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A Case Study of Chemical Characteristics of Daytime and Nighttime Ambient Particles in Shanghai, China

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Abstract: Ambient daytime and nighttime PM_{2.5} (particulate matter with aerodynamic diameter less than 2.5 μm) and TSP (the total suspended particulates) samples were collected at two sites (named Pudong and Jinshan) in Shanghai. The concentrations of PM_{2.5} and TSP were lower at Pudong than at Jinshan. Higher PM_{2.5} and TSP concentrations were observed during daytime than nighttime for both sites. Carbonaceous aerosol and secondary sulfate were the most abundant components. Larger enrichment factor (EFs) of Zn, Pb, Cl, and S for Jinshan nighttime were observed than for other sampling periods. PM_{2.5} showed higher relative spatial uniformity (the coefficients of divergence, COD = 0.18) than TSP (COD = 0.23) during the sampling period. The variations of chemical components and the species ratios showed

that the contributions of primary particulate emissions in Jinshan (industrial zone) were more significant than in Pudong (residential zone).

Keywords: PM_{2.5}; TSP (the total suspended particulates); carbonaceous fractions; ions; elements; Shanghai

1. Introduction

Atmospheric PM_{2.5} (particulate matter with aerodynamic diameter less than 2.5 μm) and TSP (the total suspended particulates) have been found to be associated with air pollution and human health [1–5]. Previous studies reported that carbonaceous matter and water soluble ions are the major components of atmospheric particulate matter in many urban areas [6–10]. Attributing to the urbanization of China with rapid industrial development, the identification and quantification of the aerosol components are needed to determine the severity of urban air pollution, and to develop strategies for urban air quality improvement.

Shanghai is an industrial base with China's largest petrochemical complex and other major industries. Rapid economic growth and urbanization have sharply increased fossil fuel consumption, which can contribute to air pollution [2]. Previous studies have revealed that organic matter and sulfate are the most abundant components and which exist distinctly in fine and coarse modes in Shanghai. However, most of these studies were based on filter sampling with low time-resolution [11,12]. The data was scarce in particle size distributions of chemical composition both during the daytime and nighttime for various urban functional zones. In order to understand the aerosol chemistry in depth in Shanghai, a sampling campaign was deployed simultaneously at two urban sites (Pudong and Jinshan).

Here, we presented the data of the mass and chemical components of PM_{2.5} and TSP for daytime and nighttime. The objective of this study is to provide the distributions and relationships of PM_{2.5} and TSP as well as the major components for different urban zones in Shanghai.

2. Experimental Section

2.1. Sample Collection

Shanghai represents a typical urban environment in eastern China (Figure 1). PM_{2.5} were collected on quartz and teflon filters simultaneously by using four mini-Volume samplers, and TSP were collected on quartz filters by two mini-Volume samplers with the flow rate of 5 L·min⁻¹ at Pudong (residential zone) and Jinshan (industrial zone) from 1 to 20 September 2009, respectively. Aerosol sampling was carried out over a period of 20 days, daytime samples were collected from 8:00 to 20:00 (local time) and those for nighttime samples were from 20:00 to 8:00. The meteorological data was also collected during the sampling period. All quartz filters were pre-heated at 900 °C for 3 h and then stored in aluminum foil before sampling. The quartz and teflon filters were stored in a refrigerator after sampling.

Filters were analyzed gravimetrically for PM_{2.5} and TSP mass concentrations on a Sartorius MC5 electronic micro balance with ±1 μg sensitivity (Sartorius, Göttingen, Germany) after 24 h equilibration at temperatures between 20 °C and 23 °C and RH between 35% and 45%. Each filter was weighed at least three times before and after samplings, and the net mass was obtained by subtracting the difference

between the averaged pre- and post-sampling weights. The precision of mass measurement before and after sampling based on replicate weighting is 15 and 20 μg per filter, respectively.

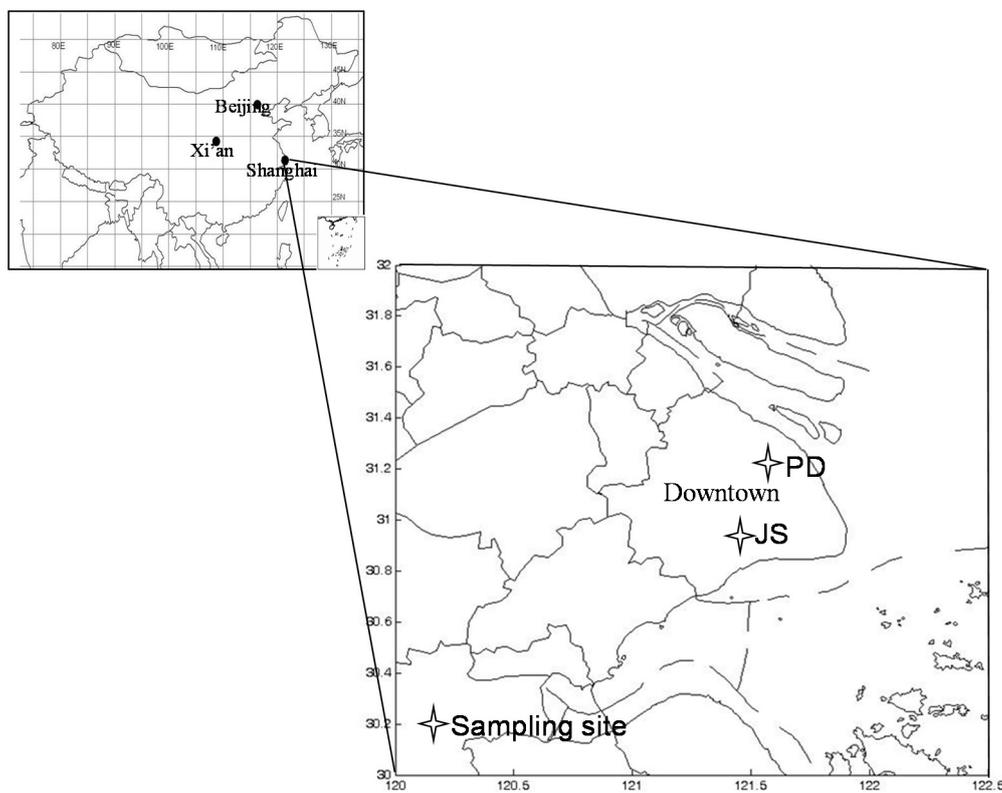


Figure 1. Location of the sampling sites in Shanghai (PD: Pudong, JS: Jinshan).

2.2. Carbonaceous Aerosol Measurement

All the $\text{PM}_{2.5}$ and TSP quartz filters were analyzed for carbon fractions using a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). Using a punch from the quartz filter, three elemental carbon (EC) fractions and four organic carbon (OC) fractions were analyzed following the IMPROVE-A (Interagency Monitoring of Protected Visual Environments) thermal/optical reflectance (TOR) protocol [13]. The method produced data for four OC fractions (OC1, OC2, OC3, and OC4 in a helium atmosphere at 140, 280, 480, and 580 $^{\circ}\text{C}$, respectively), a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 in a 2% oxygen/98% helium atmosphere at 580, 740 $^{\circ}\text{C}$, and 840 $^{\circ}\text{C}$, respectively). The IMPROVE (Interagency Monitoring of Protected Visual Environments) protocol defined OC as $\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OP}$ and EC as $\text{EC1} + \text{EC2} + \text{EC3} - \text{OP}$. The EC fraction was also divided into char and soot. Char is defined as EC1 minus OP, and soot is defined as the sum of EC2 and EC3 [14,15]. The blank filters were also analyzed for quality control and the sample results were corrected by the average of the blank concentrations, which were 0.96 and 0.23 $\mu\text{g}\cdot\text{m}^{-3}$ for OC and EC, respectively. The detailed quality assurance/quality control (QA/QC) procedures are described elsewhere [16].

2.3. Ion Analyses

The concentrations of three anions (Cl^- , NO_3^- and SO_4^{2-}) and five cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) were determined in aqueous extracts of the sample filters by using a Dionex-600 Ion Chromatograph (Dionex Inc., Sunnyvale, CA, USA). Standard solution and blank test were performed before sample analysis and the result of correlation coefficient of standard samples was more than 0.999. One in 10 extracts was reanalyzed and none of the differences between these replicates exceeded precision intervals. All the reported data of water solvable ions were corrected by the filter blanks. Minimum detection limits were as follows: $0.001 \mu\text{g}\cdot\text{mL}^{-1}$ for Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} ; $0.008 \mu\text{g}\cdot\text{mL}^{-1}$ for Cl^- , $0.025 \mu\text{g}\cdot\text{mL}^{-1}$ for NO_3^- ; and $0.027 \mu\text{g}\cdot\text{mL}^{-1}$ for SO_4^{2-} . Standard reference materials produced by the National Research Center for Certified Reference Materials (Beijing, China) were analyzed for quality control and quality assurance purposes. The experimental uncertainties were ± 0.04 for NO_3^- and SO_4^{2-} , ± 0.03 for Ca^{2+} , ± 0.02 for Cl^- , ± 0.01 for NH_4^+ , K^+ and Mg^{2+} , and ± 0.004 for Na^+ .

2.4. Element Analyses

An energy-dispersive X-ray fluorescence (ED-XRF) was used to determine the concentrations of the elements collected on the $\text{PM}_{2.5}$ Teflon fibre filters. The characteristic X-ray radiation is detected by a germanium detector (PAN 32). A spectrum of X-ray counts versus photon energy was acquired during analysis, with the individual peak energies matching to specific elements, and peak areas corresponding to elemental concentrations [17]. In total, 15 interested elements were discussed in the paper. Minimum detection limits were as follows: $0.115 \mu\text{g}\cdot\text{cm}^{-2}$ for Al, $0.007 \mu\text{g}\cdot\text{cm}^{-2}$ for K and Ca, $0.011 \mu\text{g}\cdot\text{cm}^{-2}$ for Fe, $0.093 \mu\text{g}\cdot\text{cm}^{-2}$ for Si, $0.032 \mu\text{g}\cdot\text{cm}^{-2}$ for S, $0.008 \mu\text{g}\cdot\text{cm}^{-2}$ for Zn, $0.003 \mu\text{g}\cdot\text{cm}^{-2}$ for Ni, $0.010 \mu\text{g}\cdot\text{cm}^{-2}$ for Cu, $0.014 \mu\text{g}\cdot\text{cm}^{-2}$ for Mn, $0.015 \mu\text{g}\cdot\text{cm}^{-2}$ for Sr and Pb, $0.003 \mu\text{g}\cdot\text{cm}^{-2}$ for Cl, $0.004 \mu\text{g}\cdot\text{cm}^{-2}$ for As, and $0.005 \mu\text{g}\cdot\text{cm}^{-2}$ for Ti, respectively.

3. Results and Discussion

3.1. Characteristics of $\text{PM}_{2.5}$ and TSP for Daytime and Nighttime

The average $\text{PM}_{2.5}$ and TSP obtained during the sampling periods reached $45.3 \mu\text{g}\cdot\text{m}^{-3}$ and $89.8 \mu\text{g}\cdot\text{m}^{-3}$ for daytime, and those were $32.8 \mu\text{g}\cdot\text{m}^{-3}$ and $67.0 \mu\text{g}\cdot\text{m}^{-3}$ for nighttime at Pudong, respectively. The concentrations of $\text{PM}_{2.5}$ and TSP were $49.3 \mu\text{g}\cdot\text{m}^{-3}$ and $135.3 \mu\text{g}\cdot\text{m}^{-3}$ in daytime, $49.8 \mu\text{g}\cdot\text{m}^{-3}$ and $88.0 \mu\text{g}\cdot\text{m}^{-3}$ in nighttime at Jinshan, respectively. $\text{PM}_{2.5}$ experienced lowest concentrations for Pudong nighttime and highest value for Jinshan nighttime. Higher TSP concentrations were observed in daytime than nighttime for both sites. The variations of TSP showed a slight increase at Jinshan, which may be attributed to the local primary sources. The ratios of $\text{PM}_{2.5}$ to TSP (~ 0.51 and ~ 0.49 for daytime and nighttime at Pudong, ~ 0.36 and ~ 0.57 for daytime and nighttime at Jinshan, respectively) were obtained at both sampling sites. The average $\text{PM}_{2.5}$ concentration is much higher than the USEPA (United States Environmental Protection Agency) National Ambient Air Quality Standards (NAAQS) ($15 \mu\text{g}\cdot\text{m}^{-3}$), indicating very serious potential environmental and health impacts for local residents.

Variations of $\text{PM}_{2.5}$ and TSP mass with wind speed and wind direction were plotted in Figure 2. High wind speeds during daytime (~ 2.0 and $\sim 2.7 \text{ m}\cdot\text{s}^{-1}$ for Pudong and Jinshan, respectively) and low values

during nighttime ($0.98 \text{ m}\cdot\text{s}^{-1}$ and $1.62 \text{ m}\cdot\text{s}^{-1}$ for Pudong and Jinshan, respectively) were observed during the sampling periods, which was shown to be inversely related with the corresponding mass concentrations. A sharp increase of the mass was observed when the wind direction was $>180^\circ$, which was consistent with the previous study [18].

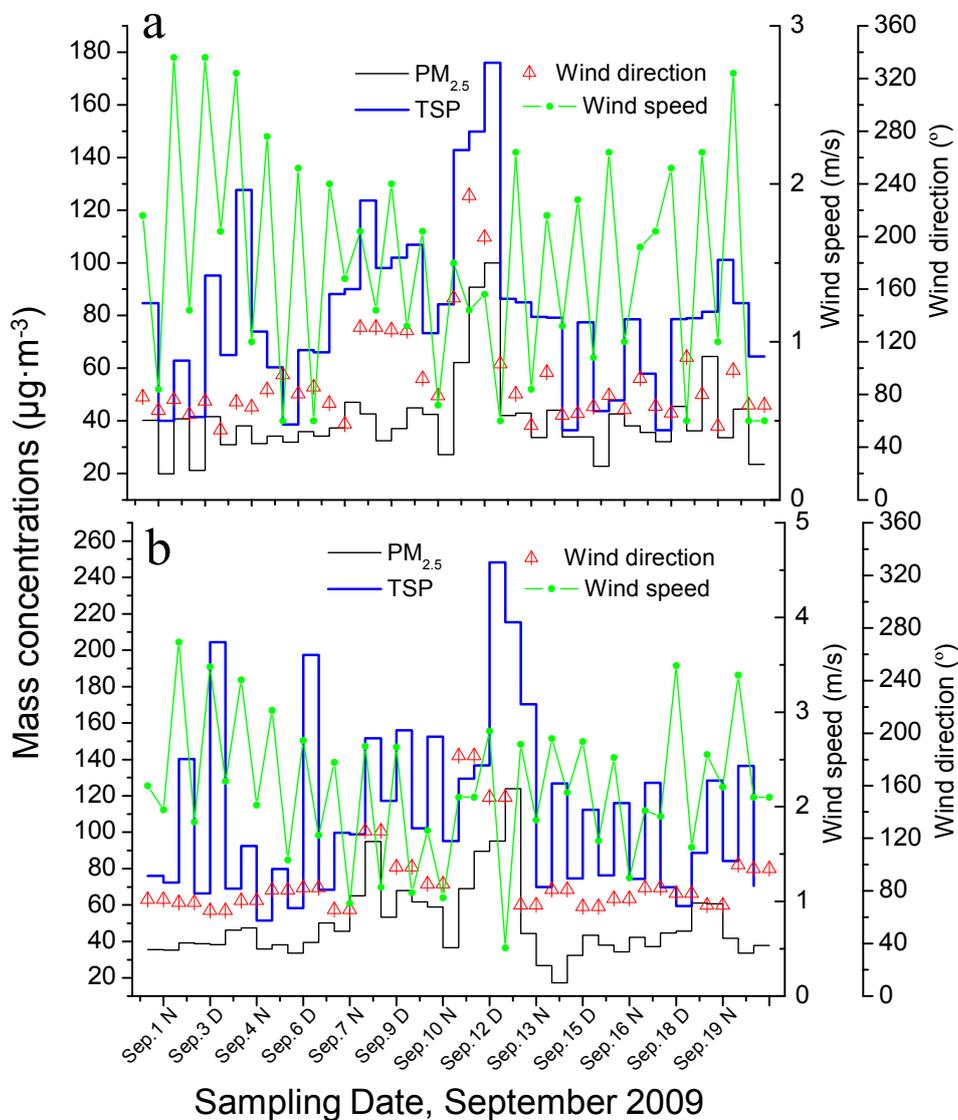


Figure 2. The concentrations of $\text{PM}_{2.5}$ and TSP vs the wind speed and wind direction during daytime and nighttime. (a) Pudong, (b) Jinshan.

The coefficients of divergence (COD) was applied to sites within study areas as a relative measure of particulate concentration uniformity [19]. To further investigate the similarities among the sites in Shanghai, the coefficients of divergence (COD_{pj}) between Pudong and Jinshan were calculated by using the average concentrations of $\text{PM}_{2.5}$ and TSP, respectively. The COD is defined mathematically as:

$$\text{COD}_{pj} = \sqrt{\frac{1}{m} \sum_{i=1}^m [(x_{ip} - x_{ij}) / (x_{ip} + x_{ij})]^2} \tag{1}$$

where x_{ip} and x_{ij} represent the 24 h average particulate concentration for sampling day i at sampling sites Pudong and Jinshan, and m is the number of observations. A COD of zero means there are no differences between concentrations at the sites, while a value approaching one indicates maximum differences and absolute heterogeneity. Values of CODs coefficients lower than 0.2 indicates a relatively homogeneous spatial distribution [20]. In the present study, the values of the CODs calculated for the both sites are 0.18 and 0.23 for PM_{2.5} and TSP, respectively, suggesting that the area investigated is characterized by a relatively homogeneous distribution of PM_{2.5}, but not for TSP during the sampling period.

3.2. Variations of OC and EC

OC and EC are the major components of aerosols that originate from natural and anthropogenic sources. Total carbon (the sum of OC and EC) contribution to urban aerosol mass ranges from 20% to 50% in both fine and coarse fractions in China [21–24]. The average concentrations of PM_{2.5} carbonaceous species were given in Table 1. The average OC and EC concentrations were 8.0 and 1.7 $\mu\text{g}\cdot\text{m}^{-3}$ for Pudong daytime and 5.7 and 1.7 $\mu\text{g}\cdot\text{m}^{-3}$ for Pudong nighttime, respectively. The corresponding concentrations were 14.5 and 2.3 $\mu\text{g}\cdot\text{m}^{-3}$ for Jinshan daytime and 19.1 and 2.9 $\mu\text{g}\cdot\text{m}^{-3}$ for Jinshan nighttime. Lower OC and EC concentrations were observed in Pudong than in Jinshan. Carbonaceous aerosol contribute ~30% of PM_{2.5} and ~23% of TSP at Pudong, respectively. The contributions were ~48% and ~31% for PM_{2.5} and TSP at Jinshan, respectively. The contributions of carbonaceous materials to PM_{2.5} were higher than those for TSP, which was consistent with the previous research [8]. The concentrations of OC and EC for daytime and nighttime at Pudong and Jinshan were comparable to previous results of Shanghai, Beijing and Guangzhou [25–27].

The ratios of OC to EC were 4.8 and 4.5 in daytime, 3.5 and 4.1 in nighttime for PM_{2.5} and TSP at Pudong, respectively. Those for Jinshan were 6.0 and 6.4 in daytime, 5.9 and 7.2 in nighttime for PM_{2.5} and TSP, respectively. Higher OC/EC ratio at Jinshan denoted a significant contribution of primary (from biomass burning and residue incineration) and secondary OC. The little difference for ratios of OC to EC between PM_{2.5} and TSP from Pudong indicated the secondary organic carbon contribution. Significant variations were observed for Jinshan nighttime, which may be attributed to primary emissions.

Table 1. The average concentrations of OC, EC for PM_{2.5} and TSP at Pudong and Jinshan ($\mu\text{g}\cdot\text{m}^{-3}$).

Size	Carbon Fraction	Pudong Daytime			Pudong Nighttime			Jinshan Daytime			Jinshan Nighttime		
		Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.
PM _{2.5}	OC	8.0	14.6	3.9	5.7	10.8	2.8	14.5	32.7	7.7	19.1	45.8	6.7
	EC	1.7	3.8	1.0	1.7	2.8	0.9	2.3	4.8	0.9	2.9	5.1	1.4
TSP	OC	11.6	19.0	6.1	9.6	15.0	4.1	30.6	55.3	14.6	37.1	62	14
	EC	2.7	4.9	1.5	2.5	4.2	1.2	3.9	7.9	1.5	4.4	8.2	2.2

3.3. Variations of Water Soluble Ions

The average concentrations of water soluble inorganic species in PM_{2.5} collected during daytime and nighttime are presented in Table 2. The concentrations of SO₄²⁻ (10.0 $\mu\text{g}\cdot\text{m}^{-3}$ for Pudong daytime, 8.6 $\mu\text{g}\cdot\text{m}^{-3}$ for Pudong nighttime, 10.3 $\mu\text{g}\cdot\text{m}^{-3}$ for Jinshan daytime and 10.2 $\mu\text{g}\cdot\text{m}^{-3}$ for Jinshan nighttime) showed high concentration during daytime, which may be attributed to more secondary species

production. SO_4^{2-} accounted for ~40% and ~36% of the total mass of inorganic ions for Pudong and Jinshan, respectively. The average NO_3^- concentrations were $5.8 \mu\text{g}\cdot\text{m}^{-3}$ for daytime and $4.7 \mu\text{g}\cdot\text{m}^{-3}$ for nighttime at Pudong, and $5.5 \mu\text{g}\cdot\text{m}^{-3}$ for daytime and $6.9 \mu\text{g}\cdot\text{m}^{-3}$ for nighttime at Jinshan, respectively. NO_3^- accounted for ~23% (Pudong daytime), ~21% (Pudong nighttime), ~20% (Jinshan daytime) and ~23% (Jinshan nighttime) of the total mass of the inorganic ions, respectively. Significant increases of NO_3^- and NH_4^+ were observed during nighttime at Jinshan.

Table 2. The concentrations of water soluble ions for $\text{PM}_{2.5}$ at Pudong and Jinshan ($\mu\text{g}\cdot\text{m}^{-3}$).

Ions	Pudong Daytime			Pudong Nighttime			Jinshan Daytime			Jinshan Nighttime		
	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.	Ave.	Max.	Min.
Cl^-	4.36	8.05	3.14	3.85	6.45	2.80	4.22	5.88	3.11	4.87	6.94	3.94
NO_3^-	5.82	15.79	3.49	4.74	7.78	2.57	5.53	11.60	n.a.	6.97	16.24	2.86
SO_4^{2-}	10.03	23.25	2.35	8.56	19.68	1.90	10.30	18.59	3.73	10.18	18.92	3.48
Na^+	0.69	2.35	n.a.	0.75	2.60	n.a.	0.53	1.40	0.15	0.63	0.90	0.22
NH_4^+	0.85	1.91	n.a.	0.79	3.64	n.a.	0.49	1.80	n.a.	1.16	5.72	n.a.
K^+	0.52	1.04	n.a.	0.39	0.79	n.a.	0.38	1.33	n.a.	0.27	0.54	n.a.
Mg^{2+}	1.02	2.70	n.a.	1.33	3.72	n.a.	0.29	1.24	n.a.	0.29	1.04	n.a.
Ca^{2+}	2.40	7.45	n.a.	1.82	7.87	n.a.	6.08	18.14	0.13	5.67	13.92	2.04

n.a.: under the method detection limit.

The concentrations of Ca^{2+} , increased from Pudong samples (2.4 and $1.8 \mu\text{g}\cdot\text{m}^{-3}$ for daytime and nighttime, respectively) to Jinshan samples (6.0 and $5.7 \mu\text{g}\cdot\text{m}^{-3}$ for daytime and nighttime, respectively), which accounted for ~9% and ~20% of the total inorganic ions for Pudong and Jinshan, respectively. The concentrations of Mg^{2+} in $\text{PM}_{2.5}$ were higher for Pudong than for Jinshan. The sea salt contribution to Na^+ should not be neglected at coastal sites. In this study, the concentrations of Na^+ for $\text{PM}_{2.5}$ were $0.7 \mu\text{g}\cdot\text{m}^{-3}$ (Pudong daytime), $0.8 \mu\text{g}\cdot\text{m}^{-3}$ (Pudong nighttime), $0.5 \mu\text{g}\cdot\text{m}^{-3}$ (Jinshan daytime), and $0.6 \mu\text{g}\cdot\text{m}^{-3}$ (Jinshan nighttime), respectively. The concentrations of K^+ were lower than other ions, and showed higher concentrations during daytime than nighttime at both sampling sites. The result is somewhat consistent with the previous study [26].

SO_4^{2-} was the most abundant anion followed by secondary contribution of NO_3^- during daytime and nighttime for Pudong. The concentrations of Ca^{2+} at Jianshan were significantly higher than those of Pudong, which may be attributed to the emission of local construction activities and soil dust at Jinshan. The concentrations of ions (except Na^+ and Mg^{2+}) are higher during daytime than nighttime at Pudong, while those for Jinshan were SO_4^{2-} , K^+ and Ca^{2+} . The result of ionic balance showed an anion deficit in the present study, which may indicate the presence of calcium carbonates combined with the large concentrations of Ca^{2+} [28].

The much distinct contents of ions in $\text{PM}_{2.5}$ and TSP were Ca^{2+} and NO_3^- . It was noteworthy that Ca^{2+} abundances in TSP increased by twice or more than that of $\text{PM}_{2.5}$ (Figure 3), which may be explained as a consequence of the lifting of dust due to municipal engineering. Enhanced Cl^- and Mg^{2+} concentrations in TSP were also found in the present study. Na^+ and Cl^- existed in both TSP and $\text{PM}_{2.5}$, which suggested that sea salt aerosols and anthropogenic emissions were factors to affect the distributions. The variations of NO_3^- and SO_4^{2-} in both sizes seem to indicate that NO_3^- was more abundant in coarse fraction than SO_4^{2-} .

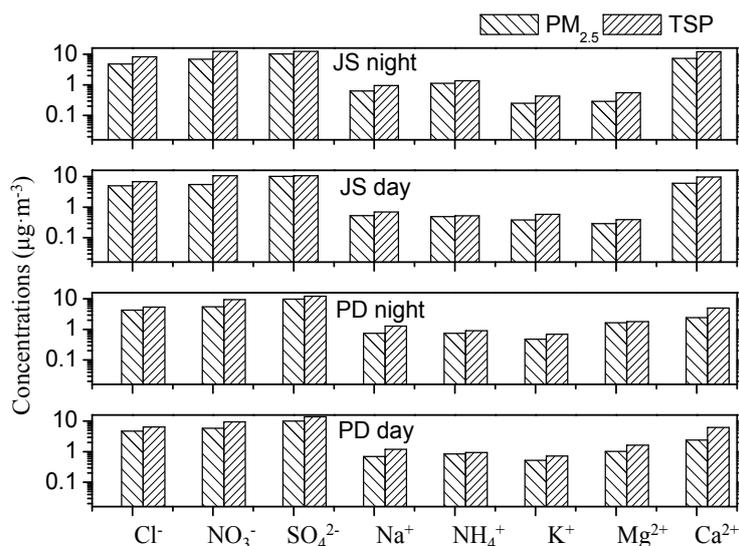


Figure 3. The major ions concentrations in daytime and nighttime for PM_{2.5} and TSP at Jinshan (JS) and Pudong (PD).

3.4. The Variations of Elemental Compositions

Figure 4 showed the element concentrations of PM_{2.5} in daytime and nighttime for Pudong and Jinshan, respectively. The elements are divided into two groups: major (Al, K, Ca, Fe and Si) and sub-major elements (S, Zn, Ni, Cu, Mn, Sr, Pb, Cl, As and Ti). The average concentrations of the major elements for daytime and nighttime at Pudong were 1.6 and 1.1 µg·m⁻³, respectively, and those of sub-major elements were 3.1 and 2.7 µg·m⁻³, respectively. In comparison, the average concentrations of the major elements were 1.8 and 1.5 µg·m⁻³ for daytime and nighttime at Jinshan, respectively, and those of sub-major elements were 3.5 and 3.6 µg·m⁻³, respectively. The ratios of Jinshan to Pudong for major elements were 1.2 for daytime and 1.3 for nighttime, respectively, and those of the sub-major were 1.1 and 1.3, respectively. Higher concentrations of major and sub-major elements at Jinshan were observed than Pudong.

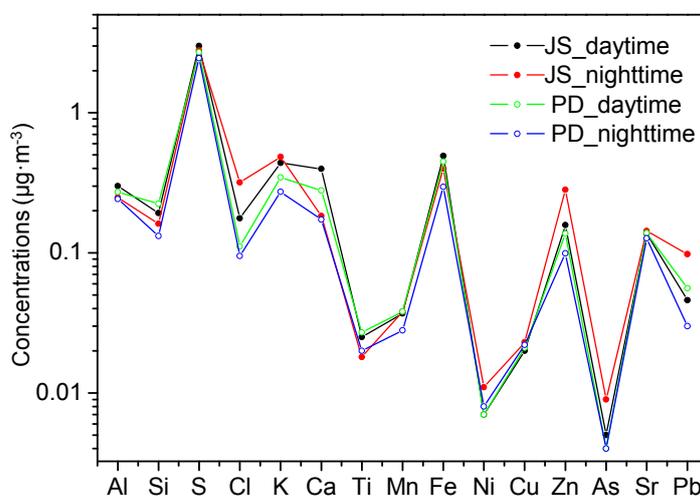


Figure 4. Concentrations of elements in PM_{2.5} during daytime and nighttime at Pudong and Jinshan.

The enrichment factor (EF) method was applied to obtain qualitative information on natural and anthropogenic origins of the elements. High values of the enrichment factor indicated a prevailing anthropogenic origin. The enrichment factor (EF) for the i -th sampling day (with $i = 1, \dots, n$; n = number of observations) and for a generic element X in comparison with a crustal reference element Y is defined as:

$$EF_X^i = \frac{(X^i / Y^i)_{air}}{(X / Y)_{crust}} \quad (2)$$

in which $(X^i / Y^i)_{air}$ is the concentration ratio calculated starting from X^i -concentration and Y^i -concentration measured in the i -th aerosol sample, and $(X / Y)_{crust}$ is the concentration ratio in the crust. In this study, Ti was used as the crustal reference element based on chemical composition of the Earth's crust [29]. The uncertainties of EFs arising from the choice of the reference element were commonly observed in previous study [30]. In the present study, EFs will be much lower or larger if Fe or Al was used as reference element. Si was not chosen as reference element because of its low concentrations due to a lower content in the soil around the sites. EF_X values ≈ 1 indicate that crustal soils are likely the predominant source for element X , while EF_X values >10 suggest that the element X has mainly non-crustal origins.

The EFs of elements were shown in Figure 5. Si, Al, Ca, Fe and K had EFs of <10 , indicating that these elements were mostly from crustal dust. The low EF of Si can be attributed to some complicated factors, such as the low concentration of Si in the soils around the measurement areas. The EFs of Ni, Sr, Cu, Zn, Pb, Cl, and S during daytime and nighttime of Pudong and Jinshan were greater than 10 and even greater than 100, indicating these elements were mainly from the anthropogenic pollution source. The EFs of these elements for Jinshan nighttime were much higher than those for other sampling periods, which further indicated that these elements were partly attributed to local emissions of industries, construction activities and residue combustion.

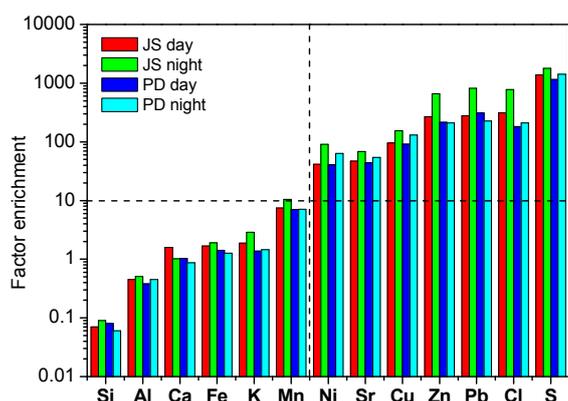


Figure 5. Enrichment factors of elements.

3.5. Indications of the Major Components Ratios

The ratios of special components may give some indications as to the source and chemical reaction of aerosol. NO_3^- and SO_4^{2-} are the major secondary species and mainly from the oxidation of NO_x and SO_2 , respectively. Some studies have used $\text{NO}_3^-/\text{SO}_4^{2-}$ mass ratio to identify the relative importance of aerosol particles from mobile sources vs. stationary sources for sulfur and nitrogen in the atmosphere [31].

The previous study indicated that solar-absorption efficiency was positively correlated with the ratio of $\text{SO}_4^{2-}/\text{EC}$ [32]. Al is quite stable in the atmosphere and its concentration is not influenced by chemical reactions. Therefore, the ratios of NO_3^-/Al and $\text{SO}_4^{2-}/\text{Al}$ can be used to show the degree of concentration variations due to the chemical reactions. Ca^{2+} is usually considered to derive from construction materials and soil dust, and the ratio of Ca^{2+}/Al is a tracer to indicate the emission of construction materials in urban aerosol [9,33]. The species ratios for daytime and nighttime at Pudong and Jinshan were presented in the study.

The chemical species ratios ($\text{SO}_4^{2-}/\text{K}^+$, Cl^-/K^+ , NO_3^-/Al , $\text{SO}_4^{2-}/\text{Al}$, Ca^{2+}/Al , $\text{NO}_3^-/\text{SO}_4^{2-}$, NO_3^-/EC , and $\text{SO}_4^{2-}/\text{EC}$) of $\text{PM}_{2.5}$ and TSP were calculated and compared in Figure 6. $\text{NO}_3^-/\text{SO}_4^{2-}$ for $\text{PM}_{2.5}$ were lower than the corresponding values for TSP in daytime and nighttime, respectively. The average values of $\text{PM}_{2.5}$ $\text{NO}_3^-/\text{SO}_4^{2-}$ were ~ 0.58 and ~ 0.56 for daytime and nighttime at Pudong, respectively. Those were ~ 0.54 and ~ 0.69 for daytime and nighttime at Jinshan, respectively. Comparing with $\text{PM}_{2.5}$, higher values of TSP $\text{NO}_3^-/\text{SO}_4^{2-}$ were observed at both sites, which indicated that NO_3^- is more abundant in coarse fraction than SO_4^{2-} [28].

As shown in Figure 6, the ratios of $\text{PM}_{2.5}$ NO_3^-/Al for both sites were ~ 20 , except Jinshan nighttime with 28. The ratios of $\text{SO}_4^{2-}/\text{Al}$ for both sites were similar, which were among 34–44. The results showed the variations of NO_3^-/Al and $\text{SO}_4^{2-}/\text{Al}$ were similar for daytime and nighttime at Pudong, while the ratios were lower for daytime than for nighttime at Jinshan. $\text{SO}_4^{2-}/\text{K}^+$ and Cl^-/K^+ for daytime and nighttime were comparable at Pudong, respectively, but higher ratios were observed during nighttime than daytime at Jinshan.

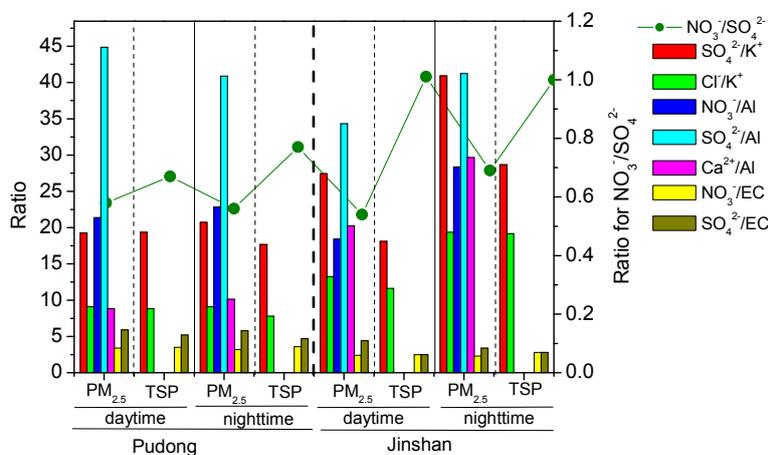


Figure 6. The variations of chemical species ratios in Shanghai.

The ratios of $\text{PM}_{2.5}$ Ca^{2+}/Al at Pudong were 8.8 and 7.6 for daytime and nighttime, respectively. Higher values were observed at Jinshan, which for daytime and nighttime were 20.3 and 22.7, respectively. The results indicated that the abundance of Ca^{2+} may be attributed to the emissions from local construction activities at Jinshan.

Higher ratios of NO_3^-/EC and $\text{SO}_4^{2-}/\text{EC}$ were found at Pudong (with ~ 3.5 and ~ 5.5 , respectively) than those for Jinshan (with ~ 2.5 and ~ 3.2 , respectively) (Figure 5). There was no notable variance for NO_3^-/EC and $\text{SO}_4^{2-}/\text{EC}$ between daytime and nighttime. The ratios of $\text{SO}_4^{2-}/\text{EC}$ in $\text{PM}_{2.5}$ were higher than those in TSP, indicating that the chemical formation processes of sulfate were more dominant in

fine particles. Attributing to primary emissions from construction activities and waste incineration, lower ratios of NO_3^-/EC and $\text{SO}_4^{2-}/\text{EC}$ were observed at Jinshan. The study showed that reducing the secondary production at Pudong and mitigating primary emissions at Jinshan are likely to be effective strategies to improve air quality.

4. Conclusions

The concentrations of $\text{PM}_{2.5}$ were lowest for Pudong nighttime and highest for Jinshan nighttime, respectively. Lower contributions of carbonaceous matter to $\text{PM}_{2.5}$ and TSP were observed at Pudong (~30% and ~23%, respectively) than Jinshan (~48% and ~31% for $\text{PM}_{2.5}$ and TSP, respectively), which indicated high carbonaceous pollution in Shanghai. Higher spatial uniformity ($\text{COD} = 0.18$) for $\text{PM}_{2.5}$ was observed than for TSP ($\text{COD} = 0.23$) during the sampling period. SO_4^{2-} was the most abundant anion followed by NO_3^- . The abundance of Ca^{2+} and elements at Jianshan may be attributed to local sources. Higher EFs of Zn, Pb, Cl, and S for Jinshan nighttime were observed than for other sampling periods. The results suggest that stringent controls on aerosol precursors could be an efficient measure to reduce secondary aerosol production in urban residential zones, and control of primary local emissions could be an efficient strategy in industrial zones.

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Author Contributions

Chongshu Zhu and Junji Cao designed and wrote the paper. Suixin Liu, Ting Zhang, Zhuzi Zhao, and Jiamao Zhou performed the gravimetric and chemical analyses. All authors reviewed and commented on the paper.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Charlson, R.J.; Scharwitz, S.E.; Hales, J.M.; Cess, R.D.; Coakley, J.A., Jr.; Hansen, J.E.; Hofman, D.J. Climate forcing by anthropogenic aerosols. *Science* **1992**, *255*, 423–430.
2. Ye, B.M.; Ji, X.L.; Yang, H.Z.; Yao, X.H.; Chan, C.K.; Cadle, S.H.; Chan, T.; Mulaw, P.A. Concentration and chemical composition of $\text{PM}_{2.5}$ in Shanghai for a 1-year period. *Atmos. Environ.* **2003**, *37*, 499–510.
3. Zhang, M.G.; Han, Z.W.; Zhu, L.Y. Simulation of atmospheric aerosols in East Asia using modeling system RAMS-CMAQ: model evaluation. *China Particuology* **2007**, *5*, 321–327.

4. Zhang, R.J.; Ho, K.F.; Cao, J.J.; Han, Z.W.; Zhang, M.G.; Cheng, Y.; Lee, S.C. Organic carbon and elemental carbon associated with PM₁₀ in Beijing during spring time. *J. Hazard. Mater.* **2009**, *172*, 970–977.
5. Cao, J.J.; Xu, H.M.; Xu, Q.; Chen, B.H.; Kan, H.D. Fine particulate matter constituents and cardiopulmonary mortality in a heavily polluted Chinese city. *Environ. Health Persp.* **2012**, *120*, 373–378.
6. Jacobson, M.C.; Hansson, H.C.; Noone, K.J.; Charlson, R.J. Organic atmospheric aerosols: Review and state of the science. *Rev. Geophys.* **2000**, *38*, 267–294.
7. Cao, J.J.; Lee, S.C.; Ho, K.F.; Zou, S.C.; Fung, K.; Li, Y.; Watson, J.G.; Chow, J.C. Spatial and seasonal variations of atmospheric organic carbon and elemental carbon in Pearl River Delta Region, China. *Atmos. Environ.* **2004**, *38*, 4447–4456.
8. Cao, J.J.; Wu, F.; Chow, J.C.; Lee, S.C.; Li, Y.; Chen, S.W.; An, Z.S.; Fung, K.K.; Watson, J.G.; Zhu, C.S.; Liu, S.X. Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China. *Atmos. Chem. Phys.* **2005**, *5*, 3127–3137.
9. Shen, Z.X.; Cao, J.J.; Arimoto, R.; Zhang, R.J.; Jie, D.M.; Liu, S.X.; Zhu, C.S. Chemical composition and source characterization of spring aerosol over Horqinsandland in northeastern China. *J. Geophys. Res.* **2007**, *112*, D14315, doi:10.1029/2006JD007991.
10. Shen, Z.X.; Cao, J.J.; Tong, Z.; Liu, S.X.; Reddy, L.S.S.; Han, Y.M.; Zhang, T.; Zhou, J. Chemical characteristics of submicron particles in winter in Xi'an. *Aerosol Air Qual. Res.* **2009**, *9*, 80–93.
11. Yang, F.; He, K.; Ye, B.; Chen, X.; Cha, L.; Cadle, S.H.; Chan, T.; Mulawa, P.A. One-year record of organic and elemental carbon in fine particles in downtown Beijing and Shanghai. *Atmos. Chem. Phys.* **2005**, *5*, 1449–1457.
12. Feng, Y.L.; Chen, Y.J.; Guo, H.; Zhi, G.R.; Xiong, S.C.; Li, J.; Sheng, G.Y.; Fu, J.M. Characteristics of organic and elemental carbon in PM_{2.5} samples in Shanghai, China. *Atmos. Res.* **2009**, *92*, 434–442.
13. Chow, J.C.; Yu, J.Z.; Watson, J.G.; Ho, S.S.H.; Bohannan, T.L.; Hays, M.D.; Fung, K.K. The application of thermal methods for determining chemical composition of carbonaceous aerosols: A review. *J. Environ. Sci. Health* **2007**, *42*, 1521–1541.
14. Han, Y.M.; Cao, J.J.; Chow, J.C.; Watson, J.G.; Fung, K.K.; Jin, Z.D.; Liu, S.X.; An, Z.S. Evaluation of the thermal/optical reflectance method for discrimination between soot- and char-EC. *Chemosphere* **2007**, *69*, 569–574.
15. Han, Y.M.; Lee, S.C.; Cao, J.J.; Ho, K.F.; An, Z.S. Spatial distribution and seasonal variation of char-EC and soot-EC in the atmosphere over China. *Atmos. Environ.* **2009**, *43*, 6066–6073.
16. Chow, J.C.; Watson, J.G.; Robles, J.; Wang, X.; Chen, L.W.; Trimble, D.L.; Steven, D.K.; Richard, J.T.; Kochy, K.F. Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon. *Anal. Bioanal. Chem.* **2011**, *401*, 3141–3152.
17. Brouwer, P. *Theory of XRF: Getting Acquainted with the Principles*; PANalytical: Almelo, The Netherlands, 2003; pp. 50–58.
18. Shan, W.P.; Lu, H.X.; Huo, S.Y.; Huang, Z.X.; You, L.N. Analysis of a high PM₁₀ episode observed at a coastal site nearby Shanghai, China. *Environ. Monit. Assess.* **2010**, *163*, 337–345.
19. Contini, D.; Belosi, F.; Gambaro, A.; Cesari, D.; Stortini, A.M.; Bove, M.C. Comparison of PM₁₀ concentrations and metal content in three different sites of the Venice Lagoon: An analysis of possible aerosol sources. *J. Environ. Sci.* **2012**, *24*, 1954–1965.

20. Wilson, J.G.; Kingham, S.; Pearce, J.; Sturman, A.P. A review of intraurban variations in particulate air pollution: Implications for epidemiological research. *Atmos. Environ.* **2005**, *39*, 6444–6462.
21. He, K.; Yang, F.; Ma, Y.; Zhang, Q.; Yao, X.; Chan, C.K.; Cadle, S.; Chan, T.; Mulawa, P. The characteristics of PM_{2.5} in Beijing, China. *Atmos. Environ.* **2001**, *35*, 4959–4970.
22. Cao, J.J.; Lee, S.C.; Chow, J.C.; Watson, J.G.; Ho, K.F.; Zhang, R.J.; Jin, Z.D.; Shen, Z.X.; Chen, G.C.; Kang, Y.M.; *et al.* Spatial and seasonal distributions of carbonaceous aerosols over China. *J. Geophys. Res.* **2007**, *112*, D22S11.
23. Shen, Z.X.; Cao, J.J.; Liu, S.X.; Zhu, C.S.; Wang, X.; Zhang, T.; Xu, H.M.; Hu, T.F. Chemical composition of PM₁₀ and PM_{2.5} collected at ground level and 100 meters during a strong wintertime pollution episode in Xi'an, China. *J. Air Waste Manag. Assoc.* **2011**, *61*, 1150–1159.
24. Tao, J.; Shen, Z.X.; Zhu, C.S.; Yue, J.H.; Cao, J.J.; Liu, S.X.; Zhu, L.H.; Zhang, R.J. Seasonal variations and chemical characteristics of sub-micrometer particles (PM₁) in Guangzhou, China. *Atmos. Res.* **2012**, *118*, 222–231.
25. Cao, J.J.; Lee, S.C.; Ho, K.F.; Zhang, X.Y.; Zou, S.C.; Fung, K.K.; Chow, J.C.; Watson, J.G. Characteristics of carbonaceous aerosol in Pear River Delta Region, China during 2001 winter period. *Atmos. Environ.* **2003**, *37*, 1451–1460.
26. Cao, J.J.; Zhu, C.S.; Tie, X.X.; Geng, F.H.; Xu, H.M.; Ho, S.S.H.; Wang, G.H.; Han, Y.M.; Ho, K.F. Characteristics and sources of carbonaceous aerosols from Shanghai, China. *Atmos. Chem. Phys.* **2013**, *13*, 803–817.
27. Duan, F.K.; He, K.B.; Ma, Y.L.; Yang, F.M.; Yu, X.C.; Cadle, S.H.; Chan, T.; Mulawa, P.A. Concentration and chemical characteristics of PM_{2.5} in Beijing, China: 2001–2002. *Sci. Total Environ.* **2006**, *355*, 264–275.
28. Contini, D.; Cesari, D.; Genga, A.; Siciliano, M.; Ielpo, P.; Guascito, M.R.; Conte, M. Source apportionment of size-segregated atmospheric particles based on the major water-soluble components in Lecce (Italy). *Sci. Total Environ.* **2014**, *472*, 248–261.
29. Taylor, S.R.; McLennan, S.M. *The Continental Crust: Its Composition and Evolution*; Blackwell Scientific Publications: Oxford, UK, 1985.
30. Cesari, D.; Contini, D.; Genga, A.; Siciliano, M.; Elefante, C.; Baglivi, F.; Daniele, L. Analysis of raw soils and their re-suspended PM₁₀ fractions: Characterisation of source profiles and enrichment factors. *Appl. Geochem.* **2012**, *27*, 1238–1246.
31. Arimoto, R.; Duce, R.A.; Savoie, D.L.; Prospero, J.M.; Talbot, R.; Cullen, J.D.; Tomza, U.; Lewis, N.F.; Ray, B.J. Relationships among aerosol constituents from Asia and the North Pacific during PEM-West A. *J. Geophys. Res.* **1996**, *101*, 2011–2023.
32. Ramana, M.V.; Ramanathan, V.; Feng, Y.; Yoon, S.C.; Kim, S.W.; Carmichael, G.R.; Schauer, J.J. Warming influenced by the ratio of black carbon to sulphate and the black-carbon source. *Nat. Geosci.* **2010**, *3*, 542–545.
33. Wang, Y.; Zhuang, G.; Sun, Y.; An, Z. The variation of characteristics and formation mechanisms of aerosols in dust, haze, and clear days in Beijing. *Atmos. Environ.* **2006**, *40*, 6579–6591.