The Chemical Composition of Inorganic and Carbonaceous Materials in PM_{2.5} in Nanjing, China

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Abstract

PM_{2.5} samples were collected at an urban and a suburban site in Nanjing, China in 2001. They were analyzed for inorganic ions, elemental carbon, organic carbon (OC), water-soluble organic carbon (WSOC), and individual WSOC and nonpolar organic species. Sulfate and organic matter were the two most abundant constituents in these samples. Sulfate accounted for an average of 23% (urban site) and 30% (suburban site) of the identified aerosol mass. Organic matter accounted for an average of 37% (urban) and 28% (suburban) of the identified aerosol mass. WSOC was a significant portion of OC, accounting for about one-third of OC at the urban site and 45% of OC at the suburban site. The suburban-urban gradient in the WSOC/OC ratio also reflected that the aerosol OC was more aged at the suburban location. The correlations of WSOC with sulfate and nitrate suggest that the WSOC fraction was dominated by secondary organics. More than 30 individual WSOC species in the compound classes of organic anions, amino acids, aliphatic amines, and carbohydrates were quantified, accounting for approximately 8% of the WSOC on a carbon mass basis. In addition, 46 individual nonpolar organic compounds in the compound classes of *n*-alkanes, hopanes, and polycyclic aromatic hydrocarbons were quantified using an in-injection port thermal desorption technique. These nonpolar organic species accounted for less than 7% of the OC on a carbon mass basis. The quantification of individual compounds allowed the identification of major aerosol sources through principal component analysis. Coal combustion, vehicular emissions, secondary inorganic and organic aerosols, and road/sea salt were the major contributing sources to the identified PM_{2.5} aerosol mass.

Keywords: Aerosol chemical composition; Water soluble organic compounds; Chinese aerosols; coal combustion; Principal component analysis; Aerosol source identification.

1. Introduction

Ambient aerosols play important roles in global radiative forcing by scattering or absorbing light directly or indirectly through modulating cloud condensation nuclei (CCN) and they consequently have an impact on climate change (IPCC, 2001). Aerosols aerodynamically smaller than 2.5 μm (i.e., PM_{2.5}) are of particular concern because they are the major culprit in visibility degradation (Watson, 2001) and because of their established harmful effects on human health (NRC, 1998).

As the most populated country and one of the fastest growing economies in the world, China is important in assessing the impact of anthropogenic pollution on the global environment. There have been an increasing number of studies on Chinese aerosols in the recent decade; however, our knowledge of the physical and chemical properties of ambient aerosols in China remains rather limited. Many of the published studies on Chinese aerosols have focused

mainly on the elemental constituents and major inorganic ions (e.g., Zhang and Friedlander, 2000 and references therein). In comparison, studies on the composition of the carbonaceous fraction of aerosols in China have been scant, with the number increasing only in recent years. Organic carbon (OC) and elemental carbon (EC) data have been collected mostly in large cities and in economically developed areas, such as Beijing (Bergin et al., 2001; He et al., 2001; Dan et al., 2004;), the Yangtze Delta region (Shanghai, Linan, Sheshan, Changshu) (Xu et al., 2002; Ye et al., 2003), and the Pearl River Delta region (Hong Kong, Guangzhou, Shenzhen, and Zhuhai) (Ho et al., 2003; Cao et al., 2003, 2004; Yu et al., 2004). Studies on the chemical composition of the OC fraction on a molecular level are especially sparse. Measurements of a limited number of organic compound classes have been documented only for a few large cities including Beijing (e.g., Simoneit et al., 1991; Yao et al., 2003), Qindao (Guo et al., 2003), Nanjing (Wang et al., 2002b), Shanghai (Yao et al., 2002), Guangzhou (e.g., Bi et al., 2002), and Hong Kong (e.g., Zheng et al., 2000).

In this study, we collected PM_{2.5} aerosol samples in Nanjing, a metropolitan area in the Yangtze Delta, in February and September of 2001. We report here on the concentrations of OC, EC, and water-soluble organic carbon (WSOC) in addition to the concentrations of major inorganic cations and anions in these aerosol samples. We also determined the concentrations of nonpolar organic species including *n*-alkanes, hopanes and PAHs as well as the concentrations of low-molecular weight carboxylic acids, amino acids, aliphatic amines in the WSOC fraction. As far as we are aware, this is one of the most comprehensive measurements of the chemical composition in PM_{2.5} aerosols in China. Our work adds to the increasing chemical database on Chinese aerosols.

2. Experimental section

2.1 Sample collection

PM_{2.5} aerosol samples were collected from two sites in Nanjing in the winter (February) and the fall (September) of 2001. One site was on the campus of Nanjing University (NJU) in the downtown area of the city. The campus is surrounded by residential areas, heavily trafficked roads and commercial centers, representing a typical urban location. The sampler was set up on the rooftop of a two-storey building, 8 to 10 m above the ground. The PM_{2.5} samples were collected at this location during 1-6 February and 21-28 September 2001. The second site was at the Purple Mountain Observatory (PMO) of the Chinese Academy of Sciences, about five kilometers to the east of the NJU site and in a suburban area of the city. The observatory is located on Zijin Mountain (118°49' E, 32°04' N, 267 m ASL) amid suburban residential surroundings and a lake at the foot of the mountain. The mountain and the observatory are largely covered with trees. The sampler was set up on the rooftop of an approximately 6 m high building inside the observatory. Samples were collected at this site from 7 to 13 February 2001. The air masses in the

three intensive sampling periods were mostly continental according to ten-day isentropic back trajectories obtained from the NOAA Climate Monitoring and Diagnostics Laboratories (CMDL) (available at <http://www.cmdl.noaa.gov>) (Harris and Kahl, 1994).

Sampling started at around 8 am and ended at around 8 pm everyday; each sample was collected for 12 h. The sampler (Andersen Instruments, Smyrna, GA, USA) was equipped with a slot inlet of 2.5 μm cut size and operated at a flow rate of 1.11 m^3/min . All the collection substrates were 20 $\times$ 25 cm quartz fiber filters, prebaked at 550°C overnight to remove any absorbed organic materials. The filters were stored and transported to the field in annealed aluminum foil pouches. After the sampling was completed, the 20 $\times$ 25 cm filters were folded in half such that the side with the sample on it was folded onto itself and stored in the annealed aluminum pouches. All the filter samples were stored at -4°C in a freezer until analysis.

2.2 Sample analysis

2.2.1 OC, EC and WSOC

OC, EC, and WSOC concentrations were determined using a thermal/optical aerosol carbon analyzer (Sunset Laboratory, Forest Grove, OR, USA) (Birch and Cary, 1996). For the determination of OC and EC concentrations, a filter punch 1.45 cm^2 in size was removed from the 20 $\times$ 25 cm filter and loaded into the aerosol carbon analyzer. The thermal analysis conditions (i.e., temperature program and the type of atmosphere) employed were similar to those adopted by all research groups that participated in the carbon analysis of the ACE-Asia samples (Schauer et al., 2003). Duplicate measurements of OC and EC were made on every sample, and the average relative standard deviations were 4% and 9% for OC and EC, respectively. For the determination of WSOC concentrations, 20 filter pieces, each piece 1.45 cm^2 in size, were randomly removed from each 20 $\times$ 25 cm parent filter and extracted with two portions of 10 ml ultra pure water in a sonication bath for 15 min for each extraction. The water extracts were filtered and concentrated using a rotary evaporator to 0.5 ml before carbon analysis. The WSOC content was determined by the carbon analyzer using the same thermal analysis conditions as those for EC and OC determination. The details of the method for the WSOC determination were described in our previous paper (Yang et al., 2003).

2.2.2 Analysis of individual inorganic and organic compounds

Inorganic ions and low molecular weight organic acids were determined using a Dionex DX 500 Ion Chromatograph (IC) System. An analytical column (AS11, 4 mm) with a guard column (AG11, 4 mm) and an anion trap column was used for organic acid and inorganic anion detection with gradient elution from 0.2 mM to 5 mM NaOH. A cation analytical column (CS12, 4 mm) with a guard column (CG12, 4 mm) was used to analyze inorganic cations with an eluent of 20 mM methanesulfonic acid. Carbohydrates were degraded to formaldehyde, followed by the determination of formaldehyde as its 2,4-dinitrophenylhydrazine derivative using an HP 1100 high-pressure

liquid chromatography (HPLC) system with photo diode array detection at 360 nm (Johnson and Sieburth, 1977). Free amino acids and aliphatic amines were converted into fluorescent derivatives and determined using a Waters HPLC system with fluorescent detection at 395 nm (Cohen and Michaud, 1993). Details of the method were given in our previous work (Mader et al., 2004).

Concentrations of nonpolar aerosol organics, including *n*-alkanes, hopanes, and PAHs, were analyzed by thermally desorbing a filter strip 2.9 cm² in size in the injection port of an HP 5890 gas chromatography (GC) system followed by GC separation and mass spectrometric detection. The method details and performance characterization are described elsewhere (Ho and Yu, 2004). Due to a lack of authentic standards, hopane concentrations were estimated by assuming the same response factors as the respective *n*-alkanes of the same carbon number.

3. Results and discussion

3.1 Major chemical constituents

Table 1 gives the concentrations of the major inorganic ionic species, EC, and OC in the PM_{2.5} aerosols. Due to a lack of a suitable balance at the time of the experiments, aerosol mass concentrations were not determined. The aerosol mass concentrations discussed hereafter were reconstructed from the measured chemical species, including sulfate, nitrate, chloride, ammonium, Na⁺, K⁺, Ca²⁺, Mg²⁺, EC, and organic matter (OM). A ratio of 1.6 is assumed to calculate the OM mass from the OC mass (Turpin and Lim, 2001). The average reconstructed PM_{2.5} aerosol mass was 80.5, 67.1, and 46.9 μg m⁻³ in the PMO-February, NJU-February, and NJU-September samples, respectively. Figure 1 shows contributions of the major constituents in individual samples in a bar chart format. Rain and snow events occurred during or immediately before the two February sampling periods. The wet scavenge effect was most clearly seen in the samples after a heavy rain event starting in the afternoon of 11 February and followed by snow on the night of 12 February. The reconstructed aerosol mass concentrations of these samples were reduced to less than one-quarter of the pre-rain maximum concentration (Figure 1). Wang et al. (2003) measured the major inorganic ionic species in eight samples collected at each of five selected locations in the same city; the eight samples were distributed across four seasons in the period of February-December 2001. Our ionic concentrations were in general in agreement with their measurements.

Sulfate and OM were the two most abundant constituents. Sulfate accounted for 30%, 21%, and 24% of the total identified mass in the PMO-February, NJU-February, and NJU-September samples, respectively. OM accounted for 28%, 37%, and 37% of the total identified mass in the PMO-February, NJU-February, and NJU-September samples, respectively. While sulfate and OM had mass percentage contributions of a comparable magnitude, sulfate contributed more at the suburban site and OM contributed more at the urban site, reflecting heavier influences from

combustion sources in the urban area on one hand and increased sulfate formation at the suburban site on the other hand.

Ammonium and nitrate were the next two most abundant constituents, taking up 8-15% and 7-16% of the total reconstructed mass, respectively. The average concentration of ammonium was similar to that of nitrate in each of the three sample sets. It is known that the filter-only sampling technique could lead to negative sampling artifacts due to evaporative loss of aerosol nitrate or positive artifacts due to gaseous nitric acid retained on the filter through adsorption or chemical reactions with alkaline aerosol constituents (e.g., Appel and Tokiwa, 1983, Zhang and McMurry, 1992; Cheng and Tsai, 1997). It is generally accepted that nitrate loss through evaporation is increased under conditions of high temperatures or low humidity. It has also been reported that nitrate losses are lower with increasing PM_{2.5} mass (Kim et al., 1999; Chang et al., 2000). As a result of the dependence on atmospheric conditions, the magnitude of evaporative loss of nitrate could vary from being negligible to substantial (e.g., Kim et al., 1999). The varying nature of nitrate's negative artifact makes it difficult to assess the degree to which our nitrate concentrations were underestimated. However, the significant presence of nitrate on the filters indicates that future studies should adopt artifact-minimizing measures for nitrate in order to obtain accurate relative contributions of the major constituents of PM_{2.5} in Nanjing.

It was found that SO₄²⁻, NO₃⁻, and NH₄⁺ were well correlated, with a correlation coefficient (r^2) of 0.82 between SO₄²⁻ and NH₄⁺ and 0.76 between NO₃⁻ and NH₄⁺ for the consolidated data set that included all the three subsets of samples. NH₄⁺ concentrations are known to track SO₄²⁻ since aerosol NH₄⁺ is mainly produced by the reaction between gaseous NH₃ and acidic sulfate particles. As a result, the two aerosol species are expected to have a good correlation. The good correlation has been abundantly demonstrated in many locations around the world, for example, in Chongju, Korea (r^2 : 0.48-0.98) (Lee and Kang, 2001), in Shanghai and Beijing (r^2 : 0.88-0.94) (Yao et al., 2002), and in Helsinki (Pakkanen et al., 2001). Considering the known atmospheric chemistry of sulfate and NH₄⁺, we in turn confirm that our measurements were reasonable.

Chloride was found to exceed the expected level if sea salt were the sole source of chloride. Non-sea-salt (nss) chloride is believed to be associated with coal burning (Yao et al., 2002) and was calculated as total Cl⁻ minus the product of the Na⁺ concentration and 1.17, the molar ratio of Cl⁻ to Na⁺ in seawater. The nss-Cl⁻ was on average 0.34, 1.33, and 0.11 μg m⁻³, accounting for 12%, 40%, and 6% of the total Cl⁻ in the PMO-February, NJU-February, and NJU-September samples, respectively. The much elevated nss-Cl⁻ level in the winter month was consistent with the higher contribution from coal burning coupled with a lower atmospheric mixing layer. In addition, chloride was found to correlate with a few PAHs (e.g., a correlation coefficient (r^2) of 0.59 with benzo[*e*]pyrene and of 0.62 with picene), further supporting the possibility of a combustion emission source.

EC was a minor component of the identified PM_{2.5} mass and also a minor fraction of aerosol carbon. EC made up on average 17%, 17%, and 27% of the total carbon in the PMO-February, NJU-February, and NJU-September samples, respectively. The EC concentrations ranged from 0.61 to 6.27 $\mu\text{g m}^{-3}$. The average EC concentrations measured in our study (2.88–4.01 $\mu\text{gC m}^{-3}$) were similar to those measured elsewhere at a few locations in the Yangtze Delta region (3.4 $\mu\text{gC m}^{-3}$) (Xu et al., 2002) and in Shanghai (4.4 $\mu\text{gC m}^{-3}$) (Ye et al., 2003), but much lower than those reported for a few locations in Beijing (15.2 $\mu\text{gC m}^{-3}$ by Dan et al., 2004 and 8.7 and 10.1 $\mu\text{gC m}^{-3}$ by He et al., 2001). We note that different thermal methods were used in these studies and that EC/OC measurements are operationally defined and method dependent (e.g., Chow et al., 2001). The large difference seen between EC concentrations in Beijing in the north and the measurements in the Yangtze Delta in the south (Nanjing included) was most likely a combined result of measurements by different thermal methods and different EC emission sources. Total carbon (TC), sum of EC and OC, could be accurately determined independent of thermal analysis methods. The TC concentrations in our Nanjing samples (15.0–18.8 $\mu\text{gC m}^{-3}$) were similar to those in Shanghai (18.7 $\mu\text{gC m}^{-3}$) (Ye et al., 2003), but much smaller than those in Beijing (39.2 $\mu\text{gC m}^{-3}$ by He et al., 2001 and 51.9 $\mu\text{gC m}^{-3}$ by Dan et al., 2004) and in the agricultural areas of the Yangtze Delta (47.4 $\mu\text{gC m}^{-3}$) (Xu et al., 2002).

The urban-suburban contrast was seen most clearly in the much higher contributions of sulfate at the suburban location (30% vs. 21%). Nitrate and ammonium also contributed more to the aerosol mass at the suburban site (16% vs. 12% for nitrate and 15% vs. 13% for ammonium). The higher contributions of SO_4^{2-} , NO_3^- and NH_4^+ were consistent with the secondary nature of these aerosol constituents. An additional urban-suburban contrast was a higher EC contribution (5.0% vs. 3.6%) observed at the urban site, in line with EC as a primary pollutant.

3.3 Molecular composition of the WSOC fraction

Due to their affinity with water, WSOC substances play a similarly important role to that of sulfate in aerosol-cloud interactions, wet scavenging of atmospheric particles, and the formation of haze. While the atmospheric behaviors of sulfate are reasonably well understood as a result of a few decades of studies, our understanding about WSOC is very limited and one of the major stumping blocks is a lack of knowledge on its chemical composition. The number of studies on measurements of WSOC and its components has increased only in recent years, and the measurements were mainly made on the European Continent (e.g., Zappoli et al., 1999; Krivacsy et al., 2001).

Table 2 summarizes the average concentrations of WSOC and individual WSOC species, together with the contribution of WSOC to OC and TC. The WSOC level at the suburban location was higher than that at the urban location. The percentage contribution of WSOC to OC at the suburban site was more than 10% higher than that at the

urban location. This was likely a combined result of more aged aerosols and higher contributions of biomass burning aerosols at the suburban location. The latter was evidenced by higher K^+ concentration seen at the suburban location (Table 1). Stronger biogenic emission could also be a factor as free amino compounds were found at higher concentrations in the suburban aerosols than the urban aerosols (Table 2). The WSOC/TC ratios ranged from 20% to 44%, in agreement with values (14-67%) reported in the literature for urban locations (Mader et al., 2004 and references therein). Our WSOC concentrations ($1.01\text{--}14.5\ \mu\text{gC m}^{-3}$) were lower than those ($17.4\text{--}19.6\ \mu\text{gC m}^{-3}$) reported by Wang et al. (2002a) for four $\text{PM}_{2.5}$ samples collected in February 2001 in Nanjing. Aerosol sampling in our work and in the work by Wang et al took place at different locations in Nanjing and also on different days, although in the same calendar month. In addition, each of our samples was collected for 12 h and there was a day sample and a night sample on each sampling day while Wang et al collected only day samples (a sampling duration of 8 h from 8:30 am to 4:30 pm). The spatial and temporal differences in aerosols were expected to at least partly contribute to the differences on the reported WSOC concentrations.

By multiplying WSOC by a factor of 2.1 (Kiss et al., 2002; Turpin and Lim, 2001), the average mass concentrations of water-soluble organic compounds were estimated to be 13.5, 9.9, and $7.2\ \mu\text{g m}^{-3}$ in the PMO-February, NJU-February, and NJU-September samples, respectively. These values were one-half to two-thirds of the respective sulfate concentrations. The comparable abundance of WSOC to that of sulfate suggests that WSOC cannot be overlooked in studying aerosols' interactions with water vapor.

WSOC was found to have the strongest correlation with two secondary inorganic aerosol components (i.e., sulfate and nitrate) among all the measured constituents (Figure 2). The correlation coefficient (r^2) was 0.78 with sulfate and 0.86 with nitrate. This may suggest that the dominant constituents of the WSOC fraction were secondary organic products formed through formation pathways similar to those of sulfate and nitrate. A similar conjecture on the significant presence of secondary components in WSOC was reached by Sullivan et al. (2004) through measurements of WSOC, OC, EC, and ozone in St. Louis, MO, U.S.A.

Four compound classes in the WSOC fraction were quantified for individual compounds, including monocarboxylic acids, dicarboxylic acids, aliphatic amines, and amino acids. A total of 32 individual WSOC compounds were identified to be present in the aerosol samples, accounting for approximately 5% the WSOC on a carbon mass basis (Table 2). The detected ionic forms of mono- and di-carboxylic acids included formate, acetate, methanesulfonate, oxalate, malonate, maleate, succinate, and glutarate. Maleate appeared as a front shoulder peak of sulfate. The much larger sulfate peak makes it difficult to quantify maleate accurately. Consequently, its quantification was not attempted.

Oxalate was the most abundant WSOC species, ranging from 67.2 to 826 ng m⁻³. The mass concentrations of individual mono- and di-carboxylic acids detected in Nanjing PM_{2.5} samples were comparable to those we detected in PM_{2.5} samples collected from Jeju Island during ACE-Asia (Yang et al., 2004). The mass concentrations of individual dicarboxylic acids also fell in the concentration ranges reported by other studies in the East Asian region (Wang et al., 2002b; Kawamura et al., 2003; Yao et al., 2002 and references therein).

Three aliphatic amines (i.e., methyl amine, ethyl amine, and ethanol amine) and twenty amino acids were identified and quantified. The three most abundant amino acids were cystine, glycine, and valine. Most individual amino acids and aliphatic amines were more abundant at PMO than at NJU, and were more abundant in February than in September at NJU.

A fifth group of WSOC determined was monomeric carbohydrate (e.g., glycerol, glucose). Only the total monomeric carbohydrate was determined by oxidizing each mole of monomeric carbohydrate into two moles of formaldehyde through a series of well-defined reactions followed by the determination of formaldehyde using an HPLC method (Johnson and Sieburth, 1977). A lower-limit estimate of the mass concentration of the total monomeric carbohydrate was calculated by assuming that a C₃-sugar alcohol (i.e., glycerol) represented the monomeric carbohydrates. On the carbon mass basis, monomeric carbohydrate accounted for 4.6%, 4.1% and 2.5% of the WSOC in the PMO-February, NJU-February, and NJU-September samples, respectively.

The detailed chemical speciation work identified only 7-10% of the WSOC mass on a carbon mass basis, leaving the majority of WSOC unidentified. Recent chemical characterization work elsewhere has provided evidence that humic-like polymeric substances account for a considerable portion (20-60%) of WSOC (Kiss et al., 2002; Krivácsy et al., 2001; Zappoli et al., 1999). A significant presence of humic-like substances would explain the low percentage of WSOC identified at the molecular level in our work. Carbon thermograms of the aerosol water extracts in this study appeared to be in line with the possibility of a large presence of polymeric substances. It was found that the evolution of roughly half of WSOC from the filter substrate to the carrier gas during its thermal analysis required a temperature higher than 615°C followed by an oxidation step at temperatures higher than 575°C. Figure 3 shows an example of a WSOC thermogram. The fact that the low molecular weight WSOC species only accounted for a minor percentage of the WSOC suggests that future chemical characterization efforts need to be directed towards polymeric substances.

3.4 *n*-Alkanes, hopanes, and PAHs

Three classes of nonpolar aerosol organic compounds were quantified and their concentrations are listed in Table 3. A total of 21 *n*-alkanes (C₁₆-C₃₆), 10 hopanes and 16 PAHs were identified to be present in the aerosol samples. Together with the identified WSOC compounds, 8.3%, 9.5%, and 5.7% of the OC on the carbon mass basis

were identified as individual compounds in the PMO-February, NJU-February, and NJU-September samples, respectively. This demonstrates the extremely complex make-up of the aerosol OC and that our knowledge of OC chemical composition at a molecular level is far from being complete.

The total *n*-alkane concentrations ranged from 64 to 1407 ng/m³. The abundance in the NJU-February samples was twice that in the PMO-February samples, indicating stronger alkane sources in the urban area. The main sources of *n*-alkanes include petroleum residues and biogenic emissions (e.g., plant wax and wood burning). *n*-Alkanes from the two sources exhibit different homologue distributions. While *n*-alkanes of petroleum origin have shorter carbon chain lengths and show no odd carbon number predominance, those of biogenic origin have strong odd number carbon predominance above C₂₅ (Mazurek and Simoneit, 1984; Simoneit, 1986). Strong odd number carbon predominance above C₂₇ was observed in all three sets of samples, indicating the presence of plant wax emissions at both sites and in both seasons. The carbon preference index (CPI), defined as the concentration ratio of the sum of odd number alkanes to the sum of even number alkanes, is an indicator for the relative contributions of anthropogenic and biogenic sources to the total aerosol alkane mass. The CPI value was 1.1 in the winter samples, indicating the dominant influence of anthropogenic emissions. In comparison, the CPI in the NJU-September samples was 1.7. The higher CPI value suggests more biogenic emissions in September than in February, in line with the expectation of the seasonality of plant-related emissions. In the winter samples, more than 50% of the *n*-alkane mass was associated with *n*-alkanes smaller than *n*-C₂₆, and the most abundant *n*-alkane (i.e., C_{max}) was C₂₂, while in the September samples, most of the *n*-alkanes mass was associated with *n*-alkanes larger than *n*-C₂₃ and C_{max} was C₃₁. The cause for the seasonal variation could be attributed to the higher ambient temperature in September than in February and consequently more of the semi-volatile *n*-alkanes resided in the gas phase in February.

Hopanes are known molecular markers of aerosol emissions from fossil fuel utilization (e.g., Simoneit et al., 1991). In this study the total hopane concentrations ranged from 10 to 65 ng m⁻³. The concentrations of individual hopanes in the NJU-February samples were generally twice those in the PMO-February samples. The C₂₇ to C₃₀ hopane concentrations in the NJU-February samples were roughly double the concentrations in the NJU-September samples while C₃₁ to C₃₂ hopane concentrations were of a similar magnitude in the two seasons.

Sixteen PAHs have been identified in our samples (Table 3). One PAH compound, picene, was identified through interpretation from its mass spectrum fragmentation pattern and its retention time relative to other known PAHs (Grimmer et al., 1983). The identification of other 15 PAH compounds were verified with authentic standards. Concentrations of picene were estimated assuming the same response factor as that of dibenz[*a,h*]anthracene, which has the same molecular weight of 278. The total PAH concentrations ranged from 34 to 433 ng m⁻³, comparable to those determined in TSP samples collected in Beijing, Guiyang, and Guangzhou (30 – 490 ng m⁻³) (Simoneit et al.,

1991; Bi et al., 2003), and more recent measurements at Qingdao ($2.2 - 241 \text{ ng m}^{-3}$) (Guo et al., 2003). The average total PAH concentration in the NJU-February samples was twice that in the PMO-February samples and three times that in the NJU-September samples. Picene, a known tracer for coal burning (Grimmer et al., 1983, Oros and Simoneit, 2000), were detected in the NJU-February samples, but not in the other two sets of samples. These observations were consistent with the expected urban-suburban difference in influences by primary combustion sources and the seasonal dependence of particle PAHs.

3.5 Source identification by principal component analysis

Principal component analysis (PCA) has been demonstrated to be a useful data analysis tool to reduce the dimensionality of a large number of interrelated aerosol components for the purpose of source identification (e.g., Simcik et al., 1999, Jeon et al., 2001, Larsen and Baker, 2003). The combined data sets of the three intensive sampling periods were analyzed using PCA. Table 4 lists the first four factor loadings for individual aerosol components after Varimax rotation of the data matrix. Factors 1 to 4 explain 36.7%, 18.5%, 17.2%, and 8.4%, respectively, of the total variance in the data sets. Factor 2 is loaded with sulfate, nitrate, ammonium, and WSOC, signifying an association with secondary sources. In factor 4, the high loading components are Na^+ , Mg^{2+} , and Ca^{2+} , suggesting a source linked to road /sea salt (Harrison et al., 1996). An $\text{Mg}^{2+} : \text{Na}^+$ mass ratio of 0.18 was found for the aerosol samples. This value exceeded the ratio of 0.13 for seawater, suggesting that sea salt was not the only source contributing to this factor.

Factors 1 and 3 are both loaded with alkanes, hopanes, and PAHs, but of different compounds within the same homolog series. Factor 1 is characterized by high loading values on $\text{C}_{17}\text{-C}_{29}$ *n*-alkanes, $\text{C}_{27}\text{-C}_{30}$ hopanes, and PAHs compounds including phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*e*]pyrene, and picene. In addition, chloride has a high loading value in Factor 1. The high loading values in picene and chloride suggests that factor 1 is related to coal combustion. Chloride emissions from coal combustion have been documented in the literature (e.g., McCulloch et al., 1999; Watson et al., 2001; Ninomiya et al., 2004). Factor 3 is characterized by high loading values in EC, $\text{C}_{32}\text{-C}_{33}$ *n*-alkanes, $\text{C}_{30}\text{-C}_{32}$ hopanes, and PAHs including benzo[*a*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, and benzo[*ghi*]perylene. The high loading value in EC associates factor 3 with automobile exhausts. The homohopane index [$\text{S}/(\text{S}+\text{R})$] was also in accordance with the identification of vehicular exhaust. The homohopane index ranged from 0.52 to 0.65 (Table 3), more in line with the typical value (0.6) for petroleum (Seifert and Moldowan, 1978), rather than for coal smoke samples (0.05-0.35) (Oros and Simoneit, 2000). The ratio of $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane to $17\alpha(\text{H}), 21\beta(\text{H})$ -22R homohopane also supported the association of factor 3 with petroleum use. This ratio was 4.4, 5.5, and 3.4 in the February-PMO, NJU-February, and NJU-September samples, respectively, more in line with the typical ratio for gasoline- and diesel-

powered vehicle exhaust (2.2-2.9) (Rogge et al., 1993). In comparison, the typical ratios were reported to be 0.1-2.6 for coal smokes (Oros and Simoneit, 2000).

Multiple linear regression analysis (MLRA) of the factor scores was used to estimate the source contribution, following a similar procedure adopted by Larsen and Baker (2003). MLRA was run with the identified aerosol mass as the dependent variables and the absolute factor scores as independent variables. The mean percent contribution was calculated to be 7.5% for coal combustion, 74% for secondary inorganic and organic aerosols, 9.4% for automobile emissions, and 5.2% for road/sea salt. A quick inspection of the major chemical constituents listed in Table 1 verifies the dominance of the secondary components (i.e., sulfate, nitrate, ammonium, and WSOC) in the identified aerosol mass. We note that crustal materials (e.g., Al, Si, Fe) were not measured in this study and therefore their contribution to the aerosol mass could not be assessed.

4. Conclusions

We determined the chemical composition of the inorganic ionic and carbonaceous materials in $PM_{2.5}$ samples collected from an urban and a suburban location in Nanjing in February and September 2001. This is one of the most comprehensive speciation studies on Chinese $PM_{2.5}$ aerosols, with a particular effort to characterize the water-soluble organic carbon fraction. Sulfate and organic matter were the two most abundant $PM_{2.5}$ components. Nitrate was less abundant, but still a significant fraction (7-16%) of the identified $PM_{2.5}$ mass. Consequently, it is important to implement measures to minimize sampling artifacts for nitrate in future studies of $PM_{2.5}$ in Nanjing. Chloride was found in excess of the expected level from sea salt. Its correlation with PAHs and seasonality indicated coal combustion as a likely important source. Water-soluble organic carbon accounted for 30-45% of OC. The water-soluble organic materials had comparable abundance to that of sulfate, implying that their roles could not be neglected in studies of aerosol-water interactions. Only a small fraction of the WSOC could be identified as individual species, mainly low-molecular weight compounds. The thermal evolution behaviors of the WSOC suggested that the unidentified WSOC mass was largely made of thermally recalcitrant substances, likely polymeric in nature. Future chemical characterization efforts need to be directed towards these polymeric organic substances. The good correlation of WSOC with sulfate and nitrate, together with the higher WSOC and WSOC/OC observed at the rural sites, tend to suggest that secondary organics were a dominant component of the WSOC fraction.

The quantification of individual nonpolar organic compounds, together with the inorganic constituents, allows the identification of major aerosol sources through PCA. Four sources, coal combustion, secondary aerosols, vehicular exhaust, and road/sea salt, were found to account for 81% of the total variance of the data matrix. The source contributions to the identified aerosol mass were estimated using MLRA to be 7.5% for coal combustion, 74%

for secondary inorganic and organic aerosols, 9.4% for automobile emissions, and 5.2% for road/sea salt. In light of sulfate and OM being either the most abundant or the second most abundant component of PM_{2.5}, future work is suggested to identify and quantify major SO₂ sources and organic aerosol sources in this city.

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Figure Captions

Figure 1. Concentrations of major constituents of PM_{2.5} aerosols

(The sample names on the X-axis are sampling dates in mm/dd followed by D (day) or N (night). Day samples started at 8 am and ended at 8 pm while night samples started at 8 pm and ended at 8 am.)

Figure 2. Correlation plots of WSOC versus sulfate and nitrate.

Figure 3. Carbon thermogram of an aerosol water extract sample. (Thermal analysis conditions: In the helium stage, the temperature was initially 50°C, followed by four temperature steps at 310, 450, 615, and 870°C for a residence time of 60, 60, 60, and 110 s, respectively; the O₂/He stage used six temperature steps at 540, 600, 660, 720, 780, and 840°C, each step for 30 s, and a final temperature step at 890°C for 150 s.)

Table 1. Concentrations ($\mu\text{g m}^{-3}$) of major chemical constituents in PM_{2.5} aerosols

	PMO-February ($n=12$) ^a		NJU-February ($n=10$) ^a		NJU-September ($n=14$) ^a	
	Average	Range	Average	Range	Average	Range
Temperature (°C)	4.2	0.0-11.0	5.7	1.0-8.5	23.2	21.3-26.6
EC	2.88 (3.6%) ^c	0.61-6.27	3.33 (5.0%)	1.19-5.69	4.01 (8.6%)	2.63-5.54
1.6*OC ^b	22.7 (28.2%)	4.05-49.9	25.0 (37.3%)	16.8-32.2	17.3 (36.9%)	11.6-23.0
SO ₄ ²⁻	24.4 (30.3%)	7.50-43.0	14.0 (20.9%)	9.60-21.5	11.5 (24.5%)	6.13-18.9
NO ₃ ⁻	12.9 (16.0%)	1.86-30.1	8.06 (12.0%)	5.12-12.4	3.24 (6.9%)	1.64-8.34
Cl ⁻	1.09 (1.4%)	0.33-1.95	2.62 (3.9%)	1.77-4.07	1.12 (2.4%)	0.41-2.53
NH ₄ ⁺	12.1 (15.0%)	4.50-21.0	8.40 (12.5%)	6.07-11.0	3.55 (7.6%)	0.58-7.35
Na ⁺	0.64 (0.8%)	0.39-1.19	1.01 (1.5%)	0.29-2.96	0.86 (1.8%)	0.55-1.31
K ⁺	2.44 (3.0%)	0.45-5.73	2.07 (3.1%)	0.92-4.83	2.57 (5.5%)	0.81-5.81
Mg ²⁺	0.13 (0.2%)	0.04-0.24	0.18 (0.3%)	0.03-0.51	0.15 (0.3%)	0.08-0.23
Ca ²⁺	1.18 (1.5%)	0.36-1.89	2.34 (3.5%)	0.31-5.42	2.60 (5.5%)	0.81-4.57
Total identified mass	80.5	21.2-160	67.1	46.8-82.0	46.9	31.6-72.1

^a PMO denotes Purple Mountain Observatory. NJU denotes Nanjing University. The numbers inside parenthesis refer to the number of PM_{2.5} samples collected.

^b A ratio of 1.6 is assumed to calculate the organic matter mass from organic carbon (Turpin and Lim, 2001).

^c The percentage inside the parenthesis represents the mass percentage of the given aerosol species.

Table 2. Concentrations of WSOC and individual WSOC species

	PMO-February		NJU-February		NJU-September	
	Average	Range	Average	Range	Average	Range
WSOC ($\mu\text{gC m}^{-3}$)	6.42	1.01-14.5	4.70	3.16-6.57	3.45	1.85-5.41
WSOC/OC	45%	40-51%	30%	22-38%	32%	23-40%
WSOC/TC	38%	32-44%	25%	20-32%	23%	17-29%
Compound	Concentration (ng m^{-3})					
Acetate	92.7	0-456	32.8	0-114	4.5	0-62.4
Formate	61.3	23.4-127	107	20.9-236	17.3	0-50.7
Methanesulfonate	55.1	11.1-164	31.1	0-59.6	29.1	0-65.9
Σmonocarboxylic acids	209	34.5-743	171	20.9-369	50.8	0-123
Σmonocarboxylic acids/WSOC^b	0.8%	0.2-1.6%	0.9%	0.2-2.2%	0.3%	0.0-0.8%
Oxalate	299	67.2-826	220	134-280	299	133-593
Malonate	75.2	15.1-227	26.5	14.2-41.0	32.9	6.0-70.7
Succinate	74.6	22.4-118	69.3	39.9-99.4	23.3	7.5-45.0
Glutarate	48.4	8.9-109	25.9	9.2-68.3	21.2	1.5-67.8
Σdicarboxylic acids	497	144-1158	341	211-460	376	152-774
Σdicarboxylic acids/WSOC^b	2.8%	1.7-4.4%	2.4%	1.8-3.5%	3.1%	1.8-4.9%
Methyl amine	19.0	4.0-54.4	12.5	4.9-27.0	5.5	0.5-20.2
Ethyl amine	8.7	2.4-20.9	6.7	3.2-9.1	3.7	1.3-9.8
Ethanol amine	5.7	1.9-14.4	4.0	1.8-7.6	1.6	0.3-4.3
Σaliphatic amine	33.5	8.3-77.3	23.2	9.9-43.6	10.9	2.3-33.5
Σaliphatic amine/WSOC^b	0.2%	0.1-0.4%	0.2%	0.1-0.3%	0.1%	0.04-0.3%
Alanine	12.6	0-36.1	7.3	0-13.4	5.4	1.1-14.4
β -Alanine	14.1	0-42.2	7.0	0-17.8	2.9	0-9.0
α -Aminobutyric acid	2.0	0-4.8	1.6	0-6.6	1.0	0-3.0
Arginine				bdl ^a		
Asparagines	2.6	0-7.4	3.4	1.0-5.0	5.0	2.6-10.1
Cystine	27.5	8.4-60.6	23.1	15.4-39.1	16.4	7.6-31.6
Galactosamine	6.4	0-23.4	3.5	1.6-6.2	1.9	0.6-3.6
Glutamic acid	0.1	0-1.2	2.7	0-5.6	3.5	1.1-5.4
Glycine	61.8	15.0-165	18.6	12.0-25.8	4.7	1.5-11.9
Histidine	2.2	0.6-4.1	0.8	0-1.6	1.4	0-3.6
Isoleucine	4.0	1.1-7.7	3.5	2.1-4.9	2.2	1.1-4.2
Leucine	3.5	0.7-9.9	4.4	2.4-6.5	2.9	1.3-4.8
Lysine	10.5	2.4-26.8	8.8	0-15.2	6.7	3.4-13.3
Methionine	0.5	0-2.8	0.2	0-1.9	0.2	0-1.7
Ornithine	0.1	0-1.2	1.5	0-4.6	1.6	0-3.7
Phenylalanine	11.7	1.1-50.6	9.4	2.9-17.3	5.8	0.8-26.7
Proline	bdl		7.3	0-40.8	9.0	0-27.4
Serine	5.5	1.3-14.8	2.9	1.0-6.1	2.6	1.2-4.2
Threonine	bdl		bdl		1.1	0-5.3
Tyrosine	5.8	1.4-12.6	5.2	2.9-8.2	3.5	1.8-5.5
Valine	18.1	7.0-46.3	18.2	8.6-35.8	7.1	1.3-22.3
Σfree amino acids^c	189	58.5-396	129	81.9-188	84.9	39.3-162
Σfree amino acids/WSOC^b	1.4%	0.6-2.3%	1.3%	0.8-2.3%	1.1%	0.6-1.5%
Σmonomeric carbohydrates	323	90.9-533	218	131-274	117	23.3-229
Σmonomeric carbohydrates/WSOC^b	4.6%	2.7-7.0%	4.1%	2.2-6.1%	2.5%	0.7-5.0%

^a Below detection limit.^b The percentage contribution is on a carbon mass basis.^c The sum of free amino acids.

Table 3. Concentrations of nonpolar OC compounds

OC/TC	PMO-February		NJU-February		NJU-September	
	Average	Range	Average	Range	Average	Range
	83%	80~85%	83%	77~90%	73%	69~79%
Compound	Concentration (ng m ⁻³)					
<i>n</i> -hexadecane (C-16)	ND		ND		2.0	0.0-6.5
<i>n</i> -heptadecane (C-17)	10.0	4.0-18.1	36.4	12.2-89.8	2.6	0.0-8.2
<i>n</i> -octadecane (C-18)	15.3	5.9-26.3	75.1	25.8-210	0.9	0.4-1.8
<i>n</i> -nonadecane (C-19)	13.7	3.6-23.0	54.4	17.8-130	0.6	0.2-1.6
<i>n</i> -eicosane (C-20)	25.5	6.6-40.0	75.6	33.3-146	1.0	0.4-4.4
<i>n</i> -heneicosane (C-21)	32.2	11.4-57.0	78.5	48.4-119	1.6	0.6-5.1
<i>n</i> -docosane (C-22)	42.3	13.6-78.9	83.5	47.4-111	2.0	0.6-10.4
<i>n</i> -tricosane (C-23)	37.9	11.2-73.3	68.7	39.1-88.7	4.1	1.3-21.4
<i>n</i> -tetracosane (C-24)	36.8	10.0-78.0	63.3	38.1-80.9	7.6	2.2-32.6
<i>n</i> -pentacosane (C-25)	36.2	7.9-75.7	59.0	36.3-77.3	11.4	3.4-50.6
<i>n</i> -hexacosane (C-26)	23.8	5.0-52.7	40.4	25.3-55.0	10.3	3.0-32.9
<i>n</i> -heptacosane (C-27)	25.1	4.5-54.5	45.0	26.6-58.2	9.7	3.5-30.2
<i>n</i> -octacosane (C-28)	22.1	3.1-58.3	38.9	24.1-59.1	7.7	2.6-20.5
<i>n</i> -nonacosane (C-29)	23.5	2.7-55.1	56.4	30.9-90.5	19.3	7.4-37.9
<i>n</i> -triacontane (C-30)	8.2	1.4-21.8	15.0	1.1-23.9	9.9	3.5-21.0
<i>n</i> -hentriacontane (C-31)	11.6	1.9-22.9	32.8	15.6-67.8	25.1	11.8-38.9
<i>n</i> -dotriacontane (C-32)	3.0	0.0-7.6	9.3	4.4-14.6	8.8	4.3-17.2
<i>n</i> -tritriacontane (C-33)	3.1	0.0-7.3	11.8	5.4-25.9	19.0	9.9-33.4
<i>n</i> -tetratriacontane (C-34)	ND		ND		8.3	3.7-15.1
<i>n</i> -pentatriacontane (C-35)	ND		ND		6.4	0.0-14.4
<i>n</i> -hexatriacontane (C-36)	ND		ND		1.5	0.0-3.6
Σn-alkanes	370	118-695	844	458-1407	145	63.9-350
Σn-alkanes/OC^b	2.5%	1.9-4.0%	4.5%	3.4-6.6%	1.2%	0.8-2.2%
CPI	1.10	0.96-1.30	1.10	1.05-1.16	1.74	1.34-2.83
C_{max}	22		22		31	
18α(H)-22,29,30-trisnorhopane (Ts) (C27)	1.5	0.4-3.1	2.3	1.5-3.4	0.68	0.41-0.98
17α(H)-22,29,30-trisnorhopane (Tm) (C27)	1.8	0.7-3.9	3.6	2.4-4.9	1.16	0.79-1.96
17α(H),21β(H)-30-norhopane (C29)	5.1	1.9-10.4	9.8	6.0-13.6	4.91	3.52-8.86
17β(H),21α(H)-30-norhopane (C29)	0.8	0.0-1.4	1.9	1.2-3.2	0.79	0.52-1.38
17α(H),21β(H)-hopane (C30)	7.7	2.6-16.5	15.1	9.5-19.7	9.22	6.16-15.0
17β(H),21α(H)-hopane (C30)	1.4	0.4-3.1	2.7	1.6-3.8	1.72	1.01-3.11
17α(H),21β(H)-22S-homohopane (C31)	2.3	0.9-5.0	3.6	1.7-5.6	3.58	2.28-5.79
17α(H),21β(H)-22R-homohopane (C31)	1.7	0.6-3.5	3.0	1.3-4.6	2.75	1.76-4.50
17α(H),21β(H)-22S-bishomohopane (C32)	1.7	0.0-3.4	3.0	1.1-4.7	3.19	2.09-5.55
17α(H),21β(H)-22R-bishomohopane (C32)	1.2	0.0-2.4	2.4	1.0-3.9	2.53	1.73-4.47
Σhopanes	29.2	9.6-64.8	47.5	28.3-64.8	30.5	21.3-49.7
Σhopanes/OC^b	0.17%	0.12-0.33%	0.27%	0.16-0.43%	0.25%	0.17-0.36%
Homohopane index, C31 [S/(S+R)]	0.57	0.53-0.65	0.55	0.52-0.58	0.57	0.53-0.59
C30αβ /C31αβR	4.4	3.3-6.2	5.5	3.9-7.9	3.4	2.5-4.0
Fluorene	3.3	0.3-6.8	5.5	1.9-9.9	2.3	0.0-12.2
Phenanthrene	21.6	2.2-42.9	30.2	14.6-53.9	8.5	4.5-15.5
Anthracene	2.3	0.3-3.9	3.2	2.0-4.2	0.7	0.4-1.2
Fluoranthene	29.5	3.3-60.7	47.4	30.0-73.9	11.0	7.3-16.1
Pyrene	23.3	3.3-42.2	33.8	19.1-52.3	7.7	5.3-11.9
Benzo[a]anthracene	11.8	1.5-31.4	30.6	19.0-41.0	4.1	2.4-7.9
Chrysene	32.2	7.0-59.1	54.6	35.4-68.3	6.4	4.3-12.4
Benzo[b]fluoranthene	29.8	9.2-49.3	65.8	44.1-96.6	28.9	20.2-49.6
Benzo[k]fluoranthene	1.2	0.6-1.8	4.4	1.9-19.1	1.3	0.3-2.2
Benzo[e]pyrene	6.1	2.8-9.0	21.1	13.5-27.5	10.6	6.3-19.0
Benzo[a]pyrene	1.9	0.7-3.0	7.8	5.5-11.9	8.3	3.8-16.5
Perylene	0.3	0.2-0.5	1.1	0.7-1.4	0.7	0.1-2.1
Indeno[1,2,3-cd]pyrene	0.2	0.0-0.7	6.2	2.9-10.7	6.2	1.7-10.6
Dibenz[ah]anthracene	0.2	0.1-0.2	4.1	2.4-5.9	1.9	0.0-4.4
Picene	ND		0.71	0.45-0.99	ND	
Benzo[ghi]perylene	0.4	0.2-1.1	7.6	2.5-14.2	6.8	2.5-11.0
ΣPAH	164	33.6-298	323	219-433	105	65.9-175
ΣPAH/OC^b	1.2%	0.7-2.0%	2.0%	1.6-2.7%	1.0%	0.5-1.9%

^a Not determined due to the lack of standards.^b The percentage contribution is on a carbon mass basis.

Table 4. Factor loadings from principal component analysis of the combined data after Varimax rotation

Components	F1	F2	F3	F4
Estimated source %variance	Coal 36.7%	secondary 18.5%	vehicle 17.2%	Road/Sea salt 8.4%
Sulfate	–	0.953	–	–
Nitrate	0.345	0.876	–	–
Chloride	0.755	–	0.306	–
Na+	0.231	–	0.316	0.846
NH4+	<u>0.414</u>	0.844	–	–
K+	–	<u>0.530</u>	0.616	–
Mg2+	0.269	–	0.233	0.877
Ca2+	–	–	<u>0.518</u>	0.707
EC	–	0.416	<u>0.590</u>	0.351
OC	<u>0.473</u>	0.725	0.338	–
WSOC	0.287	0.896	–	–
Lactate	<u>0.558</u>	–	–	–
Acetate	–	0.673	–	–
Formate	0.699	–	–	<u>0.586</u>
MSA	–	0.832	–	–
Glutarate	–	0.871	–	–
Succinate	0.603	0.648	–	–
Malonate	–	0.829	–	–
Oxalate	–	0.295	–	–
<i>n</i> -C17 alkane	0.764	–	–	<u>0.594</u>
<i>n</i> -C18 alkane	0.750	–	–	<u>0.585</u>
<i>n</i> -C19 alkane	0.793	–	–	<u>0.568</u>
<i>n</i> -C20 alkane	0.896	–	–	<u>0.409</u>
<i>n</i> -C21 alkane	0.965	–	–	–
<i>n</i> -C22 alkane	0.956	0.232	–	–
<i>n</i> -C23 alkane	0.935	0.310	–	–
<i>n</i> -C24 alkane	0.906	0.369	–	–
<i>n</i> -C25 alkane	0.860	<u>0.408</u>	–	–
<i>n</i> -C26 alkane	0.846	0.393	–	–
<i>n</i> -C27 alkane	0.896	0.336	–	–
<i>n</i> -C28 alkane	0.827	<u>0.423</u>	–	–
<i>n</i> -C29 alkane	0.810	–	0.233	0.295
<i>n</i> -C30 alkane	<u>0.484</u>	0.298	0.261	–
<i>n</i> -C31 alkane	0.397	–	<u>0.431</u>	<u>0.493</u>
<i>n</i> -C32 alkane	–	–	<u>0.572</u>	–
<i>n</i> -C33 alkane	–	–	<u>0.488</u>	0.275
18 α (H)–22,29,30-trisnorhopane (Ts) (C27)	0.801	0.381	0.328	–
17 α (H)–22,29,30-trisnorhopane (Tm) (C27)	0.840	–	<u>0.419</u>	–
17 α (H),21 β (H)–30-norhopane (C29)	0.702	0.233	0.636	–
17 β (H),21 α (H)–30-norhopane (C29)	0.768	–	<u>0.519</u>	–
17 α (H),21 β (H)–hopane (C30)	0.593	–	0.741	–
17 β (H),21 α (H)–hopane (C30)	<u>0.555</u>	–	0.781	–
17 α (H),21 β (H)–22S-homohopane (C31)	–	–	0.930	–
17 α (H),21 β (H)–22R-homohopane (C31)	–	–	0.893	–
17 α (H),21 β (H)–22S-bishomohopane (C32)	–	–	0.918	–
17 α (H),21 β (H)–22R-bishomohopane (C32)	–	–	0.877	0.310
Fluorene	<u>0.421</u>	–	–	0.306
Phenanthrene	0.756	<u>0.448</u>	–	0.394
Anthracene	0.834	<u>0.424</u>	–	–
Fluoranthene	0.811	0.342	–	0.326
Pyrene	0.843	<u>0.401</u>	–	0.261
Benzo[<i>a</i>]anthracene	0.907	–	–	–
Chrysene	0.891	0.338	–	–
Benzo[<i>b</i>]fluoranthene	0.789	–	<u>0.534</u>	–
Benzo[<i>k</i>]fluoranthene	0.355	–	–	–
Benzo[<i>e</i>]pyrene	0.710	-0.248	0.613	–
Benzo[<i>a</i>]pyrene	–	-0.392	0.838	–
Perylene	0.397	-0.366	0.658	–
Indeno[123- <i>cd</i>]pyrene	–	<u>-0.551</u>	0.602	0.282
Dibenzo[<i>ah</i>]anthracene	0.609	<u>-0.454</u>	<u>0.492</u>	–
Picene	0.893	-0.247	–	–
Benzo[<i>ghi</i>]perylene	–	<u>-0.509</u>	<u>0.586</u>	<u>0.408</u>

Note: Bold and underlined values represent factor loadings higher than 0.60 and 0.4–0.6, respectively. Factor loadings less than 0.23 are omitted.

Figure 1. Concentrations of major constituents of $\text{PM}_{2.5}$ aerosols

(The sample names on the X-axis are sampling dates in mm/dd followed by D (day) or N (night). Day samples started at 8 am and ended at 8 pm while night samples started at 8 pm and ended at 8 am.)

Figure 2. Correlation plots of WSOC versus sulfate and nitrate.

Figure 3. Carbon thermogram of an aerosol water extract sample. (Thermal analysis conditions: In the helium stage, the temperature was initially 50°C, followed by four temperature steps at 310, 450, 615, and 870°C for a residence time of 60, 60, 60, and 110 s, respectively; the O₂/He stage used six temperature steps at 540, 600, 660, 720, 780, and 840°C, each step for 30 s, and a final temperature step at 890°C for 150 s.)