PM$_{2.5}$ characterization and source-receptor relations in South Carolina

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Abstract: Ambient PM$_{2.5}$ aerosol samples were collected at three sites at Clemson University during January and June of 2001. The PM$_{2.5}$ mass concentrations averaged 12.2 μg/m^3 in January and 21.2 μg/m^3 in June. Chemical characterization of the samples identified an average of 99% of the fine particulate matter collected in January and 96% in June. The primary ingredients of the PM$_{2.5}$ aerosol were organic carbon compounds (49% in January and 44% in June) and sulfates (21% in January and 33% in June). Total heavy metals on average contributed 0.3% of the fine aerosol mass. Source-receptor reconciliation was completed for the fine aerosol using a chemical mass balance model, Chemical Mass Balance v. 8 (CMB8). In January, approximately 105% of the measured mass was accounted for, and the major sources were soil dust, ammonium sulfate, and ammonium nitrate. In June, an average of 80% of the measured mass was accounted for, and the major sources were the same as in January, except that the contribution of ammonium nitrate was negligible. A composite source of organic compounds that includes gasoline vehicle exhaust, meat cooking, cigarette smoke, and wood burning, was one of the major sources for both June and January seasons.

Key words: PM$_{2.5}$, CMB8, source receptor modeling.

Résumé : Des échantillons de particules en suspension PM$_{2.5}$ dans l'air ambiant ont été recueillis à trois sites de l'université Clemson en janvier et juin 2001. La moyenne des concentrations massiques des PM$_{2.5}$ était de 12,2 μg/m^3 en janvier et de 21,2 μg/m^3 en juin. La caractérisation chimique des échantillons a permis d'identifier une moyenne de 99 % des matières particulaires fines collectées en janvier et 96 % en juin. Les ingrédients principaux des particules en suspension PM$_{2.5}$ étaient les composés carbonés organiques (49 % en janvier et 44 % en juin) et des sulfates (21 % en janvier et 33 % en juin). Les métaux lourds totaux ont contribué en moyenne 0,3 % de la masse de particules fines en suspension. Les données source-récepteur pour les particules fines en suspension ont été rapprochées en utilisant un modèle de bilan massique chimique (« CMB — Chemical Mass Balance »), le CMB8. En janvier, environ 105 % de la masse mesurée était comptabilisée et les sources majeures étaient la poussière du sol, le sulfate d'ammonium et le nitrate d'ammonium. En juin, une moyenne de 80 % de la masse mesurée était comptabilisée, et les sources majeures étaient les mêmes qu'en janvier, sauf que la contribution du nitrate d'ammonium était négligeable. Une source composite de composés organiques, qui comprend l'échappement des véhicules à essence, la cuisson de la viande, la fumée de cigarette et le brûlage du bois, était l'une des sources principales pour juin et janvier.

Mots clés : PM$_{2.5}$, modèle CMB8, modélisation de la relation source-récepteur.

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Introduction

Fine particulate matter, or PM$_{2.5}$, has been a topic of much interest in recent years. These particles are capable of causing a variety of adverse health and environmental effects. Anthropogenic PM$_{2.5}$ comes primarily from combustion of fossil fuels, such as in transportation, manufacturing, and power generation. Some particles are released directly into the atmosphere, while others may form in the atmosphere as secondary pollutants. Fine PM mass is generally dominated by sulfates, nitrates, and organic compounds, with soil dust making up a small but measurable fraction. PM$_{2.5}$ is largely responsible for the visibility reduction commonly associated with polluted areas, and its deposition onto surfaces and materials may cause damage to them (Wark et al. 1998). The potential health effects of PM$_{2.5}$ are a concern because the particles are small enough to be inhaled

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deeply into the lungs, where they may deposit and cause damage. A number of studies have indicated that increased levels of particulate matter lead to adverse health effects (Dockery et al. 1993; Pope et al. 1995). A recently published study followed 500 000 adults beginning in 1982 and linked risk factor data with air pollution, vital status, and cause of death data for the participants through the end of 1998. This study found that for every 10 $\mu g/m^3$ increase in long-term $PM_{2.5}$ exposure levels, the risk of cardiopulmonary related death increased by 6%, while the risk of death resulting from lung cancer increased by 8% (Pope et al. 2002). In addition, the health effects resulting from $PM_{2.5}$ exposure might be exacerbated if the particulate matter contains toxic heavy metals.

In response to increasing concerns from the scientific community, on 18 July 1997 the U.S. Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for $PM_{2.5}$ and ozone. The new NAAQS for $PM_{2.5}$ sets the allowable limit at a maximum annual average concentration of 15 $\mu g/m^3$.

Should the NAAQS for $PM_{2.5}$ be exceeded, it would be necessary to control the $PM_{2.5}$ concentration at the sources of the emissions. These sources must therefore be identified. The first step in source identification is the collection and chemical characterization of the particulate matter. Sampling and analysis methods employed in this study were consistent with previous research, in which $PM_{2.5}$ was collected and characterized (Solomon et al. 1998; Christoforou et al. 2000; Andrews et al. 2000; Ligocki et al. 1993; Polissar et al. 2001). The data resulting from the analyses can then be used in source–receptor models. Mass balance source–receptor models take the composition profiles of various sources and attempt to find a linear combination of sources whose emissions account for the ambient aerosol. While some recent studies have utilized these models with specific organic compounds as tracers (Schauer et al. 1996; Schauer and Cass 2000), modeling here was carried out using more general species, as has been also successfully employed (Salmon et al. 1995; Friedlander 1973; Cass and McRae 1983).

This paper presents the mass concentrations and chemical composition of ambient $PM_{2.5}$ on the campus of Clemson University. Chemical Mass Balance v. 8 (CMB8), a source–receptor model (Watson et al. 2001) is used to determine the primary sources contributing to the ambient fine aerosol.

Experimental methods

Sample collection

Three sites were selected for ambient sampling, all on the campus of Clemson University: under the stands of the football stadium, under the soccer stadium stands, and under a sheltered portion of a nearby loading dock. The three sites were approximately 750 m apart from each other.

All sampling events were 24 h in length, with the samplers running from midnight to midnight every other day in order to associate each sampling event with a calendar day. Three sampling events were carried out in January 2001 (21st, 23rd,

25th) and five sampling events were carried out in June 2001 (17th, 19th, 21st, 23rd, 25th).

The sampling system used is similar to those used in the past for particulate matter collection and characterization studies (Solomon et al. 1988; Ligocki et al. 1993; Polissar et al. 2001; Schauer et al. 1996; Salmon et al. 1995). In the current work, fine PM samples were collected after air was drawn through a glass inlet tube and passed through a Teflon-coated AIHL cyclone separator operated at 26 L/min to remove particles larger than approximately 2.1 μm (John and Reischl 1980). From the cyclone, the flow passed through Teflon tubing to four parallel 47-mm filter holders. Two contained quartz fiber filters (Pallflex® Tissuequartz 2500 QAO-UP) to collect samples for carbon analysis and two contained Teflon membrane filters (Teflo® 1.0 or 2.0 μm pore size) to collect samples for gravimetric, ion chromatographic, and XRF analyses.

Total suspended particulate (TSP) samples were also collected during this study. The data obtained were used primarily in consistency checks of the $PM_{2.5}$ data. The samples were analogous to the fine PM samples, with 4 filters (2 Teflon and 2 quartz) from each sampling event at each location. Samples were collected on filters in four open-face filter holders. The filters were treated identically to those from fine PM sampling in terms of preparation, collection, preservation, and analysis.

Quality assurance – quality control

A number of measures were taken in this study for the purposes of QA–QC. All quartz filters were baked at 550 °C overnight prior to sampling to lower residual carbon levels. Additionally, the quartz filters were stored prior to sampling in plastic petri dishes sealed with Teflon tape and lined with aluminum foil discs that had also been baked overnight at 550 °C to reduce contamination. All Teflon filters were pre-weighed as they were used in gravimetric analysis, and were stored prior to sampling in plastic petri dishes sealed with Teflon tape. After sampling, all filters were replaced in their original petri dishes and frozen upright until re-weighing and analysis.

Both laboratory and field blanks were used to account for inherent blank contamination and potential field contamination. Laboratory blanks remained in the laboratory until analysis, and this measure accounted for inherent filter contamination. Field blanks were used to check for potential contamination in the field due to loading–unloading practices or conditions. For each sampling event, one filter of each type was taken into the field, placed into the filter holder of the sampling apparatus, and removed to serve as a field blank. These filters remained in their petri dishes in the field for the duration of the sampling event and were retrieved and stored in the same manner as actual samples. The site at which the field blanks were loaded and unloaded was rotated each day in order to check for any site-specific contamination.

The flow rate through each filter assembly was controlled by a critical orifice following the filter assembly, and the flow rate was measured before and after each sampling event by a DryCal DC-Lite Primary Flow Meter (Model No. DCLT20K Rev. 1.08).

Timers were used to control the systems (Grasslin Controls Corporation, Model FM/1 digi 20), and counters were used to ensure that the systems ran for 24 h (Redington Counters, Inc., Model 710-0035).

Sample analysis

Out of every sampling set, both Teflon filters were analyzed gravimetrically to determine the mass concentration of particulate matter. Prior to weighing, these filters were equilibrated for 24 h in a room maintained at 70–80°F (21–27 °C) and 45±5% relative humidity. Filters were weighed before and after sampling on a Mettler-Toledo UMT-2 microbalance, which reports masses at the level of 0.1 μg. Mass concentrations were then determined by difference by dividing the mass of PM collected by the volume of air sampled as determined by the average of the two flow measurements (before and after sampling) for each filter.

One of the quartz filters from each set were shipped with cold packs to the Environmental Quality Laboratory, California Institute of Technology (Pasadena, Calif.) for elemental carbon – organic carbon (EC–OC) analysis. These filters were analyzed with a thermal-optical technique according to the method of Birch and Cary (1996). During the procedure, a small portion from the filter being analyzed is placed into an oven, in which analysis proceeds in two steps. First, the temperature is raised under a pure helium atmosphere to volatilize organic carbon, which is catalytically converted to methane and detected by a flame ionization detector (FID). Some of the organic carbon may, however, be pyrolytically converted to char (elemental carbon). To correct for this charring effect, a laser is used to measure the filter transmittance throughout the procedure. When organic carbon is pyrolized to char, the transmittance decreases. The second step occurs under a mixture of oxygen and helium, and the amount of carbon that is detected up to the point that the transmittance returns to its original value is counted as organic carbon, with the remaining carbon being detected as elemental carbon (Birch and Cary 1996).

Of the Teflon filters from each sampling set, one of the two was analyzed by ion chromatography (IC) for water soluble ions, while the other was analyzed for 23 elements by X-ray fluorescence (XRF) spectroscopy. The filters analyzed for ions were first extracted with 200 μL of ethanol (to wet the hydrophobic filter surface), followed by 9 mL of distilled, deionized (DDI) water (Derrick and Moyers 1981). The filters were then placed on a shaker table operating at 150 rpm for 3 h to complete the extraction. Aliquots were subsequently removed for IC analysis. Ion analysis was completed with the use of a Waters IC-Pak Cation M/D column (WAT036570) for cations and a Waters IC-Pak Anion HR column (WAT026765) for anions. A Waters 432 conductivity detector was used for ion detection. Analysis was completed for Na^+, K^+, NH_4^+, Mg^{+2}, Ca^{+2}, Cl^-, NO_3^-, PO_4^{-3}, and SO_4^{-2}.

X-ray fluorescence analysis was completed with the use of a wavelength dispersive XRF (WDXRF) spectrometer (Rigaku RIX 3000). Calibration was achieved with the use of thin-film standards (Micromatter Company). Seven of the elements measured were used to determine the crustal dust component of the particulate matter. In this determination, it was assumed that these elements were present as their common oxides (Al_2O_3, SiO_2, K_2O, CaO, TiO_2, MnO_2, and Fe_2O_3), and the crustal dust is the sum of those oxides (Christoforou et al. 2000; Andrews et al. 2000).

Results and discussion

Mass concentrations

Figure 1 shows the mass concentration of PM$_{2.5}$ at each of the three sites for all sampling events. The heavy line indicates the NAAQS limit of 15 μg/m^3 as a yearly average.

The concentrations were quite similar between sites for each sampling event. It is also apparent that the PM$_{2.5}$ concentration was substantially higher on both June 19th and June 21st. The PM$_{2.5}$ concentrations were greatly decreased on June 23rd and 25th, but this was most likely due to a rain event that occurred on June 22nd. The overall winter average was 12.2 μg/m^3, while the overall summer average was 21.2 μg/m^3. Across all sampling events and locations, the average mass concentration was 16.7 μg/m^3.

Total suspended particulate measurements showed a qualitatively similar pattern to the above mentioned fine PM data. On average, approximately 48% of the TSP was in the fine mode.

Chemical characterization

Figure 2 shows the charge balance for both PM$_{2.5}$ and TSP as determined by ion chromatography. The solid line represents neutrality, and the locations are denoted by FS (football stadium), SS (soccer stadium), and LD (loading dock).

Two distinct regions are apparent. The upper cluster consists entirely of the particulate matter collected on June 19th and 21st at all three sites. This result highlights the increased mass concentrations found on those days, as discussed previously. In addition, it can be seen that the samples from those two days were slightly anion deficient, while the lower cluster indicates that the majority of the other samples were essentially neutral. On the whole, charge neutralization averaged 98.5%, indicating that all major ionic species were properly accounted for in the analyses and that the aerosol was essentially neutral.

Table 1 shows the chemical characterization of the PM$_{2.5}$ aerosol, arranged by location and sampling event. The largest component of PM$_{2.5}$ mass in January was organic carbon compounds, followed by sulfate, ammonium, and nitrate. The composition was reasonably similar at each site, with organic compounds making up a slightly larger portion at the soccer stadium and the loading dock than at the football stadium. In general, the aerosol was well-characterized at all sites, with a mass balance closure of 99%.

In June, the composition profiles were again quite similar. Organic compounds contributed the largest portion of the aerosol mass, though slightly less than in the January samples. Sulfate contributed the next largest portion, and the percentage was

Fig. 1. PM$_{2.5}$ ambient concentrations at the three sampling locations. The solid horizontal line at 15 μg/m^3 denotes the annual average for PM$_{2.5}$ taken from the EPA.
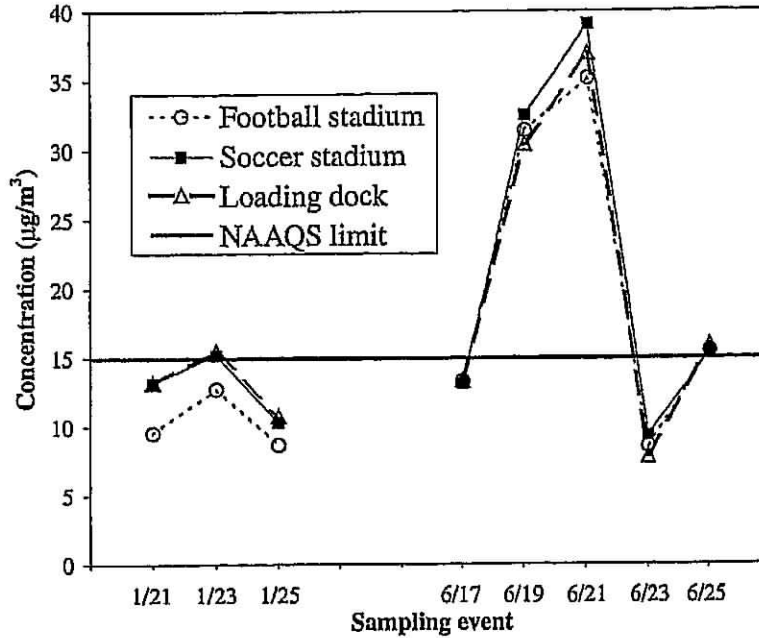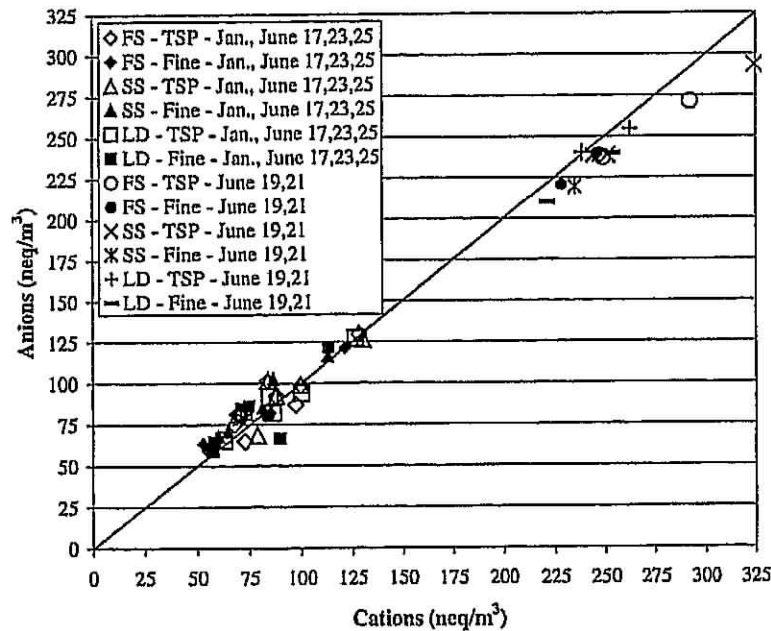

Fig. 2. Charge balance of ambient particulate matter. Sulfate and nitrate are included in the anions, while ammonium is the only cation used. The solid line represents neutrality.

higher than that found during January, suggesting that sulfate levels increased in June. Mass closure on these samples averaged 96%. At each site, there was only a small amount of nitrate present (less than 1%), unlike the January samples, in which nitrate comprised 9% of the aerosol. This lack of nitrate is likely due to the equilibrium behavior of the particulate species. The primary fine particulate form of nitrate is as ammonium nitrate, but this exists in equilibrium with gaseous ammonia and nitric acid. The equilibrium is somewhat complex, and it is highly dependent on ambient temperature and relative humidity (Watson et al. 1994). Chow and Watson (1998) note that it has been estimated that at temperatures about 30 °C, most of the nitrate will

Table 1. Chemical characterization of $PM_{2.5}$ aerosol.

	Date	Mass	EC	OC^a	NH_4^+	NO_3^-	SO_4^{-2}	Crustal[b]	Other identified[c]	Trace metals[d]	Not identified
Football stadium	21-Jan	9.57	0.08	3.34	1.03	0.66	2.53	0.25	0.39	0.06	1.23
	23-Jan	12.79	0.30	6.73	0.93	1.04	2.02	0.38	0.25	0.02	1.09
	25-Jan	8.70	0.12	3.99	0.91	1.01	2.02	0.26	0.24	0.52	0.00
	17-June	13.33	0.00	9.20	1.41	0.00	3.93	0.48	0.54	0.00	0.00
	19-June	31.44	0.25	9.63	3.82	0.10	10.53	0.49	1.31	0.31	5.00
	21-June	35.18	0.46	10.66	4.08	0.29	11.30	0.61	1.50	0.02	6.27
	23-June	8.57	0.01	4.78	0.96	0.00	2.93	0.17	0.21	0.00	0.00
	25-June	15.55	0.06	4.96	1.87	0.00	5.83	0.47	0.89	0.00	1.48
Soccer stadium	21-Jan	13.16	0.25	6.18	1.40	0.90	3.34	0.66	0.29	1.19	0.00
	23-Jan	15.23	0.43	8.92	1.09	1.22	2.45	0.29	0.17	0.00	0.68
	25-Jan	10.34	0.13	5.28	0.94	1.39	2.18	0.44	0.14	0.59	0.00
	17-June	13.13	0.00	5.93	1.40	0.00	3.91	0.36	0.59	0.00	0.94
	19-June	32.53	0.14	9.64	3.86	0.00	10.54	0.62	1.31	0.03	6.40
	21-June	39.07	0.44	14.97	4.09	0.17	11.33	0.96	1.41	0.14	5.54
	23-June	9.37	0.08	5.35	0.99	0.00	2.88	0.46	0.24	0.00	0.00
	25-June	15.47	0.06	5.22	1.92	0.00	5.59	0.50	0.53	0.15	1.53
Loading dock	21-Jan	13.21	0.46	5.58	1.28	0.91	3.43	0.36	0.24	0.00	0.94
	23-Jan	15.54	0.38	10.34	1.31	1.22	2.27	0.30	0.50	0.20	0.00
	25-Jan	10.79	0.17	5.51	0.98	1.36	2.06	0.26	0.18	0.14	0.13
	17-June	13.38	0.07	8.19	1.37	0.00	3.89	0.31	0.49	0.00	0.00
	19-June	30.46	0.15	10.83	3.75	0.00	10.11	0.41	1.53	0.00	3.67
	21-June	36.97	0.13	12.09	3.98	0.07	11.47	0.62	1.71	0.11	6.78
	23-June	7.82	0.09	5.94	0.98	0.00	2.82	0.16	0.30	0.03	0.00
	25-June	15.93	0.09	6.92	1.90	0.00	5.85	0.22	0.56	0.02	0.38

Note: All units in $\mu g/m^3$.

[a] Organic compounds, uses 1.4 as conversion factor in January and 2.0 in June.

[b] Sum of oxides of Al, Fe, Si, Mn, Ti, K, Ca, as determined by XRF and IC.

[c] Cl^-, Mg^{2+}, Na^+, and excess sulfur (above SO_4^{-2} from IC), as determined by XRF and IC.

[d] Pb, Cr, Co, Ni, Se, As, Ga, Te, Cu, Hg, U determined by XRF.

exist in the gas phase as nitric acid. Below that point, the relative amount of particulate ammonium nitrate present in the aerosol increases until most of the nitrate is present in particulate form at approximately 15 °C or below (Chow and Watson 1998). During the sampling events in June, the average temperature at the time of filter collection was 29 °C, so it is reasonable that significant amounts of nitrate were not found in the analysis of the fine particulate matter collected in June. In January, the average temperature during filter collection was 9 °C, so all of the nitrate present should have been in the particulate form.

Nitrate can also exist as a coarse species. Coarse particulate nitrate is generally more stable, and this form results from the reaction of nitric acid vapor on the surface of existing coarse particles (Pakkanen 1996). Sodium nitrate is a common nitrate form that exists primarily in the coarse mode, but smaller amounts may also be found in the fine mode, as with soil dust. Therefore, the appearance of small amounts of nitrate, possibly as sodium nitrate, in the fine mode is reasonable.

An important consideration in chemical characterization is the organic compound component. In completing the chemical characterization, the EC–OC procedure only reports the mass of organic carbon present. In ambient particulate matter, though, organic carbon is actually present in compounds that include varying amounts of oxygen and hydrogen. A conversion factor from organic carbon mass to organic compound mass is therefore required, and many studies have used a factor of 1.4, a value determined from two measurements of TSP gathered in Los Angeles in 1973 (Gray et al. 1986; Grosjean and Friedlander 1975; White and Roberts 1977).

In recent years, this value has been questioned (Andrews et al. 2000; Saxena et al. 1995; Hegg et al. 1997; Turpin and Lim 2001), and the prevailing opinion seems to be that there is no universal factor. The value of the factor will vary depending on the level of oxidation of the organic compounds. More highly oxidized (polar) organic compounds will have a higher mass and, therefore, larger conversion factor associated with them than less polar organic compounds. Less polar compounds are generally most associated with urban areas, while less urbanized areas often contain more polar organic compounds (Hegg et al. 1997). This may be the result of transport and atmospheric oxidation of the compounds from urban areas to non-urban areas, or of direct release of natural organic compounds, which tend to be more polar (Saxena et al. 1995). Turpin and Lim (2001) completed a review of existing data and recommend a

value of 1.6 ± 0.2 for urban areas and 2.1 ± 0.2 for non-urban areas, but they note that the actual factor will likely vary with location, season, and even time of day.

For the current study, a factor of 1.4 was applied to the data, and provided a good fit for the aerosol collected in January. Use of this factor for samples taken in June, however, resulted in an average mass balance closure of only 83%. The lack of a mass balance closure in June suggests that a higher factor may be appropriate. Application of a factor of 2.0 to the data collected in June resulted in a mass balance closure of 96%. The use of a higher factor is reasonable because the more intense sunlight and higher temperatures of June are expected to lead to greater photochemical oxidation of organic compounds present in the atmosphere as they are transported.

Heavy metal concentrations

Individual heavy metal concentrations were generally low, on the order of $0.01 - 0.14 \mu g/m^3$, and total heavy metals on average contributed approximately 0.3% of the fine PM mass.

Comparison of the contribution of heavy metals to PM mass in this study to other published results is complicated by the fact that different metals were often examined in various studies. $PM_{2.5}$ studies conducted in California, Colorado, and Illinois, as summarized by Chow and Watson (1998), provide some basis for comparison to the results of the present study. For the same metals examined in those studies, results from this work show an average contribution to fine PM mass of $0.11 \pm 0.18\%$ versus 0.04% for California, 0.09% for Colorado, and 0.18% for Illinois (Chow and Watson 1998). This comparison suggests that the results from the current study are in the same general range.

Source-receptor reconciliation

The theory behind the operation of chemical mass balance models has been presented in a variety of sources (Schauer et al. 1996; Schauer and Cass 2000; Salmon et al. 1995; Cass and McRae 1983) and is summarized here. In these models, the mass concentration of each chemical species in the ambient aerosol is assumed to be a linear combination of the emissions of those species from individual sources. Therefore, source emission profiles are an essential part of these models. The basic equation used in these models is shown below:

$$[1] \qquad c_{ik} = \sum_{j=1}^{m} a_{ij} f_{ijk} s_{jk}$$

where c_{ik} is the mass fraction of chemical species i in ambient sample k, a_{ij} is the mass fraction of chemical species i in emissions of source j, f_{ijk} is the fractionation coefficient for species i as it travels from source j to ambient location k, s_{jk} is the mass fraction of ambient sample k that is due to all of the chemical species in emissions of source j, i.e., the fraction of the ambient sample mass that is contributed by source j.

The unknowns in this analysis are the values of s_{jk} for the m sources that combine to give the ambient aerosol. The fractionation coefficient, f_{ijk}, is used to account for differential removal of selected species from the emission of a source as the emitted aerosol travels to the ambient sample site. For this project, it was assumed that all species are removed from the atmosphere at equal rates during transport, i.e., $f_{ijk} = 1.0$ in all cases. For each ambient sample, eq. [2] is written n times — once for each species included in the analysis. For the models to work, n must match or exceed m, i.e., the system of linear equations must be exactly specified or over-specified. A linear regression analysis is then used to solve the system of equations and determine the combination of sources, and their respective contributions, that explains the composition of the ambient aerosol with the minimum square residual error.

The computer model used in this work was CMB8 (Watson et al. 2001), distributed by the U.S. Environmental Protection Agency. The input to the program consists of the ambient data and source profiles as well as the uncertainties in each species, and the effective variance weighted least-squares technique is used in the solution of the system of equations. In this technique, the inclusion of uncertainties provides a better estimate of the uncertainties in the source contributions. The technique also gives greater influence to those species that are known with more precision in both ambient data and source profiles (Watson et al. 1984). The model output then consists of the contribution of each source to the ambient aerosol and the uncertainty in that estimate.

Included in the CMB8 distribution package is a set of source profiles gathered during a study in the San Joaquin Valley in California in the late 1980s. One of the provided source profiles for agricultural soil was used in this work due to the lack of a full soil source profile for the Clemson area. More recent source profiles for automobile emissions, cigarette smoke, medium-duty diesel trucks, wood burning (oak), and meat charbroiling were also added (Kleeman 2002). Cigarette smoke and meat cooking were added because significant cigarette smoking was known to occur in the immediate area of the sampler at the loading dock, and Hildemann et al. (1994) found that meat cooking was the single largest contributor to organic carbon compounds in the Los Angeles aerosol in 1982. Added in the source profiles are ammonium sulfate, ammonium nitrate, and sodium nitrate. These are all secondary aerosols and, therefore, have no specific source, but they have been included to represent inorganic secondary aerosols.

One of the issues involved in using CMB8 with only general source profiles (rather than with specific organic compounds as tracers) is that those profiles should be chemically distinct. If two or more sources are too similar in chemical composition, it is impossible for the program to distinguish between the two. The similar sources are said to be collinear and a solution to the system giving the contribution of each individual source cannot be found. Frequently, this condition results in one of the collinear sources being estimated as a negative quantity, which

Table 2. Source contributions to ambient aerosol as determined by CMB8.

	Football stadium (avg±σ in $\mu g/m^3$)		Soccer stadium (avg±σ in $\mu g/m^3$)		Loading dock (avg±σ in $\mu g/m^3$)	
	January 21–25	June 17–25	January 21–25	June 17–25	January 21–25	June 17–25
Agricultural soil dust	0.41±0.40	1.45±0.77	1.46±1.02	1.50±0.48	1.60±0.53	0.31±0.94
Ammonium sulfate	2.75±0.25	9.12±0.75	3.18±0.32	9.14±0.74	3.46±0.31	9.04±0.71
Ammonium nitrate	1.10±0.16	—	1.37±0.26	—	1.13±0.27	—
Sodium nitrate	—	0.13±0.20	0.07±0.10	0.02±0.05	0.35±0.10	0.02±0.14
Diesel vehicle exhaust	0.10±0.57	0.20±0.97	0.06±0.60	0.19±0.52	0.46±0.57	0.07±0.58
Other[a]	5.80±0.97	6.87±1.71	8.55±1.22	7.21±1.45	6.54±0.94	5.77±1.08
Sum of identified sources	10.17±0.88	17.77±1.99	14.70±1.48	18.07±1.65	13.54±0.98	15.21±1.45
Measured mass	10.35±0.77	20.81±1.50	12.91±0.46	21.91±2.02	13.18±1.06	20.91±2.91
Total mass explained	98%	85%	114%	82%	103%	73%
R^2	0.99	0.99	0.98	1.00	1.00	1.00
χ^2	0.47	0.28	1.78	0.16	0.01	0.06

Note: σ denotes the uncertainty in the estimate from CMB8. R^2 is the correlation coefficient, showing the goodness of fit of the model to the data.
χ^2 is the sum of the square of the residual errors between data and model predictions.
[a] Includes gasoline vehicle exhaust, meat cooking, cigarette smoke, and wood burning.

is meaningless and would require the model to be run again without the negative source included. To circumvent the estimation of negative source contributions, this version of CMB allows the simulation to be run with the option for sources with negative contributions to be automatically eliminated in subsequent iterations. In this way, the most likely sources with positive contributions are always selected (Watson et al. 2001). This option was used in the current work. An important point to recognize, however, is that this method leads to an estimate of the contribution of only one of the collinear sources, when in reality the true contribution is likely some combination of all of the collinear sources. A number of sources in this work exhibited this behavior. The source profiles for automobile emissions, meat cooking, cigarette smoke, and wood burning were dominated by organic carbon and were all sufficiently similar to cause collinearity problems.

When simulations were run without the CMB program option involving automatic removal of sources with negatively estimated contributions in subsequent iterations, the model estimated some of the organic carbon sources as having unreasonably high contributions (i.e., greater than the total mass of the aerosol), while other organic carbon sources were estimated as having large negative contributions. As discussed earlier, CMB8 was unable to determine the individual contribution of the organic carbon sources with similar source profiles, i.e., automobile exhaust, meat cooking, cigarette smoke, and wood burning. Between these effects and the similarity in the source profiles themselves, it was determined that the aforementioned organic carbon sources were sufficiently collinear that CMB could not distinguish between the individual contributions of each.

Due to the relatively rural nature of Clemson, S.C., biogenic organic carbon emissions might also contribute to the ambient aerosol. Such emissions are typically gases, which are then photochemically oxidized to form secondary organic carbon particulate matter. No source profile could be found for such emissions, so this source was not included in the modeling. In addition, even if a source profile had been available, it would very likely have suffered from collinearity as discussed above, making the determination of its individual contribution to the aerosol difficult.

In modeling the aerosol, the data were averaged by season but kept separate by location, so that six distinct ambient data sets were modeled. The source profiles employed were ammonium sulfate, ammonium nitrate, sodium nitrate, meat charbroiling, cigarette smoke, automobile exhaust, medium-duty diesel truck exhaust, agricultural soil dust, and wood smoke. The source profiles available for automobile emissions were for cars with catalytic converters and without catalytic converters (Kleeman 2002). In an attempt to mitigate the collinearity effects of the automobile sources, the simplifying assumption was made that the distribution of cars in the Clemson University area was approximately 80%–20% catalytic to non-catalytic converter-equipped cars.

Table 2 shows the contribution of each identified source to the ambient aerosol during each season at each site. The total mass estimated by the model was somewhat more accurate for the January samples than for the June samples, averaging 105% in January and 80% in June, although the uncertainty of the model estimates was on the order of 10%–20%. The correlation coefficient (R^2) was close to 1 for each location, which implies that the model provided a good fit to the data in all cases. Chi-square (χ^2) is the weighted sum of the squares of the deviations between the measured and predicted species concentrations. Ideally, therefore, this value would be zero for a perfect fit. In general, a value less than 1.0 represents a very good fit to the data, while a value between 1 and 2 is acceptable. For simulations like those performed in this study, χ^2 values of this size are not statistically different from zero at the 99% confidence level (Watson et al. 2001), indicating that the model predictions explain the ambient aerosol well.

Table 3. PM$_{2.5}$ species concentrations as measured and as predicted by CMB8.

|	Football stadium (average±σ in μg/m^3)			
	January 21–25		June 17–25	
	Measured	Predicted by CMB8	Measured	Predicted by CMB8
Nitrate	0.9030±0.1039	0.8689±0.0854	0.0788±0.1484	0.1118±0.0104
Sulfate	2.1922±0.1908	2.1141±0.2001	6.9019±0.5532	6.8004±0.6632
Ammonium	0.9588±0.0284	0.9659±0.0791	2.4274±0.0781	2.4345±0.2491
Sodium	ND	0.0010±0.0002	0.1702±0.1782	0.0428±0.0036
Elemental carbon	0.1689±0.3362	0.1184±0.0006	0.1556±0.5500	0.1545±0.0020
Organic carbon	3.3476±0.5363	3.3672±0.0048	3.9225±0.9264	3.9210±0.0156
Potassium	0.0602±0.0102	0.0594±0.0015	0.0525±0.0242	0.0532±0.0052
Titanium	ND	0.0034±0.0004	0.0104±0.0305	0.0121±0.0013
Manganese	0.0314±0.0263	0.0006±0.0001	0.0163±0.0197	0.0019±0.0001
	Soccer stadium (average±σ in μg/m^3)			
	January 21–25		June 17–25	
	Measured	Predicted by CMB8	Measured	Predicted by CMB8
Nitrate	1.1736±0.1754	1.1187±0.1066	0.0335±0.0355	0.0353±0.0048
Sulfate	2.6545±0.2499	2.5581±0.2315	6.8477±0.5526	6.7725±0.6646
Ammonium	1.1422±0.0319	1.1484±0.0923	2.4514±0.0672	2.4552±0.2496
Sodium	0.0285±0.0284	0.0313±0.0020	0.1010±0.1536	0.0144±0.0009
Elemental carbon	0.2675±0.3361	0.2660±0.0024	0.1445±0.2967	0.1447±0.0021
Organic carbon	4.8507±0.6590	4.8563±0.0166	4.1120±0.7990	4.1099±0.0162
Potassium	0.0695±0.0319	0.0752±0.0053	0.0549±0.0140	0.0553±0.0054
Titanium	0.0540±0.0545	0.0142±0.0013	0.0194±0.0533	0.0126±0.0014
Manganese	0.0779±0.0354	0.0020±0.0002	0.0091±0.0131	0.0020±0.0002
	Loading dock (average±σ in μg/m^3)			
	January 21–25		June 17–25	
	Measured	Predicted by CMB8	Measured	Predicted by CMB8
Nitrate	1.1643±0.1993	1.1406±0.0916	0.0149±0.1051	0.0204±0.0015
Sulfate	2.5888±0.1747	2.5706±0.2518	6.8281±0.4044	6.7668±0.6573
Ammonium	1.1902±0.0313	1.1921±0.0980	2.3949±0.0702	2.4021±0.2468
Sodium	0.0957±0.0265	0.0967±0.0094	0.1732±0.3528	0.0063±0.0005
Elemental carbon	0.3396±0.3256	0.3383±0.0023	0.1048±0.3338	0.1040±0.0004
Organic carbon	5.1011±0.6901	5.1046±0.0173	4.3974±0.7997	4.3992±0.0040
Potassium	0.0992±0.0141	0.0991±0.0058	0.0526±0.0288	0.0523±0.0011
Titanium	0.0109±0.0340	0.0135±0.0014	ND	0.0032±0.0003
Manganese	ND	0.0021±0.0002	ND	0.0004±0.0001

Note: ND, below method detection limit. σ - 1 standard deviation for measured concentrations or uncertainty in prediction as calculated by CMB8.

The primary contributions to the aerosol in January were made by soil dust, ammonium sulfate (secondary aerosol), ammonium nitrate (secondary aerosol), and a source consisting primarily of organic carbon. As discussed earlier, CMB8 was unable to determine the individual contribution of sources with similar source profiles. The program, therefore, identified only one source as making the last contribution, e.g., cigarette smoke at the loading dock. Since it is unlikely that the single identified source made such a large contribution to the aerosol at each site, the contributions were reported in Table 2 in an "other" category. In the modeling, this category included automobile exhaust, meat cooking, cigarette smoke, and wood burning. In reality, all of these sources probably contributed to the aerosol. It is also likely that biogenic secondary organic compounds contributed, as well. Due to their secondary nature and the lack of a source profile, this source was not included in the modeling, but it could be considered to be a part of the "other" category, since its inclusion would not have changed the output of CMB8.

In June, the main contributions were similar to those in January, except that the contribution of ammonium nitrate was neg-

Fig. 3. Comparison of measured and predicted concentrations by CMB8 of selected particulate matter constituents.
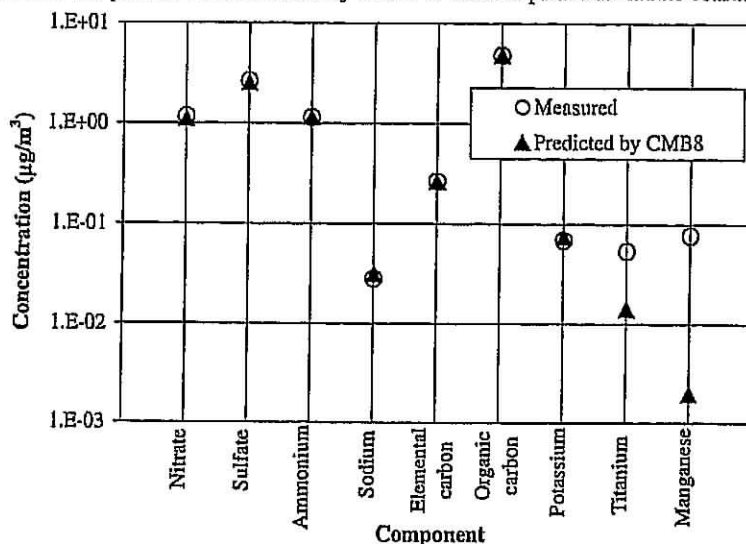
ligible. Similarly to the January data, the actual contributions of automobile exhaust, meat cooking, and cigarette smoke (as well as the likelihood of biogenically derived organic compounds) could not be determined, so the contribution was attributed to the "other" category. The inability of the program to determine the individual contributions of sources with similar source profiles highlights the utility of using specific organic compounds as tracers, as this type of data would facilitate a differentiation between the individual contributions of similar sources.

In all cases, diesel exhaust was identified as a contributing source, but only at levels below the uncertainty associated with the estimate. This condition indicates that the contribution is below a limit of detection. The contribution made by sodium nitrate (secondary aerosol) is similar, though in several cases the levels are closer to the uncertainty than in the case of diesel exhaust. In such cases, it can be assumed that the upper limit of the source contribution is two or three times the uncertainty estimate (Watson et al. 2001). The small contributions made by sodium nitrate are supported by the previous discussion on the relative thermodynamic stability of the predominant fine species, ammonium nitrate, and the more stable predominantly coarse species, sodium nitrate.

In using CMB8, fitting species must be selected. These species are the components used in fitting the model to the data and determining the quality of the fit. The fitting species, therefore, must have been quantified in both the ambient aerosol samples and in all of the source profiles. Subject to this constraint, nine fitting species were chosen, and the species concentrations, as measured and as predicted by CMB8, are shown in Table 3. In most cases, the agreement between measured and calculated concentrations was good, as expected from the R^2 and χ^2 values presented earlier. The primary exceptions were manganese and to a lesser extent titanium. Except for the cases where a measurable level was not detectable, the calculated concentration

of manganese was lower than the measured concentration by a factor ranging from 5 to 52. Inspection of the uncertainty estimates for the measured concentrations indicates, however, that actual differences may be much smaller or even insignificant in some cases. The discrepancy may be due to a difference in the manganese and titanium content of the soil in the Clemson area versus the California soil that was used as a source profile. As a typical illustration of the agreement between measured and calculated concentrations, Fig. 3 shows the comparison between the two for the average January aerosol at the soccer stadium.

Conclusions

Ambient $PM_{2.5}$ and TSP aerosol samples were taken at three sites on the campus of Clemson University during January and June of 2001. On average, approximately 48% of the TSP was in the fine mode. Chemical characterization of the samples indicated that in both seasons, $PM_{2.5}$ mass was dominated by organic carbon compounds and sulfate, with smaller but still significant contributions by ammonium, soil dust, and nitrate (in January only). On average, 99% of the gravimetrically determined $PM_{2.5}$ mass was chemically identified in the January samples, with 96% identified in the June samples. The average mass concentration was higher in June than in January, with an average value of 12.2 $\mu g/m^3$ in January and 21.2 $\mu g/m^3$ in June, resulting in an overall average of 16.7 $\mu g/m^3$. It appears that an increase in sulfate was largely responsible for the higher mass concentrations found in June than in January, and this may be due to greater photochemically enhanced production of secondary sulfates (Polissar et al. 2001).

In determining the mass composition of the fine and TSP aerosol, a factor of 1.4 was used for the January samples to convert from organic carbon (the measured component) to organic compounds, while a factor of 2.0 for the June samples provided a better fit to the gravimetrically determined mass.

These factors correspond well to the values recommended by Turpin and Lim (2001), and by the greater photochemical oxidation occurring in June than in January, which would result in the formation of more highly oxididized organic compounds, thus giving them a higher average molecular weight.

Due to health-related concerns over the association of toxic heavy metals with fine PM, chemical characterization included heavy metal analysis. Individual heavy metal concentrations were relatively low, on the order of $0.01–0.14 \ \mu g/m^3$, and total heavy metals on average contributed 0.3% of the fine aerosol mass.

If future control of fine PM is to be practiced, the sources of the aerosol must be determined since control of an ambient aerosol is only possible at the level of the source. Source-receptor reconciliation was completed for the fine aerosol in this study using a chemical mass balance model, CMB8. Modeling results show that the major sources of the ambient aerosol sampled in this work were soil dust, ammonium sulfate, ammonium nitrate (only in January), and a single source at each site consisting primarily of organic carbon. The identification of a single source is a consequence of the similarity (collinearity) of the source profiles for automobile exhaust, meat cooking, cigarette smoke, and wood burning. In reality, it is highly likely that all of the collinear sources actually contributed to the aerosol, in addition to the likely contribution of biogenic secondary organic carbon. Therefore, results were reported with a composite source of organic compounds that included all of the collinear sources. To determine the individual contribution of each source to the aerosol, specific organic compounds would have to be used as tracers in source-receptor reconciliation.

Acknowledgements

References

Andrews, E., Saxena, P., Musarra, S., Hildemann, L.M., Koutrakis, P., McMurry, P.H., Olmez, I., and White, W.H. 2000. Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements. J. Air Waste Manage. Assoc. 50: 648–664.

Birch, M.E., and Cary, R.A. 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Sci. Technol. 25: 221–241.

Cass, G.R., and McRae, G.J. 1983. Source-receptor reconciliation of routine air monitoring data for trace metals: an emission inventory assisted approach. Environ. Sci. Technol. 17(3): 129–139.

Chow, J.C., and Watson, J.G. 1998. Guideline on Speciated Particulate Monitoring, Draft 3. U.S. Environmental Protection Agency. Prepared for Office of Air Quality Planning and Standards (MD-14).

Christoforou, C.S., Salmon, L.G., Hannigan, M.P., Solomon, P.A., and Cass, G.R. 2000. Trends in fine particle concentration and chemical composition in southern California. J. Air Waste Manage. Assoc. 50: 43–53.

Derrick, J., and Moyers, J. 1981. Precise and sensitive water soluble ion extraction method for aerosol samples collected on polytetrafluorethylene filters. Anal. Lett. 14(A19): 1637–1652.

Dockery, D.W., Pope, C.A., III, Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Jr., and Speizer, F.E. 1993. An association between air pollution and mortality in six U.S. cities. N. Engl. J. Med. 329(24): 1753–1759.

Friedlander, S.K. 1973. Chemical element balances and identification of air pollution sources. Environ. Sci. Technol. 7(3): 235–240.

Gray, H.A., Cass, G.R., Huntzicker, J.J., Heyerdahl, E.K., and Rau, J.A. 1986. Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles. Environ. Sci. Technol. 20(6): 580–588.

Grosjean, D., and Friedlander, S.K. 1975. Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere. J. Air Pollut. Control Assoc. 25(10): 1038–1043.

Hegg, D.A., Livingston, J., Hobbs, P.V., Novakov, T., and Russell, P. 1997. Chemical apportionment of aerosol column optical depth off the mid-Atlantic coast of the United States. J. Geophys. Res. 102(D21): 25293–25303.

Hildemann, L.M., Klinedinst, D.B., Klouda, G.A., Currie, L.A., and Cass, G.R. 1994. Sources of urban contemporary carbon aerosol. Environ. Sci. Technol. 28(9): 1565–1576.

Imboden, A.S. 2001. Atmospheric Dry Deposition of Nitrogen to Lake Greenwood, South Carolina. M.Sc. thesis, Environmental Engineering and Science, Clemson University, Clemson, South Carolina.

John, W., and Reischl, G.A. 1980. cyclone for size-selective sampling of ambient air. J. Air Pollut. Control Assoc. 30(8): 872–876.

Kleeman, M.J. 2002. Personal communication. University of California, Davis.

Ligocki, M.P., Salmon, L.G., Fall, T., Jones, M.C., Nazaroff, W.W., and Cass, G.R. 1993. Characteristics of airborne particles inside southern California museums. Atmos. Environ. 27A(5): 697–711.

Pakkanen, T.A. 1996. Study of formation of coarse particle nitrate aerosol. Atmos. Environ. 30: 2475–2482.

Polissar, A.V., Hopke, P.K., and Poirot, R.L. 2001. Atmospheric aerosol over Vermont: chemical composition and sources. Environ. Sci. Technol. 35(23): 4604–4621.

Pope, C.A., III, Dockery, D.W., and Schwartz, J. 1995. Review of epidemiological evidence of health effects of particulate air pollution. Inhal. Toxicol. 7: 1–18.

Pope, C.A., III, Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., and Thurston, G.D. 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. J. Am. Med. Assoc. 287: 1132–1141.

Salmon, L.G., Christoforou, C.S., Gerk, T.J., Cass, G.R., Casuccio, G.S., Cooke, G.A., Leger, M., and Olmez, I. 1995. Source contributions to airborne particle deposition at the Yungang Grottoes, China. Sci. Total Environ. 167: 33–47.

Saxena, P., Hildemann, L.M., McMurry, P.H., and Seinfeld, J.H. 1995. Organics alter hygroscopic behavior of atmospheric particles. J. Geophys. Res. 100(D9): 18755–18770.

Schauer, J.J., and Cass, G.R. 2000. Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers. Environ. Sci. Technol. 34(9): 1821–1832.

Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. Atmos. Environ. 20(22): 3837–3855.

Solomon, P.A., Fall, T., Salmon, L., Lin, P., Vasquez, F., and Cass, G.R. 1988. Acquisition of acid vapor and aerosol concentration data for use in dry deposition studies in the south coast air basin. Vol. 1. Environmental Quality Laboratory, California Institute of Technology, Report 25.

Turpin, B.J., and Lim, H.-J. 2001. Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass. Aerosol Sci. Technol. 35: 602–610.

Wark, K., Warner, C.F., and Davis, W.T. 1998. Air Pollution – Its Origin and Control, 3rd ed. Addison Wesley Longman Inc., Reading, Mass.

Watson, J.G., Cooper, J.A., and Huntzicker, J.J. 1984. The effective variance weighting for least squares calculations applied to the mass balance receptor model. Atmos. Environ. 18: 1347–1355.

Watson, J.G., Chow, J.C., Lurmann, F., and Musarra, S. 1994. Ammonium nitrate, nitric acid, and ammonia equilibrium in wintertime Phoenix, AZ. Air Waste, 44: 261–268.

Watson, J.G., Robinson, N.F., Chow, J.C., Fujita, E.M., and Lowenthal, D.H. 2001. CMB8 User's Manual Draft. EPA-454/R-01-XXX, U.S. Environmental Protection Agency, Research Triangle Park, N.C.

White, W.H., and Roberts, P.T. 1977. On the nature and origins of visibility-reducing aerosols in the Los Angeles air basin. Atmos. Environ. 11: 803–812.