies met to participate in the Pittsburgh Air Quality Study (PAQS),

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a research program funded by the Department of Energy (DOE) and the Supersite Program of the EPA. This was a 1-month intensive measurement campaign to test and compare innovative particle measurement methods, and to improve our scientific understanding of atmospheric particles. Several sites were included in PAQS, with the main site about 5 km east of downtown Pittsburgh. That location was adjacent to the Carnegie Mellon University (CMU) campus in Schenley Park. One of the additional sampling sites was located at the National Energy Technology Laboratory (NETL), located in the suburban area about 18 km south of downtown Pittsburgh. This paper compares the diurnal patterns in $PM_{2.5}$ concentration and chemical composition (including semi-volatile components lost from particles during sampling) at the PAQS site and the NETL site for samples collected using the Particle Concentrator—Brigham Young University Organic Sampling System (PC-BOSS) (Modey et al., 2001; Lewtas et al., 2001).

2. Experimental

2.1. The NETL sampling site

This site is located at 40.31 N latitude and 79.98 W longitude on an open hill at the NETL facility. The site is in a suburban portion of Pittsburgh, 18 km south of the downtown Pittsburgh area, Fig. 1. The location of the sampling station was chosen to take advantage of an existing meteorological tower which supplies full weather data for the program. Two experimental combustors, located at the NETL facility just 200 m east of the site, occasionally burn a variety of fuels ($230\,kg\,h^{-1}$ of coal and about $20\,kg\,h^{-1}$ of various other fuels). About 600 m ESE is a coal-fired steam plant which burns up to $900\,kg\,h^{-1}$ to provide heating for the NETL facility. Considering the infrequent occurrence of winds from the direction of these two facilities, and the short time period when these winds are present, the contribution of these nearby sources to $PM_{2.5}$ at the NETL site appears to be negligible (Anderson et al., 2002). High concentrations of NO_x and CO identify when these sources impact the NETL site. This occurs less than 0.2% of the time and the $PM_{2.5}$ concentration during these time periods changes less than $2\,\mu g\,m^{-3}$. Major coal-fired power plants, iron and coke processing facilities, and chemical manufacturing plants are located along the Ohio River Valley to the west and southwest of the NETL site. Some coke and iron processing facilities are also located along the Monongahela River to the east of the facility and on the Ohio River to the north of the facility. These are all potential sources of transported pollutants to the site.
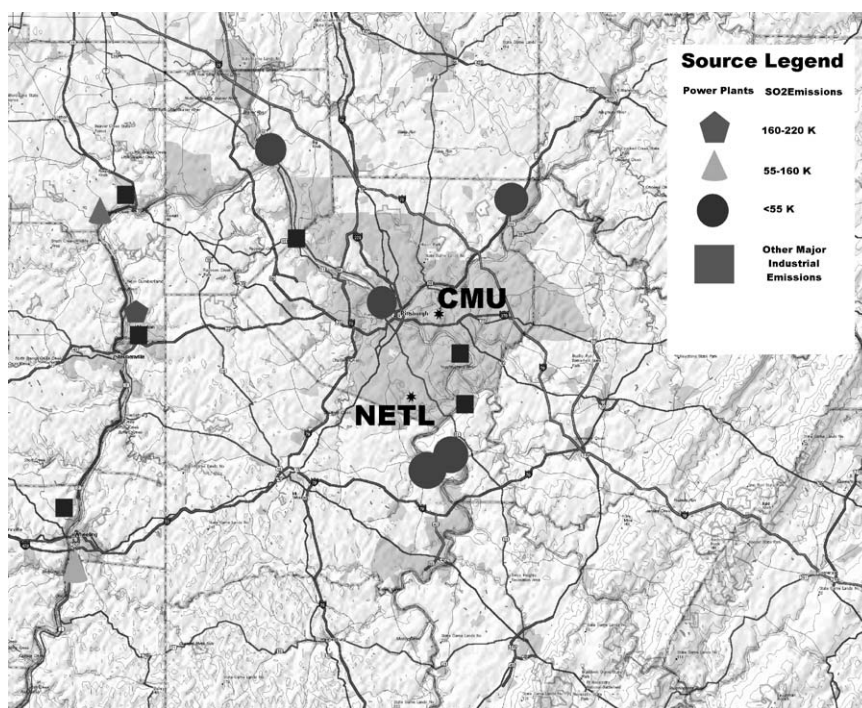

Fig. 1. Map showing location of the CMU and NETL sites in the metropolitan Pittsburgh area (gray shaded in center of figure), main point sources and 100 m contour lines in the region around Pittsburgh.

2.2. The Carnegie Mellon University PAQS site

The CMU PAQS site is located at 40.44 N latitude and 79.94 W longitude in the middle of the Pittsburgh urban area. The site is about 2 km from the heavily populated and trafficked area of Pittsburgh known as Oakland and 5 km east of the downtown area, Fig. 1. The Bellefield boiler, a small steam heating plant that burns a mixture of bituminous coal and natural gas, is located about 1 km to the west. The site is also influenced by minor emissions from the CMU campus. Like the NETL site, the prevailing winds at the CMU site are frequently from the southwest to northwest directions. Many of the same distant industrial sources influencing the NETL site are also likely to impact the CMU site.

Fig. 1 also contains 100 m topographical contours. These data emphasize that the region to the southwest becomes quite hilly, as the foothills of the central Pennsylvania mountains appear. In addition, the regions surrounding the city to the southwest and north have significant hills (on a 100 m contour basis). However, the Pittsburgh metropolitan area is much less influenced by hills. While the city is hilly, these height variations are not significant at the 100 m level.

2.3. Sampling protocols

Five sets of PC-BOSS samples were collected each day at the CMU site. The time periods (EST) were: 12:00 a.m. to 6:00 a.m.; 6:00 a.m. to 10:00 a.m.; 10:00 a.m. to 2:00 p.m.; 2:00 p.m. to 6:00 p.m.; and 6:00 p.m. to 12:00 a.m. Because of limitations on site access each day, only four sample sets were collected each day at the NETL site using a nearly identical PC-BOSS. The sampling time periods (EST) at this site were: 5:00 a.m. to 10:00 a.m.; 10:00 a.m. to 2:00 p.m.; 2:00 p.m. to 7:00 p.m.; and 7:00 p.m. to 5:00 a.m. the next day. The differences in sampling times between the two sites thus include only one sample collected at night at the NETL site versus two night samples at the CMU site and a 1-h earlier start and end time for the NETL early morning and late evening samples. The latter differences were chosen to match the expected earlier start and end of the morning and evening commutes at the NETL site.

2.4. The PC-BOSS Samplers

Details of the PC-BOSS sampler used at both sampling sites have been previously published (Lewtas et al., 2001; Modey and Eatough, 2003). Ambient aerosols were drawn through an inlet that removed particles greater than $\sim 2.5\,\mu m$ in aerodynamic diameter from the air stream. The inlet on the CMU PC-BOSS was an MSP Corporation $PM_{2.5}$ virtual impactor (MSP Corporation, Minneapolis, MN, USA) with a $2.5\,\mu m$

cut, and that on the NETL PC-BOSS was a Bendix cyclone with a $2.4\,\mu m$ cut (Chan and Lippmann, 1977). Inlet flows were $140–150\,l\,min^{-1}$.

After the inlet and a small mixing chamber, $15\,l\,min^{-1}$ was removed into a side flow manifold which held a single filter pack containing a 47-mm diameter Whatman Nuclepore filter ($0.4\,\mu m$ pore, Whatman Inc., Clifton, NJ) for sulfate determination, and a 47-mm diameter charcoal-impregnated glass fiber filter (CIG) (Schleicher and Schuell, Dassel, Germany) for volatile organic material (VOM) determination. Samples collected on the Nuclepore filters were concentrated in a 4-cm^2 area on the filter using a stainless steel masking disk, positioned underneath the Nuclepore filter. The remainder of the sampled air stream entered a virtual-impactor particle concentrator whose design and evaluation have been described (Sioutas et al., 1994; Ding et al., 2002). The particle concentrator separated 75% of the gas phase material into the major flow and left particles larger than the cut point ($> 0.1\,\mu m$) along with a significantly reduced fraction of the gas phase material in the minor flow channel. The minor flow stream containing concentrated particles entered a diffusion denuder comprised of parallel strips of charcoal-impregnated cellulose fiber filter (CIF, Schleicher and Schuell, Keene, NH) which were separated at the long edges by 2-cm diameter glass rods. With most of the gas phase species removed through the particle concentrator prior to passage of aerosol through the denuder, efficiency of the denuder for removal of gas phase SO_2, HNO_3, and organic compounds is expected to equal or exceed 99% (Lewtas et al., 2001; Eatough et al., 1999; Ding et al., 2002).

The denuder was followed by two parallel filter packs. One contained a 47-mm Pallflex quartz filter (Gelman Sciences, Ann Arbor, MI) followed by a 47-mm diameter CIG filter. The first filter was used to determine fine particulate elemental carbon (EC), and nonvolatile organic material (NVOM), sulfate and nonvolatile nitrate concentrations. The CIG filter was used to capture semi-volatile organic material (SVOM) evolved from the quartz filter. Particulate samples collected on both of these filters were concentrated on a 4-cm^2 area on the filters using the mask described earlier for the Nuclepore filter. The other parallel filter pack contained a 47-mm diameter ring-supported Teflon filter (Whatman Inc.) followed by a 47-mm diameter Nylasorb filter (Gelman Sciences). Unlike sample collection on the quartz and CIG filter pack, collection on the Teflon and Nylasorb filters was over the entire filter surfaces. The Teflon filters were analyzed for sulfate and nonvolatile nitrate, and the Nylasorb filters were analyzed for nitrate lost from particles during sampling. With these combinations of sample analysis techniques on both parallel channels of the minor flow of the sampler, negative and positive sampling artifacts were minimized.

The sulfate determination on the side flow Nuclepore filter allowed for the direct determination of the particle concentrator efficiency and losses (Lewtas et al., 2001; Modey et al., 2001) when regressed against sulfate determinations on the minor flow quartz and Teflon filters. Previous studies in similar environments in the eastern United States (Pang et al., 2002; Modey et al., 2001) have shown that efficiencies calculated from sulfate, OM or EC data are all similar. However, only sulfate data were available for this calculation in the data reported here. Particle size dependence of the fine particle components indicated that the mass median diameters for sulfate and carbon materials are similar and also, not close to the lower cut point of the particle concentrator, indicating efficiencies for all components should be comparable (Cabada et al., 2004).

2.5. Filter pre-treatment

All quartz filters were baked in an oven at $800^\circ C$ for 10 h before use. Such treatment is likely to alter the sorption sites for SVOM, and cause higher SVOM losses from the quartz filters. This may account for differences in the split between NVOM and SVOM determined with the PC-BOSS, compared to the simultaneous sampling with a diffusion denuder system (Subramanian et al., 2004). However, the sum of EC, NVOM and SVOM determined by the two systems in 24-h sampling periods agreed ($n = 14$, $R^2 = 0.92$, regression slope = 1.01). This is a further indication that the particle concentrator efficiency based on sulfate measurements was also valid for the carbonaceous material. The CIG sorbent filters used in the study were baked in an oven at $340^\circ C$ for 24 h in an atmosphere of nitrogen. Such treatments were to ensure that the filters contained minimal residual organic material prior to being used for sampling. The Nuclepore, Teflon, and Nylasorb filters and the denuder CIF strips were used as received from the manufacturers without any pre-treatment.

2.6. Analysis of collected carbonaceous material

A 2-cm^2 portion from the center of each quartz filter were analyzed for elemental carbon (EC) and nonvolatile organic material (NVOM) by thermal desorption of the collected materials using temperature programmed volatilization (Eatough et al., 1993; Ellis and Novakov, 1982). Similarly sized portions from the centers of the CIG filters were analyzed for semi-volatile organic material (SVOM). Both EC and NVOM or SVOM were converted to CO_2 over a barium chromate combustion catalyst (UIC Inc., IL) at $800^\circ C$ and the CO_2 concentration was then determined using non-dispersive infrared (NDIR) detection on an ULTRA-MAT 3 - Gas Analyzer (Siemens Inc., GA). The NDIR

detector was calibrated using three certified CO_2 standards which spanned the analysis concentration range. The CIG filters were heated from $50^\circ C$ to $340^\circ C$ at a ramp rate of $15^\circ C\,min^{-1}$ in a stream of nitrogen. The maximum temperature for the CIG analysis was imposed by the fact that degradation of the filter charcoal began $10–20^\circ C$ below the maximum analysis temperature. Collected SVOM lost from the particles were evolved from the CIG between $200^\circ C$ and $300^\circ C$. The quartz filters were heated from $50^\circ C$ to $800^\circ C$ at a ramp rate of $28^\circ C\,min^{-1}$ in a stream of N_2/O_2 (70:30% v/v). Soot was estimated from the high temperature (usually above $440^\circ C$) peak (Ellis and Novakov, 1982) on the thermogram obtained from the quartz filter analysis. Because of the frequent presence of high concentrations of nonvolatile organic material that evolve at a temperature just below that for EC, the uncertainty in this estimate varied from about 30–70%. However, EC was a small fraction of the total carbonaceous material. The shape of the thermograms indicated that all collected organic compounds and soot were evolved from the collection matrix at the maximum temperatures used. No evidence for the high-temperature evolution of CO_2 from inorganic carbonates was seen. Field handled blank determinations were made for both quartz and CIG filters. The blank filter thermograms were used to correct the sampled filter thermograms for blank filter material. The variability in blank filters was less than $\pm 3\,\mu g\,C\,filter^{-1}$, corresponding to an uncertainty in the blank correction of less than $0.4\,\mu g\,C\,m^{-3}$.

2.7. Analysis for nitrate and sulfate

Sulfate and nitrate analysis was by ion chromatography. All ion chromatographic analyses were performed using a Dionex LC20 Chromatograph equipped with a CD20 conductivity detector. The eluant was a 3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$ solution used at a flow rate of 1.2 ml min^{-1}. An anion self-generating suppressor was used. One 2-cm^2 punch of the quartz filters was extracted by ultrasonication with deionized water in a monovette (Sarstedt, Newton, NC). The extracted solution was analyzed for sulfate and nitrate. Whole Teflon filters and half of each Nuclepore filter were also extracted by ultrasonication in deionized water in a monovette and analyzed for sulfate and nitrate. Whole Nylasorb filters were extracted ultrasonically in the ion chromatography eluant solution and analyzed for nitrate. Field handled blank determinations were made for all filters.

2.8. O_3, NO_x and NO_2 Data

Hourly averaged concentrations of O_3, NO_x and NO_2 were determined by NETL (Anderson et al., 2004) and

CMU (Wittig et al., 2004) using continuous gas monitors. These data were combined to give average concentrations of each gas phase species for the various PC-BOSS sampling times.

3. Results and discussion

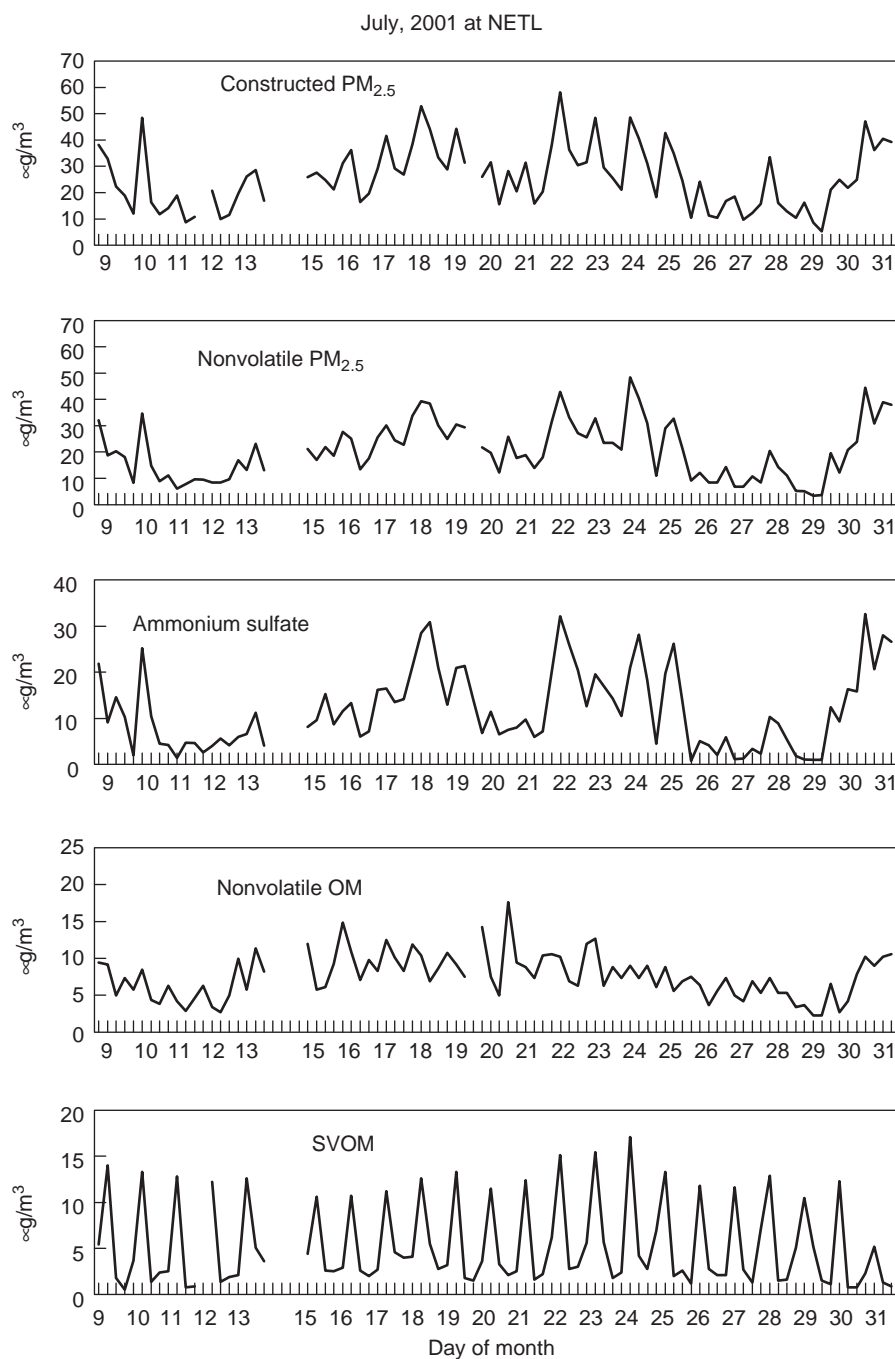Results for the studies conducted at both sites showed periods lasting over 24 h when peak constructed $PM_{2.5}$

Fig. 2. $PM_{2.5}$ concentrations at the NETL and Carnegie Mellon University PAQS sites from 9–31 July, 2001. At the NETL site, the first tick mark for each day on the horizontal axes is for the first sampling period starting from 5:00 a.m. to 10:00 a.m. At the PAQS site the first tick mark for each day on the horizontal axes is for the first sampling period starting from 12:00 a.m. to 6:00 a.m.
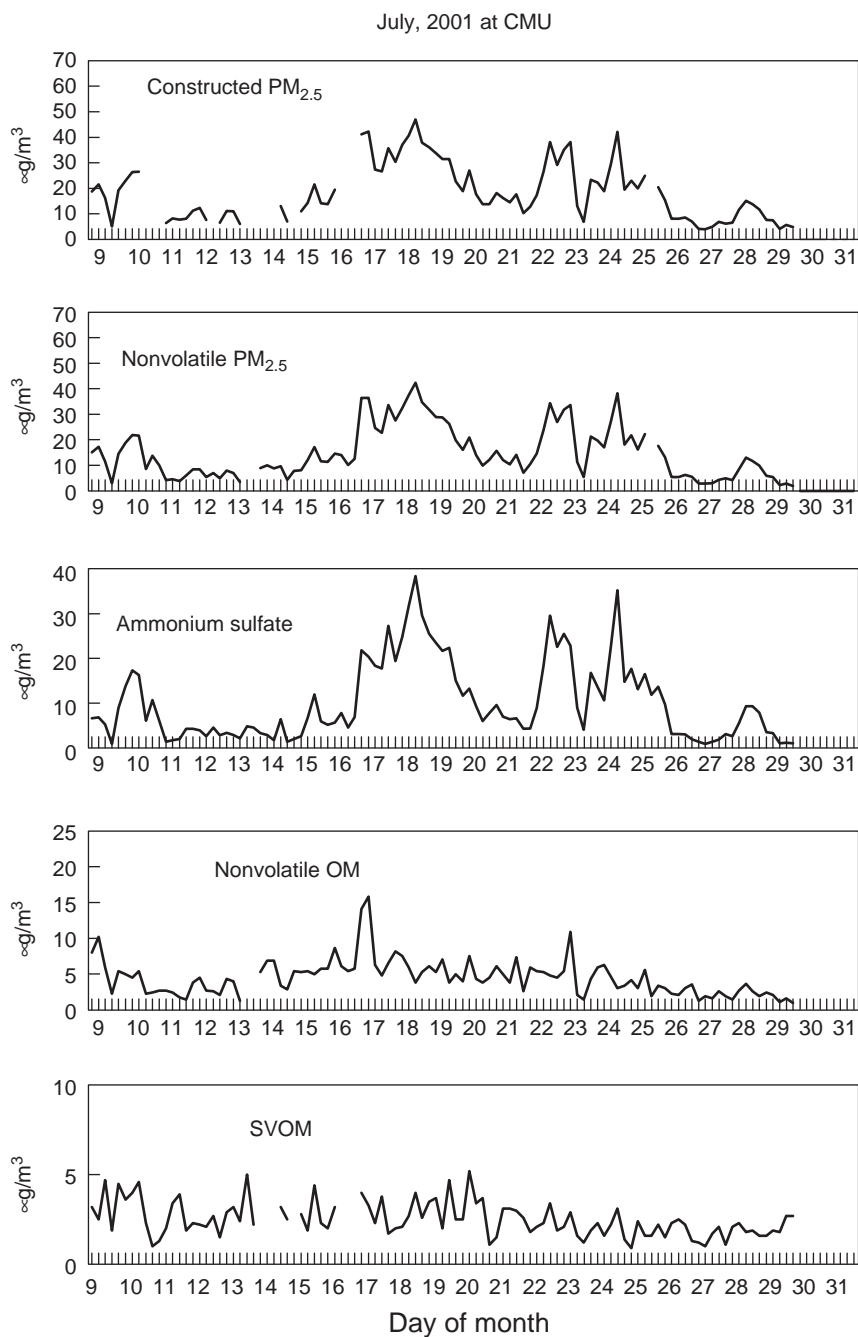
July, 2001 at CMU

Fig. 2 (*continued*).

concentrations exceeded $30.0\,\mu g\,m^{-3}$, which is considered to be an episode. Constructed nonvolatile $PM_{2.5}$ was calculated as the sum of the concentrations of ammonium sulfate and ammonium nitrate determined on the Teflon filter, and EC, and nonvolatile organic material (NVOM) determined on the quartz filter. Constructed $PM_{2.5}$ was then calculated as the sum of

the constructed nonvolatile $PM_{2.5}$ concentration, and lost ammonium nitrate and SVOM determined on the Nylasurb and CIG filters, respectively. It was assumed that gas phase VOM and particulate nonvolatile NVOM and SVOM were 61% carbon by mass (Turpin and Lim, 2001). The same factor was used to convert OC to OM for the VOM, NVOM and SVOM fractions, since the

Table 1
Diurnal concentrations in $\mu g\, m^{-3}$ for constructed $PM_{2.5}$ and the three major $PM_{2.5}$ components and for gas phase VOM ($\mu g\, m^{-3}$) and NO_x (ppb)

Period of day	Category	Constructed $PM_{2.5}$	$(NH_4)_2SO_4$	NVOM	SVOM	VOM	NO_x
(a) NETL site in Pittsburgh							
5:00 a.m. to 10:00 a.m	Average	24.4	10.2	8.9	3.7	13.9	17.2
	Maximum	47.1	32.6	14.9	7.1	23.1	32.4
	Minimum	10.4	0.8	3.3	1.1	5.6	6.8
10:00 a.m. to 2:00 p.m.	Average	34.9	13.0	7.8	12.4	13.5	8.7
	Maximum	58.1	32.2	12.7	17.1	25.2	18.3
	Minimum	16.2	1.1	2.8	5.2	7.1	4.1
2:00 p.m. to 7:00 p.m.	Average	23.3	13.8	6.0	2.8	10.6	6.0
	Maximum	44.0	30.9	11.4	5.7	17.2	8.9
	Minimum	8.6	1.0	2.2	0.8	4.1	2.9
7:00 p.m. to 5:00 a.m.	Average	20.7	10.4	7.7	2.0	15.9	12.4
	Maximum	39.1	26.6	17.6	4.0	24.2	26.0
	Minimum	5.2	1.0	2.3	0.5	11.1	9.1
(b) Carnegie Mellon University PAQS site in Pittsburgh							
12:00 a.m. to 6:00 a.m.	Average	22.1	11.4	5.9	2.6	24.0	24.4
	Maximum	48.9	36.0	14.1	5.0	53.8	46.8
	Minimum	4.0	1.4	1.3	0.9	8.2	6.6
6:00 a.m. to 10:00 a.m.	Average	21.3	10.5	6.5	3.1	28.1	28.6
	Maximum	42.1	24.8	15.8	6.2	68.3	68.5
	Minimum	3.9	0.9	1.9	1.0	5.3	5.9
10:00 a.m. to 2:00 p.m.	Average	20.6	12.0	4.9	3.0	24.3	10.7
	Maximum	43.2	31.7	10.8	8.4	59.6	24.2
	Minimum	4.0	1.0	1.1	1.6	5.2	5.1
2:00 p.m. to 6:00 p.m	Average	22.3	11.8	4.2	3.7	18.7	7.7
	Maximum	65.1	49.6	12.9	7.9	44.4	13.6
	Minimum	5.0	0.9	1.4	1.1	2.1	5.0
6:00 p.m. to 12:00 a.m.	Average	16.4	10.0	3.6	2.0	20.5	14.3
	Maximum	37.9	29.5	6.5	4.5	48.3	24.2
	Minimum	4.7	0.9	0.8	1.0	4.0	6.3

Maximum concentrations given are for the entire period for the given sampling period.

relative importance of primary and secondary organic material in these fractions is not identifiable from the data given here. However, if the SVOM is dominantly secondary in nature, as suggested in the discussion, the factor used to convert from SVOC to SVOM may be too small and the SVOM concentrations may be relatively somewhat higher than given here (Turpin and Lim, 2001). Sulfate and nitrate determined by ion chromatography were assumed to be present as ammonium sulfate and ammonium nitrate, respectively. These same assumptions and calculations were used for both the NETL and Carnegie Mellon PAQS site PC-BOSS data. The resulting concentrations are shown in Fig. 2 with average, maximum and minimum concentrations given in Table 1.

3.1. Gas phase NO_x and VOM diurnal patterns

The diurnal variations in NO_x and VOM gas phase concentrations are given in Figs. 3 and 4, respectively.

Sampling period average, maximum and minimum concentrations of these species are given in Table 1. The diurnal variations in the concentrations of both these species will be dependent on a combination of diurnal variations in emission and in meteorology. For species which are emitted in the metropolitan area, if emission rates are constant, concentrations will be the highest during the night-time, with the presence of a stable night-time mixed layer, and lowest during midday and afternoon when the atmosphere is well mixed. For species associated with mobile emissions, concentrations will be high during the early morning commute, and low during the middle of the day when traffic density is lower and the atmosphere is well mixed. Concentrations would also be expected to be low during the evening commute because of the well-mixed atmosphere. However, even though traffic is reduced during the night, concentrations may increase due to the presence of a relatively shallow, stable mixed layer. Examination of the data in Table 1 and in Fig. 3 both
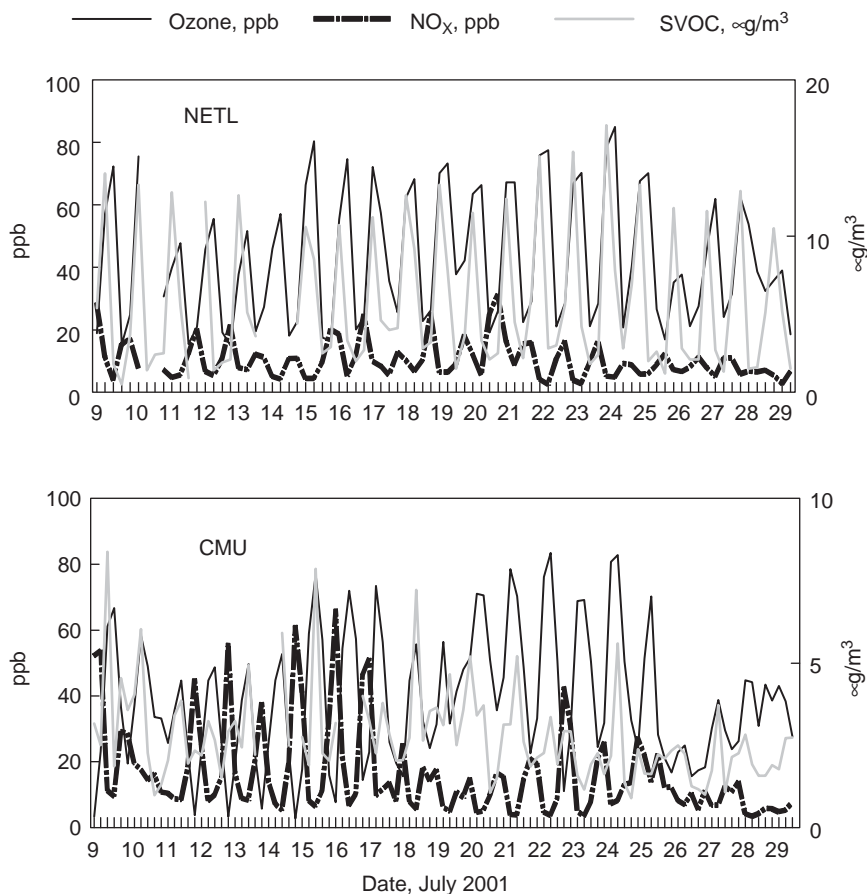
Fig. 3. Diurnal NO_x, Ozone and SVOM concentrations at the two sampling sites.

suggest this is the case for NO_x at both the NETL and CMU sites, indicating mobile emissions are a significant contributor to NO_x at both sites. Furthermore, the concentrations of NO_x are consistently higher at the CMU, compared to the NETL site, especially for the early morning time period, consistent with the higher traffice density in the downtown region close to the CMU site, compared to the more suburban NETL site, Fig. 1. The picture is similar for VOM with highest concentrations always present at the CMU site, compared to the NETL site. However, the significant drop in concentrations of NO_x seen in the mid-day, compared to early morning samples, is less pronounced for VOM. This suggests other mid-day VOM sources may be present, for example vegetative emissions, or increased emissions of VOM compared to NO_x from combustion sources, including mobile sources as the day progresses. There is, however, no reason to believe vegetative sources will be more important at either one of the two sites. The increased importance of VOM, relative to NO_x, may reflect a changing composition of mobile sources as the morning commute passes.

3.2. $PM_{2.5}$ diurnal distribution

Fig. 2 shows the diurnal patterns for constructed $PM_{2.5}$ mass concentrations and composition at the two sampling sites. Highest constructed $PM_{2.5}$ concentrations at the NETL site were observed during the sample collection period each day from 10.00 a.m. to 2.00 p.m. (indicated by the second and third vertical tick marks each day). These maxima are greatly influenced by the striking pattern in SVOM concentrations shown at the bottom of Fig. 2. In contrast, the constructed $PM_{2.5}$ concentrations at the CMU site do not show a strong diurnal variation. Averages, maxima and minima in the different patterns between the two sites are given in Table 1. The NETL site shows an average SVOM concentration of $12.4\,\mu g\,m^{-3}$ and an average constructed $PM_{2.5}$ mass concentration of $34.9\,\mu g\,m^{-3}$ during 10:00 a.m.–2:00 p.m., both values well above the averages for any of the other time periods. The CMU site shows very similar average SVOM and constructed $PM_{2.5}$ concentrations in all five time periods. Table 1 indicates that ammonium sulfate is the largest single component
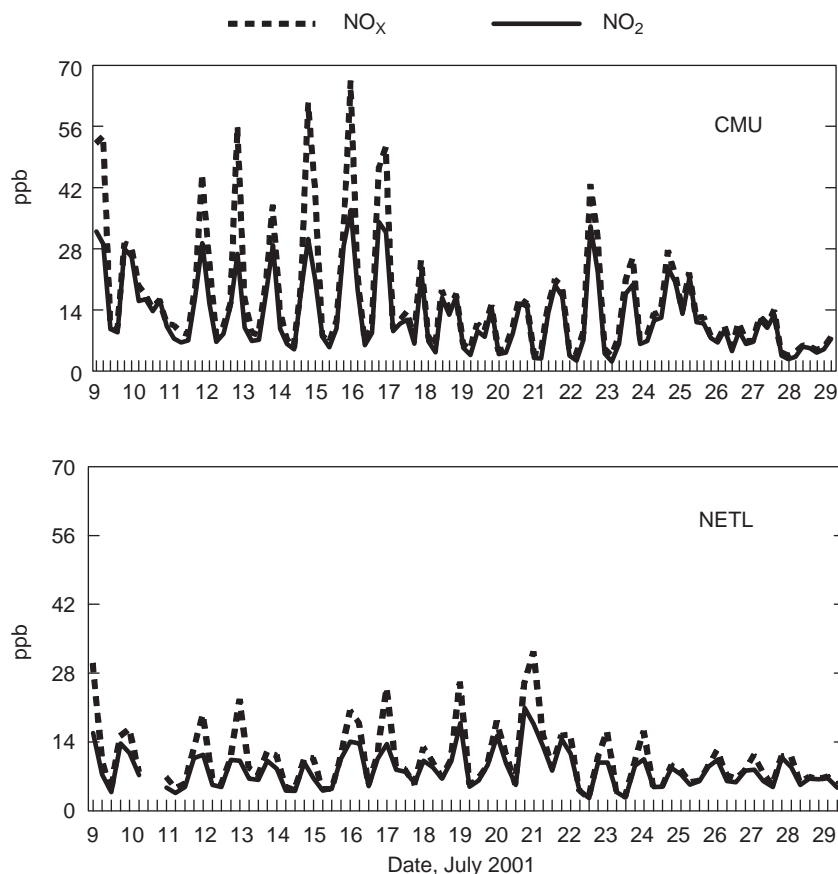
Fig. 4. Diurnal concentrations of NO_x and NO_2 at the two sampling sites.

affecting constructed $PM_{2.5}$ concentrations at both sites. The high SVOM concentration at the NETL site during the peak time period is also a significant contributor to constructed $PM_{2.5}$ at that site. A comparison of the diurnal variations in SVOM, ozone (Fig. 3), and NO_x at the two sampling sites shows that maximum SVOM concentrations coincide with high ozone concentrations during mid-day, possibly indicating a high occurrence of secondary SVOM. It is clear that this high SVOM is not associated with the morning commute since maximum ozone and SVOM concentrations are observed hours after maximum NO_x concentrations as shown in Fig. 3 and Table 1. NO_x is principally associated with fresh or primary emissions, and maximum concentrations are observed during early morning and night-time periods as discussed above. The lack of a continued rise in SVOM, with continued high ozone concentrations, during the late afternoon suggests that the apparent conversion of VOM to SVOM at the NETL site is rapid, and does not involve VOM emitted later in the day, e.g. from vegetative sources. Fig. 4 (trends in NO_x at the two sampling sites) and Fig. 5 (trends in VOM, and SVOM

at the two sampling sites) in combination with Fig. 3 suggest the importance of NO_x, compared to SVOM chemistry at the CMU site but a shift to more SVOM chemistry at the NETL site. A connection between the two phenomena is not obvious, and it is not expected that the two different phenomena would occur in the same city. The observed differences are, presumably, linked to the differences in the importance of organic versus NO_x emissions by nearby sources at the two sampling sites. For example, higher concentrations of NO_x at the CMU site may favor NO_x over organic compound chemistry. The high concentrations and regular diurnal pattern of SVOM at the NETL site may be due to a suburban source, but the nature of this source is presently unknown.

High concentrations of NVOM were frequently observed during the time period from 5.00 a.m. to 10.00 a.m. (9, 11, 12, 15, 16, 18, 19, 26, 27 July), and occasionally in the night-time (20, 21, 31 July). As discussed above, the NVOM measured at these times is likely to be associated with local sources. But Fig. 6 shows that concentrations at the NETL site were
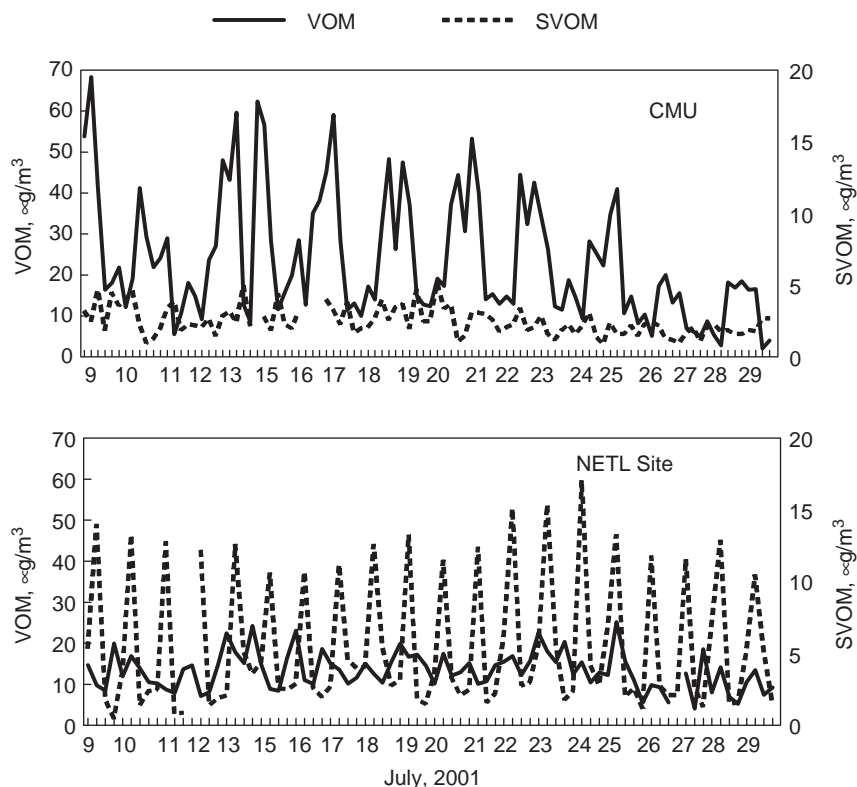
Fig. 5. Diurnal concentrations of gas phase volatile organic material (VOM) and SVOM at the two sampling sites.

consistently higher than those at CMU for all sampling time periods. Therefore, it is possible that OM emission sources near the NETL site may be lower in NO_x content, or that organic material impacting the NETL site includes more secondary material. This would be consistent with the increased importance of secondary SVOM at the NETL site as noted above.

Fig. 6 shows that ammonium sulfate concentrations during the midday and late afternoon sampling periods at both sites were comparable for most of the samples, suggesting similar concentrations over a large region which is probably due to long-range transport. The sulfate formed during long-range transport will be dominated by homogeneous chemistry. The transported sulfate observed at the site is formed during and is present at the site in clear sky conditions, in advance of, not associated with a frontal passage. Thus, homogeneous chemistry would be expected to dominate in the formation of sulfate. This expectation is also consistent with the low MMD observed for sulfate under these conditions (Cabada et al., 2004). However, during the early morning sampling period, differences in ammonium sulfate concentrations at the two sites were observed, consistent with the decoupling of surface air

from elevated layers and the importance of varying low concentrations of sulfate from local sources. When pollutants are locally generated, they are likely to be non-uniformly distributed at the two sites because the source contributions impacting the sites may be diverse in nature.

3.3. Meteorological influence on $PM_{2.5}$ distribution and episode occurrence

Previous work has explored the relationship between meteorology and the occurrence of fine particle episodes in the Pittsburgh area (Anderson et al., 2002). The use of surface weather maps (UNISYS, 2002) and the HYSPLIT back-trajectory model (NOAA, 2002) indicated that high $PM_{2.5}$ episodes in Pittsburgh were associated with transitions from locally high pressure to low pressure regimes, and that fine particle episodes were most commonly associated with pollutant transport from the west, southwest, and northwest (Anderson et al., 2002; Modey and Eatough, 2002). Similar transport patterns were observed in the present study. For example, the high concentration of particulate matter observed at both sampling sites on 18 July was preceded by a period of high pressure on 16 and
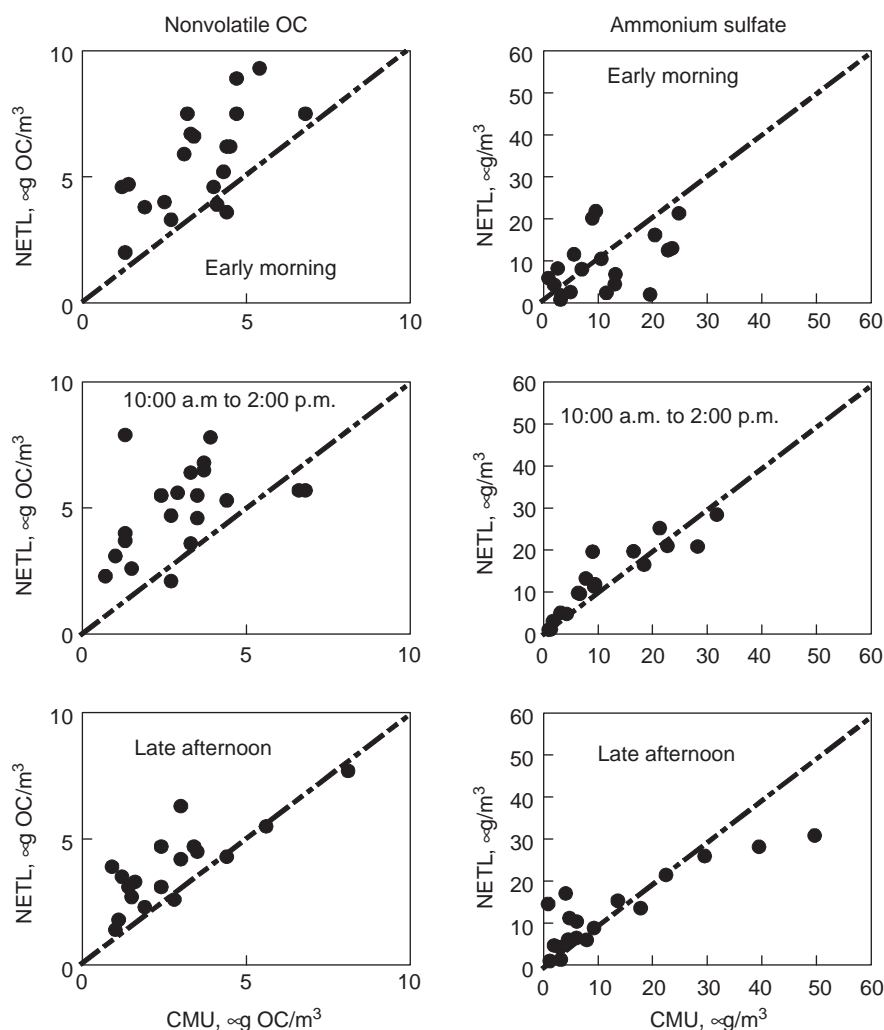
Fig. 6. Plots showing the diurnal distribution of ammonium sulfate and NVOM at both sampling sites. The 1:1 line represents data from Carnegie Mellon University (CMU) PAQS site, and data points in closed circles represent data from the NETL site.

17 July. Pollutant concentrations increased with the approach of a frontal system and the development of low pressure on 18 July. In the previous studies (Anderson et al., 2002; Modey and Eatough, 2003), high concentrations similar to that reported for 18 July were generally shown to be associated with transport from the southwest and the west. In contrast, transport at the start of the episode on 18 July was from the east, with short-term $PM_{2.5}$ concentrations exceeding $50 \,\mu g \, m^{-3}$ at both sites. Peak concentrations of ammonium sulfate exceeded $30 \,\mu g \, m^{-3}$ (Fig. 2), with 24-h averages above $24 \,\mu g \, m^{-3}$ (Table 2). Transport from the east may include emissions from the Monongahela River coke and steel industries (Fig. 1) as well as from coal-fired power plants east of Pittsburgh.

In this study, comparably high concentrations of ammonium sulfate were also observed at both sampling sites during pollutant transport from the west (9, 10, 17, 24, 25 July) and southwest (16, 22, and 23 July) (Table 2). Transport from these directions may include emissions from coal-fired power plants and the various coke processing and steel manufacturing plants located along the Ohio River valley to the west of both sampling sites, Fig. 1. Much lower pollutant concentrations were seen with transport from the NW (12, 13, 15, and 26 July) as shown in Table 2, and from the SE (19, 20, 27 July). Similarly, low ammonium sulfate concentrations were also associated with some incidences of transport from the southwest (16 July), and the west (9 July).

In contrast to episodes of long-range transported pollutants, the episode on 31 July was locally influenced.

Table 2
Relationship between the frequent meteorological transport pathways and composition of constructed $PM_{2.5}$ and the major components

Dates	24-h Back-trajectory	Specie	Concentration
(a) NETL site in Pittsburgh			
July 9, 10, 17, 24, 25	West	Constructed $PM_{2.5}$	27.4
		Ammonium sulfate	14.2
		Nonvolatile OM	7.4
		SVOM	4.8
July 16, 22, 23	Southwest	Constructed $PM_{2.5}$	31.1
		Ammonium sulfate	15.9
		Nonvolatile OM	9.3
		SVOM	5.0
July 12, 13, 15, 26	Northwest	Constructed $PM_{2.5}$	17.8
		Ammonium sulfate	5.8
		Nonvolatile OM	6.9
		SVOM	4.2
July 18	East	Constructed $PM_{2.5}$	39.8
		Ammonium sulfate	24.4
		Nonvolatile OM	9.3
		SVOM	5.3
(b) Carnegie mellon PAQS site in Pittsburgh			
July 9, 10, 17, 24, 25	West	Constructed $PM_{2.5}$	24.4
		Ammonium sulfate	15.1
		Nonvolatile OM	5.9
		SVOM	2.9
July 16, 22, 23	Southwest	Constructed $PM_{2.5}$	21.5
		Ammonium sulfate	12.9
		Nonvolatile OM	5.5
		SVOM	2.3
July 12, 13, 15, 26	Northwest	Constructed $PM_{2.5}$	11.7
		Ammonium sulfate	4.3
		Nonvolatile OM	3.9
		SVOM	2.7
July 18	East	Constructed $PM_{2.5}$	40.8
		Ammonium sulfate	29.9
		Nonvolatile OM	6.8
		SVOM	3.2

Average daily species concentration for each type of transport is given in $g\,m^{-3}$.

Prior to this date, transport from the southeast to the NETL site occurred at very low altitude. But a stable air mass with little wind was present at the NETL site throughout 31 July, leading to high $PM_{2.5}$ concentrations, with average 24-h constructed $PM_{2.5}$, ammonium sulfate, and nonvolatile organic material (NVOM) concentrations reaching $40\,\mu g\,m^{-3}$, $27\,\mu g\,m^{-3}$, and $10\,\mu g\,NVOM\,m^{-3}$, respectively. However, the locally dependent pollutant concentration observed on 21 July was characterized by lower $PM_{2.5}$ concentrations.

4. Conclusions

The concentration and composition of $PM_{2.5}$ impacting the NETL PM characterization site and Carnegie Mellon University EPA PAQS site were dependent on meteorological conditions. High-pressure conditions were characterized by low concentrations of ammonium sulfate and high concentrations of nonvolatile organic material. High concentrations of ammonium sulfate were generally associated with transport of pollutants to the sampling sites during transition from high pressure to low pressure regimes, thus suggesting the transport of sulfur oxide emissions from distant sources. Therefore, such pressure transitions could be used to predict the occurrence of fine particulate $PM_{2.5}$ episodes around the Pittsburgh area. Trends in VOM and SVOM at the two sampling sites in combination with trends in NO_x suggested the importance of NO_x chemistry at the CMU site but organic chemistry at the NETL site. This was reflected in higher concentrations of NVOM and SVOM

at the NETL site. The details of differences in emissions and atmospheric chemistry which lead to these observed differences in fine particulate organic material at the two sites are not yet known.

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