



Chemical Composition of PM_{2.5} Based on Two-Year Measurements at an Urban Site in Beijing

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ABSTRACT

In this study, the daily PM_{2.5} atmospheric aerosols were collected on quartz and PTFE filters simultaneously from January 2008 to December 2009. Organic carbon (OC) and elemental carbon (EC), water-soluble ions including SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺ were analyzed for the samples. The annual average mass concentration of PM_{2.5} for PTFE was 79 μg m⁻³. The OC, SO₄²⁻, NO₃⁻, NH₄⁺ accounted for about 75 % of PM_{2.5}, and secondary organic carbon (SOC) was estimated about 50% of OC. Monthly averages of SO₄²⁻, NO₃⁻, NH₄⁺, K⁺ were maximum in June and minimum in October, but EC, Cl⁻ displayed the highest in December and the lowest in July, which is related to the coal-combustion emission from heating. Three groups with high, medium and low PM_{2.5} concentrations were categorized. SO₄²⁻, NO₃⁻, OC and NH₄⁺ accounted for 24%, 20%, 21% and 11% of sum of defined components in the high concentration days. In the medium and low concentrations, OC occupied large fractions of defined components. Mass closure was obtained for PTFE, but not for quartz. The PM_{2.5} mass concentrations on quartz filters were about 50 μg m⁻³ higher than that on PTFE. The concentrations of water soluble ions on quartz filters were about 60–70% of that on PTFE filters. About 15–30% of PM_{2.5} was considered as the contribution of water vapor, the artifact of water vapor on quartz filter should be noted in later research works. PM_{2.5} displayed neutral during the year of 2008 and appeared acidic at the next year according to the calculation of cations/anion, concentration of hydrogen and acidic purity. Carbonaceous aerosols occupied same fractions in neutral and acidic aerosols. While sulfate and nitrate contributed 32% and 21% to PM_{2.5} for acidic aerosols, and 22%, 17% of PM_{2.5} from sulfate and nitrate for neutral aerosols.

Keywords: PM_{2.5}; OC; Water-soluble ions; Pollution; Acidity.

INTRODUCTION

Atmospheric aerosols are largely responsible for air quality deterioration, visibility reduction (Watson, 2002; Molina and Molina, 2004) and has an adverse effect upon human health ((Pope III *et al.*, 2002). Particulate Matter (PM) with the diameter less than 10 μm (PM₁₀) and 2.5 μm (PM_{2.5}) are widely used to investigate the chemical, physical and optical properties of atmospheric aerosols. Organic matters (Cao *et al.*, 2004) and water-soluble ions are major constituents (Putaud *et al.*, 2004; Yang *et al.*, 2011), which influence the absorption and scattering properties, resulting in hazy days. Moreover, acidic aerosols cause harm to human health and contribute to acid deposition and the ecological system damage (Bouwman *et al.*, 2002). Beijing, as the capital and the center of politics, economics and culture in China, has

experienced effects of serious PM pollution such as haze. Although the government has devoted itself to improving air quality and numerous studies have been conducted, Beijing is still suffering with serious hazy days nowadays, some essential questions remain unknown (Zhang *et al.*, 2013). Therefore, comprehensive investigation of PM_{2.5} and obtain the mass concentration of these main components are the key method to track the emission sources, understand their formation process and supply the references of reducing the pollutions.

A number of studies have dedicated to the characterization of particulate matter in recent years based on filters measurement and analysis in Beijing (He *et al.*, 2001; Dan *et al.*, 2004; Sun *et al.*, 2004; Wang *et al.*, 2005; Duan *et al.*, 2006; Wu and Wang, 2007; Zhang *et al.*, 2007; Pathak *et al.*, 2009; Cao *et al.*, 2012; Wang *et al.*, 2013; Zhao *et al.*, 2013; Hu *et al.*, 2014). These studies reported a lot of valuable results on PM and chemical composition in different years which make us understand aerosols properties better, but most of them focus on the characterization of aerosol at short-term measurements representing one or two seasons. Seldom researches covered more than one-year

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measurements. For limited samples and short monitoring time would make deliberate source identification and trend estimation difficult (Wang *et al.*, 2013), a set of two-year monitoring data would be more representative to evaluate the pollution situation and sources identification.

In this paper, we report the results of a two-year study carried out in Beijing using MiniVol sampling instruments to collect PM_{2.5} on both quartz and PTFE filters during 2008–2009. First of all, the differences of PM_{2.5} mass concentration and water-soluble ions between quartz and PTFE filters are surveyed. The temporal variation of mass concentrations and their chemical components are investigated. Based on the national air quality standards for PM_{2.5} (35 µg m⁻³ for first grade, and 75 µg m⁻³ for second grade), three groups of days with high, medium and low PM_{2.5} concentrations were categorized, the chemical components related with polluted formation, source emissions and mass closures are discussed. Finally, the mass concentrations of hydrogen ions and acidic purity, the aerosol acidities are estimated via the ratio of cations to anions. These results are valuable for describing the general level of PM_{2.5}, understanding the chemical composition in different polluted cases relating to local sources and atmospheric transformation processes. It also supplies a reference for the formulation of effective air quality management strategies.

METHODOLOGY

Measurement Site and Sampling

During this research project, three side-by-side MiniVol™ air samplers (Airmetrics, Oregon USA) were placed at the top of a 9 story building (39°56'N, 116°24'E, 35 m a.s.l.) in the campus of the China Meteorological Administration (CMA) of Beijing, which is believed to represent the typical urban environment in Beijing (Zhang *et al.*, 2011). The atmospheric aerosols were collected on filtration media, operating for 24 h from 09:00 a.m. to 09:00 a.m. (Beijing time) at the following day, with ambient air flow rate of 5 L min⁻¹ between 1 January 2008 and 31 December 2009. The 47mm Whatman quartz microfiber filters (QMA) were baked at 800°C for 3 h to remove the potential OC interferences before use PTFE filters with 2 µm pore size and diameter of 46.2 mm with the supported PP ring (Whatman Inc., Clifton, NJ, USA) were also used. From 1 January 2008 to 30 April 2009 (period 1), aerosols were collected every day except rainy day, and sampled every Tuesdays and Thursdays from 1 May 2009 afterwards (period 2). All of these filters were weighted before and after the ambient sampling to obtain the mass concentration of PM_{2.5}.

Data Analysis

The filters were weighted with an electronic microbalance (Sartorius-ME5, ± 1 µg) after equilibrating the filter under constant temperature (25 ± 1°C) and relative humidity (30 ± 2%) for over 24 h. Quartz samples were used for organic carbon (OC) and elemental carbon (EC) analysis by means of a DRI 2000A carbon analyzer (Desert Research Institute, Reno, NV, USA) following the IMPROVE protocol (Chow *et al.*, 2001). Both quartz and PTFE filters were analyzed

by ion chromatography using ICS 3000 (Dionix Corp., Sunnyvale, CA, USA), water-soluble ions were extracted from one fourth of each filter with 10 mL ultraclean water. All the samples were extracted at an ice-water ultrasonic bath at 0°C for 1.5 hours to avoid the losses of ions. The solution was filtered by a syringe filter and then analyzed the concentration of cations (Ca²⁺, Mg²⁺, K⁺, Na⁺, NH₄⁺) and anion (SO₄²⁻, NO₃⁻, Cl⁻) by ICS 3000 (Zhang *et al.*, 2012b).

In order to estimate the primary OC (POC) and secondary OC (SOC), the minimum OC/EC ratio method was used with the following equation (Turpin and Huntzicker, 1995; Castro *et al.*, 1999): SOC = OC – EC × (OC/EC)_{min} (Cao *et al.*, 2004). In this work, the observed minimum OC/EC ratio 2.13 was used for SOC calculation.

To better understand the acidity or neutralization status of PM, the concentration of hydrogen ion (H⁺) and acid purity (*f*) in each sample were calculated using all measured ions. The concentration of hydrogen ion (H⁺) in each sample is calculated using all measured ions (Schwab *et al.*, 2004; Hu *et al.*, 2014). $[H^+] = 2[SO_4^{2-}] + [NO_3^-] + [Cl^-] - 2[Ca^{2+}] - 2[Mg^{2+}] - [K^+] - [Na^+] - [NH_4^+]$. The brackets represent concentrations in molar units. This equation assumes that the unmeasured ions (except [H⁺]) are negligible compared to the measured ions. The acid purity is assumed as the ratio of [H⁺] to the sum of all cation concentrations according to the formula $f = [H^+]/([H^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + [K^+] + [Na^+] + [NH_4^+])$ (Stevens *et al.*, 1980).

RESULT AND DISCUSSIONS

Comparison of PM_{2.5} on Quartz and PTFE FILTERS

The scatter plot of PM_{2.5} mass concentrations on Quartz filters verse on PTFE filters was shown in Fig. 1. PM_{2.5} mass concentration on Quartz and PTFE filters shows an acceptable correlation with the correlation coefficient ($r^2 = 0.73$), the fitting curve slope of 0.99, and the intercept is 48.8 µg m⁻³, suggesting the mass concentration on the quartz filters is much higher than that on the PTFE filters. The

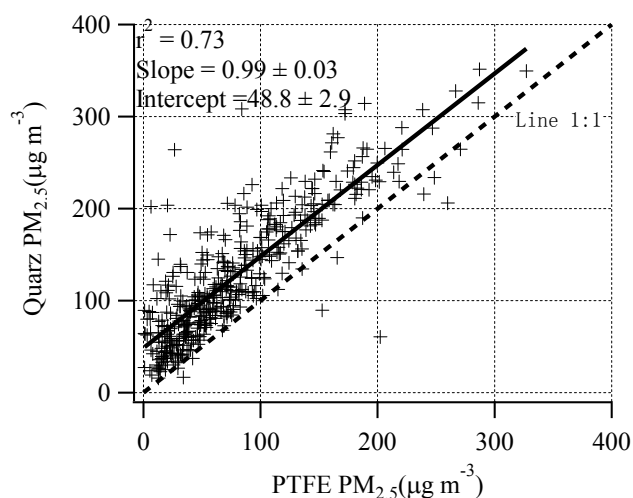


Fig. 1. Scatter plot of mass concentration of PM_{2.5} between quartz and PTFE filters, the uncertainty in the regression slope is at the 68% confidence interval.

hydrophobic nature of PTFE filters prevents water and water molecules remain linked to the dust particle until the end of the sampling (Zdziennicka *et al.*, 2009), but quartz filters are more sensitive of absorbing organics vapor and water vapor would be the main reason. So the data reported by quartz filters may overestimate the concentration of $PM_{2.5}$. On the purpose of surveying the collection efficiencies of different water-soluble ions on quartz filters, regarding the ions concentration of PTFE as reference, the relationships for $PM_{2.5}$ chemical species between the quartz and PTFE filters are plotted in Fig. 2. There are moderate correlations in which the squares of correlation coefficient for SO_4^{2-} , NH_4^+ , NO_3^- , Cl^- and K^+ are 0.76, 0.74, 0.55, 0.69 and 0.78, respectively. However, for Ca^{2+} , Mg^{2+} , the correlations are not good, and there is even no relationship for Na^+ in this campaign. The concentrations of chemical species on quartz filters are general lower than on PTFE filters, which is 0.77, 0.66, 0.76 and 0.56 of that on PTFE filters for sulfate, nitrate, ammonium and chloride respectively. These differences between quartz and PTFE filter samples could be caused different recovery/extraction efficiency, and mass size distributions of aerosol. Moreover,

the sampling flow rate and specification of quartz or PTFE filters may influence the collection efficiency of Quartz or PTFE filters for aerosol. Wake (*et al.*, 1994) suggested that deposition of HNO_3 didn't influence the nitrate concentration for 47mm PTFE filters. Volatilization loss of NH_4NO_3 from the filter has been found during sampling, especially during the warm months and during the warmest periods of the day (Chow *et al.*, 2005), which might also influence the concentration of nitrate and ammonium in quartz filters.

According to the comparison between quartz and PTFE filters, PTFE filters are more optimize to report the concentration of $PM_{2.5}$ and water-soluble ions, and quartz filters are suitable to obtain the concentration of OC and EC. Here, we combined the data of $PM_{2.5}$, water-soluble ions from PTFE and the data of OC, EC from quartz filters to discuss the characterization of $PM_{2.5}$.

Temporal Variation of $PM_{2.5}$ and Their Compositions

The concentration time series of daily $PM_{2.5}$ mass and of soluble species (SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , K^+ , Na^+ , Ca^{2+} and Mg^{2+}) based on PTFE filters, and that of OC, EC, and

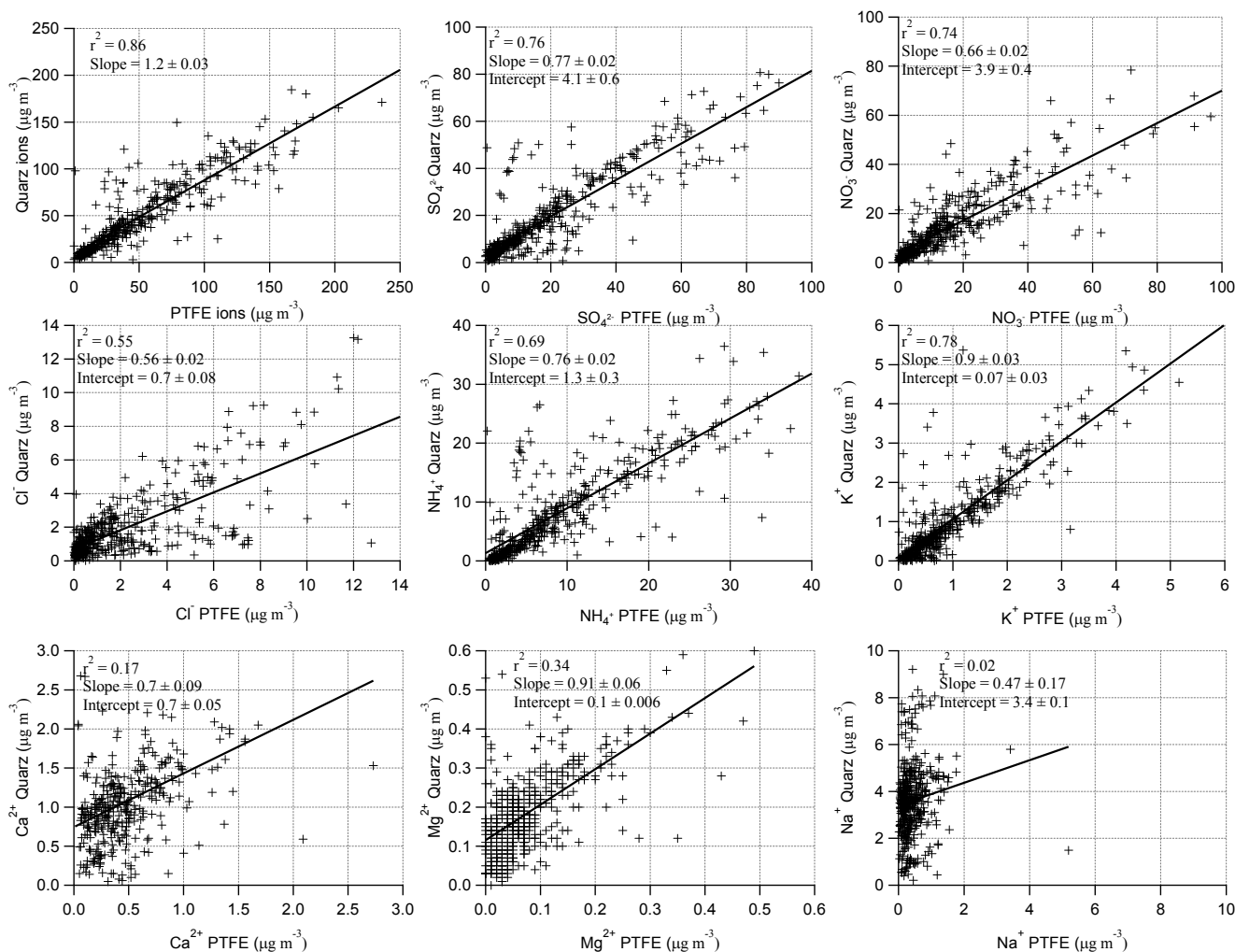


Fig. 2. Comparison of water-soluble ions in quartz and PTFE filters, the uncertainties in the regression slopes are at the 68% confidence interval.

calculated SOC, POC based on quartz filters are plotted in Fig. 3. The average mass concentrations for PM_{2.5} and their chemical composition during period 1 are summarized in Table 1. The average mass concentration of PM_{2.5} was 77.9 $\mu\text{g m}^{-3}$, varied from 0.8 $\mu\text{g m}^{-3}$ to 372 $\mu\text{g m}^{-3}$, which is about twice of the annual PM_{2.5} national air quality standards in China (35 $\mu\text{g m}^{-3}$). The mass loadings of OC, SO₄²⁻, NO₃⁻, and NH₄⁺ also varied from several $\mu\text{g m}^{-3}$ to hundred $\mu\text{g m}^{-3}$ with the average level of 17.3 $\mu\text{g m}^{-3}$, 18.4 $\mu\text{g m}^{-3}$, 14.6 $\mu\text{g m}^{-3}$ and 8.3 $\mu\text{g m}^{-3}$ respectively. Table 2

summarized the published dataset of PM_{2.5} and their chemical compositions from 2001 to 2010 in Beijing. It reveals that the annual PM_{2.5} decrease from 150 $\mu\text{g m}^{-3}$ during 2001–2003 (Wang *et al.*, 2005) to 78 $\mu\text{g m}^{-3}$ during 2008–2009, and then increase to 123 $\mu\text{g m}^{-3}$ in 2009 (Zhao *et al.*, 2013) and 98 $\mu\text{g m}^{-3}$ in 2010–2011 (Wang *et al.*, 2013). Amongst the studies, the concentration of PM_{2.5} for this work is the lowest, which is about half of that during 2001–2003, and about 40% lower than in 2009. As the host city of the 29th Olympic Game in 2008, many measures of

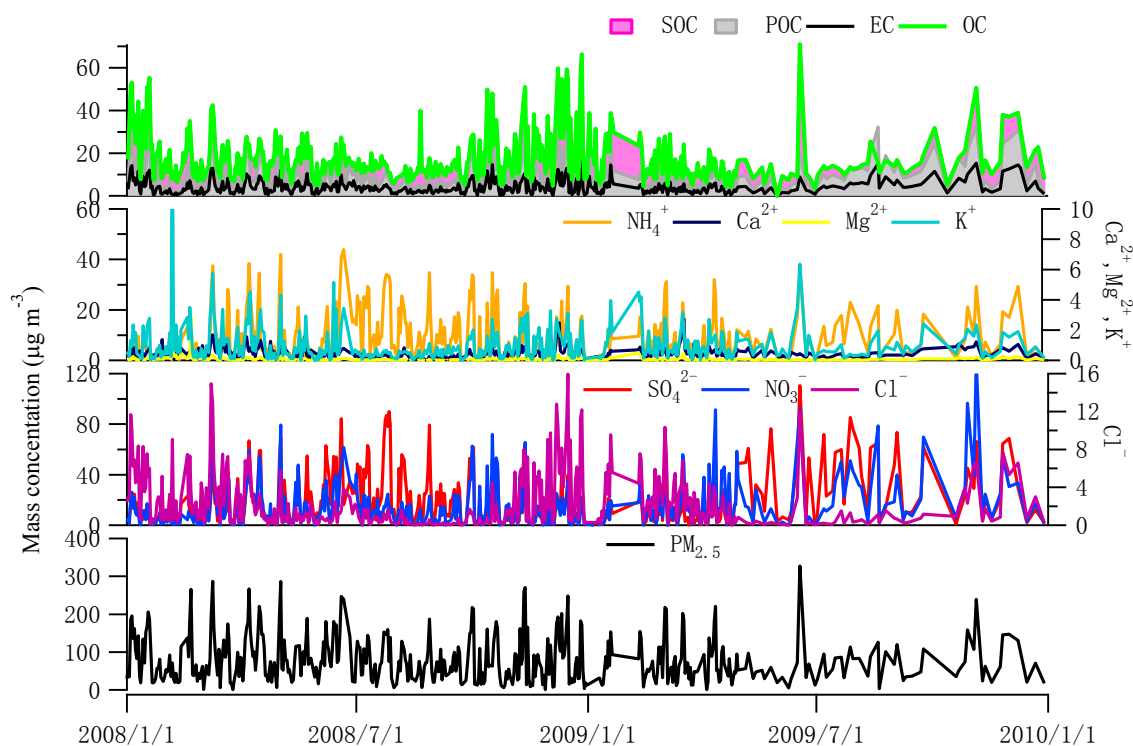


Fig. 3. Time series of mass concentration of PM_{2.5} and their chemical components.

Table 1. Summary of chemical components in PM_{2.5} quartz filter from 1 January 2008 to 30 April 2009 (period 1).

Species	numbers	Mean	SD	Min	Max
mass ($\mu\text{g m}^{-3}$)	433	77.9	46.1	0.8	327.2
OC ($\mu\text{g m}^{-3}$)	444	17.3	10.5	4.2	66.3
EC ($\mu\text{g m}^{-3}$)	444	3.9	2.9	0.2	16.7
POC ($\mu\text{g m}^{-3}$)	444	8.3	6.1	0.4	35.6
SOC ($\mu\text{g m}^{-3}$)	444	9.1	5.5	0.3	36.2
SO ₄ ²⁻ ($\mu\text{g m}^{-3}$)	434	18.1	19.6	n.a.	110.7
NO ₃ ⁻ ($\mu\text{g m}^{-3}$)	433	14.6	17.2	n.a.	129.9
Cl ⁻ ($\mu\text{g m}^{-3}$)	433	2.1	2.7	n.a.	15.9
NH ₄ ⁺ ($\mu\text{g m}^{-3}$)	430	8.3	8.1	n.a.	41.2
Mg ²⁺ ($\mu\text{g m}^{-3}$)	432	0.1	0.2	n.a.	2.8
Ca ²⁺ ($\mu\text{g m}^{-3}$)	399	0.5	0.4	n.a.	2.7
K ⁺ ($\mu\text{g m}^{-3}$)	430	1.0	1.2	n.a.	15.7
Anion ($\mu\text{g m}^{-3}$)	430	32.7	34.6	0.7	214.5
Cation ($\mu\text{g m}^{-3}$)	399	11.2	10.2	0.2	48.9
M _{anion} ($\mu\text{mol m}^{-3}$)	430	0.6	0.7	0.03	4.1
M _{cation} ($\mu\text{mol m}^{-3}$)	399	0.6	0.5	0.01	2.6
H ⁺ ($\mu\text{mol m}^{-3}$)	399	0.1	0.3	-0.8	1.9
<i>f</i>	399	0.1	1.5	-2.9	24.4

Table 2. Summary for studies on PM_{2.5} from this work and other research works.

Location	Period	PM _{2.5} ± SD	PM _{2.5} ions ± SD	OC ± SD	EC ± SD	Sulfate ± SD	Nitrate ± SD	Ammonium ± SD	Reference
Annual									
urban site	2001–2003	154.3 ± 145.7				17.1 ± 16.5	11.5 ± 11.4	8.7 ± 7.7	Wang et al., 2005
CAMS	2008–2009	77.9 ± 46.1	44.7 ± 40.0	17.3 ± 10.5	3.9 ± 2.9	18.1 ± 19.6	14.6 ± 17.2	8.3 ± 8.1	This work
BJ urban	2009	123		18.2 ± 13.8	6.3 ± 2.9	19.1 ± 16.4	20.5 ± 18.1	6.4 ± 3.9	Zhao et al., 2013
Embassy station	2010–2011	98.9							Wang et al., 2013
Spring									
BJ urban	2001–2003	162.1 ± 179.9				13.5 ± 13.9	11.9 ± 11.8	6.5 ± 6.8	Wang et al., 2005
BNU	2003	80.2 ± 80.2	12.6 ± 5.8	7.2 ± 8.5					Dan et al., 2004
CAMS	2008–2009	81.1 ± 60.2	30.1 ± 25.5	15.4 ± 7.3	3.8 ± 2.6	16.4 ± 17.0	16.9 ± 17.4	8.9 ± 8.8	This work
BJ urban	2009	123		15.8	5.2	16.4	20.4	6.77	Zhao et al., 2013
Summer									
BNU	2001	104.1 ± 45.1	17.1 ± 4.1	4.9 ± 5.4					Dan et al., 2004
BNU	2001–2002	106.9				10.6	7.8	5.5	Duan et al., 2006
BJ urban	2002	91.1 ± 30.9	10.7 ± 3.6	5.7 ± 2.9					Dan et al., 2004
BNU	2002	99.4 ± 33.9	11.5 ± 3.8	5.2 ± 2.4					Dan et al., 2004
CGZ	2002	96.6				9.9	6.9	5.8	Duan et al., 2006
BJ urban	2001–2003	93.3 ± 56.3				18.4 ± 15.3	11.2 ± 10.4	10.1 ± 6.9	Wang et al., 2005
BNU	2002–2003	106				23.2	14.6	11.7	Sun et al., 2004
BJ urban	2005	59.2				16.2	5.5		Wu and Wang, 2007
CAMS	2008–2009	81.2 ± 56.9	47.2 ± 42.0	13.2 ± 4.9	3.3 ± 1.7	31.9 ± 25.5	16.4 ± 17.2	12.8 ± 10.6	This work
CAMS	2009	129.7	53.2			26.1	12.7	9.1	Hu et al., 2014
BJ urban	2009	115		10.13	5.9	33.76	22.76	8.43	Zhao et al., 2013
Fall									
BJ urban	2001–2003	105.2 ± 39.0				12.7 ± 12.9	9.1 ± 10.3	6.3 ± 5.8	Wang et al., 2005
BJ urban	2003	123.6	50.4			21.3	13.4	9.6	Cao et al., 2012
CAMS	2008–2009	70.9 ± 58.7	71.2 ± 48.9	18.3 ± 10.4	4.1 ± 2.9	16.3 ± 17.4	17.8 ± 22.2	8.5 ± 8.8	This work
CAMS	2009	114	35.7			20.1	6.1	4.3	Hu et al., 2014
BJ urban	2009	120		20.16	7.06	11.53	21.54	5.01	Zhao et al., 2013
Winter									
BNU	2001	257.6 ± 85.8	41.2 ± 20.8	31.6 ± 31.0					Dan et al., 2004
BNU	2002	151.4 ± 126.8	36.6 ± 26.2	12.9 ± 10.4					Dan et al., 2004
BJ urban	2002	168.8 ± 114.1	36.7 ± 19.4	15.2 ± 11.1					Dan et al., 2004
BJ urban	2001–2003	214.2 ± 159.3				20.9 ± 19.7	12.3 ± 12.1	10.6 ± 8.8	Wang et al., 2005
CAMS	2008–2009	76.8 ± 60.1	46.9 ± 48.3	22.1 ± 14.3	4.3 ± 3.7	9.6 ± 9.8	8.4 ± 8.7	6.1 ± 6.0	This work
BJ urban	2009	125		26.8	7.14	14.23	17.09	5.21	Zhao et al., 2013

BJ urban: sites in urban area of Beijing; BNU: Beijing normal university; CGZ: Chegongzhuang; CAMS: Chinese Academy of meteorological Sciences.

improving air quality were carried out before, during and after the Game in Beijing (Zhang *et al.*, 2009), which resulted in the reduced concentrations of particulate matter in this study. Seasonally, it is surveyed that the highest $PM_{2.5}$ always occurred in winter and lowest in spring and fall for the published works, but no obvious increasing or decreasing trends were found within the ten years. Multiple factors such as different monitoring periods for concerned studies, changes of source emissions, photochemical processes and the variation of meteorological conditions and so on could have effects on the aerosol concentration from year to year.

As for the carbonaceous aerosols, the average OC and EC in $PM_{2.5}$ was $17.3 \mu\text{g m}^{-3}$ and $3.9 \mu\text{g m}^{-3}$ respectively. The OC concentration is same as the previous results in 2009 (Zhao *et al.*, 2013), while the EC is lower than that in 2009 due to the strict traffic constrain measures. In Beijing, the coal combustion and diesel traffic are considered as main contributions to the primary organic aerosol with 35% and 25% (Zhang *et al.*, 2012a). As precursors of SOC, Volatile organic compounds (VOCs) mainly come from industrial (13%), housing waste disposal (12%), combustions of gasoline (14%) and diesel (12%) (Zhang *et al.*, 2012a). The OC concentrations during 2009 (Zhao *et al.*, 2013) display about twice of those in 2004 (Dan *et al.*, 2004). With the increase number of vehicles in Beijing (<http://www.bjstats.gov.cn>), the contribution of vehicles to the OC could not be ignored.

In terms of inorganic species, sulfate, nitrate and ammonium were the major ions, accounting for 90% of ions and 55% of PM (Table 1). The average mass concentrations of sulfate, nitrate and ammonium in $PM_{2.5}$ was $18 \mu\text{g m}^{-3}$, $15 \mu\text{g m}^{-3}$, $8 \mu\text{g m}^{-3}$ respectively (Table 2). They are similar as that reported by Wang *et al.* (2005) and Zhao *et al.*

(2013). In summer, it is higher than other studies, but lower than others in winter. As the main precursor of sulfate, it was reported that 27% and 26% of SO_2 from industrial coal and coke combustion (Zhang *et al.*, 2012a). Beijing stated that during the 11th five-year (2006–2010) plan, both coal and natural gas have been developed for heating in the city, and modification of desulfurization and dedusting for boilers have been accelerated. Small coal-burning boilers have been replaced by electric boilers (Zhang *et al.*, 2012c). These measures would work on reducing the local emission of SO_2 and result in lower sulfate in winter. But in summer, photochemical reaction, meteorological situation and regional transportation would attribute to the high concentration for this study.

Monthly Variations of Chemical Components in $PM_{2.5}$

Monthly cycles of chemical components concentration including OC, EC, POC, SOC and water soluble species of $PM_{2.5}$ are plotted in Fig. 4. The result shows the inorganic species such as sulfate, nitrate, ammonium and potassium appear higher levels in summer and lower levels in winter. However, OC, EC and chloride present higher levels in winter and lower levels in summer. In summer, high temperature and intensive radiation are beneficial for secondary aerosol formation from its precursors by gas-particle transformation, resulting in the high concentrations of these secondary inorganic species. On the other hand, higher concentration of nitrate would relate with the artifact of HNO_3 from the evaporation of nitrate ammonium under the high temperature. Many earlier studies have also observed higher inorganic species concentrations in summer at Xi'an and Beijing (Duan *et al.*, 2006; Cao *et al.*, 2012; Hu *et al.*, 2014).

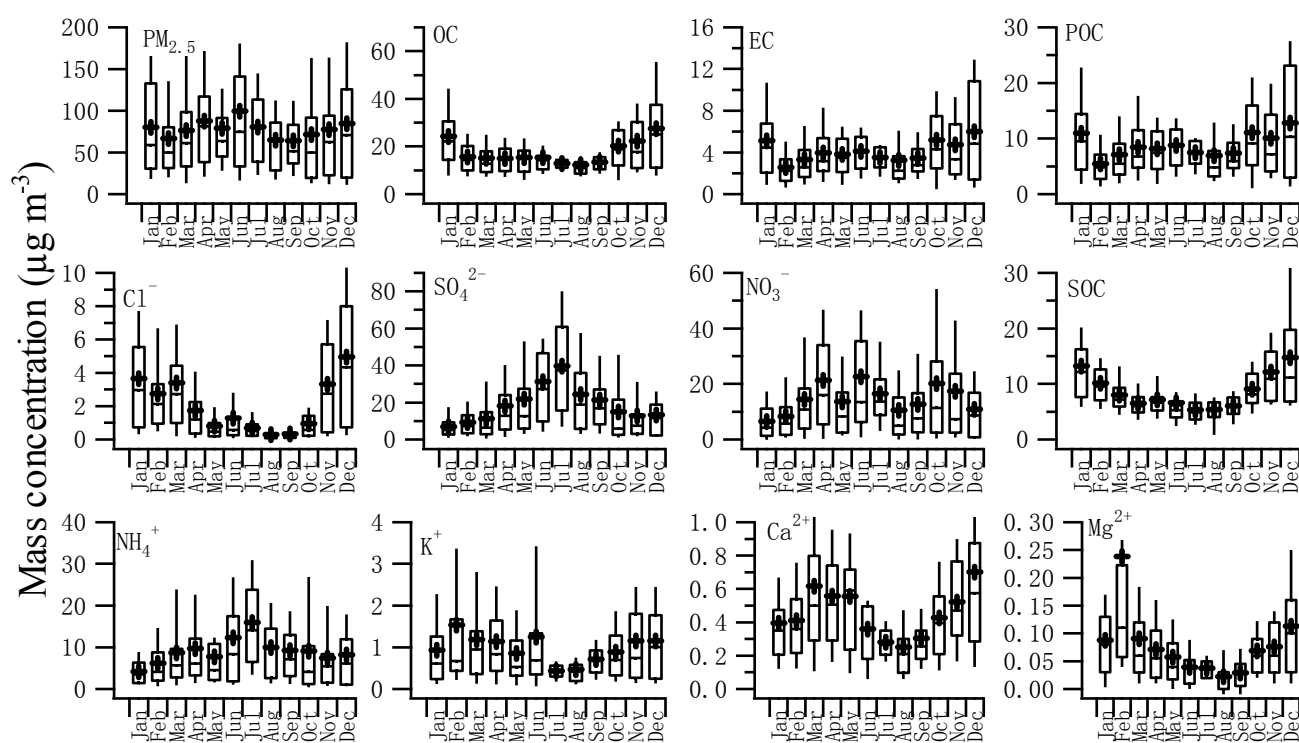


Fig. 4. Monthly variations of $PM_{2.5}$ and their chemical components.

The high loadings of OC, EC and chloride in winter are likely related with vehicles, combustion emissions and the low temperature. Coal combustion for heating in winter contributes more to the primary organic matter than other seasons. In addition, low temperature benefits the condensation of VOCs on the existed particles and enhances the gas-particle transformation process of organic matters. The fact that chloride levels are higher in winter and lower in summer may have been caused by higher emission from combustion in winter (Sun *et al.*, 2013) and higher extent of chloride depletion and evaporation of ammonium chloride during hot seasons. In terms of SOC, higher concentrations were found in winter, which could be explained to some extent by that semi-volatile organics prefer to stay in particle phase due to low temperature.

Potassium is accepted as a marker of biomass burning (Cao *et al.*, 2006). In our study, the potassium concentration showed the higher concentrations in June, which are in good agreement with the wheat harvest season in North China Plain (Qu *et al.*, 2012). A previous study mentioned that the field open burning of wheat straws in the North China Plain during May–June 2006 influenced urban areas such as Beijing (Li *et al.*, 2007).

Characterization of Chemical Components during Different Polluted Cases

In previous section, dramatic variations for mass concentration of PM and their chemical components were observed in our study. The differences on day by day basis are linked with sources emission, pollutant formation process, human activities, meteorological situation etc. To clarify the contributions of chemical components to these different polluted cases, three types of polluted cases were categorized based on the first grade (daily average $< 35 \mu\text{g m}^{-3}$) and second grade (daily average $< 75 \mu\text{g m}^{-3}$) of national air quality standard of $\text{PM}_{2.5}$. High concentrations were selected from days with $\text{PM}_{2.5}$ concentration higher than $75 \mu\text{g m}^{-3}$, and medium concentrations were days with $\text{PM}_{2.5}$ concentration

higher than $35 \mu\text{g m}^{-3}$ and less than $75 \mu\text{g m}^{-3}$. The days that $\text{PM}_{2.5}$ mass concentration less than $35 \mu\text{g m}^{-3}$ were defined as low concentrations. Table 3 summarized the average mass concentration of chemical components in the three types of polluted cases.

It is concluded that, during the study period, 74% of days were influenced by high concentration and 21% were at medium concentration, while only 5% days were at low concentration. The average mass concentrations of $\text{PM}_{2.5}$ in low, medium and high were $17 \mu\text{g m}^{-3}$, $31 \mu\text{g m}^{-3}$ and $95 \mu\text{g m}^{-3}$ respectively.

The contributions of chemical components to $\text{PM}_{2.5}$ under high, medium and low concentration days are plotted in Fig. 5(a). The pie charts demonstrate that the unidentified parts of $\text{PM}_{2.5}$ on PTFE filters under high, medium and low concentrations was 14%, 16% and 21% respectively. In this study, OC, EC and water-soluble ions were analyzed, and to our knowledge, the unidentified parts should include oxygen in metal oxides from mineral aerosols, water vapor and some non-C atoms organic matters (including H, O, N atoms, etc.) excluding organic carbon. It was reported that mineral elements contribute less (0.5%) to $\text{PM}_{2.5}$ (Zhang *et al.*, 2012b). The ratio of organic matter (OM) to organic carbon (OM: OC) could vary from 1.4 to 2.0 in Beijing (Xing *et al.*, 2013). Provided that OM equal to twice of OC, 13%, 19% and 20% of $\text{PM}_{2.5}$ could be defined as non-C atoms organic matters. Based on this calculation, mass closures were obtained for high and low concentrations and 3% was overestimated for medium concentrations may come from the analysis errors.

For quartz filters were also used to report the mass concentration of $\text{PM}_{2.5}$, water-soluble ions, EC and OC by some measurements, in order to evaluate the impact of water vapor on mass closures for quartz filters, the mass closures of $\text{PM}_{2.5}$ using all the data (mass concentration of $\text{PM}_{2.5}$, water-soluble ions and EC OC) from quartz filters under high, medium and low concentrations were also calculated and plotted in Fig. 5(b). The result revealed that

Table 3. Average mass concentrations of chemical components in high, medium and low $\text{PM}_{2.5}$ concentration cases.

	High		Medium		Low	
	numbers	Mean	numbers	Mean	numbers	Mean
mass	369	95.5	104	30.8	24	16.8
OC	369	19.8	104	10.8	24	7.3
EC	369	4.8	104	1.9	24	1.0
POC	368	10.2	104	4.1	24	2.2
SOC	368	9.5	104	6.7	24	5.1
SO_4^{2-}	366	22.7	97	5.5	24	2.3
NO_3^-	366	18.9	97	3.7	24	0.9
Cl^-	365	2.6	99	0.6	24	0.2
NH_4^+	358	11.4	94	2.6	23	0.9
Mg^{2+}	358	0.1	94	0.0	23	0.0
Ca^{2+}	358	0.5	94	0.3	23	0.2
K^+	363	1.2	98	0.4	22	0.2
$M_{\text{anion}} (\mu\text{mol m}^{-3})$	366	1.1	97	0.3	24	0.1
$M_{\text{cation}} (\mu\text{mol m}^{-3})$	358	0.9	94	0.2	23	0.1
$\text{H}^+ (\mu\text{mol m}^{-3})$	358	0.3	94	0.1	23	0.1
f	358	0.2	94	0.4	23	0.7

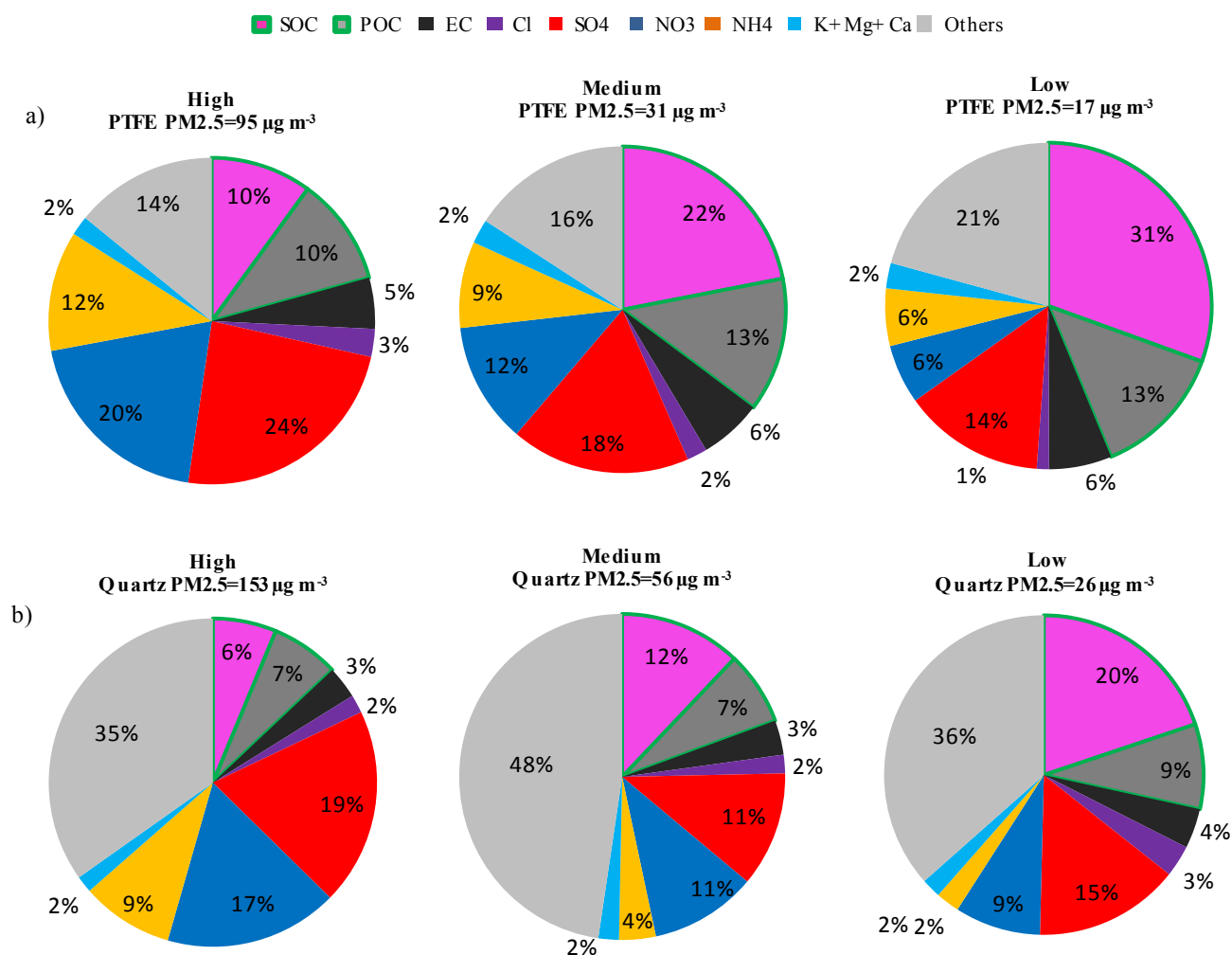


Fig. 5. Percentages of different chemical components in the three polluted cases a) for PTFE filters and b) for quartz filters.

about 35%, 48% and 36% of PM_{2.5} was unidentified under high, medium and low concentration days. The hydrophilic nature of quartz filters and their wettability (Zdziennicka *et al.*, 2009) facilitate the transfer of water molecules from the particles to the filters (Perrino *et al.*, 2013), and the water vapor would contribute to the undefined mass. Comparing the undefined parts of quartz and PTFE filters, it infers that about 21%, 32% and 15% of PM_{2.5} in quartz filters from water vapor during different polluted cases. And this number should be noted for the measurements using quartz filters.

In addition to the undefined parts in the filters, the chemical components displayed different performances in the three types of polluted cases. In the high concentrations, sulfate, nitrate, OC and ammonium ranked as the four highest components in the three types of cases, and the respective mass concentrations of these four chemical components were 23 μg m⁻³, 19 μg m⁻³, 20 μg m⁻³ and 11 μg m⁻³. Ignoring the undefined parts, the total mass concentration of defined components (ΣDC) was 82 μg m⁻³, and sulfate, nitrate, OC and ammonium account for 24%, 20%, 21% and 11% of ΣDC in the high concentration days. In the medium and low concentrations, the percentage of inorganic components to ΣDC decreases, while the OC increases, suggesting their

different roles in the different types of cases. For PM_{2.5}, similar results show that inorganic components play more important roles in polluted cases, while the role of OC increases in clean cases.

Aerosol Acidity, Hydrogen Ion (H⁺) and Acidity Purity (f) in PM_{2.5}

Aerosol acidity influences aerosol hygroscopicity (Khlystov *et al.*, 2005), and secondary aerosol formation. The ratio of total anions to total cations in PM is commonly used to evaluate the aerosol acidity (Kerminen *et al.*, 2001; Zhang *et al.*, 2008). If the cations concentration is significantly (25% or more) lower than the anions concentration, then a particle is considered highly acidic. If the ratio of cation to anion is 0.75, roughly 50% of SO₄²⁻ is considered to be in the form of bisulfate (HSO₄⁻) and another 50% in the form of (NH₄)₂SO₄. Another method evaluating the extent of aerosol neutralization is to use the concentration of hydrogen ions (H⁺) and acidity purity (*f*) (Hu *et al.*, 2014).

The scatter plot between cations (NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺) and anions (SO₄²⁻, NO₃⁻, Cl⁻) for PM_{2.5} is shown in Fig. 6. There are two groups with different ratios of cations to anions, one follows line 1:1 and another tracks line 1:2,

suggesting the samples for group 1 are neutral and that for group 2 are highly acidic. Two pie charts for chemical components of group 1 and group 2 are plotted in Fig. 6. Sulfate and nitrate contribute 31% and 28% to the $PM_{2.5}$ in group 2, but 22% and 17% in group 1. No obvious differences for ammonium and carbonaceous aerosols are observed between two groups. That means the acidic compounds in group 2 play significant roles on the acidity of $PM_{2.5}$.

The daily values of the estimated hydrogen $[H^+]$ and acid purity (f) in $PM_{2.5}$ are shown in Figs. 7(a) and 7(b). During period 2 (1 May 2009–end), the concentration of $[H^+]$ was higher than that period 1 (1 January 2008–30 April 2009), and the average concentration of $[H^+]$ during period 1 and period 2 was $0.2 \pm 0.3 \mu\text{mol m}^{-3}$ and $0.75 \pm 0.5 \mu\text{mol m}^{-3}$ respectively. This $[H^+]$ value in period 1 is comparable to the results from the semi-continuous measurement of Ambient Ion Monitor (AIM) (URG 9000D Series, USA) at the same site in Beijing (Hu *et al.*, 2014), an urban site in Shanghai (Pathak *et al.*, 2009). The $[H^+]$ is nearly 2 times of that at

Mount Tai, and almost ten times of those at some sites in the US (Zhang *et al.*, 2007; Murray *et al.*, 2009), South Korea (Lee *et al.*, 1999) and Japan (Shimohara *et al.*, 2001). Higher $[H^+]$ couple with the lower ratio of cation to anion for period 2 may be related with sampling time, increasing emission and some meteorological situation comparing with more strict controlling measures for period covered Olympic Games in 2008.

On average, the calculated acidity purity (f) for period 1 and period 2 was 0.2 and 0.5 respectively. The different acidity purity suggest that sulfate may exist as a mix of $(NH_4)_2SO_4$ and NH_4HSO_4 in most bulk aerosols during different periods. It was presumed that when $f=0.5$, the bulk aerosol existed as a mixture of chemical species including $(NH_4)_2SO_4$, NH_4HSO_4 and H_2SO_4 , and exhibits the properties of NH_4HSO_4 . In period 1, $PM_{2.5}$ could be considered as letovicites with chemical formula $(NH_4)_3H(SO_4)_2$ (Ziemia *et al.*, 2007), and in period 2, $PM_{2.5}$ would be exist as NH_4HSO_4 and H_2SO_4 for the higher acidic environment.

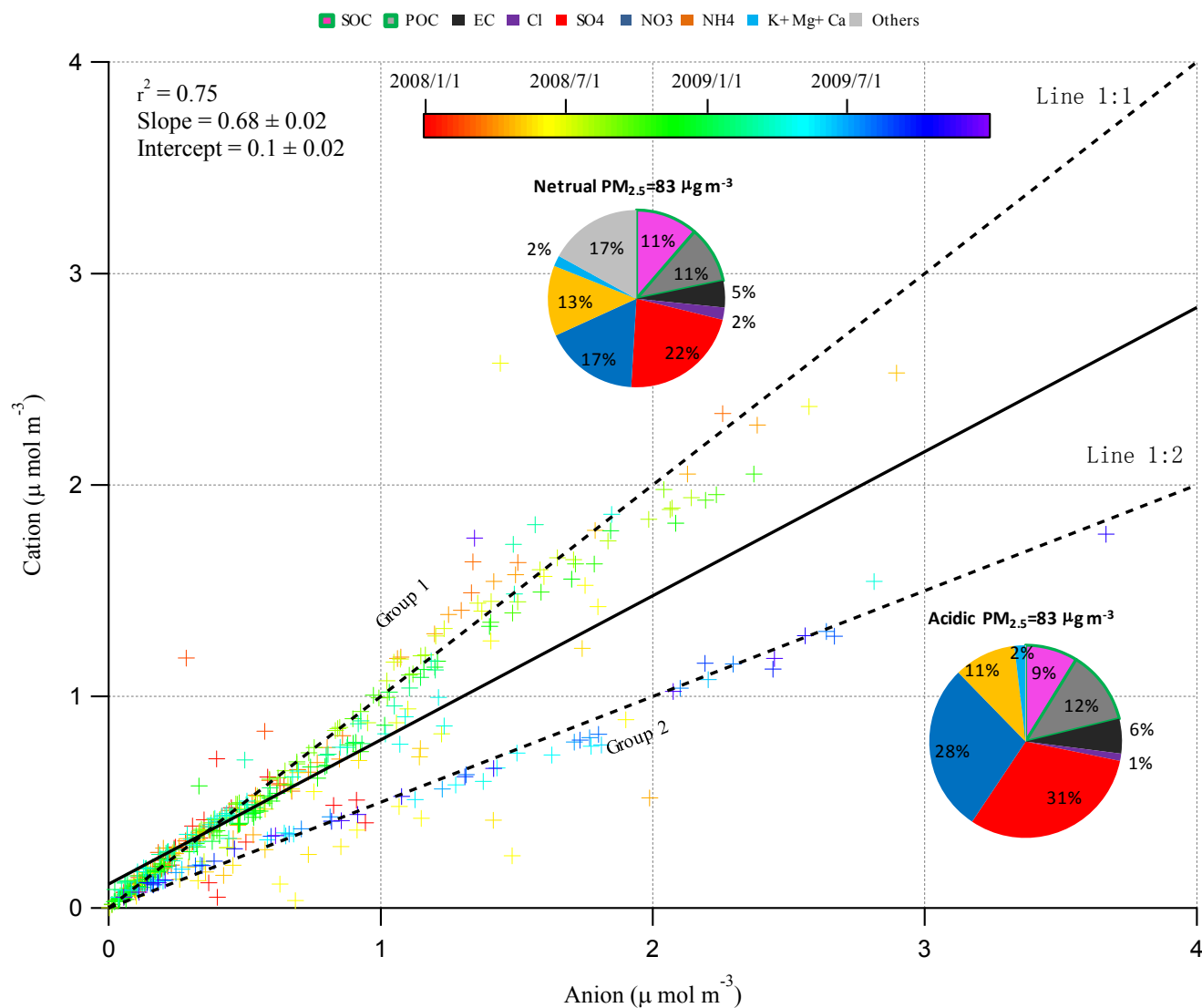


Fig. 6. Scatter plot of cations versus anions and chemical components in two groups, the uncertainty in the regression slope is at the 68% confidence interval.

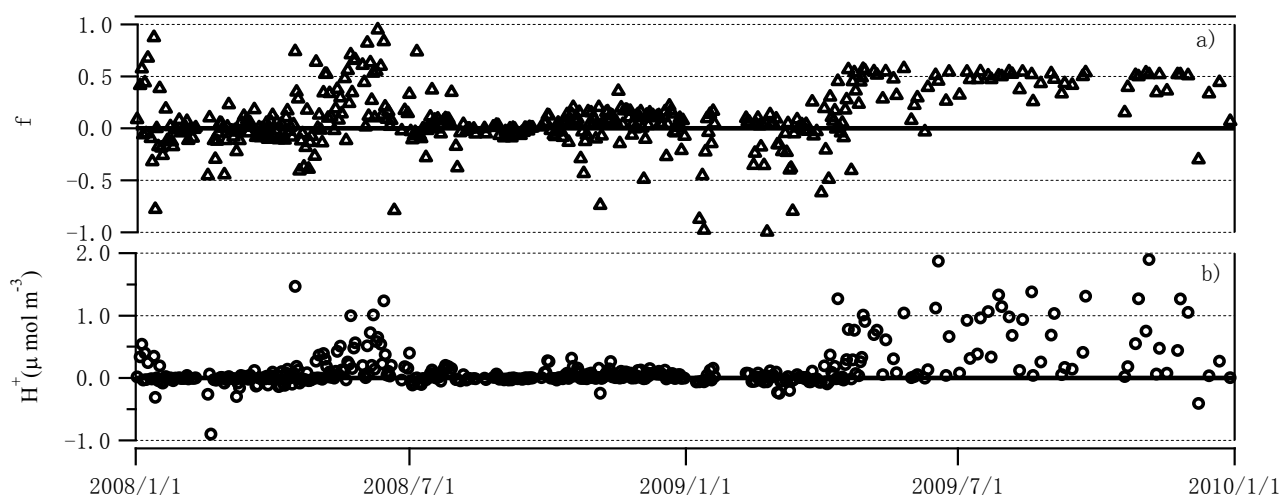


Fig. 7. Time series of H^+ and f in $PM_{2.5}$.

SUMMARY AND CONCLUSION

In this study, $PM_{2.5}$ collected on quartz and PTFE filters were simultaneously by two side-by-side MiniVol sampling instruments during 2008–2009 in Beijing. Reasonable correlations between quartz and PTFE filters were found from the comparison of mass concentration and their chemical compositions for two types of filters. The water vapor and organic vapor in the atmosphere result in higher $PM_{2.5}$ concentration for Quartz filter. The concentrations of different ions on quartz filters were general lower than in PTFE filters, which was 0.77, 0.66, 0.76 and 0.56 of in PTFE filters for sulfate, nitrate, ammonium and chloride respectively.

The mass concentrations of $PM_{2.5}$, their chemical components, monthly variation and their acidities are discussed. It was shown that $PM_{2.5}$ varied dramatically day by day throughout the entire study by about 3 orders. The average $PM_{2.5}$ was $79 \mu\text{g m}^{-3}$ which is about twice of national air quality standard of $PM_{2.5}$. Water-soluble ions and OC were the major components, accounting for 75% of $PM_{2.5}$. About 50% of OC were formed by secondary formation process. Seasonally, it was surveyed that the highest $PM_{2.5}$ always occurred in winter and lowest in spring and fall for the published works, but no obvious increasing or decreasing trends were found within the ten years. The OC concentrations display about twice of those in 2004 and the contribution of vehicles to the OC could not be ignored. Decrease trend of sulfate in winter was observed from the summary of previous works on $PM_{2.5}$ in Beijing, while higher concentration of sulfate, nitrate and carbonaceous aerosol were found in summer.

Significant monthly cycles of chemical components concentration were found. Inorganics species such as sulfate, nitrate, ammonium and potassium appear higher in summer and lower in winter, but OC, EC and chloride were higher in winter and lower in summer.

High, medium and low concentration cases were categorized based on the first grade of national air quality standard of $PM_{2.5}$. It was shown that 74% of days

influenced by high concentration and 21% were at medium concentration, while only 5% of points throughout the entire study were in low concentration. Mass closures for PTFE filters were obtained during different polluted cases, the non-C atom organic matter and water vapor influenced the undefined parts of quartz filters. The ratio of cations to anion was employed to evaluate the acidity of PM. Samples displayed neutral for period 1 and acidic for period 2. The average concentration of $[H^+]$ in period 1 and period 2 was $0.2 \pm 0.3 \mu\text{mol m}^{-3}$ and $0.75 \pm 0.5 \mu\text{mol m}^{-3}$ respectively, and the acidic purity was 0.2 and 0.5. The controlling measures during the Olympic Games in 2008 and the meteorological situation result in the different acidity of $PM_{2.5}$.

ACKNOWLEDGMENTS

This work is supported by the Natural Science Foundation of China (NSFC41275141), and National Basic Research Program of China (grant Nos. 2014CB441303 and 2011CB403401).

REFERENCES

- Bouwman, A.F., Van Vuuren, D.P., Derwent, R.G. and Posch, M. (2002). A Global Analysis of Acidification and Eutrophication of Terrestrial Ecosystems. *Water Air Soil Pollut.* 141: 349–382.
- Cao, G., Zhang, X. and Zheng, F. (2006). Inventory of Black Carbon and Organic Carbon Emissions from China. *Atmos. Environ.* 40: 6516–6527.
- Cao, J.J., Lee, S.C., Ho, K.F., Zou, S.C., Fung, K., Li, Y., Watson, J.G. and Chow, J.C. (2004). Spatial and Seasonal Variations of Atmospheric Organic Carbon and Elemental Carbon in Pearl River Delta Region, China. *Atmos. Environ.* 38: 4447–4456.
- Cao, J.J., Shen, Z.X., Chow, J.C., Watson, J.G., Lee, S.C., Tie, X.X., Ho, K.F., Wang, G.H. and Han, Y.M. (2012). Winter and Summer $PM_{2.5}$ Chemical Compositions in Fourteen Chinese Cities. *J. Air Waste Manage. Assoc.* 62: 1214–1226.

- Castro, L.M., Pio, C.A., Harrison, R.M. and Smith, D.J.T. (1999). Carbonaceous Aerosol in Urban and Rural European Atmospheres: Estimation of Secondary Organic Carbon Concentrations. *Atmos. Environ.* 33: 2771–2781.
- Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H. and Merrifield, T. (2001). Comparison of Improve and Niosh Carbon Measurements. *Aerosol Sci. Technol.* 34: 23–34.
- Chow, J.C., Watson, J.G., Lowenthal, D.H. and Magliano, K.L. (2005). Loss of PM_{2.5} Nitrate from Filter Samples in Central California. *J. Air Waste Manage. Assoc.* 55: 1158–1168.
- Dan, M., Zhuang, G., Li, X., Tao, H. and Zhuang, Y. (2004). The Characteristics of Carbonaceous Species and Their Sources in PM_{2.5} in Beijing. *Atmos. Environ.* 38: 3443–3452.
- Duan, F.K., He, K.B., Ma, Y.L., Yang, F.M., Yu, X.C., Cadle, S.H., Chan, T. and Mulawa, P.A. (2006). Concentration and Chemical Characteristics of PM_{2.5} in Beijing China: 2001–2002. *Sci. Total Environ.* 355: 264–275.
- He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C.K., Cadle, S., Chan, T. and Mulawa, P. (2001). The Characteristics of PM_{2.5} in Beijing, China. *Atmos. Environ.* 35: 4959–4970.
- Hu, G., Zhang, Y., Sun, J., Zhang, L., Shen, X., Lin, W. and Yang, Y. (2014). Variability, Formation and Acidity of Water-Soluble Ions in PM_{2.5} in Beijing Based on the Semi-Continuous Observations. *Atmos. Res.* 145–146: 1–11.
- Kerminen, V.M., Hillamo, R., Teinila, K., Pakkanen, T., Allegrini, I. and Sparapani, R. (2001). Ion Balances of Size-Resolved Tropospheric Aerosol Samples: Implications for the Acidity and Atmospheric Processing of Aerosol. *Atmos. Environ.* 35: 5255–5265.
- Khlystov, A., Stanier, C.O., Takahama, S. and Pandis, S.N. (2005). Water Content of Ambient Aerosol during the Pittsburgh Air Quality Study. *J. Geophys. Res.* 110, doi: 10.1029/2004JD004651.
- Lee, H.S., Kang, C.M., Kang, B.W. and Kim, H.K. (1999). Seasonal Variations of Acidic Air Pollutants in Seoul, South Korea. *Atmos. Environ.* 33: 3143–3152.
- Li, X., Wang, S., Duan, L., Hao, J., Li, C., Chen, Y. and Yang, L. (2007). Particulate and Trace Gas Emissions from Open Burning of Wheat Straw and Corn Stover in China. *Environ. Sci. Technol.* 41: 6052–6058.
- Molina, M.J. and Molina, L.T. (2004). Megacities and Atmospheric Pollution. *J. Air Waste Manage. Assoc.* 54: 644–680.
- Murray, G.L.D., Kimball, K., Bruce Hill, L., Allen, G.A., Wolfson, J.M., Pszenny, A., Seidel, T., Doddridge, B.G. and Boris, A. (2009). A Comparison of Fine Particle and Aerosol Strong Acidity at the Interface Zone (1540 M) and within (452 M) the Planetary Boundary Layer of the Great Gulf and Presidential-Dry River Class I Wildernesses on the Presidential Range, New Hampshire USA. *Atmos. Environ.* 43: 3605–3613.
- Pathak, R.K., Wu, W.S. and Wang, T. (2009). Summertime PM_{2.5} Ionic Species in Four Major Cities of China: Nitrate Formation in an Ammonia-Deficient Atmosphere. *Atmos. Chem. Phys.* 9: 1711–1722.
- Perrino, C., Canepari, S. and Catrambone, M. (2013). Comparing the Performance of Teflon and Quartz Membrane Filters Collecting Atmospheric PM: Influence of Atmospheric Water. *Aerosol Air Qual. Res.* 13: 137–147.
- Pope III, C.A., 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.
- Putaud, J.P., Dingenen, R.V., Dell'Acqua, A., Raes, F., Matta, E., Decesari, S., Facchini, M.C. and Fuzzi, S. (2004). Size-Segregated Aerosol Mass Closure and Chemical Composition in Monte Cimone (I) during Minatroc. *Atmos. Chem. Phys.* 4: 889–902.
- Qu, C., Li, B., Wu, H. and Giesy, J.P. (2012). Controlling Air Pollution from Straw Burning in China Calls for Efficient Recycling. *Environ. Sci. Technol.* 46: 7934–7936.
- Schwab, J.J., Felton, H.D. and Demerjian, K.L. (2004). Aerosol Chemical Composition in New York State from Integrated Filter Samples: Urban Rural and Seasonal Contrasts. *J. Geophys. Res.* 109: doi: 10.1029/2003JD004078.
- Shimohara, T., Oishi, O., Utsunomiya, A., Mukai, H., Hatakeyama, S., Eun-Suk, J., Uno, I. and Murano, K. (2001). Characterization of Atmospheric Air Pollutants at Two Sites in Northern Kyushu, Japan-Chemical Form, and Chemical Reaction. *Atmos. Environ.* 35: 667–681.
- Stevens, R.K., Dzubay, T.G., Shaw, R.W., McClenny, W.A., Lewis, C.W. and Wilson, A.W.E. (1980). Characterization of the Aerosol in the Great Smoky Mountains. *Environ. Sci. Technol.* 14: 1491–1498.
- Sun, Y., Zhuang, G., Wang, Y., Han, L., Guo, J., Dan, M., Zhang, W., Wang, Z. and Hao, Z. (2004). The Air-Borne Particulate Pollution in Beijing: Concentration, Composition, Distribution and Sources. *Atmos. Environ.* 38: 5991–6004.
- Sun, Y.L., Wang, Z.F., Fu, P.Q., Yang, T., Jiang, Q., Dong, H.B., Li, J. and Jia, J.J. (2013). Aerosol Composition, Sources and Processes during Wintertime in Beijing, China. *Atmos. Chem. Phys.* 13: 4577–4592.
- Turpin, B.J. and Huntzicker, J.J. (1995). Identification of Secondary Aerosol Episodes and Quantification of Primary and Secondary Organic Aerosol Concentrations during Scaqs. *Atmos. Environ.* 29: 3527–3544.
- Wake, C.P., Dibb, J.E., Mayewski, P.A., Zhongqin, L. and Zichu, X. (1994). The Chemical Composition of Aerosols over the Eastern Himalayas and Tibetan Plateau during Low Dust Periods. *Atmos. Environ.* 28: 695–704.
- Wang, J.F., Hu, M.G., Xu, C.D., Christakos, G. and Zhao, Y. (2013). Estimation of Citywide Air Pollution in Beijing. *PLoS ONE* 8: e53400.
- Wang, Y., Zhuang, G., Tang, A., Yuan, H., Sun, Y., Chen, S. and Zheng, A. (2005). The Ion Chemistry and the Source of PM_{2.5} Aerosol in Beijing. *Atmos. Environ.* 39: 3771–3784.
- Watson, J.G. (2002). Visibility: Science and Regulation. *J. Air Waste Manage. Assoc.* 52: 628–713.
- Wu, W.S. and Wang, T. (2007). On the Performance of a

- Semi-Continuous PM_{2.5} Sulphate and Nitrate Instrument under High Loadings of Particulate and Sulphur Dioxide. *Atmos. Environ.* 41: 5442–5451.
- Xing, L., Fu, T.M., Cao, J.J., Lee, S.C., Wang, G.H., Ho, K.F., Cheng, M.C., You, C.F. and Wang, T.J. (2013). Seasonal and Spatial Variability of the OM/OC Mass Ratios and High Regional Correlation between Oxalic Acid and Zinc in Chinese Urban Organic Aerosols. *Atmos. Chem. Phys.* 13: 4307–4318.
- Yang, F., Tan, J., Zhao, Q., Du, Z., He, K., Ma, Y., Duan, F. and Chen, G. (2011). Characteristics of PM_{2.5} Speciation in Representative Megacities and across China. *Atmos. Chem. Phys.* 11: 5207–5219.
- Zdziennicka, A., Szymczyk, K. and Janczuk, B. (2009). Correlation between Surface Free Energy of Quartz and Its Wettability by Aqueous Solutions of Nonionic, Anionic and Cationic Surfactants. *J. Colloid Interface Sci.* 340: 243–248.
- Zhang, K., Wang, Y., Wen, T., Meslmani, Y. and Murray, F. (2007). Properties of Nitrate, Sulfate and Ammonium in Typical Polluted Atmospheric Aerosols (PM₁₀) in Beijing. *Atmos. Res.* 84: 67–77.
- Zhang, L., Vet, R., Wiebe, A., Mihele, C., Sukloff, B., Chan, E., Moran, M.D. and Iqbal, S. (2008). Characterization of the Size-Segregated Water-Soluble Inorganic Ions at Eight Canadian Rural Sites. *Atmos. Chem. Phys.* 8: 7133–7151.
- Zhang, R., Jing, J., Tao, J., Hsu, S.C., Wang, G., Cao, J., Lee, C., Zhu, L., Chen, Z. and Zhao, Y. (2013). Chemical Characterization and Source Apportionment of PM_{2.5} in Beijing: Seasonal Perspective. *Atmos. Chem. Phys.* 13: 7053–7074.
- Zhang, X., Zhang, Y. and Cao, G. (2012a). Aerosol Chemical Compositions of Beijing PM₁ and Its Control Countermeasures. *J. Appl. Meteorol. Sci.* 23: 257–264.
- Zhang, X.Y., Wang, Y.Q., Lin, W.L., Zhang, Y.M., Zhang, X.C., Gong, S.L., Zhao, P., Y., Y., Wang, J.Z., Hou, Q., Zhang, X.L., Che, H.Z., Guo, J.P. and Li, Y. (2009). Changes of Atmospheric Compositions and Optical Property over Beijing: 2008 Olympic Monitoring Campaign. *Bull. Am. Meteorol. Soc.* 90: 1633–1651.
- Zhang, X.Y., Wang, Y.Q., Niu, T., Zhang, X.C., Gong, S.L., Zhang, Y.M. and Sun, J.Y. (2012b). Atmospheric Aerosol Compositions in China: Spatial/Temporal Variability, Chemical Signature, Regional Haze Distribution and Comparisons with Global Aerosols. *Atmos. Chem. Phys.* 12: 779–799.
- Zhang, Y.M., Zhang, X.Y., Sun, J.Y., Lin, W.L., Gong, S.L., Shen, X.J. and Yang, S. (2011). Characterization of New Particle and Secondary Aerosol Formation during Summertime in Beijing, China. *Tellus Ser. B* 63: 382–394.
- Zhang, Y.M., Sun, J.Y., Zhang, X.Y., Shen, X.J., Wang, T.T. and Qin, M.K. (2012c). Seasonal Characterization of Components and Size Distributions for Submicron Aerosols in Beijing. *Sci. China Earth Sci.* 55: 1–11.
- Zhao, P.S., Dong, F., He, D., Zhao, X.J., Zhang, X.L., Zhang, W.Z., Yao, Q. and Liu, H.Y. (2013). Characteristics of Concentrations and Chemical Compositions for PM_{2.5} in the Region of Beijing, Tianjin, and Hebei, China. *Atmos. Chem. Phys.* 13: 4631–4644.
- Ziemba, L.D., Fischer, E., Griffin, R.J. and Talbot, R.W. (2007). Aerosol Acidity in Rural New England: Temporal Trends and Source Region Analysis. *J. Geophys. Res.* 112, doi: 10.1029/2006JD007605.

Received for review, November 16, 2014

Revised, February 8, 2015

Accepted, April 27, 2015