Water-soluble organic carbon (WSOC) and its temperature-resolved carbon fractions in atmospheric aerosols in Beijing

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ABSTRACT

Investigation of temperature-resolved carbon fractions of water-soluble organic carbon (WSOC) can improve our understanding of the chemical properties, formation processes and sources of WSOC in aerosols. We developed a method that can examine different temperature-resolved carbon fractions of WSOC and used this method to characterize aerosol samples ($n = 102$) collected from an urban site in Beijing in 2010–2011. The aerosol composition data including inorganic ions, elements and temperature-resolved carbon fractions of WSOC were used as input of positive matrix factorization (PMF) model to investigate the sources of WSOC. The results showed that the mean concentrations of WSOC were $10.2 \mu\text{g m}^{-3}$ with increased values in winter and decreased values in summer, while WSOC/OC ratios (mean: 51.7%) were higher in spring and summer than in fall and winter. The sampling artifacts of WSOC (18.2%) were higher than those of OC (13.4%). Though WSOC was significantly influenced by biomass burning in spring and winter, the strong correlations between WSOC and other secondary components suggested that WSOC was secondary in nature. Results of temperature-resolved carbon fractions of OC and WSOC showed that WSOC/OC ratios for different carbon fractions had the highest value of 0.92 and lowest value of 0.30. PMF analysis identified four factors, three of which were associated with three organic polar compounds groups (low, medium, and high molecular weight compounds) based on their thermal evolution features, and one of which was attributed to inorganic secondary formation processes. Annually, the contributions of four factors were 20.5%, 46.2%, 12.4% and 20.9%, respectively.

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1. Introduction

Aerosols contain a wide variety of inorganic and organic compounds, and organics account for up to 70% of the fine aerosol mass (Jacobson et al., 2000). Organic carbon is classified into two groups: water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WIOC) (Sullivan and Weber, 2006). WSOC accounts for 20–70% of organic carbon, and it is of interest because it can affect the aerosol's hygroscopicity and ability to serve as cloud condensation nuclei (CCN), and thus impacts climate change (Asa-Awuku et al., 2009).

It is well known that WSOC consists of oxygenated compounds containing functional groups such as COOH, COH, C=O, COC, CONO₂, CNO₂, and CNH₂ (Saxena and Hildemann, 1996). Sources of WSOC have been shown to be complex. They are emitted directly from combustion, industrial, and natural sources (primary) and/or formed through secondary processes such as homogeneous gas-phase and/or heterogeneous aerosol-phase oxidation (secondary) (Claeys et al., 2004; Koch et al., 2007; Schichtel et al., 2008). Although the primary sources such as

biomass burning may be important for WSOC loadings (Graham et al., 2002), it is suggested that a major fraction of WSOC is from secondary organic aerosol (SOA) formation (Aggarwal and Kawamura, 2009; Kondo et al., 2007). Sullivan et al. (2004) found correlated diurnal variations between ratio of WSOC/OC and O₃ in summer, indicating that a significant fraction of WSOC was originated from secondary formation. Studies have also shown that WSOC strongly correlated with secondary species such as inorganic ions and oxalate (Du et al., 2014; Zhang et al., 2012). The correlation between WSOC and SOA estimated by elemental carbon (EC)–tracer method provided additional evidence for secondary nature of WSOC (Cheng et al., 2011; Du et al., 2014). In addition, many field measurements of Aerosol Mass Spectrometer (AMS) suggested that the majority of oxygenated organic aerosol (OOA) was associated with SOA, and most of OOA was found to be water-soluble (Timonen et al., 2013; Xiao et al., 2011). These findings suggested that SOA, OOA, and WSOC were very similar in their chemical characteristics in the urban atmosphere (Pathak et al., 2011).

One challenge for carbonaceous aerosol sciences is the large discrepancy between modeled and measured SOA concentrations (Heald et al., 2005). Current knowledge of SOA, including its precursors, production pathways and atmospheric evolution, is still very limited (Hallquist

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et al., 2009; Yu et al., 2014). There is no direct method to reliably quantify the SOA mass. Indirect techniques such as WSOC measurement and elemental carbon (EC)-tracer method have been used to estimate SOA (Du et al., 2014). Organic aerosols are comprised of numerous individual organic compounds, whereas only a small fraction (of the order of 10%) can be identified at a molecular level (Hallquist et al., 2009). Thermal-optical analysis is widely used for completely separation of organic and elemental carbon in carbonaceous aerosols (Turpin et al., 2000). OC/EC measurement by IMPROVE_A protocol is one of the most representative heating programs used in many previous studies (Chow et al., 2007). Using this method, several carbon fractions including four OC carbon fractions (OC1–OC4) and three EC fractions (EC1–3), as well as the pyrolyzed organic carbon (OP) are measured at different temperature steps (Cao et al., 2005; Chow et al., 2007; Wang et al., 2014). Carbon abundances in each of these fractions vary with different carbon sources (Watson et al., 1994), therefore, the eight carbon fractions have been used as source markers for carbon appointment by chemical mass balance (CMB) and PMF model (Kim and Hopke, 2004; Kim et al., 2004; Lewtas, 2002; Liu et al., 2006). However, investigation of WSOC fraction evolved at different heating temperature step and its application to source appointment in long period of measurements is sparse. So far, most studies have measured a bulk WSOC value by method based on total organic carbon analyzer (TOC) after water extraction and filtration of filter samples (Du et al., 2014; Salma et al., 2007; Wozniak et al., 2012). Limited studies (Matsumoto et al., 2014; Yu et al., 2004) have been done to demonstrate that the thermal characteristics of WSOC altered with the particle size and sampling season, and that the thermal characteristics may reflect the formation processes and sources of the WSOC. Therefore, the data about temperature-resolved carbon fractions of WSOC may provide useful information to model simulations to estimate secondary organic carbon formation and assess their effects on climate and air quality (Martinez et al., 2016).

Another challenge for the measurement of carbonaceous aerosol is the sampling artifacts (Turpin et al., 2000). On the one hand, positive artifacts may occur due to the absorption of some gaseous compounds (mainly volatile organics) to the collection substrate and/or collected particles; on the other hand, negative bias may be caused by the volatilization of organic condensable constituents of the aerosol (like semi-volatile organics) during the sampling (Subramanian et al., 2004). Artifacts may be quantified by deploying different types of sampling setups including diffusion denuders to remove gaseous OC and the use of front and backup filters, impregnated or not by different adsorbents (Mader et al., 2003). Factors that control the occurrence and magnitude of artifacts include the sampling conditions (such as air temperature and relative humidity), sampling location (concentrations of volatile organic compounds and their sources) and sample storage (Viana et al., 2007). However, the studies about the artifacts of OC, especially WSOC, were not sufficiently investigated.

Although a number of studies have focused on chemical characteristics and sources of WSOC (Cheng et al., 2012; Huang et al., 2006; Miyazaki et al., 2007; Park et al., 2015), studies about the artifacts of WSOC during sampling, thermal characteristics of WSOC and its application to source appointment were limited. In our study, we developed a method to obtain the temperature-resolved carbon fractions of WSOC. This paper presents the results from the sampling and determination of carbonaceous species (OC, EC, and WSOC), water-soluble ions and elements in an urban site of Beijing during four seasons in 2010–2011. Sampling artifacts of OC and WSOC were evaluated and seasonal variations of the carbonaceous species were discussed. Furthermore, we estimated secondary organic carbon (SOC) by EC-tracer method and compared SOC with WSOC to understand the sources and formations of WSOC. Finally, the temperature-resolved carbon fractions of WSOC were applied to positive matrix factorization (PMF) model to identify source contributions of WSOC. Our main goals were to investigate the characteristics of temperature-resolved carbon fractions of WSOC to offer insights to the characteristics of chemical composition and sources

of WSOC, and to provide data which may be useful in atmospheric models to better estimate secondary organic carbon formation.

2. Methods

2.1. Sample collection

PM₁₀ samples were collected on the roof of a building (about 15 m above ground level) in the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (40° 00' 28" N, 116° 20' 15" E), which is located between the 4th and 5th ring road in the outskirts of Beijing urban area.

We used PM₁₀ sampler (LB, USA) with two parallel sampling channels without denuders to collect aerosol samples at a flow rate of 16.7 L min^{−1}. Samples were collected twice a week on Wednesday and Sunday from January 2010 to January 2011. The sample duration was 24 h with runs beginning and ending at 9:00 a.m. (local time, GMT + 0800). Totally 102 sets of samples were collected.

We used the two parallel sampling channels (Fig. S1) to evaluate the possible artifacts of carbonaceous aerosols. Each of the channels was operated at 8.35 L min^{−1}. Channel 1 collected aerosols on a quartz filter (47 mm diameter; Gelman, USA), and Channel 2 collected aerosols on a Teflon filter (2 μm pore size; 47 mm diameter; Gelman, USA) with a backup quartz filter. Channel 2 was arranged with a Teflon-quartz (TQ) configuration, since this configuration was better than the QQ (quartz-quartz) configuration for estimating adsorbed vapor on a quartz filter (Mader et al., 2003; Salma et al., 2007; Turpin et al., 2000).

Another two sets of aerosol samples were also collected on quartz filter (Gelman, USA) with a large exposed area (~419 cm²) for developing the method of WSOC determination, since multiple punches of filter samples were needed to determine the appropriate water volume for extraction (see below). The samples were collected on 6 August and 28 October by a high volume sampler (HV-150 SIBETA, flow rate: 556 L m^{−3}) with duration time of 48 h to obtain high aerosol loadings.

All the filter samples were packed and sealed in plastic bags, and were stored at −20 °C before chemical analysis. The aerosol samples collected on the quartz filters were measured for OC, EC and WSOC. The samples collected on Teflon filters were determined for PM₁₀ mass, water-soluble ions and elements. Quartz filters were baked at 800 °C for 4 h to remove absorbed organics before sampling. Field blanks for each filter medium were analyzed to correct their background levels. Meteorological data (including wind speed, temperature and relative humidity) were obtained from the website (<http://www.wunderground.com>).

2.2. Sample analysis

2.2.1. OC/EC

OC and EC were determined by a DRI-2001A OC/EC Analyzer following IMPROVE_A heating procedure (Chow et al., 2007), which assumes carbonates carbon in the sample is negligible. A 0.51 cm² punch of each quartz filter was heated stepwise in a pure helium atmosphere at 140 °C (OC1), 280 °C (OC2), 480 °C (OC3), and 580 °C (OC4), and then in 2%O₂/98% He atmosphere at 580 °C (EC1), 740 °C (EC2), and 840 °C (EC3). The particulate carbon in the filter was converted to CO₂, and then was reduced to CH₄ and quantified by a flame ion detector. OC can evolve as pyrolysis carbon (OP) during the heating process. To correct OC, light reflectance was monitored during the procedure. OP was determined when reflected laser light attained its original intensity after oxygen was added to the analysis atmosphere. OC is the sum of OC1, OC2, OC3, OC4 and OP. EC is the sum of EC1, EC2 and EC3 minus OP.

2.2.2. WSOC

To determine WSOC, another punch from the samples was used for the water extraction and then submitted for the same thermal-optical analysis. The decrease of five OC carbon fractions (OC1–4 and OP) on

the filter before and after water extraction is the water-soluble part of organic carbon. By this indirect method, we obtained WSOC1, WSOC2, WSOC3, WSOC4 and WSOP, which represents the temperature-resolved carbon fractions of WSOC.

The extraction of WSOC was conducted using a filtration apparatus. A punch of aerosol sample (1.8 cm in diameter) was mounted between a funnel and a borosilicate glass sieve (2.5 cm in diameter, with quartz filter disc, 1.6 cm in diameter) connected with a filtering flask. The funnel and sieve were held together with a clamp to avoid any water leakage. All the glassware was pre-baked (4 h, 500 °C). The samples were first soaked with 300 μL water for 20 min to allow WSOC to fully desorb. Milli-Q deionized water ($\text{DOC} < 5$ ppb) was then added into the funnel. After the water passed through the filter, the filter was dried in a desiccator and submitted for the OC/EC thermal-optical analysis.

It is important to determine the volume of water for the extraction of WSOC. The volume of water should be enough to desorb WSOC and allow WSOC to be fully washed away without any retention on the filter. However, it has not escaped our notice that a slight decrease of EC occurred at the same time. When choosing the optimal water volume, one seeks to balance the two effects. Fig. 1 shows the percentage of OC and EC reduction after extraction treatment with different water volume. It can be seen that WSOC was nearly fully desorbed and washed away when water volume reached 20 mL while EC was subjected to a minimal loss. More loss of EC was observed when water volume was > 20 mL.

There were three possible reasons for the observation of EC reduction. One reason may be the uncertainty of OC/EC split, since water soluble inorganic constituents (such as ammonium bisulfate) which may influence OC charring behavior were also washed away by water (Yu et al., 2002). However, Yang et al. (2003) showed that the method based on TOC analyzer and OC/EC carbon analyzer gave equivalent measurement results when determining water extracts of WSOC. Second, one should admit that the loss of EC may be caused by “under catch” and breakthrough effects of particulates on the filter, as suggested by Wang et al. (2014). Finally, one reason might be the nature of EC. Wozniak et al. (2008) found that approximately 1–4% of the peaks in the aerosol-derived WSOC mass spectra were classified as black carbon (BC) on the basis of double bond equivalents calculated from the assigned molecular formulas, suggesting that part of EC may be also soluble. In fact, if this is the case, the now widely used TOC method would have been suffered from this problem when extracting WSOC. However, it remains to be further investigated whether EC were partially water-soluble and led to the overestimation of WSOC.

To minimize the possible interference discussed above during the extraction, deliberate efforts were made. The water distilled slowly

from the filter with the average velocity of about 0.5 mL min^{-1} . In addition, 5 mL of the water volume was selected based on our experiment results (Fig. 1) and the reported fast first order kinetics of the desorption of WSOC by Wozniak et al. (2012). This water volume was chosen because the daily aerosol samples had generally lower loadings compared with the samples used in the above experiments. In this method, standard compounds spiked onto filters showed satisfactory recovery (87%–104%, $n = 7$). Triplicate sets of samples were determined, and the standard error was about 5%. The procedure blank of WSOC was about $0.3 \mu\text{g m}^{-3}$ and was subtracted from the measured WSOC. Merits of this method include the use of identical carbon analyzer for quantification of the derived CH_4 , and the relatively low WSOC loadings.

2.2.3. Inorganic ions and elements

We used a microbalance ($1 \mu\text{g}$ sensitivity) to weigh the Teflon filters which had been conditioned for 24 h in a clean chamber (relative humidity of 40% and temperature of 20 °C). Water-soluble inorganic ions were analyzed using similar methods in our previous studies (Lun et al., 2003; Tang et al., 2016). Water extracts of Teflon filters were analyzed for anions (SO_4^{2-} , NO_3^- , Cl^-) and cations (Na^+ , Mg^{2+} , K^+ , Ca^{2+} , NH_4^+) by a Dionex model ICS-120 ion chromatograph equipped with a conductivity detector (ASRS-ULTRA). Twenty elements (Na, K, Ca, Mg, S, Cl, Al, Si, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Pb) were measured by particle induced X-ray emission (PIXE) method in a 2×1.7 MV tandem electrostatic accelerator, which belonged to the College of Nuclear Science and Technology of Beijing Normal University, China (Yu et al., 2013).

2.3. Data analysis

We used PMF model (USEPA PMF 5.0) to identify sources and their contributions to WSOC. PMF is a multivariate receptor model that estimates the source profiles and their contributions based on a weighted least-squares approach (Norris et al., 2014). The dataset used for PMF analysis consisted of 102 samples and 29 variables (WSOC, WSOC1–4, WSOP, EC, eight water-soluble ions and fourteen trace elements). According to the review of Reff et al. (2007), elements such as Na, K, Ca, Mg, S, Cl were not included in the PMF analysis to avoid double counting of mass concentrations (i.e. pairs of elemental and ionic species such as Na and Na^+ , K and K^+ , or Ca and Ca^{2+} are both used). The uncertainties for chemical species were calculated according to the user guide of PMF model. Method detections were $< 0.2 \mu\text{g m}^{-3}$ for ions, 0.2 to $0.3 \mu\text{g m}^{-3}$ for carbonaceous species, and 6 to 27 ng m^{-3} for elements. The concentration data that below the detection limit were replaced with half of the detection limit, and their estimated errors were evaluated as 5/6 of the detection limit (Polissar et al., 1998). The uncertainties fractions were about 5% for ions, 10% for carbonaceous species, and 10–15% for elements. An extra model uncertainty of 5% was also set to account for errors that are not covered in the input uncertainty values (Reff et al., 2007). We run the model several times using 3–7 factors to obtain the best solutions. Uncertainty and stability with the resolved factor profiles were also estimated and assessed using three error estimation methods, i.e. displacement (DISP) analysis, bootstraps (BS) method and a combination of DISP and BS methods. Finally, a four-factor solution provided the most physically realistic source profiles.

3. Results and discussion

3.1. Sampling artifacts of OC and WSOC

Concentrations of OC, WSOC and the ratio of WSOC/OC for the front and back filters, along with the artifacts of OC and WSOC in standard seasons are presented in Table 1. OC concentrations (mean $\pm$ standard deviation) on backup filter corresponded to $2.5 \pm 0.7 \mu\text{g m}^{-3}$, $2.3 \pm 0.5 \mu\text{g m}^{-3}$, $1.9 \pm 0.8 \mu\text{g m}^{-3}$ and $2.0 \pm 1.1 \mu\text{g m}^{-3}$ in spring, summer, fall and winter, respectively. As expected, EC concentrations detected on

Fig. 1. Fractions of reduced OC or EC versus water volume washed out through samples collected on 6 August and 28 December. Reduced OC or EC fractions was the ratio of OC or EC difference measured before and after extraction treatment to OC or EC value before treatment. Error bars represent standard errors of triplicate analyses.

Table 1

Mean concentrations of OC, WSOC and the ratio of WSOC/OC, as obtained by the samplings of parallel channels (Channel 1: one front quartz filter; Channel 2: one front Teflon filter and back up quartz filter) for the front and back quartz filter samples, along with the artifacts (mean $\pm$ standard deviation) for 102 urban-type PM₁₀ samples collected in different seasons. OC and WSOC artifacts were quantified by calculating the percentage of their concentrations on backup filters to front filters.

Season	OC ($\mu\text{g m}^{-3}$)		Artefact (%)	WSOC ($\mu\text{g m}^{-3}$)		Artefact (%)	WSOC/OC (%)		N
	Front	Back		Front	Back		Back	Front	
Spring	16.9 $\pm$ 8.6	2.5 $\pm$ 0.7	17.4 $\pm$ 6.7	9.6 $\pm$ 5.3	1.8 $\pm$ 0.6	22.2 $\pm$ 11.3	68.9 $\pm$ 12.5	56.5 $\pm$ 8.2	20
Summer	14.3 $\pm$ 4.0	2.3 $\pm$ 0.5	17.0 $\pm$ 4.0	8.1 $\pm$ 2.8	1.5 $\pm$ 0.5	20.1 $\pm$ 8.7	62.4 $\pm$ 14.8	55.5 $\pm$ 8.2	26
Fall	18.0 $\pm$ 9.0	1.9 $\pm$ 0.8	12.1 $\pm$ 5.7	9.5 $\pm$ 6.2	1.4 $\pm$ 0.7	18.4 $\pm$ 10.2	75.1 $\pm$ 20.1	51.6 $\pm$ 8.0	21
Winter	27.9 $\pm$ 25.1	2.0 $\pm$ 1.1	9.2 $\pm$ 6.3	12.3 $\pm$ 8.8	1.5 $\pm$ 0.9	14.4 $\pm$ 8.8	73.6 $\pm$ 15.3	46.2 $\pm$ 9.3	35
Annual	20.2 $\pm$ 16.8	2.2 $\pm$ 0.9	13.4 $\pm$ 6.7	10.1 $\pm$ 6.6	1.5 $\pm$ 0.7	18.2 $\pm$ 9.9	70.1 $\pm$ 16.4	51.7 $\pm$ 9.5	102

the backup filters were negligible (mean: $0.10 \mu\text{g m}^{-3}$). During our field measurements, OC artifacts were higher (*t*-test, $p < 0.01$) in spring (17.4%) and summer (17.0%) than in fall (12.2%) and winter (9.2%), which are comparable to those in other sites in China and other countries (Cheng et al., 2009; Vecchi et al., 2009).

Similar with the seasonal trends of OC artifacts, WSOC artifacts were higher (*t*-test, $p < 0.07$) in spring (22.2%), summer (20.1%) and fall (18.4%) than those of winter (14.4%). However, the seasonal differences of WSOC artifacts were not as significant as those of OC artifacts, indicating that the formation of the absorbed WSOC on the filter had a more stable emission source in different season or the absorbed WSOC was less temperature-dependent.

Possible explanation for the seasonal patterns of artifacts may be the enhanced emissions of volatile organic compounds (VOCs) and absorptions of volatile organics on the filter in warm seasons (Viana et al., 2007). Alternatively, our data might be interpreted as that the enhanced evaporation of organic carbon collected on the front filter contributed to the backup filter in warm seasons. Unfortunately, the denuder set-up were not arranged to remove the gaseous organics before the collection of aerosols on the filter to assess the magnitude of the positive or negative artifacts. However, our results highlighted the importance of proper sampling and artifacts correction method for the measurements of organic compounds especially for WSOC in urban environments, since WSOC artifacts (18.2%) were significantly (*t*-test, $p < 0.01$) larger than those of OC (13.4%).

WSOC/OC ratios on back filter were 70.1%, showing the organic compounds contributing to the adsorptive sampling artifacts were more soluble, which may contain more polar or oxidized functional groups. This high ratios are expected, since quartz fiber filters may primarily adsorb polar (i.e. more water soluble) organic compounds (Salma et al., 2007). OC and WSOC on the backup quartz filter was dominated by OC1 and OC2, suggesting that organic artifacts were mainly associated with OC fractions evolving at lower temperatures. While only little contribution from PC (<1%) was observed on backup filters. This may be due to the nature of absorbed organic compounds themselves that may not be susceptible to pyrolysis and/or the absence of inorganic constituents favoring pyrolysis (Vecchi et al., 2009).

3.2. Temporal variations of WSOC and WSOC/OC ratio

Fig. 2 shows the temporal profiles of PM₁₀ mass, WSOC, OC, EC and ratios of WSOC/OC and OC/EC, as well as meteorological parameters (temperature, relative humidity and wind speed) during the measurement period. OC and WSOC concentrations were not corrected for possible artifacts because there was uncertainty in assessing positive or negative artifacts in this study and our uncorrected results were more reasonable to compare with other studies that did not usually use tandem filters during sample collection. WSOC concentrations varied from 2.7 to $35.9 \mu\text{g m}^{-3}$ (mean $\pm$ SD: $10.1 \pm 6.6 \mu\text{g m}^{-3}$). OC concentrations varied from 4.6 to $137.2 \mu\text{g m}^{-3}$ ($20.2 \pm 16.8 \mu\text{g m}^{-3}$) and EC concentrations were from 1.1 to $35.2 \mu\text{g m}^{-3}$ ($6.7 \pm 4.5 \mu\text{g m}^{-3}$). WSOC was strongly correlated with OC ($r = 0.8602$, $n = 102$), suggesting their similar primary emission sources and/or similar secondary processes.

The seasonal variations of carbonaceous species and the ratios of WSOC/OC and OC/EC are shown in Fig. 3. Overall, carbonaceous species decreased in spring and summer and increased in fall and winter. WSOC concentrations in PM₁₀ were 9.60 ± 5.31 , 8.05 ± 2.78 , 9.48 ± 6.24 and $12.27 \pm 8.81 \mu\text{g m}^{-3}$ in spring, summer, fall and winter, respectively. OC and EC had similar seasonal variations. The seasonality of carbonaceous compounds may be regulated by the variability in emission strengths and meteorology. The elevated WSOC, OC and EC concentrations in winter were mainly due to the intensive burning of coal during heating period in the northern China (Lin et al., 2009). Weather conditions may also have important influences on the carbonaceous concentrations, since other sources of carbonaceous species, such as vehicle emissions may not have distinct seasonal changes. The relatively stagnant air masses in fall (Fig. S2) were favorable for air pollution accumulation, leading to elevated concentrations of carbonaceous species. In contrast, the frequent precipitation events in summer and higher wind speed in spring were favorable for the scavenging and dispersion of pollutants, which led to lower concentrations of carbonaceous species.

Fig. 2 shows that the WSOC/OC ratios varied from 0.26 to 0.73 with a mean of 0.52. These values were comparable to those measured in other urban sites (Cho and Park, 2013; Tao et al., 2013). WSOC/OC ratios were higher (*t*-test, $p < 0.05$) in spring (56.5%) and summer (55.5%) than in fall (51.6%) and winter (46.2%). The high WSOC/OC ratio has been used to infer great extent of secondary aerosol formation and/or aging of aerosols during long-range transport (Ram et al., 2012). Therefore, the high WSOC/OC ratios in summer were likely due to active SOA formation associated with higher O₃, solar radiation, and VOC emissions (Sun et al., 2015; Wang et al., 2015b). In addition, the high acidity in particulate in the summer of Beijing, which can enhance the production of secondary organic aerosols through heterogeneous acid-catalyzed chemistry (Pathak et al., 2011; Rengarajan et al., 2011), may be another reason. Interestingly, the spring also had high WSOC/OC ratios. The relatively strong solar radiation and high concentrations of ozone in spring (Sun et al., 2015; Wang et al., 2015b) were plausible reasons. Other important factors may be the prevalent dust and relatively high wind speed in this season. One the one hand, SOA formation in particles was likely driven by the acid-base reactions involving the acidic organics formed by photochemical reactions of VOCs and the preexisting dust (Cachier, 2005; Guinot et al., 2007; Liu et al., 2013; Wang et al., 2015a). On the other hand, high wind speed in spring was favorable for the long-range transport of aging aerosols with great proportion of WSOC/OC fractions from remote region (Salma et al., 2007).

OC/EC ratios mostly fell within the range of 2.0–5.0 (Fig. 2) and had higher (*t*-test, $p < 0.01$) values in spring (4.1 ± 1.6), and winter (3.3 ± 0.7) than in summer (2.5 ± 0.4) and fall (2.7 ± 0.7) (Fig. 3). These values are similar to those in previous studies (Duan et al., 2005; Yang et al., 2005). OC/EC ratios exceeding 2.0 have been used to identify secondary organic aerosol formation (Chow et al., 1994) and the secondary organic carbon (SOC) were estimated in the next section. The elevated OC/EC ratios in spring may be due to the influence of dust particles, which could be illustrated when investigating the relationship of OC and EC (Fig. 4). Three data points with high OC/EC ratios (6.7–7.85) was circled with an ellipse in Fig. 4 and dust storm events were observed on the three days (21 March, 31 March and 10 May). This is

Fig. 2. Temporal profiles of WSOC, OC, EC, PM₁₀ mass concentrations, ratios of WSOC/OC and OC/EC, and meteorological parameters.

consistent with the study of Guinot et al. (2007), who reported lower BC/TC (i.e. higher OC/EC ratios) during dust periods and suggested that the scavenging of semi-volatile organic gases by dust particles were the reason of OC enhancement. Also, recent evidence suggests that mineral dust has the potential to participate in the atmospheric heterogeneous photochemical processes (Nie et al., 2014) and therefore can promote secondary aerosol formation of OC. In our study, the relatively high OC/EC ratios in winter reflected the potential contributions of coal burning, which was reported to have elevated OC/EC ratios (12.0) (Cao et al., 2005). The lowest OC/EC ratios in summer may be due to frequent rain events since EC could not be efficiently scavenged by rain as OC.

3.3. SOC estimation and correlation of WSOC and SOC

The relationship of OC and EC reflects the origins of carbonaceous aerosols. The regression analysis of OC and EC are shown in Fig. 4. Good OC and EC correlations were observed for all four seasons ($r > 0.84$), suggesting that OC and EC might have similar sources and their relationship could be used for the estimation of secondary organic

formation. As EC is resistant to chemical reactions, it is a good indicator of primary anthropogenic pollutants and it has often been used as a tracer of primary OC (Turpin and Huntzicker, 1991). OC/EC ratios exceeding 2.0 have been used to identify secondary organic aerosol formation (Chow et al., 1994). High OC/EC ratios were found among four seasons in our study, indicating the formation of SOC. Turpin and Huntzicker (1995) suggested an equation below to identify the SOC:

$$\text{OC}_{\text{sec}}(\text{SOC}) = \text{OC} - \text{EC} * (\text{OC}/\text{EC})_{\text{pri}} \quad (1)$$

where OC_{sec} is the SOC, which is the difference between measured OC and primary OC. The OC_{pri} is obtained by:

$$\text{OC}_{\text{pri}}(\text{POC}) = a + b * \text{EC} \quad (2)$$

where a and b are the intercept and slope, respectively. The primary OC can be divided into two categories—that associated with the elemental carbon ($b * \text{EC}$) and the remainder (a). The organic carbon in the term $b * \text{EC}$ includes combustion generated organic carbon (e.g., coal and traffic emissions). The remainder, a , is an aggregate of non-combustion

Fig. 3. Seasonal variations of carbonaceous species and ratios of WSOC/OC and OC/EC. The central lines and dots are the seasonal medians and means, respectively. The bottoms and tops of boxes are the 25th and 75th percentile.

sources (e.g., biogenic OC, etc.) or primary OC background concentrations.

This method assumes that the relationship between primary OC and EC (the OC/EC ratio) and OC background concentrations are stable at certain locations (Cao et al., 2007). However, the primary OC/EC ratios are not easy to determine because they are influenced by source emissions and meteorological conditions. Therefore, special efforts were made to apply this method. First, OC and EC with lowest probability of SOC production were identified. Samples collected in days that meteorological conditions and oxidative factors (relatively low ozone concentrations, solar radiation and unstable air mass for good dispersion) did not favor SOC formation were used to calculate primary OC/EC ratios (Duan et al., 2005). In addition, the primary OC/EC ratio is season-dependent (Yuan et al., 2006). So the season-specific primary OC/EC ratios were obtained using samples with the lowest ~20% OC/EC ratios (Lim and Turpin, 2002; Yuan et al., 2006) for regression analysis. Samples collected on days with rain events were excluded in the regression analysis of primary OC and EC (Cabada et al., 2004). As shown in Fig. 4, the primary ratios varied from 1.73 to 2.77 in four seasons. By this estimate, SOC accounted for 24.7%, 28.4%, 21.1% and 23.0% of OC in spring, summer, fall and winter, respectively. Summer had the highest SOC fraction which is consistent with the fact that the potential photochemistry is high in summer.

Correlation analysis of WSOC with other components may reflect different sources of WSOC, such as primary emissions (fossil fuel combustion and biomass burning) and/or secondary formation. As shown in Table 2, WSOC concentrations were strongly ($r = 0.55$ – 0.82) correlated with estimated SOC, suggesting that secondary sources were important for WSOC formation. Correlations of WSOC with secondary inorganic ions (sulfate and nitrate) were also investigated. Good correlations between WSOC and sulfate were found in spring ($r = 0.6627$) and winter ($r = 0.7382$), while this correlations were found to be weak in summer ($r = 0.2328$) and fall ($r = 0.2651$). Similar results were found in the study of Du et al. (2014), who found weaker correlations of sulfate with WSOC in summer than other seasons in Beijing. Du et al. (2014) also suggested that the different formation pathway of WSOC and sulfate in summer may be the reason, since aqueous reactions were important production pathway of both sulfate and WSOC,

while the photochemical reactions could also have important contributions to WSOC in summer. WSOC and nitrate also exhibited good correlations in all seasons except for summer in our study. Possible reasons may be the unfavorable weather conditions for the formation of fine nitrate and the significant sampling artifacts of nitrate in summer. The strong correlation of WSOC with K^+ in spring ($r = 0.8935$) and winter ($r = 0.8654$) suggested the contribution of biomass burning in the two seasons, since K^+ has been widely used as a source tracer of biomass burning and has been applied in several source appointment studies (Cheng et al., 2015; Duan et al., 2004; Sun et al., 2010; Zhang et al., 2008). Our findings were also supported by the study of Zhang et al. (2008), who found significant contribution of biomass burning in October, November and May using another better indicator levoglucosan. Straw that was leftover on the field of the previous year were usually burned in spring (Duan et al., 2004) and agricultural waste and fallen leaves were usually combusted in late fall (Zheng et al., 2005). In addition, field observations suggested that there are secondary organic formations during the aging process of biomass burning plumes (Vakkari et al., 2014; Yao et al., 2016). Therefore, WSOC were secondary in nature but were also influenced by biomass burning in spring and winter. In contrast, WIOC appeared to be strongly associated with primary emissions annually, showing strong correlations with EC ($r = 0.9216$) and POC ($r = 0.8949$).

3.4. Characteristics of temperature-resolved carbon fractions of WSOC

Characteristics of temperature-resolved carbon fractions of WSOC may reflect the chemical properties, formation mechanisms and sources of WSOC. It was suggested that the evolution features of carbon, such as the number and position of the peaks, are greatly influenced by the chemical composition of the aerosols (Yu et al., 2002). Investigation of thermograms of single standards of water-soluble organic species found that organics evolved at lower temperatures (such as oxalic acid, adipic acid and glucose) are generally associated with low molecular weight polar organic and organics evolved at higher temperatures (such as humic acid) might be associated with high molecular weight polar compounds (Matsumoto et al., 2014; Miyazaki et al., 2007; Yu et al., 2004). Therefore, the carbon fractions of WSOC in ascending

Fig. 4. Regression analysis of OC and EC in each season (using all data in each season, including data with both solid and empty symbols) and the primary OC and EC regression analysis (using data with solid symbols, excluding rain events data with “+” symbols). Three data points in summer and two data points in autumn were excluded in the primary OC and EC regression analysis because of the rain events. The data collected in dust events were circled with an ellipse.

Table 2

Regression analysis of WSOC and SOC, K^+ , SO_4^{2-} , and NO_3^- , and regression analysis of WIOC and POC and EC.

Season	Correlation coefficient (r) between WSOC and				Correlation coefficient (r) between WIOC and		N
	SOC	K^+	SO_4^{2-}	NO_3^-	POC	EC	
Spring	0.5479	0.8935	0.6627	0.7418	0.6771	0.6758	20
Summer	0.7014	0.3032	0.2328	0.0469	0.7205	0.7194	26
Fall	0.6872	0.4556	0.2651	0.6340	0.8794	0.8669	21
Winter	0.8178	0.8654	0.7382	0.8207	0.9502	0.9492	35
Annual	0.7411	0.7477	0.3576	0.5531	0.9216	0.8949	102

order (WSOC1–4 to WSOP) were associated with gradually high molecular weight polar compounds.

The concentrations of each carbon fractions of OC and WSOC and WSOC/OC of each carbon fractions are shown in Fig. 5. As can be seen, there was substantial seasonal variability in carbon fraction concentrations and WSOC/OC ratios of each carbon fraction. Annually, OC4 fraction dominated in both OC and WSOC concentrations. The second highest concentrations of OC fraction were OC3 fraction; however, concentrations of WSOC3 were lower than those of WSOC2 because of the lower ratio of WSOC/OC in OC3 fraction. Overall, WSOC/OC in different carbon fractions had a wide range from 0.30 (OC3 in winter) to 0.92 (OC1 in spring), suggesting the large temporal variability in emission source and their strength, and the contribution from SOA at our urban sampling site.

WSOC/OC ratios may be a possible indicator of aerosol sources. Previous studies suggested that WSOC/OC ratios for vehicular emissions were generally low compared to those from biomass burning emissions. For example, roadside measurements in Paris showed a value of 0.12 for WSOC/OC (Ruellan and Cachier, 2001), while WSOC/OC ratios were reported to be ranged from 0.40 to 0.45 in aerosols collected during peak of biomass burning season in the Brazilian Amazon region (Mayol-Bracero et al., 2002). Other evidence was provided by Saarikoski et al.

(2008), who reported the value of 0.27 for vehicular emissions over an urban environment in Helsinki, in contrast to the value of 0.4 for biomass burning. It is generally acknowledged that WSOC/OC ratios are relatively high in SOA aerosol (Saxena and Hildemann, 1996), as confirmed by the study of Saarikoski et al. (2008), who reported that WSOC/OC ratio had a value of 0.8 for secondary organic aerosol. Therefore, it is likely a reasonable assumption that the enhanced WSOC/OC ratios suggest the contribution of secondary formation or biomass burning emissions, while low WSOC/OC ratios indicate the contribution of vehicular emissions.

According to Fig. 5, annually, OC1 fraction had the highest WSOC/OC ratios (0.74), while OC3 fraction had the lowest ratio (0.33). This suggests that the high volatile organic fraction (OC1) was more soluble than other OC fractions. In addition, we found that OC1 fraction had enhanced concentrations and proportions in both OC and WSOC during spring and winter. Interestingly, WSOC correlated well with the biomass-burning marker (K^+) in spring and winter as discussed in Section 3.3. Therefore, OC1 fraction could be attributed to biomass burning, which is consistent with the study of Cao et al. (2005), who reported higher OC1 fraction in biomass burning samples. In contrast, our results showed OC3 had the lowest WSOC/OC ratios in all seasons, implying the least soluble nature of this OC fraction. Therefore, this OC fraction may be associated with vehicle emissions based on the above assumption. This is in agreement with the study of Cao et al. (2006) and Liu et al. (2006), who found enhanced OC3 in vehicle emissions.

OC2 fraction has relatively high WSOC/OC ratios (0.5) in the entire study. One interesting finding about this carbon fraction in our study is that the ratio dropped significantly in winter (0.34) compared with other seasons (>0.57). On the one hand, the coal burning during the winter heating period seemed to be the most possible reason. OC2 in OC was therefore related with coal burning, which was in line with other studies (Cao et al., 2005; Matsumoto et al., 2014). On the other hand, in other seasons, WSOC2 seemed

Fig. 5. Different carbon fractions concentrations in OC and WSOC and the ratios of WSOC/OC in different carbon fraction. Error bar = $0.2 \times SD$.

Fig. 6. Composition profiles of four factors resolved by PMF. WSOC1, WSOC2, WSOC3, WSOC4, and WSOP denote temperature-resolved carbon fractions of WSOC.

to be influenced by the possible oxidation of VOCs, since WSOC/OC ratios for OC2 were very high (0.70) and WSOC2 fractions in WSOC had enhanced concentrations and proportions during summer. This speculation seems reasonable because the oxidants levels were supposed to be the highest in summer and VOCs such as the biogenic VOCs had the highest emission strength during summer in Beijing (77% of annual emissions) (Wang et al., 2003). This possible influence was supported by the study of Ehn et al. (2014), who found that the biogenic VOCs contributed to the formation of secondary organic aerosols by producing large amounts of low-volatility vapors that condense irreversibly onto aerosol surface. OC4 fraction had WSOC/OC ratios of 0.53 and this carbon fraction accounted for the highest proportions of both OC and WSOC annually. Finally, the OP, the charring part of organic carbon, had a value of 0.60 for WSOC/OC ratios. Yu et al. (2004) studied direct thermal characteristics of WSOC and suggested that the charring part of

organic carbon were associated with high molecular weight polar compounds like humic-like substances and secondary organic aerosols. OP had the lowest WSOC/OC ratios in winter, which was consistent with the fact that secondary organic formation is lower in winter than in other seasons.

It should be noted that our data must be interpreted with caution. The temperature-resolved carbon fraction were not speciated into functional groups and could not be characterized at the molecular level in this study, since until now the analysis of individual substances in single fraction at molecular level is still challenging and unrealistic (Grabowsky et al., 2011). Therefore, the chemical characteristics and the formation of temperature-resolved carbon fraction are still unclear. However, our data provided important information about the relative abundance of the temperature-resolved carbon fractions and their solubility, and therefore may offer some insights to the source identifications.

Fig. 7. Time series of the mass concentrations of each factor contributing to WSOC.

3.5. Source apportionment of WSOC by PMF

Measurements of aerosol organic carbon (OC) fractions evolved at different heating temperature step were widely used in source identification (Chow et al., 2007; Zhu et al., 2014); however, investigation of temperature-resolved carbon fractions of WSOC has rarely been applied to the source identification. In this study, temperature-resolved carbon fractions of WSOC were used to better understand the sources of WSOC and four factors were identified by the PMF analysis. Composition profiles for four factors are shown in Fig. 6 and their contributions to WSOC throughout the sampling period are presented in Fig. 7.

Factor 1 is characterized by the high loadings of WSOC1, suggesting a link of this factor with as the low molecular weight polar compounds. K^+ also had important contributions in this factor, indicating that this factor was likely attributed to biomass burning. Annually, about 20.5% of WSOC was represented in this factor, demonstrating that the influence of biomass burning were important in Beijing. The winter had high (32.8%) biomass burning contribution, which is consistent with the study of Du et al. (2014).

Factor 2 is dominated by WSOC2–4, suggesting this factor was related to medium molecular weight polar groups. This factor was also influenced by high loadings of Mg^{2+} , Ca^{2+} , suggesting the influence of soil dust, which could enhance the formation of secondary organic carbon as suggested in Section 3.2. Factor 2 also had some contributions from EC, As, Se, and Pb. Here we tentatively identify factor 2 as secondary organic formation of organic precursors from anthropogenic sources (coal burning and vehicle exhaust). Annually, 46.2% of WSOC were associated with this factor.

Factor 3 is characterized by high levels WSOP, suggesting this factor was associated with high molecular weight polar groups. We found that the extent of charring (defined as the ratio of WSOP/WSOC) positively correlates ($r = 0.6268$, $p < 0.05$) with WSOC loadings. This means that higher WSOC concentrations caused more charring during the carbon evolution process, which is consistent with the study of Yu et al. (2002). One reason for the charring of organic carbon was suggested to be associated with catalytic oxides such as Fe and Mn oxides (Wang et al., 2010). Interestingly, Factor 3 also had high values of Mn, Fe, as well as other elements such as Al, Si, Ti, V and Cr, indicating the influence of industrial dust in this factor. Annually, this factor contributes 12.4% of WSOC.

Factor 4 is characterized by high levels of SO_4^{2-} , NO_3^- and NH_4^+ , indicating the link of this factor with inorganic secondary aerosol formation processes. Annually, this factor contributes 20.9% of WSOC. The seasonal pattern of factor 4 shows that secondary aerosol production was estimated to be prevalent in summer, accounting for 40.2% of WSOC. This estimation is consistent with the fact that the secondary contribution was more important in summer.

4. Conclusions

PM₁₀ samples were collected on an urban site in Beijing from 2010 January to 2011 January and were analyzed for chemical components (inorganic ions, carbonaceous compounds and elements). A method based on OC/EC TOR analysis was developed to determine the temperature-resolved WSOC and the results were applied to PMF to reveal the sources of WSOC. The usefulness and limitations of our data for source apportionment of aerosols were briefly discussed and its applicability to PMF analysis was demonstrated.

Our results showed the sampling artifacts of WSOC and OC were relatively high, suggesting the importance of appropriate sampling and correction method for measuring organic compounds in urban environment. We revealed the seasonal patterns of WSOC/OC ratios and suggested that the preexisting dust in spring and the enhanced photochemistry reactions in summer contributed to the elevated WSOC/OC. Regression analysis of WSOC with other components suggested that WSOC were secondary in nature but were also influenced by biomass

burning in spring and winter. The substantial seasonal variability of carbon fraction concentrations and WSOC/OC ratios for each fraction suggested that this information may be useful for the identification of possible of sources. The four factors (low, medium and high molecular weight polar compounds, and inorganic secondary formation processes) identified by the PMF analysis suggested the complexity of thermal evolution features of WSOC and current limited understanding of chemical characteristics of temperature-resolved WSOC. Our study has the potential to improve the estimates of secondary organic carbon in atmospheric models to assess their effects on climate and air quality. We suggest that more source emissions studies should be conducted to better understand the thermal characteristics of WSOC and be applied to the source appointment of WSOC.

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Appendix A. Supplementary data

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