Chemical characteristics of water-soluble organic compounds (WSOC) in PM_{2.5} in Beijing, China: 2011–2012

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ARTICLE INFO

Article history:

Received 26 April 2016

Received in revised form 14 July 2016

Accepted 23 August 2016

Available online 25 August 2016

Keywords:

PM_{2.5}

Haze

OC/EC

WSOC

Seasonal variation

Beijing

ABSTRACT

PM_{2.5} filter sampling was conducted on a daily basis for one year from 2011 to 2012 at an urban site in Beijing. One-third of the samples were subjected to chemical analysis, including water-soluble inorganic ions, organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC). The results show that OM (Organic Matter = OC × 1.6; average 50.8% of PM_{2.5}) was the most abundant species, followed by SNA (SO₄²⁻ + NO₃⁻ + NH₄⁺; average 35%); however, SNA contributed more to PM_{2.5} in summer and OM contributed more in other seasons. The concentrations of nitrate were higher in summer and autumn than that in winter, suggesting that nitrate had formed in acidic and ammonium-poor environments in summer. WSOC accounted for 26.6% of OC and 8.1% of PM_{2.5} and exhibited distinct seasonal variations: the lowest concentration occurred in spring (3.90 ± 1.78 μg/m³) and the highest in autumn (5.82 ± 3.73 μg/m³). The higher WSOC/OC ratio in summer suggests that OC was more aged, oxidized and hygroscopic during this season. The seasonal trend of SOC (Secondary Organic Carbon) was the opposite of WSOC/OC, which may indicate that the OC/EC minimum ratio method was not suitable for estimating SOC in this study. Correlations between WSOC and K⁺, EC and inorganic ions indicated that WSOC was dominated by secondary formation, except that biomass burning was an important source in autumn. Aqueous chemical processes may play an important role in the formation of WSOC in winter. Meteorological conditions had an important influence on WSOC: positive correlations were observed between WSOC and relative humidity, but there was a negative correlation when humidity was higher than 80% in summer.

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1. Introduction

Ambient aerosols have received much attention due to their potential influence on air quality, climate change and human health (ICPP, 2001). Water-soluble inorganic ions (WSI) are major components of fine particles and account for about 50% of PM_{2.5} (Cao et al., 2004; Tan et al., 2009a, 2009b). Water-soluble inorganic ions can affect the size, composition, number, acidity and lifetime of aerosols due to their strong hygroscopic property (Wang et al., 2003). Carbonaceous species are another important fraction in the atmosphere (Yu et al., 2004). Based on thermal and optical properties, carbonaceous aerosols can be divided into EC and OC. EC can be emitted directly by incomplete combustion of e.g., biomass and fossil fuel. It is not readily oxidized, and nor does it participate in photochemical reactions; thus it can be regarded as a tracer of primary anthropogenic sources (Cao et al., 2003, 2004; Duan et al., 2007). OC is emitted by fossil fuel combustion or is formed by a

complex process of secondary formation, including of a vast array of individual organic species, such as formaldehyde, acetone and PAHs (Cao et al., 2003; Tang et al., 2006; Yang et al., 2011). Most organic species are harmful to human health.

OC has been divided into a number of sub-groups, such as hydrocarbon organic aerosol (HOA) versus oxygenated organic aerosol (OOA). OOA tends to follow the classification of water-insoluble organic carbon (WIOC) and water-soluble organic carbon (WSOC). WSOC, accounting for 10–80% of particulate organics in the atmosphere, can potentially alter the hygroscopicity, surface tension and density of aerosols, and thereby can have an important effect on the formation of CCN (Decesari et al., 2001; Duarte and Duarte, 2011). Some of the WSOC, such as HULIS, can contribute to the absorption of ultraviolet light and the visible spectral region (Hoffer and Gelencsér, 2006). On the other hand, the wet deposition of WSOC is an important source of OC for surface water and can play an important role in the global carbon cycle (Jurado et al., 2008). Many studies have focused on the structural characterization and physical-chemical properties of WSOC (Decesari et al., 2000; Duarte et al., 2007; Chalbot et al., 2014). Decesari et al. (2000)

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confirmed that WSOC is predominantly composed of aliphatic or oxygenated aliphatic compounds (alcohols, carboxylic acids, etc.), with a minor content of aromatic rings carrying carboxylic and phenolic groups. Dinar et al. (2008) found that WSOC can affect the ability of particles to act as CCN. However, the sources and formation mechanisms of WSOC are not well understood, and data on the seasonal variation of atmospheric WSOC in Beijing are still limited.

China is the most populated and fastest developing country in the world. Over the past several decades, it has suffered from poor air quality caused by fine particles, as a consequence of rapid economic growth and a drastic increase in the number of vehicles. Beijing (39.8°N, 116.5°E) is the political and cultural center of China, with a population of over 19.61 million. Affected by regional and complex air pollution, the city experiences hazy conditions for about one-third of the year. Numerous studies have been conducted of the chemical characteristics and source apportionment of fine particles in Beijing in order to provide a theoretical basis for decision-making related to air quality improvement (Duan et al., 2012, 2014; Du et al., 2014; Hu et al., 2014; Tao et al., 2015, 2016; Tan et al., 2014; Tan et al., 2016; Yang et al., 2015). However, most of the available data cover a limited measurement period and focus mainly on the inorganic component of PM_{2.5}; in addition, knowledge of carbonaceous species, especially WSOC, is still limited. Here we present the results of an investigation of the annual cycle of WSOC, in order to obtain comprehensive information on their properties, sources, and atmospheric processing.

2. Data and methods

2.1. Aerosol sampling

This study is a part of the project entitled “Insight into Physical and Chemical Properties of Aerosol in Beijing” (IPCPA-Beijing), which focused on identifying and understanding all possible physical characteristics and chemical components of PM_{2.5} in Beijing. Collaborators include Tsinghua University, University of Chinese Academy of Sciences and Chinese Research Academy of Environmental Sciences. The sampling site was on the campus of the Chinese Research Academy of Environmental Sciences, located 4 km to the north of the 5th ring road, 15 km from the city center, and 5.8 km from the National Olympic Stadium (the “Bird’s Nest”). It is surrounded by high-density roads, residential buildings, and business offices. There are no obvious industrial and local sources of aerosols in the vicinity. Aerosol samplers were located at the super-observatory site of a four-floor building.

24-h samples of PM_{2.5} were collected daily using a high volume air sampler (Graseby-Andersen, GMW High Volume Air Sampler), operating at a flow rate of 1.13 m³ min⁻¹. A total of 324 samples were obtained from 6 July 2011 to 6 July 2012, and approximately one-third of the filters (every third day) were subjected to full chemical analysis. Whatman quartz fiber filters (QFFs) (20.3 × 25.4 cm) were heated at 450 °C for 4 h to eliminate organic species and used to collect aerosol samples. After sampling, the loaded filters were wrapped in aluminum foil and stored in a refrigerator at -18 °C before analysis in order to prevent evaporation of volatile components.

Meteorological data for Beijing during the sampling period were obtained from <http://www.wunderground.com>. The average temperature, relative humidity, visibility, and wind speed during the sampling period, are listed in Table 1.

2.2. Analyses

2.2.1. Water soluble inorganic ions

An ultrasonic method was used to extract water-soluble inorganic ions from portions of the PM_{2.5} filter samples, and normally over 98% of sulfate, nitrate, and ammonium can be extracted. The filter was submerged in a vial with 10 mL ultrapure water, sealed and subjected to ultrasound for 20 min for each extraction. The extraction was repeated

twice. The extract was filtered with a 0.45 µm Teflon filter and then analyzed by ion chromatography (Dionex ICS 600 and 2100) in order to determine the concentrations of water soluble inorganic ions. The recovery of each ion (Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺) was in the range of 90–110%. The relative standard deviation of each ion was <6% in reproducibility tests. Blank values were subtracted from sample determinations. The details are given elsewhere (Tan et al., 2009a, 2009b).

2.2.2. OC/EC

All samples were analyzed for OC and EC using a DRI Thermal/Optical Carbon Analyzer. The temperature steps of the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal evolution protocol was adopted. A punch aliquot of a sample quartz filter was heated stepwise at temperatures of 120 °C (OC1), 250 °C (OC2), 450 °C (OC3), and 550 °C (OC4) in a non-oxidizing helium (He) atmosphere, and 550 °C (EC1) and 700 °C (EC2) in an oxidizing atmosphere of 2% oxygen in a balance of helium. The carbon that evolves at each temperature is oxidized to carbon dioxide (CO₂) and then reduced to methane (CH₄) for quantification with a flame ionization detector. The analyzer was calibrated daily with CH₄. QFFs blanks, processed concurrently with field blank samples, were used to quantify detection limits. The blank-based limits of detection (LOD), calculated for each species as three times the average field blanks, were below 1.0 µg/m³ for both OC and EC. Replicate analyses were performed at the rate of one per group of 10 samples. The determined repeatability was better than 5% (Cao et al., 2003).

2.2.3. WSOC

Each filter was ultrasonically extracted with 30 mL of ultrapure water for 15 min. The extraction was filtered through a membrane filter (PVDF, German Sciences) of 0.22 µm pore size. The concentrations of WSOC were measured on a TOC Analyzer (Analytic Jena AG multi N/C 3100, Germany) using high temperature (680 °C) Pt-catalyzed oxidation coupled to non-dispersive infrared gas detection of CO₂. Calibration curves for WSOC were created using a potassium hydrogen phthalate standard. All samples for WSOC analysis were acidified to remove inorganic carbon with 2–3 drops of 2 M hydrochloric acid constituted in ultrapure water and analyzed in triplicate. Calibrations were performed for each analytical sequence. The detection limit of WSOC was 0.179 µg/m and an average blank concentration per filter area was 0.948 µg cm⁻³.

3. Results and discussion

3.1. Seasonal variations of chemical composition

The seasonal variations of major chemical species in PM_{2.5} are illustrated in Fig. 1 and listed in Table 2, while the daily variation of chemical species (WSOC, OC, EC, and WS-ions) is illustrated in Fig. 2. An OM/OC ratio of 1.6 was assumed in order to calculate OM from OC (Turpin and Lim, 2001). The concentrations of aerosol mass discussed hereafter were reconstructed from the measured chemical species, including EC, OM and water-soluble inorganic ions species (Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺). Large variations in concentration variations occurred during the four seasons.

Carbonaceous species constitute a major fraction of the fine particles, accounting for 30–50% of the total aerosol mass. The concentrations of OC range from 3.5 to 70.7 µg/m³, with an average of 20.7 ± 14.3 µg/m³, which are significantly higher than the values for 2010 in Beijing (Du et al., 2014). The concentrations of EC range from 0.61 to 13.4 µg/m³, with an average of 4.1 ± 2.6 µg/m³, slightly less than the values in 2010 in Beijing (Du et al., 2014). The average levels of carbonaceous species in Beijing are comparable to recent results from European and Chinese urban cities (Viana et al., 2008; Du et al., 2014; Huang et al., 2012). Fig. 1 and Fig. 2 clearly indicate that organic matter

Table 1
Meteorological conditions during the sampling period.

Sampling period	Date	Temp	RH	Pressure	Visibility	Wind speed	Precipitation
Summer (2011)	6 Jul–29 Oct	26.16	78.05	1005.53	5.17	7.89	
Summer (2012)	3 Jun–6 Jul	25.18	62.27	1002.36	10.6	7.67	
Autumn (2011)	1 Sep–30 Nov	12.85	68.96	1019.96	5.39	11.6	
Winter (2011)	3 Dec–28 Feb	−3.12	44.68	1029.28	5.67	10.7	0.93
Spring (2012)	2 Mar–31 May	14.16	50.2	1012.96	9.96	8	2.45

All of the meteorological data are the average of daily integrated values.

was the most abundant constituent in $PM_{2.5}$, accounting for 50.8% of $PM_{2.5}$; the ratio of OM/ $PM_{2.5}$ was as high as 60.8% in winter. In summer OM became the second largest constituent, while SNA became the dominant species in $PM_{2.5}$, comprising half of the aerosol mass. Winter-time OC ($28.16 \mu\text{g}/\text{m}^3$) was about twice that in summertime OC ($15.04 \mu\text{g}/\text{m}^3$). Autumn OC ($25.42 \mu\text{g}/\text{m}^3$) was slightly lower but close to that in winter. Several factors, such as the gas-particle partitioning of OC under lower temperatures and lower mixing height in winter, could contribute to the high concentrations of OC in winter. EC was a minor component of $PM_{2.5}$, accounting for about 16% of TC during the sampling period. Seasonal fluctuations in EC were <45%, with the highest values in autumn and the lowest in spring. EC exhibits a similar trend and is well correlated with OC, which indicates that they may have a similar primary source.

In general, the total concentration of water soluble inorganic ions contributes nearly 45% of the annual $PM_{2.5}$ mass. SNA accounts for 35% of $PM_{2.5}$ and 78% of water soluble inorganic ions. SNA and OM have a comparable magnitude of contribution to $PM_{2.5}$, SNA contributing more to $PM_{2.5}$ in summer and OM contributing more to $PM_{2.5}$ in other seasons. Sulfate had the highest concentration in summer ($15.6 \mu\text{g}/\text{m}^3$), while lower values (approximately 6.3 – $7.8 \mu\text{g}/\text{m}^3$) and small seasonal variation occurred in the other seasons. It has been suggested that SO_2 can be rapidly oxidized to SO_4^{2-} through heterogeneous or homogeneous reactions in the course of atmospheric processes in summer (Shen et al., 2008). Particulate nitrate is generally formed through the photo-oxidation of NO_2 emitted from the combustion of fossil fuels. According to thermodynamic theory, nitrate is more sensitive to temperature, and higher temperatures do not favor the formation of nitrate. However, the concentrations of nitrate are higher in summer and autumn than those in winter. Previous studies showed that the highest concentrations of NO_3^- had formed in acidic and ammonium-poor aerosol in summer in Beijing (Pathak et al., 2009; Ianniello et al., 2011; Wei et al., 2015). Nitrate was most probably formed via the heterogeneous hydrolysis of N_2O_5 on the surface of the moist and acidic aerosols (Ianniello et al., 2011; Pathak et al., 2009). The conversion of gaseous NH_3 to particulate NH_4^+ depends on the concentration of acids in the atmosphere, temperature, and water availability, as well as the flux rates of NH_3 . The seasonal trend of NH_4^+ is similar to that of NO_3^- , as indicated in Fig. 1, with the lowest value in winter and a relatively

higher concentration in other seasons. However, the ratio of $\text{NO}_3^-/\text{NH}_4^+$ (about 1.3) fluctuated weakly during the sampling periods. This is confirmed by the fact that ammonium nitrate (NH_4NO_3), which is a product of gas-phase reactions between ammonia and nitric acid, is an important speciation of NH_4^+ and NO_3^- in the atmosphere.

The concentration of chloride exhibits the following seasonal variation: winter > autumn > spring > summer. Non-sea-salt (nss) chloride is believed to be associated with coal burning, and greatly elevated nss-Cl levels in winter are consistent with a higher contribution from coal burning, coupled with a lower atmospheric mixing layer. Na^+ was a negligible component of aerosol mass during the entire year, because Beijing is an inland city and sea salt is the major source of Na^+ . K^+ can be derived from sea-salt, silicates, calcareous soils, and biogenic aerosols, as well as from biomass burning, coal combustion, and traffic emissions. However, biomass burning is regarded as the most important source for K^+ and it is usually used as an indicator of biomass burning (Andreae, 1983). The average K^+ was lowest in spring ($0.75 \mu\text{g}/\text{m}^3$), and highest in summer ($1.46 \mu\text{g}/\text{m}^3$) and autumn ($1.39 \mu\text{g}/\text{m}^3$). Mg^{2+} is derived mainly from sea salt and eroded soil particles, which were scarce in our study. Ca^{2+} originates from sea salt, eroded and airborne soil particles, and traffic dust. Ca^{2+} exhibits the highest concentration in spring, which was probably caused by a sandstorm during this season.

3.2. Seasonal variations of WSOC

The seasonal average concentration of WSOC, EC, OC, SOC and their ratio are listed in Table 2, and time series of WSOC are illustrated in Fig. 2. The concentration of WSOC was lowest in spring ($3.90 \mu\text{g}/\text{m}^3$) and highest in autumn ($5.82 \mu\text{g}/\text{m}^3$), ranging from $1.69 \mu\text{g}/\text{m}^3$ to $14.88 \mu\text{g}/\text{m}^3$, with an annual average of $5.07 \pm 2.99 \mu\text{g}/\text{m}^3$. The trend is consistent with the concentrations of OC in $PM_{2.5}$. Atmospheric particulate WSOC in Beijing is much higher than those in other European cities, such as Barcelona, Amsterdam, and the Netherlands (Viana et al., 2007).

It is evident from Fig. 2 that the concentration of WSOC varied significantly in different seasons and that it was always well correlated with $PM_{2.5}$. WSOC was generally low in spring, especially in May, which suggests that there was no dominant source of WSOC, or favorable

Fig. 1. The contributions of major chemical species to $PM_{2.5}$.

Table 2

Concentrations of carbonaceous species and the ratio among these components.

City	Time	N	WSOC	OC	EC	SOC	WSOC/OC	WSOC/SOC	OC/EC	Reference
Beijing	2011 Summer	19	4.48	13.55	3.08	3.51	0.33	1.68	4.44	This study
	2011 Autumn	27	5.82	25.42	5.40	10.80	0.25	0.76	4.62	
	2011 Winter	25	5.53	28.16	4.70	14.7	0.20	0.41	5.88	
	2012 Spring	25	3.90	16.57	2.98	5.76	0.27	0.81	5.93	
	2012 Summer	11	5.81	16.54	3.15	4.58	0.34	1.35	5.19	
Beijing	2010–2011	399	7.2	15.7	5.2		0.46			Du et al., 2014 Huang et al., 2012
Guangzhou	2006–2007 Winter	13	2.39	8.53	4.81		0.28			
	2006–2007 Summer	13	1.60	5.97	3.46		0.27			Feng et al., 2007
Shanghai	2003 Summer	7	2.2	4.9	2.1		0.45			
	2003 Winter	7	6.7	16.5	3.6		0.41			Viana et al., 2007
Amsterdam	2005 Summer	30	1.0	3.9	1.9		0.26			
	2006 Winter	30	1.9	6.7	1.7		0.28			
Barcelona	2004 Summer	30	1.6	3.6	1.5		0.44			
	2004 Winter	30	2.1	6.9	2.6		0.30			

meteorological conditions, to enhance the formation of WSOC. The high concentration of WSOC observed on March 20 and 26 may have been the result of calm weather conditions (average wind speed was <2 m/s), which favors the accumulation of air pollutants. The concentrations of

WSOC were relatively stable in the summer of 2011; however, the situation was quite different in 2012, when a significant decrease occurred from June 3 to June 15, and an abrupt increase on June 18. The wet scavenging effect of the rainfall during early June may have contributed to

Fig. 2. The seasonal variation of WSOC, OC, EC and WS-ions during the study interval.

the low concentration of WSOC. There were strong fluctuations in WSOC in autumn and biomass burning after the straw harvest may have contributed to the extremely high WSOC. Transformation and transportation of air pollutants from other areas are important processes in Beijing (Duan et al., 2014). Relatively high WSOC in winter ($5.53 \mu\text{g}/\text{m}^3$) may be caused by coal and biomass combustion as well by the relatively calm weather conditions (Shen et al., 2014). Heavy haze days, characterized by low visibility ($<4 \text{ km}$), low wind speed and high relative humidity and temperature, were observed on Oct 22, Nov 24, Jan 17 and Jun 18, in combination with significantly high WSOC.

The seasonal pattern of WSOC was similar to that of OC, but the ratio of WSOC/OC exhibited considerable temporal variations with a relatively high value in summer (average, 0.34) and a slightly low value in winter (average, 0.20). This is in agreement with the findings of previous studies (Du et al., 2014; Huang et al., 2012). It is noteworthy that the WSOC/OC ratio is usually used as an indicator of the formation of secondary organic aerosol (SOA). The increase of WSOC/OC is due to the photochemical transformation of primary organic aerosol to WSOC and/or the formation of water soluble secondary organic aerosol via gas-to-particle conversion. In this study, the highest WSOC/OC ratios occurred in summer, consistent with the results of previous studies, and are thought to be caused by strong photochemical processes. In a previous study, WSOC was largely attributed to the atmospheric oxidation of VOCs via reactions with strong oxidants (ozone and peroxide radicals) through the gas-phase conversion (Pio et al., 2007).

WSOC constitutes an important part of SOC. Due to the lack of an analytical technique for directly quantifying primary OC and SOC, the OC/EC minimum ratio method is widely used to calculate SOC. Details of the method can be found elsewhere (Turpin and Huntzicker, 1995). The level of SOC and its seasonal variation are listed in Table 2 and illustrated in Fig. 2. The seasonal variation of WSOC was similar to that of SOC in

winter, spring and autumn. However, only part of the secondary organic aerosol can be attributed to WSOC, especially in summer ($\text{WSOC}/\text{SOC} > 1$). The data in Table 2 demonstrate that the seasonal trend of WSOC/OC ratio is the inverse of that of SOC, with a low WSOC/OC ratio and a high concentration of SOC in winter; and a high WSOC/OC ratio and low concentration SOC in summer. The key step in the EC tracer method is to determine an appropriate OC/EC ratio and to use hourly data of OC/EC minimum ratio. This may suggest that the OC/EC minimum ratio method was unsuitable for estimating SOC, since the ratios of OC/EC can be affected by various factors such as meteorological conditions, seasonal fluctuations in emissions, local sources, and long-range transport (Duan et al., 2004).

3.3. Relationship between WSOC and other components

WSOC is a highly complex mixture composed of secondary organic carbon (SOC) and/or oxygenated primary organic aerosols, such as diacids, polyols, alcohols, aldehydes, and ketones (Feng et al., 2007). Due to its multiple primary and secondary formation pathways, the sources of WSOC are poorly characterized. Linear regression analysis was performed to investigate the relationship between WSOC and OC, EC, and other species; and to evaluate the possible source of WSOC during the four seasons (Fig. 3). Na^+ , Ca^{2+} and Mg^{2+} were not included because of their minor contributions to $\text{PM}_{2.5}$.

There are strong positive correlations between WSOC and OC, in both winter and summer. The annual average correlation coefficient of the two classes of components is 0.88, which may indicate that WSOC and OC have a similar source, even in different seasons. It is noteworthy that the coefficient is especially high in winter ($R^2 = 0.98$) and in summer ($R^2 = 0.97$). This is consistent with previous results indicating that photochemical reactions dominate the formation of WSOC in summer,

Fig. 3. Correlations between the major fractions of $\text{PM}_{2.5}$.

while biomass burning may contribute to a high WSOC concentration in winter; both are important sources of WSOC and OC (Zhang et al., 2012). The correlations between WSOC and EC exhibit large fluctuations in different seasons, being lowest in spring ($R^2 = 0.75$) and highest in winter ($R^2 = 0.91$). This highlights the importance of the primary source of WSOC, especially in winter.

WSOC and sulfate are strongly correlated in winter ($R^2 = 0.93$); however, the correlation is relatively weak in summer ($R^2 = 0.56$). The strong correlation between WSOC and sulfate may indicate that they had a similar source or formation pathway in winter. Peltier et al.

(2007) suggested that coal combustion was unlikely to be an important source of WSOC. In our study, WSOC is weakly correlated with chloride, which is used as a tracer of coal burning, and this may support the hypothesis of Peltier. However, numerous studies have demonstrated that sulfate is mainly derived from the conversion of sulfur dioxide emitted from coal combustion and the major production pathway of sulfate has been suggested to be aqueous phase reactions (Wei et al., 2015). In this case we can speculate that aqueous chemical processes may play an important role in the formation of WSOC in winter. The weak correlation observed in summer is reasonable since atmospheric

Fig. 4. Influence of temperature (a), RH (b) and wind speed (c) on WSOC.

photochemical processes may dominate the formation of WSOC. This hypothesis is further explored by investigating the relationship between WSOC and relative humidity.

The correlation between WSOC and nitrate is similar to that between WSOC and sulfate during the sampling period: highest in winter ($R^2 = 0.85$) and lowest in summer ($R^2 = 0.46$), with an average of 0.64. This is in agreement with the results from other studies (Du et al., 2014). Biomass burning is undoubtedly an important primary emission source of WSOC (Park and Kim, 2014), and potassium is generally considered to be an excellent tracer for biomass burning. In our study, WSOC is well correlated with K^+ ($R^2 = 0.63$), except in spring. The correlation between WSOC and potassium is especially high in summer ($R^2 = 0.89$) and winter ($R^2 = 0.91$). The correlation in autumn ($R^2 = 0.83$) was slightly weaker but similar to that in summer. Numerous studies have demonstrated that frequent biomass burning activity occurs in and around Beijing in winter, while the strong correlation in summer and autumn may be attributed to the burning of wheat residues in farmland after the harvest (Tao et al., 2016; Cheng et al., 2013).

3.4. Influence of meteorological conditions

WSOC can be produced in the atmosphere by photochemical reactions of primary precursors as well as their oxidation products. Thus meteorological parameters, such as wind speed, temperature and relative humidity, which could influence atmospheric chemistry processes and diffusion condition, can affect the level of atmospheric WSOC. In order to evaluate the effects of meteorological conditions on WSOC, correlations between WSOC and ambient temperature (T), relative humidity (RH), and wind speed were determined. The results are illustrated in Fig. 4, while the relationships between WSOC/OC ratio and meteorological parameters are illustrated in Fig. 5.

As illustrated in Fig. 4, the correlation between WSOC and the ambient temperature is weak: concentrations of WSOC were not significantly higher during warm conditions ($>25^\circ\text{C}$) which are generally considered favorable for their formation. However, more days with higher concentrations of WSOC occurred under cold conditions ($<0^\circ\text{C}$), indicating that the concentration of WSOC is strongly dependent upon atmospheric dynamics and local dispersion conditions, and these factors are not necessarily

related to temperature. However, the ratios of WSOC/OC exhibit a strong positive relationship with ambient temperature (Fig. 5a). It is well known that secondary organic aerosols can be produced by photochemical oxidation of volatile organic compounds (VOCs) and gas-to-particle conversion processes (Pathak et al., 2011). The significant positive correlation between WSOC/OC ratio and temperature further suggests that high temperatures in summer may contribute to the increased oxidation and aging of aerosol.

It is obvious that generally higher WSOC values coincide with a higher RH, especially in winter. WSOC and RH are positively correlated when the ambient relative humidity is $<80\%$ and negatively correlated when RH was higher than 80% in summer; this was also observed in Foshan city. A substantial number of studies have highlighted the importance of aerosol liquid water to the formation of SOA (Hodas et al., 2014). This is because aerosol liquid water can influence the partitioning of gas-phase water-soluble organic compounds (WSOCg) to the condensed phase, and provide the reaction medium and surface area affecting the kinetics of precursor uptake if SOA were to form through aqueous chemical processes in aerosol liquid water. The atmospheric aqueous process related to the aerosol water contributes a great deal to the total aerosol loading, since WSOC is formed by water vapor-related partitioning. The strong positive correlation of WSOC and RH is consistent with the hypothesis that WSOC formation is linked with aqueous processes. However, this trend was different in summer, which indicates the importance of photo-oxidation reaction to the formation of SOA. The depletion of oxidant might accelerate and hinder the reaction between VOCs and the oxidant in conditions of high RH ($>80\%$).

A high concentration of aerosol liquid water is observed when sulfate and nitrate were abundant in aerosol and ambient RH was high. In order to examine the influence of RH and ($\text{SO}_4^{2-} + \text{NO}_3^-$) on the concentration of WSOC we investigated the relationship between WSOC/OC and RH (Fig. 5b). The influence of ($\text{SO}_4^{2-} + \text{NO}_3^-$) on WSOC at different temperatures and RH values is illustrated in Fig. 6. As mentioned above, aerosol liquid water is influenced by the combined effects of anthropogenic sulfate, nitrate and ambient humidity (Blando and Turpin, 2000). Fig. 6 demonstrates that hygroscopic sulfate and nitrate aerosol may have a potential influence on WSOC. High levels of WSOC occurred

Fig. 5. Correlations between WSOC/OC and temperature (a), RH (b), and wind speed (c); the relationship between WSOC/EC and RH (d).

Fig. 6. Combined effects of (sulfate and nitrate), RH and T on WSOC.

at times when sulfate and nitrate were abundant in the aerosol for a given RH, especially in spring and summer.

WSOC/EC ratio was used to evaluate the influence of RH on the formation potential of WSOC, where EC was applied as an estimate of the strength of primary sources. The variation of the WSOC/EC ratio is generally consistent with RH, as illustrated in Fig. 5d. A similar trend can be observed in Fig. 5d, namely higher WSOC/EC ratios occurred in more humid conditions.

An exponential decrease of WSOC occurred with increasing wind speed, and an inverse correlation between WSOC/OC and wind speed is also evident in Fig. 5c. Thus it is apparent that most of the pollutants were diluted in strong winds.

4. Conclusions

The major chemical constituents of PM_{2.5} were investigated in an urban area in Beijing from July 2011 to July 2012, with particular emphasis on water soluble organic carbon. Overall, organic substances (average 50.8%) were the most abundant species in PM_{2.5}, followed by SNA. SNA comprised 78% of WSI and 35% of the reconstructed PM_{2.5} annually. The concentration of WSOC was lowest in spring (3.90 μg/m³) and highest in autumn (5.82 μg/m³), ranging from 1.69 μg/m³ to 14.88 μg/m³, with an annual average of 5.07 ± 2.99 μg/m³. WSOC constituted a major fraction of OC and the WSOC/OC ratio (0.12–0.43) is comparable to urban background sites in Europe and other areas in China. Higher WSOC/OC ratios in summer suggest that OC was more aged, oxidized and hygroscopic during this season. The seasonal trend of secondary organic carbon was the inverse of WSOC/OC, which may indicate that the OC/EC minimum ratio method was not suitable for estimating SOC in this study. Linear regression analysis of WSOC and other chemical compositions was performed. The strong relationship between WSOC and SNA, as well as with a biomass burning tracer (K⁺), indicates that biomass burning is an important source of WSOC in autumn; that biomass burning and aqueous chemical process are both important sources in winter; and that photochemical reaction processes are important in summer and spring. Meteorological parameters (temperature, relative humidity and wind speed) had different influences on the concentration of WSOC. It was found that RH could significantly affect the aqueous chemical reactions of WSOC precursors and the gas-to-particle conversion processes of WSOCg.

Acknowledgments

We thank the National Natural Science Foundation of China (grant nos. 41675127, 41475116, 41105111; no. 41275134) for financial

support. We also appreciate the valuable advice from the editor regarding the improvement of the manuscript.

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