The secondary nature and light absorption properties of water-soluble organic carbon in the winter of Beijing

Anna Li¹,², Xueliang Deng³*, Nana Yang¹,², Jiacheng Zhou¹,²

¹Laboratory of Atmospheric Physio-chemistry, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, 230031, Anhui, China
²Graduate School, University of Science and Technology of China, Hefei, 230026, Anhui, China
³Anhui Institute of Meteorology, Key Laboratory of Atmospheric Science and Satellite Remote Sensing, Hefei 230031, China

*Corresponding author’s e-mail: dengxueliang9989@aliyun.com (X. Deng)

Abstract: From December 26th to 28th, 2014, Beijing was hit by the regional severely polluted weather, during which the daily average mass concentration of PM₂.₅ was three times that of non-polluted days. Water-Soluble Organic Carbon (WSOC) concentrations (6.8 μg C/m³) in the polluted day were four times that of the non-polluted day (1.7 μg C/m³). The high correlation between WSOC and Secondary organic carbon (SOC) indicated that WSOC and SOC shared similar source and formation mechanism. The high correlation between WSOC and biomass burning tracer (K⁺) indicated that biomass burning was an important source of WSOC in winter. This paper measures the light absorption intensity of water-soluble brown carbon on the average light absorption (Abs₃₆₅) of WSOC between 360nm and 370 nm. The absorption spectrum analysis of WSOC showed that Abs₃₆₅ ranged from 0.80-15.26 with an average of 3.7 Mm⁻¹. The AAE value was 3.42 with the fluctuation range between 1.8 and 7.7. The mean value of MAE was 1.87 m²/g, with no significant difference between day and night. The WSOCMAE in polluted days was 1.96 m²/g and in the non-polluted day was 1.86 m²/g. In general, the absorbance capacity of WSOC in the polluted days was greater than that in the non-polluted days.

1. Introduction

The carbonaceous aerosol, which mainly includes organic carbon (OC) and elemental carbon (EC) [1], is an important component of atmospheric particulate matter. OC can be further divided into water-soluble OC (Water-Soluble Organic Carbon, WSOC) and non-water-soluble OC (Water-Soluble Inorganic Carbon, WSIC), in which the former accounts for 20% to 70% of atmospheric organic carbon (OC)[2]. The latter, WSOC, can absorb sunlight, promote the formation of clouds, and change the hygroscopic properties of aerosols, thus affecting the formation of cloud condensation nuclei (CCN) and climate change [3]. Different studies have provided evidence that WSOC is closely related to SOA (Secondary Organic Aerosol, SOA) and that WSOC in atmospheric aerosols is mainly derived from biomass combustion and secondary reactions of gaseous precursors. The result concerning WSOC is consistent with that of other research using SOA methods [4]. For example, the correlation coefficient of SOC and WSOC calculated using the OC/EC minimum ratio method in winter and summer in Tokyo is 0.75 and 0.79, respectively [5]. Carlton et al. [6] estimated the secondary organic

---

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Published under licence by IOP Publishing Ltd
aerosol (SOA) based on the OC/EC minimum ratio method, pointing out that the correlation between WSOC and SOA and inorganic ions, while that between WSOC and EC is relatively poorer, indicating that WSOC is mainly derived from secondary production.

Some organic components in WSOC can also lead to light absorption, which are called “Brown Carbon” [7]. However, the light absorption intensity and properties of water-soluble brown carbon and the relationship between it and the source have not been fully studied. Some traditional optical instruments fail to effectively distinguish the light absorption of black carbon and brown carbon in the particles. Therefore, separating the organic carbonaceous component from the elemental carbon using solvent extraction in order to conduct analysis on the light absorption characteristics of the organic carbon component has accepted as a means of studying brown carbon [8]. In order to avoid interference of the inorganic component with light absorption, this paper uses the light absorption average (Abs$_{365}$) between 360nm and 370 nm to indicate the light absorption of the water-soluble brown carbon. The absorbing capacity of water-absorbing brown carbon in Beijing is stronger light than that in upper air in Atlanta, US, Kosan, South Korea, and the Indian Ocean, equivalent to that in Los Angeles, US [9]. In addition, the absorption capacity of water-soluble brown carbon is weaker than that of methanol-extracted brown carbon [10], which may be related to the chemical composition or structure of different solvent-extracted organics. Therefore, it is of both great theoretical and practical significance to study the pollution characteristics of water-soluble organic carbon in polluted days and non-polluted days in Beijing.

2. Materials and methods

2.1 Sampling location and method

The samples were taken in the campus of the Chinese Academy of Sciences in Huairou County, Beijing (40°24’24.45”N, 116°40’32.95”E), about 60 kilometers northeast to the center of Beijing. G11 national highway with a large traffic volume is about 80 meters east to the sampling location and there are no obvious sources of industrial pollution around the sampling location. Samples (diameter of 81 mm, quartz filter) were collected using a PM$_{1.0}$ sampler, twice a day (from 08:30 to 20:30 and 20:30-8:30 Beijing time). Each collection lasted for 12 hours, and a total of 14 samples were collected.

2.2 Chemical composition analysis

2.2.1 OC/EC. The mass concentration analysis of OC and EC was conducted by adopting TOR method, and the thermo-reflective carbon analyzer. The pyrolysis temperature rising was conducted using IMPROVE-A plan (sample is heated in 4 stages in pure helium atmosphere (140 °C, 280 °C, 480 °C, 580 °C) to pyrolyze organic carbon materials, and then oxidize the carbon element in the environment of 2% oxygen and 98% helium in 3 stages (580 °C, 740 °C, 840 °C). A 1.5 m$^2$ circular filter was taken from the sampling filter for OC/EC analysis.

2.2.2 Water-soluble organic carbon. The WSOC in PM$_{1.0}$ was measured using the Sievers 900 Total Organic Carbon (TOC) supplied by GE. Before analysis, take a 1.5 cm$^2$ patch at the center of the sampling membrane, place it in a PP bottle, and add 20 ml of deionized water. After sonication for 40 minutes, filter it into a PP bottle using a 0.22 um PTF water filter.

2.2.3 Water soluble ions. The ICS-90 ion chromatograph produced by DIONEX, USA to analyze nine water-soluble ions (four anions: NO$_3^-$, SO$_4^{2-}$, F $^-$, Cl$^-$; five cations: NH$_4^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$) [11]. The cation was detected using Ionpac CS12A 4×250 mm separation column, CSRS 300-4mm suppressor, the eluent of 22 mmol/L methanesulfonic acid MSA; anion detection used Ionpac AS14A 4×250 mm separation column, ASRS 300-4mm suppressor and the eluent of the mixed solutions of 3.5 mmol/L Na$_2$CO$_3$ and 1 mmol/L NaHCO$_3$ with a mixing flow rate of 0.3 ml/min. Before analysis, a standard curve was required with the correlation coefficient reaching ≥0.999; otherwise, remake a
standard curve.

2.3 Absorption spectrum of water-soluble organic carbon

2.3.1 LWCC. The absorption spectrum of WSOC was analyzed using the Liquid Waveguide Capillary Cell (LWCC). The extract subjected to absorption spectrum analysis is the same as that for extracting water-soluble organic carbon. The LWCC-2100 was supplied by an American company called World Precision Instrument.

2.3.2 Data processing. According to Beer's Law, the light absorption $A_{\lambda}$ is the negative logarithm of the ratio of the projected light $I$ to the incident light $I_0$.

$$A_{\lambda} = -\log_{10}\left(\frac{I}{I_0}\right)$$ (1)

$\lambda$ refers to a specific wavelength; $A_{\lambda}$ the light absorption intensity of the final WSOC obtained at the corresponding atmospheric concentration; $A_\lambda$ refers to the amount of light absorption at wavelength $\lambda$; $A_{700}$ is the mean value of light absorption between 695 nm and 705 nm; $V_i$ is the volume of deionized water during extraction; $a_i$ the extracted membrane area; $V_0$ is the sample volume.; $I$ is the optical path; $A_{360}$ is the mean light absorption between 360 nm and 370 nm; $A_{365} = K_\lambda^{AAE}$. Absorption AAE (Absorption Angstrom exponent) refers to the absorption wavelength index. In order to compare the difference in light absorption capacity of water-soluble organic carbon between different samples, this study introduces the concept of Mass Absorption Efficiency (MAE). $\text{MAE}_{\text{WSOC}}$ refers to the mass absorption efficiency of WSOC at 365 nm wavelength, while $c_{\text{WSOC}}$ refers to the water-soluble organic carbon concentration (m$^2$/g).

$$A_{\lambda} = (A_{\lambda} - A_{700}) \frac{V_i a_i}{V_0 a_i} \ln(10)$$ (2)

$$\text{MAE}_{\text{WSOC}} = \frac{A_{365}}{c_{\text{WSOC}}}$$ (3)

2.4 Meteorological data
This study uses date covering ambient air pollutant concentration, surface meteorological data, and PM$_{2.5}$ quality. The pollutant data were taken from the hourly concentration information of PM$_{10}$, PM$_{2.5}$, O$_3$, SO$_2$, NO$_2$ and CO released by the China Urban Environmental Monitoring Center (http://106.37.208.233:20035/). The average concentration of PM$_{2.5}$ exceeded the daily average concentration standard (75 μg/m$^3$) specified in the Ambient Air Quality Standard (GB 3095-2012). Therefore, in this paper, the sampling days are divided into non-polluting days (PM$_{2.5} < 75$ μg/m$^3$) and polluted days (PM$_{2.5} \geq 75$ μg/m$^3$).

3. Results and discussion

3.1 Introduction to the heavy pollution incident
From December 24 to 30, 2014, a regional pollution process occurred in Beijing, lasting for 7 days. The hourly time series of meteorological parameters, gaseous pollutant concentrations, and PM$_{2.5}$ mass concentrations during observation are shown in Figure 1. Based on the daily average concentration of PM$_{2.5}$, the process can be divided into polluted days (PM$_{2.5} \geq 75$ μg/m$^3$) and non-polluted days (PM$_{2.5} < 75$ μg/m$^3$).
Figure 1. Hourly time series of meteorological parameters, gaseous pollutant concentration and PM$_{2.5}$ mass concentration during the observation period

From the perspective of three development process of pollutants, the process can be divided into three stages: (1) December 24th to 25th: pollutant development stage. With the gradual accumulation of pollution, the average concentration of PM$_{2.5}$ reached 26.70 μg/m$^3$, with the average wind speed of 1.32 m/s. (2) December 26th to 28th: pollution maintenance stage. As the temperature dropped and the humidity rose, the weak weather system featuring low temperature and high humidity pushed the pollutants to gradually accumulate and transform under inversion. The daily average PM$_{2.5}$ concentration during the second stage was 112.56 μg/m$^3$, which was significantly improved compared with the first stage. The wind speed slowed down with the average wind speed of 0.79 m/s, and the fluctuation range of 0.40-0.94 m/s. At 3:00 on December 26th, the wind speed dropped to the bottom of 0.40 m/s during the period. The pollution on the 27th was the most serious, with a maximum concentration of PM$_{2.5}$ reaching 238.56 μg/m$^3$, and the concentration of PM$_{2.5}$ on polluted days about three times that of non-polluted days. The average temperature during the pollution period was relatively low (-1.2 °C), while the relative humidity of the polluted day (46%) was 1.6 times that of the non-polluted day. In general, during the pollution period, the surface wind speed was relatively lower with lower temperature, larger relative humidity, and weaker atmospheric level diffusion ability, which was conducive to the formation and maintenance of pollution. 3) December 29th to 30th: pollution dissipation stage. The concentration of PM$_{2.5}$ dropped to 31.43 μg/m$^3$, while both temperature and relative humidity rose to some extent, thus reaching the end of the whole process. The concentration of SO$_2$, NO$_2$, CO and O$_3$ of the polluted days were 39.33, 72.93, 2.28 and 10.42 μg/m$^3$, respectively, 5.1, 2.7, 4.0 and 0.3 times of that of the non-polluting days. SO$_2$, NO$_2$ and CO mainly came from coal, mobile and industrial exhaust emissions.

3.2 Comparison of WSOC change under different pollution levels

As shown in Table 1, the average mass concentration of WSOC during the whole sampling period was 3.54 μg C/m$^3$. The peak value (9.20 μg C/m$^3$) occurred in the daytime on December 27th, 2014 while the lowest value (0.59 μg C/m$^3$) occurred in the daytime of December 30th, 2014. The WSOC concentration (5.53 μg C/m$^3$) in the polluted days was 3.6 times that of the non-polluted days.

Table 1. Mass concentration and ratio of WSOC/OC, OC/EC and WSOC/EC on polluted and non-polluted days OC (μg/m$^3$), EC (μg/m$^3$), WSOC (μg C/m$^3$)

|                | OC  | EC  | WSOC | WSOC/OC | OC/EC | WSOC/EC |
|----------------|-----|-----|------|---------|-------|---------|
| None-Polluted Days | 3.88| 0.52| 1.55 | 0.41    | 7.77  | 3.19    |
| Polluted Days     | 14.65| 1.62| 5.53 | 0.38    | 8.82  | 3.35    |
3.2.1 WSOC and OC, EC, SOC. Since EC mainly comes from combustion, it is often used as a tracer of organic carbon [12]. Therefore, OC/EC ratio can be used to distinguish the source of the carbon-containing aerosol and the generation of the secondary aerosol. Generally speaking, if the OC/EC ratio exceeds 2, there are secondary organic carbon aerosols in the atmosphere. All the ratios of OC/EC in this observation exceeded 2 (7.7 in non-polluted days and 8.82 in polluted days), indicating that SOC is one of the main causes for polluted days. Figure 2 shows how WSOC/EC, WSOC/OC, WSOC/WIOC, and OC/EC change with time. The correlation coefficients (R) of WSOC with OC, EC and SOC are listed in Table 2. The WSOC/OC fluctuation ranged between 0.36 and 0.48. WSOC had a good correlation with OC (R=0.95), which also has been approved by abundant literatures [13].

Table 2. Correlation coefficient (R) between OC, EC, WIOC, SOC, Ammonium, Nitrate, Sulfate and WSOC

|       | OC   | EC   | WIOC | SOC  | Nitrate | Sulfate | Ammonium |
|-------|------|------|------|------|---------|---------|----------|
| WSOC  | 0.95 | 0.52 | 0.74 | 0.82 | 0.65    | 0.81    | 0.63     |

This paper uses the OC/EC minimum ratio method in EC tracer method to estimate SOC (Secondary Organic Carbon). The formula is as follows:

\[
P_{OC} = EC \times (OC/EC)_{min} \tag{4}
\]

\[
SOC = OC - P_{OC} \tag{5}
\]

(OC/EC)\textsubscript{min} refers to the observed minimum OC/EC ratio. The concentration of SOC in polluted days and non-polluted days were 1.32 µg/m\textsuperscript{3} and 4.56 µg/m\textsuperscript{3}, respectively. Since the concentration of SOC in polluted days is greater than that in non-polluted days, it can be inferred that the secondary generation of particulate matter is one of the main causes of pollution in Beijing in winter. It can be seen from Table 2 that WSOC and SOC have a high correlation (R=0.82). Meantime, the high correlation between WSOC and SOC indicates that WSOC and SOC share similar source and formation mechanism. The correlation between WSOC and EC (R=0.52) is lower than that between WSOC and OC, showing that the WSOC can be used as a good tracer for SOA.

Figure 2. Time series of WSOC/EC, WSOC/OC, WSOC/WIOC and OC/EC
3.2.2 *WSOC and water-soluble inorganic ions.* The mass concentration of $\text{SO}_4^{2-}$ during pollution was 7.24 μg/m³, while that of $\text{NO}_3^{-}$ was 5.02 μg/m³, and that in polluted days were 7 times and 4 times that of the non-polluted days, respectively. Sulfate and nitrate in the particles are mainly formed by the conversion of such gaseous precursors as $\text{SO}_2$ and $\text{NO}_x$ through a secondary reaction [14]. From the China’s emissions inventory study, the precursors of Sulfate mainly come from coal combustion, while the precursors of nitrates are mainly from the emissions of motor vehicles. Abundant studies have shown that the liquid phase reaction process is considered as the main way to form sulfate [15]. Table 2 shows the correlation between WSOC and secondary inorganic ions ($\text{SO}_4^{2-}$, $\text{NO}_3^{-}$ and $\text{NH}_4^{+}$). The correlation coefficient of WSOC and $\text{SO}_4^{2-}$ during sampling was 0.81. The high correlation between WSOC and secondary inorganic ions in winter may be the result of the similar source to sulfate and nitrate.

Due to the fact that the correlation between winter WSOC and $\text{Cl}^{-}$ was weak during sampling in Beijing (R=0.09) and $\text{Cl}^{-}$ is regarded as a tracker for coal combustion, coal combustion is not the main source of WSOC in Beijing in winter. In this study, WSOC had a good correlation with $\text{K}^{+}$ (R=0.59). Since Potassium ($\text{K}^{+}$) is widely recognized as a tracer of biomass burning, biomass burning is the main cause of high concentration of WSOC.

3.3 *Optical properties of water-soluble organic carbon*

3.3.1 *Changes of Abs$_{365}$ with time.* This paper measures the light absorption intensity of water-soluble brown carbon in the sample using the average light absorption intensity (Abs$_{365}$) of WSOC between 360 nm and 370 nm. Abs$_{365}$ ranged between 0.83 and 10.26 Mm$^{-1}$, with the average value of 4.62 Mm$^{-1}$. As shown in Figure 3, the mean value of Abs$_{365}$ in non-polluting days was 3.00 Mm$^{-1}$, while that in polluted days was 2.6 times that of the former (7.85 Mm$^{-1}$). Therefore, the light absorption of water-soluble brown carbon in the particles in polluted days may have a more significant impact on the climate and atmospheric photochemical reactions in Beijing. In addition, Abs$_{365}$ in polluted days showed a similar trend with WSOC, and a high correlation was found between them (R = 0.81), as shown in Figure 4, demonstrating that water-soluble brown carbon shares a similar source with WSOC.

![Figure 3. Abs$_{365}$ changes with wavelength](image-url)
Figure 4. Correlation between WSOC and light absorption intensity

3.3.2 AAE and MAE value of WSOC light absorption and MAE. The average AAE of WSOC in PM$_{1.0}$ samples in winter was 3.42, fluctuating from 1.8 to 7.7, with no significant change during sampling. Previous studies have shown that [16] the AAE values of aerosol water extracts in different seasons in Beijing are within 5.80-11.70. During this sampling process, the AAE values in polluted days and non-polluted days were similar, around 7, showing that the sampling time and location have little effect on the AAE value of WSOC.

Figure 5 shows the change of light absorption efficiency during sampling with time. In order to compare the difference in light absorption capacity of water-soluble organic carbon between different samples, this study introduced the concept of Mass Absorption Efficiency. The calculated MAE reflects the absorption capacity of WSOC, as shown in Figure 7. The mean value of WSOC$_{MAE}$ was 1.87 m$^2$/g, with no significant difference in day and night with that in the polluted day being 1.96 m$^2$/g and that in the non-polluted day being 1.86 m$^2$/g. In general, the absorption capacity of WSOC in polluted days is higher than similar to that in non-polluted days.
4. Conclusion
(1) The daily average mass concentration of PM$_{2.5}$ was three times that of non-polluted days and the WSOC concentration ($6.8 \mu g \text{ C/m}^3$) in PM$_{1.0}$ in the polluted day was 4 times that of the non-polluted days ($1.7 \mu g \text{ C/m}^3$). The average mass concentration of WSOC during the whole sampling period was $3.2 \mu g \text{ C/m}^3$, and WSOC had a good correlation with OC ($R=0.95$), with the WSOC/OC fluctuating between 0.36 and 0.48.

(2) WSOC and SOC had a high correlation ($R=0.82$). The concentration of SOC in polluted days was greater than that of non-polluted days, indicating that the source and formation mechanism of the two were similar (mainly from secondary generation). The high correlation between WSOC and biomass burning tracer ($K^+$) indicated that biomass burning is an important source of WSOC in these sampling days.

(3) The absorption spectrum analysis of WSOC showed that Abs$_{365}$ ranged from 0.80 to 15.26 with an average of 3.7 Mm$^{-1}$. The high correlation ($R = 0.81$) between Abs$_{365}$ and WSOC indicated that WSOC and water-soluble brown carbon in the winter of Beijing shared the similar source.

(4) The AAE value was 3.42, fluctuating from 1.8 to 7.7. The WSOC$_{\text{MAE}}$ in polluted days was 1.96 m$^2/g$, while that in non-polluted days was 1.86 m$^2/g$. In general, the WSOC absorbance capacity in polluted days was higher than that in non-polluted days during sampling days.

References
[1] Custodio, D., et al., A one-year record of carbonaceous components and major ions in aerosols from an urban kerbside location in Oporto, Portugal. Science of the Total Environment, 2016. 562: p. 822-833.
[2] Rengarajan, R., M.M. Sarin, and A.K. Sudheer, Carbonaceous and inorganic species in atmospheric aerosols during wintertime over urban and high-altitude sites in North India. Journal of Geophysical Research-Atmospheres, 2007. 112(D21).
[3] Feng, J.L., et al., Properties of organic matter in PM2.5 at Changdao Island, China - A rural site in the transport path of the Asian continental outflow. Atmospheric Environment, 2007. 41(9): p. 1924-1935.
[4] Saffari, A., et al., Nighttime aqueous-phase secondary organic aerosols in Los Angeles and its implication for fine particulate matter composition and oxidative potential. Atmospheric Environment, 2016. 133: p. 112-122.
[5] Miyazaki, Y., et al., Chemical charaterization of water-soluble organic carbon aerosols at a rural site in the Pearl River Delta, China, in the summer of 2006. Journal of Geophysical Research-Atmospheres, 2009. 114.
[6] Carlton, A.G., C. Wiedinmyer, and J.H. Kroll, A review of Secondary Organic Aerosol (SOA) formation from isoprene. Atmospheric Chemistry and Physics, 2009. 9(14): p. 4987-5005.
[7] Srinivas, B. and M.M. Sarin, Brown carbon in atmospheric outflow from the Indo-Gangetic Plain: Mass absorption efficiency and temporal variability. Atmospheric Environment, 2014. 89: p. 835-843.
[8] Li, M.J., et al., Abundance and Light Absorption Properties of Brown Carbon Emitted from Residential Coal Combustion in China. Environmental Science & Technology, 2019. 53(2): p. 595-603.
[9] Cheng, Y., et al., Mass absorption efficiency of elemental carbon and water-soluble organic carbon in Beijing, China. Atmospheric Chemistry and Physics, 2011. 11(22): p. 11497-11510.
[10] Zhang, X.L., et al., Sources, Composition and Absorption Angstrom Exponent of Light-absorbing Organic Components in Aerosol Extracts from the Los Angeles Basin. Environmental Science & Technology, 2013. 47(8): p. 3685-3693.
[11] Sasaki, K. and K. Sakamoto, Diurnal characteristics of suspended particulate matter and PM2.5 in the urban and suburban atmosphere of the Kanto Plain, Japan. Water Air and Soil Pollution, 2006. 171(1-4): p. 29-47.
[12] Hecobian, A., et al., Water-Soluble Organic Aerosol material and the light-absorption characteristics of aqueous extracts measured over the Southeastern United States. Atmospheric Chemistry and Physics, 2010. 10(13): p. 5965-5977.

[13] Ye, Z.L., et al., Chemical characterization of fine particulate matter in Changzhou, China, and source apportionment with offline aerosol mass spectrometry. Atmospheric Chemistry and Physics, 2017. 17(4): p. 2573-2592.

[14] Horng, C.L., M.T. Cheng, and W.F. Chiang, Distribution of PM2.5 and gaseous species in central Taiwan during two Chinese festival periods. Environmental Engineering Science, 2007. 24(4): p. 515-524.

[15] Wang, G.H., et al., Evolution of aerosol chemistry in Xi'an, inland China, during the dust storm period of 2013-Part 1: Sources, chemical forms and formation mechanisms of nitrate and sulfate. Atmospheric Chemistry and Physics, 2014. 14(21): p. 11571-11585.

[16] Lim, S., et al., Absorption and scattering properties of organic carbon versus sulfate dominant aerosols at Gosan climate observatory in Northeast Asia. Atmospheric Chemistry and Physics, 2014. 14(15): p. 7781-7793.