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Chemical Characteristics and Sources of Water-Soluble Organic Nitrogen Species in PM_{2.5} in Nanjing, China

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Abstract: Water-soluble organic nitrogen (WSON) is an important component of PM_{2.5} which may affect air quality, climate and human health. Herein, one-year field samples of atmospheric PM_{2.5} (June 2017–May 2018) were collected in northern Nanjing. Chemical characterization of PM_{2.5} major components as well as WSON were conducted, and WSON composition and sources were further investigated via measurements by a Aerodyne soot particle aerosol mass spectrometer (SP-AMS) as well as positive matrix factorization (PMF). Inorganic ions, mainly consisting of ammonium, sulfate, and nitrate, were found to dominate PM_{2.5} mass (58.7%), followed by organic matter (OM) (22.6%), and elemental carbon (EC) (2.1%). Water-soluble OM dominated OM (65.1%), and its temporal variation was closely correlated with that of secondary organic matter, while time series of water-insoluble OM concentrations correlated tightly with that of primary organic matter. Average WSON concentration was 2.15 µg/m³, which was highest in winter and lowest in summer. Correlation analysis of WSON with PM_{2.5} components also indicated that WSON was mainly from secondary sources. SP-AMS revealed that WSON mass spectrum was composed of C_xH_yN_p⁺ (91.2%) and C_xH_yO_zN_p⁺ (8.8%), indicating dominance of amines and other oxygenated ON compounds. PMF analysis resolved two primary sources (traffic, biomass burning) and two secondary sources (less-oxidized and more-oxidized factors) of WSOM and WSON, and the secondary source dominated both WSOM and WSON. Contribution of the more-oxidized ON factor was very high in winter, and the less-oxidized factor was significant in summer, indicating a likely important role of aqueous-phase processing in winter as well as photochemical oxidation in summer to WSON.

Keywords: organic nitrogen; mass spectra; aqueous-phase oxidation; source apportionment

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1. Introduction

The nitrogen-containing components such as nitrate (NO₃[−]), ammonium (NH₄⁺), and especially organic nitrogen compounds in aerosols are chemically important, and they also possess potential toxicity [1]. Atmospheric organic nitrogen (ON) species can be present in gaseous, aqueous, or particulate phases [2–4]. Water-soluble organic nitrogen (WSON) makes up a significant fraction of total nitrogen (TN) and can account for approximately 68% WSTN [1,5–10]. WSON species are also an important contributor to light absorption in near-UV regions [11,12], and therefore might have considerable effects on solar radiative balance; WSON can affect terrestrial and aquatic ecosystems through dry and wet deposition [13].

Sources of ON include both natural and anthropogenic ones. Nitrogen in biological particulate matter such as bacteria, dust, and pollen, is emitted into the atmosphere in large quantities [14,15]. The ON species released by the degradation of microorganisms and biological metabolism in animals and plants can contribute significantly to airborne ON [16].

It has been suggested that amines and amino acids released from the fragmentation of bubbles at the surface of ocean become an important natural ON source [17,18]. Fossil-fuel combustion, biomass burning, and widespread usage of nitrogen-based fertilizer in agricultural regions can be an important source of WSON [19–21], resulting from both direct emission and secondary production of emitted volatile or semi-volatile organic compounds in related plumes [5]. The low temperature reaction of soot with NO_x and NH_3 can also produce ON [1]. In recent years, studies on isoprene derivatives of nitrate and sulfate have shown that oxidation of isoprene is an important source of ON [22], which is particularly evident in summer. Secondary organic aerosols (SOA) can further react with NH_3 or ammonium to form light absorbing nitrogen-containing substances, thus affecting the optical properties of aerosols [23]. A previous study shows that WSON was found to mainly exist in fine particles (size $< 1.9 \mu\text{m}$) and biogenic hydrocarbons served as dominant precursors of secondary WSON in summer, while coarse particulate WSON (size $> 1.9 \mu\text{m}$) was attributed from primary biological emissions in the autumn-winter seasons [24].

WSON can play an active role as hydrogen acceptor and transfer in the redox reaction cycle to generate reactive oxygen species [25]. Then, the photochemical oxidation under the presence of hydrocarbons and NO_x (NO and NO_2) can facilitate the formation of WSON in the atmosphere [26]. Besides, ON acts as the reactive nitrogen carriers such as in the formation of acetyl nitrate peroxide (PAN) and alkyl nitrate (RONO_2). Peroxyacetyl nitrates have strong oxidizing capability, which can enhance the oxidation ability of the atmosphere and have a great impact on gaseous photochemical reaction, therefore alter the chemical composition of aerosols. The amino group of ON species has an effect on the hygroscopicity and composition of particles too [27]. Kieber et al. [28] proposed that the formation of marine humus by photochemical oxidation of fatty acids and ammonia, accompanied by the formation of complex organic components of reduced nitrogen, may also occur in the atmosphere. It has been confirmed that the reduced nitrogen will be oxidized and degraded to oxidized ON in the air [1,5]. In addition, NO_x in the atmosphere can react with polycyclic aromatic hydrocarbons (PAHs) to form nitro-PAHs, nitrophenol [29] and other ON compounds, etc. [29,30]. In addition, gaseous nitric acid can react with coarse sea salt aerosols or terrestrial air, and the generated non-volatile sodium nitrate is transferred from fine particles to coarse particles [31,32].

Severe haze (or $\text{PM}_{2.5}$ pollution) events still occur in the Yangtze River Delta (YRD) region, a densely populated and developed region in China. However, chemical characteristics and source profiles of $\text{PM}_{2.5}$ ON in the YRD region are rarely investigated. Previously, we have investigated $\text{PM}_{2.5}$ WSON concentrations and its seasonal variations in Yangzhou [33]. In this study, one-year of daily $\text{PM}_{2.5}$ samples were collected from June 2017 to May 2018 in the northern suburban area of Nanjing, and concentrations of $\text{PM}_{2.5}$ major components and their correlation with WSON were investigated. The Aerodyne soot particle aerosol mass spectrometer (SP-AMS) [34,35] was used to characterize the composition of WSON. Therefore, compared with most previous literature that mainly report WSON level and its temporal variation, this work further elucidates the mass spectral features as well as the major chemical classes of WSON, and more importantly, quantifies mass contributions of primary and secondary sources to WSON, and in particular, the different roles of gaseous and aqueous-phase oxidation on secondary formation of WSON. Overall, our findings provide valuable insights into $\text{PM}_{2.5}$ WSON chemistry and its effective control in this region.

2. Experiments

2.1. $\text{PM}_{2.5}$ Sample Collection

The sampling site was set inside the campus of Nanjing University of Information Science and Technology (32.21°N , 118.72°E), locating in northern suburban Nanjing (Figure 1). Details of this site can be found in Wang et al. [36]. A total of 260 daily $\text{PM}_{2.5}$ samples were collected on quartz fiber filters (Pall Life Science, Port Washington, NY, USA) using a high volume $\text{PM}_{2.5}$ sampler (model 2031, Qingdao Laoying Ltd., Qingdao,

China) with a flow rate of $1.05 \text{ m}^3 \cdot \text{min}^{-1}$. The sampling period was a full year from 1 June 2017 to 30 May 2018. Meteorological parameters including temperature, relative humidity (RH), wind speed, and wind direction were simultaneously recorded by an automatic meteorological station in the sampling site. The $\text{PM}_{2.5}$ concentration on each filter was measured gravimetrically using a digital balance (DV215CD, OHAUS, NJ, USA, precision 0.01 mg) at RH of 45% and room temperature. All filters were sealed and stored at -18°C in a refrigerator until analysis.

Figure 1. Location of the sampling site in suburban Nanjing and its surroundings.

2.2. Chemical Analyses

The organic carbon (OC) and elemental carbon (EC) contents in each $\text{PM}_{2.5}$ sample were measured by a RT-4 carbon analyzer (Sunset Lab, Hillsborough, NC, USA) through a punch of each filter (2.27 cm^2). Four punches (diameter of 10 mm) of each filter were sonicated in 40 mL ultrapure water (EPED-E2-20 TJ, Nuoding Instrument, Shanghai, China) for 20 min and the filtrate was obtained via a 0.45 mm PTEE syringe filters (SCAA-213, ANPEL, Shanghai, China). The water-soluble OC (WSOC) and WSTN concentrations were determined by using a TOC/TN analyzer (TOC-L, Shimadzu, Tokyo, Japan). Water-soluble inorganic ions (WSIIs) including SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , K^+ , Ca^{2+} , Na^+ , and Mg^{2+} were measured by using ICS-2000 and ICS-3000 ion chromatographs (Thermo Dinoex, Ramsey, MN, USA). More details regarding instrument and operations can be found in our previous work [33].

Particularly, in this work, the chemical speciation and source apportionment of WSON were fulfilled via the SP-AMS measurement. The laser vaporizer of SP-AMS was removed and therefore the instrument was used to measure non-refractory species in the filter extracts. Such offline AMS technique has been developed in our group and applied successfully on ambient $\text{PM}_{2.5}$ water extracts [37,38] and other liquid samples [39–44]. Briefly, the aqueous solution of filter extract was drawn into an atomizer and nebulized into mist by the carrier Argon gas, the mist passed through a diffusion dryer filled with silica gel to remove moisture and leave dry particles to be loaded into the SP-AMS for analyses. The particles were first evaporated by a 600°C vaporizer and then impacted by 70 eV electron and ionized into ion fragments, the SP-AMS then outputted the mass spectrum based on the mass-to-charge (m/z) ratios of all fragments. The chemical features of water-soluble OM (WSOM) as well as WSON can therefore be investigated via mass spectral analyses.

2.3. Data Analyses

Mass concentrations of OC, EC, WSOC, WSON and ionic species were determined based on the calibration curves of corresponding instruments. The water-soluble inorganic nitrogen (WSIN) concentration was obtained from the sum of nitrogen masses in nitrate

(NO_3^-) and ammonium (NH_4^+), and then the WSON concentration found as the difference between WSTN and WSIN (Equation (1)):

$$\text{WSON} = \text{WSTN} - \text{WSIN} \quad (1)$$

The atomic nitrogen-to-carbon (N/C) ratio (denoted as $\text{N}/\text{C}_{\text{AC}}$) that represents the relative abundance of ON in OM can be calculated according to Equation (2):

$$\text{N}/\text{C}_{\text{AC}} = (\text{WSON}/14)/(\text{WSOC}/12) \quad (2)$$

The SP-AMS data were processed by a standard data analysis package (SQUIRREL version 1.56D and PIKA version 1.15D, written by Igor Pro. (Wave Metrics, Portland, OR, USA) [45]. Elemental ratios including oxygen-to-carbon (O/C) ratio, hydrogen-to-carbon (H/C) ratio and more importantly nitrogen-to-carbon (N/C) ratio (denoted as $\text{N}/\text{C}_{\text{AMS}}$) can be calculated by using the methods proposed by Canagaratna et al. [46] and Aiken et al. [47]. The organic matter to organic carbon ($\text{OM}/\text{OC}_{\text{AMS}}$) ratio can thus be obtained, and WSOM and WIOM concentrations are calculated via Equations (3) and (4):

$$\text{WSOM} = \text{WSOC} * (\text{OM}/\text{OC})_{\text{AMS}} \quad (3)$$

$$\text{WIOM} = (\text{OC} - \text{WSOC}) * 1.3 \quad (4)$$

Here 1.3 is an empirical factor to convert water-insoluble OC (WIOC) to WIOM [48]. Other terms, including primary OC (POC), secondary OC (SOC) and primary OM (POM) and secondary OM (SOM) can be calculated according to Equations (5)–(8):

$$\text{POC} = \text{EC} * (\text{OC}/\text{EC})_{\text{pri}} \quad (5)$$

$$\text{SOC} = \text{OC} - \text{POC} \quad (6)$$

$$\text{POM} = \text{POC} * 1.2 \quad (7)$$

$$\text{SOM} = (\text{WSOM} + \text{WIOM}) - \text{POM} \quad (8)$$

Here $(\text{OC}/\text{EC})_{\text{pri}}$ is typically the minimum value among all samples, representing the OC/EC ratio for primary organics.

2.4. Source Apportionment of WSOM and WSON

Positive matrix factorization (PMF) [49] was conducted on the high-resolution AMS dataset of WSOM [37,50]. Prior to the PMF analysis, ions with a signal-to-noise ratio (SNR) lower than 0.2 were removed, and those with SNR between 0.2 and 2 were properly downweighted; all isotopic ion signals were removed from the matrix because they were not directly measured. Some outliers in the data matrix were also downweighted to minimize their influence on PMF results. Only ions with m/z less than or equal to 120 were included in the analysis since large m/z ions have limited chemical resolutions. We analyzed WSOM here therefore fragments from inorganic species were not included. Following the protocol documented in Zhang et al. [51], we critically evaluated the PMF solutions with different number of factors, and finally a four-factor solution was chosen as the best solution. The four resolved factors include a hydrocarbon-like OA (HOA), a biomass burning OA (BBOA), a low oxygenated OA (LO-OOA), and a more oxygenated OA (MO-OOA). Source apportionment of WSON was then performed via analysis of the ON ions contained in these four WSOM factors.

3. Results and Discussion

3.1. Overview of $\text{PM}_{2.5}$ Concentration and Composition

As shown in Figure 2a, the annual $\text{PM}_{2.5}$ mass concentration was determined to be $75.69 (\pm 34.12)$ (mean $\pm$ one standard deviation) $\mu\text{g}\cdot\text{m}^{-3}$. In term of composition, inorganic ions dominated $\text{PM}_{2.5}$ mass (58.7%), followed by organics (22.6%) and EC (2.1%).

16.6% species that were not identified, likely including carbonate, metals, water, etc. Note the PM_{2.5} compositional structure in Nanjing determined here is generally similar to those observed in Yangzhou [37] and Changzhou [52] by our group previously, indicating a consistent regional aerosol characteristic in the YRD region.

Figure 2. Percentage of chemical composition of PM_{2.5} (a), mass contributions of individual ions in total ions (b), and WIOM and WSOM (c), and POM and SOM (d) in total OM.

The annual average concentration of total ionic species was $44.40 (\pm 18.51) \mu\text{g}\cdot\text{m}^{-3}$, ranging from 11.04 to $98.91 \mu\text{g}\cdot\text{m}^{-3}$. Concentrations of different ions followed an order of $\text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{Cl}^- > \text{K}^+ > \text{Mg}^{2+}$; the majority was so-called SNA, including sulfate (34.5%), nitrate (30.7%) and ammonium (16.4%) (Figure 2b). Again, such result was similar to that found in Yangzhou [33]. Besides SNA, Ca^{2+} also occupied a notable fraction of total ions (9.5%) probably owing to the intense municipal construction activities around the site during the sampling period.

Regarding the organic matter (OM), as shown in Figure 2c,d, WSOM dominated over WIOM (65.1% versus 34.9%), while SOM fraction exceeded POM (68.5% versus 31.5%). Further correlation analyses in Figure 3 demonstrated good linear correlations between WSOM and SOM ($r = 0.98$) and between WIOM and POM ($r = 0.94$), respectively. As SOM mass was a bit larger than that of WSOM (68.5% versus 65.1%), this finding reveals that most secondarily formed organic species are hygroscopic, and water-insoluble species was mostly from primarily emitted species. This is consistent with POM, for example from combustion sources, often contains a large amount of non-polar molecules such as PAHs and hydrocarbons. Nevertheless, a recent study [53] reveals that under very humid conditions slightly soluble POM species can chemically converted into SOM species. This process perhaps explains why SOM/WSOM concentrations were larger than those POM/WIOM observed here.

Figure 3. Linear regression analyses between WSOM and SOM (a) and between WIOM and POM (b).

Figure 4 illustrates seasonal variations of the $PM_{2.5}$ components. Overall, concentrations of $PM_{2.5}$ and its components including ions, OM and EC all peaked in winter, followed by spring, autumn and summer. This pattern is in agreement with the national average seasonal variation of $PM_{2.5}$ concentrations in China in 2018 [54]. The adverse ground-based meteorological conditions in winter are the main influencing factor to the degradation of air quality, during which the temperature inversions occur most frequently and thus the temperature and airflow remain relatively low and stable compared to other seasons. For some individual ionic species, however, the seasonal patterns might be different. Sulfate concentration varied slightly over the year and was highest in spring and lowest in autumn; its summer level was even higher than that in winter. Ca^{2+} concentration in spring was also higher than it in winter, likely reflecting influence of dust. Ammonium and nitrate concentrations follow the general pattern of $PM_{2.5}$, but the nitrate mass loading was significantly low in summer, and its thermodynamic gas/particle partitioning under high temperature might be a key factor [55]. For OM, seasonal variations of its subcomponents (WSOM, WIOM and SOM and POM) all matched that of $PM_{2.5}$, in an order of winter, spring, autumn and summer.

Figure 4. Seasonal variations in mass concentration of $PM_{2.5}$ and different components (a), ionic species (b) and organic matter (OM) (c).

The mass ratio of NO_3^-/SO_4^{2-} can reflect relative contributions from mobile and stationary sources [56]. Here the annual average NO_3^-/SO_4^{2-} ratio in Nanjing was determined to be 0.94 (Figure 5a), indicating that both vehicle and coal combustion emissions are important sources of $PM_{2.5}$ in Nanjing. The ratio was highest in winter (1.35) and lowest in summer (0.49). Except for changes in emission source of precursors (NO_2 and SO_2) and associated formation processes, particulate nitrate concentration is more significantly affected by meteorological conditions (temperature and RH) in different seasons than sulfate due to their different volatilities.

Figure 5. Seasonal distribution of (a) mean mass concentrations of $\text{NO}_3^-/\text{SO}_4^{2-}$ and (b) OC/EC ratios.

On the other hand, EC is mostly emitted from primary combustion source, while OC is from both primary and secondary sources, therefore OC/EC value is also often used as an indicator of relative contributions from primary and secondary sources [57,58]. In this work, the campaign-averaged OC/EC ratio was 6.23 (Figure 5b), indicating an overall remarkable contribution from secondary formation to the OM in Nanjing, in line with Figure 2d. Note the ratio was also notably high in winter (7.41) and lower in summer (5.01), indicating more secondary organics generated in winter than in other seasons. Sources of the water-soluble portion of OM are discussed in details in Section 3.3.2.

3.2. Characteristics of WSON

3.2.1. Seasonal Variations of WSON and WSTN Concentrations

Figure 6a,b illustrate the annual and seasonal average concentrations of WSTN and WSON, respectively. The annual average WSTN and WSON concentrations was $10.88 (\pm 6.30) \mu\text{g}\cdot\text{m}^{-3}$ and $2.15 (\pm 2.33) \mu\text{g}\cdot\text{m}^{-3}$, respectively. Such WSON levels are comparable to those reported in Yangzhou ($1.71 \mu\text{g}\cdot\text{m}^{-3}$) [33], but significantly lower than a study in Xi'an [59], conducted more than a decade ago. Compared with observations in some US and Japan sites [33], the WSON level here in Nanjing is typically much higher. Seasonal patterns of both WSTN and WSON concentrations were similar to that of $\text{PM}_{2.5}$, that was in the order of winter, spring, autumn and summer. WSON concentrations were very low in summer ($0.33 \mu\text{g}\cdot\text{m}^{-3}$), likely due to reduction of emission sources. Favorable meteorological conditions in summer may also help pollutant dispersion and therefore WSON reduction. The WSON concentrations showed negative correlations with daily average temperatures (Pearson's coefficient $r = -0.38$) and wind speed ($r = -0.26$) (not shown here); while on average, summer had relatively higher temperature and wind speed than those in other seasons (mean temperatures of 16.9°C , 26.5°C , 17.5°C and 4.4°C , mean wind speeds of 1.38 m/s , 1.54 m/s , 1.31 m/s and 1.18 m/s , in spring, summer, autumn and winter). The WSON concentrations, however, presented no correlation with RH ($r = 0.01$), consistent with previous studies [60,61]. It should be noted that, WSON concentrations in some samples were calculated to be negative, especially in summer. This is likely because WSON loading was indeed below detection limit. Of course, measurement uncertainties might also influence the results when using Equation (1), especially when both WSTN and WSIN concentrations were low (since uncertainty of WSTN or WSIN may be larger than WSON). Nevertheless, samples with negative WSON samples were less than 6% of total samples therefore influence was small; their values were assumed to zero in the following analyses. On the other hand, the maximum WSON concentration ($13.57 \mu\text{g}\cdot\text{m}^{-3}$) appeared in winter, on 23 December 2017.

Figure 6. Seasonal variation of WSTN concentration (a); Seasonal variation of WSON concentration (b); Contribution of nitrogen-containing components (NO₃⁻-N, NH₄⁺-N and WSON) in PM_{2.5} (c); Seasonal variation of N/C_{AC} (d).

Fractional contributions of WSON and other forms of WSIN to WSTN are shown in Figure 6c. The annual average WSON/WSTN was 19.8%. The contributions in winter (25.1%), spring (23.8%) and autumn (23.4%) were similar, but the value in summer (4.7%) was much lower than in other seasons. As demonstrated in Figure 5, sulfate concentration was much higher in summer than nitrate, therefore more ammonium are needed to neutralize sulfate rather than nitrate in summer than in other seasons; therefore even though nitrogen contributions from nitrate to WSTN (~20%) in summer was comparable to other seasons, the WSON contributions were decreased significantly due to increased contribution from ammonium (~75%). Figure 6d shows the annual and seasonal average N/C_{AC} values. The yearly mean value was 0.35, and in winter it was up to 0.52. Overall, this result demonstrate an overall abundance of ON species in the OM in Nanjing. However, the ratio was quite low in summer (0.06), indicating that ON is relatively not a significant PM_{2.5} component in summer compared to other seasons.

3.2.2. Relationships of WSON with PM_{2.5} Components

We further investigated the correlations of WSON with different PM_{2.5} components (total PM_{2.5}, OM, EC, NO₃⁻, SO₄²⁻, POM, SOM, WIOM and WSOM) (Figure 7). Overall, the WSON presented positively weak or moderate correlations with these components. WSON correlated with total PM_{2.5} with r of 0.50 (Figure 7a). The correlation coefficient between WSON and OM was 0.54 (Figure 7b), higher than it with EC ($r = 0.26$, Figure 7c), verifying that WSON was from mixed primary and secondary sources rather than only primary emission. Moreover, the WSON correlated better with SOM ($r = 0.57$, Figure 7d) and WSOM ($r = 0.56$, Figure 7f) than it with POM ($r = 0.26$, Figure 7e) and WIOM ($r = 0.37$, Figure 7g), further revealing that secondary production was more important than primary emission to PM_{2.5} WSON in Nanjing. We also explored the correlations between WSON and inorganic salts of nitrate (Figure 7h) and sulfate (Figure 7i). Here, the WSON showed a notably better correlation with nitrate ($r = 0.60$) than it with sulfate ($r = 0.21$), indicating

that the WSON behaved more like nitrate as a semi-volatile component. This might help explain why WSON level were very low in summer as it tended to partition into gas phase upon high temperatures.

Figure 7. Scatter plots of WSON versus (a) $PM_{2.5}$, (b) OM, (c) EC, (d) SOM, (e) POM, (f) WSOM, (g) WIOM, (h) NO_3^- , (i) SO_4^{2-} .

The acidity of an aerosol influences the generation of secondary organic aerosols, and acid-catalyzed reactions have been shown to be an important mechanism of secondary organic aerosol formation [62,63]. There have been studies on acidic aerosols in many areas of our country, such as Beijing [64], Jinan [65], Lanzhou [66], Guangzhou [66], Chongqing [64], rural areas [64], and mountainous areas [67]. SO_4^{2-} , NO_3^- and NH_4^+ were generally used to determine the magnitude of acidity of particulate matter, which is defined in Equation (9):

$$\text{Acidity} = \left[\left(\frac{SO_4^{2-}}{48} + \frac{NO_3^-}{62} - \frac{NH_4^+}{18} \right) / \left[\left(\frac{SO_4^{2-}}{48} + \frac{NO_3^-}{62} \right) \right] \right] \quad (9)$$

Here (SO_4^{2-}), (NO_3^-) and (NH_4^+) are their concentrations in each sample. We illustrated the WSON/WSTN ratios against the acidities, and found a tight and positive correlation between them ($r = 0.86$) (Figure 8). This is an interesting result, which is in some extent indicating that the acidity of particulate matter contributes to the generation of WSON, which supports the dominance of secondary sources to $PM_{2.5}$ WSON revealed by Figure 7.

Figure 8. The relationship between aerosol acidity and WSON/WSTN ratio.

3.3. Bulk Composition and Source Apportionment of WSON

3.3.1. Bulk Composition of WSON

To gain further insights into WSON composition, we used SP-AMS to determine the high-resolution mass spectrum of WSOM in each sample. The campaign-average ion-specified mass spectrometry of WSOM is shown in Figure 9a. It can be divided into six ion categories, with an inset bar plot displaying mass contributions of these ion families. $C_xH_y^+$ ion family accounted for 39.2 % of the WSOM, followed by oxygenated ion series of $C_xH_yO_1^+$ (33.6 %) and $C_xH_yO_2^+$ (15.0 %). The ON fragments ($C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$) occupied ~9% of the WSOM. The O/C of WSOM was calculated to be 0.46, which is close to those (~0.5) found in Changzhou [52], Yangzhou [37], Beijing [68] and Handan [69]; the H/C of 1.37 appeared to be lower than those (>1.5) in aforementioned studies; N/C of 0.052 was within the range (~0.04–0.06) of those studies except that in Changzhou (0.11).

Figure 9. Average high-resolution mass spectra of (a) total WSOM and (b) WSON and the percentage of each type of ion fragment.

We further extracted the ON fragments representing WSON species in Figure 9b. The oxygen-free ON fragments ($C_xH_yN_p^+$) occupied 91.2% of total WSON, while contribution from the oxygen-containing ON fragments ($C_xH_yO_zN_p^+$) was only minor (8.8%). Among $C_xH_yN_p^+$ ion family, CN^+ , CHN^+ , CH_2N^+ , CH_4N^+ , $C_2H_3N^+$, $C_2H_4N^+$, $C_2H_5N^+$ and

$C_3H_8N^+$ ions, which are likely fragments of C_1 - C_3 aminium salts (methylamine, dimethylamine, trimethylamine, ethylamine, propylamine, etc). Presence of such aminium salts is possible [70] and has been frequently observed in ambient $PM_{2.5}$ [71–74]. $CHON^+$ was the most abundant oxygen-containing ON fragment, likely from fragmentation of some oxygenated ON species (such as amino acids). The distribution of ON ions in AMS mass spectrum is similar to a previous AMS study in Beijing [75]. Note the N/C_{AMS} (0.052) was very different from the N/C_{AC} (0.35). This is because that AMS cannot measure all ionized fragments (for example, the neutral ones) and large and diverse measurement uncertainties might exist for different ON compounds [76]. In general, AMS is an effective tool for non-target quantification of OM and ON, but is very weak in molecular characterization of a certain group of compounds [77]. Other techniques, such as liquid chromatograph mass spectrometry [78–80] can be used for identification and quantification of individual ON compounds in ambient samples in future.

3.3.2. Source Apportionments of WSOM and WSON

In Section 3.1, the OC/EC variation suggests a significant role of secondary source of OM, while correlation analyses between WSON and SOM/POM also point out that WSON associates closely with secondary processes. In this section, PMF algorithm was applied on the WSOM mass spectral matrix acquired by the SP-AMS, and quantified contributions of different primary/secondary sources to WSOM as well as WSON.

Mass spectrometry of the four resolved factors with inset bar plots showing mass percentages of six ion families are presented in Figure 10. Correlation coefficients (r^2) between time series of four factors with individual ions are illustrated in Figure 11. PMF resolved two primary factors (traffic-related HOA, BBOA) and two secondary factors (LO-OOA and MO-OOA). The HOA factor had the lowest O/C of 0.28 and highest H/C of 1.55, with a dominant contribution from $C_xH_y^+$ ion category (52.9%), and the factor also had much better correlations with $C_xH_y^+$ ions (for example, r^2 of 0.61 with $C_4H_7^+$ and r^2 of 0.70 with $C_4H_9^+$) than it with oxygenated ions (Figure 11). All these features are consistent with the HOA that is related with vehicle emissions resolved in previous studies [51,81]. In addition, the HOA also had a very tight correlation with EC (r^2 of 0.85), strongly supporting that HOA mainly comes from primary emissions.

Figure 10. The high-resolution mass spectra of four factors of WSOM resolved from PMF analysis.

Figure 11. Correlations of the four factors with $C_xH_y^+$, $C_xH_yO_1^+$, $C_xH_yO_2^+$ and $C_xH_yN_p^+$ ions (colors of the ion families are the same as those in Figure 10).

The identification of BBOA was mainly attributed to highest fractions of $C_2H_4O_2^+$ and $C_3H_5O_2^+$ as well as its strongest correlations with these two ions (Figure 11) (r^2 of 0.66 with $C_2H_4O_2^+$, and r^2 of 0.81 with $C_3H_5O_2^+$) among all factors. $C_2H_4O_2^+$ and $C_3H_5O_2^+$ are fragments of levoglucosan from biomass burning, and are often used as AMS markers of BBOA [82]. The O/C of BBOA was 0.58 in this study, which is higher than the O/C values of BBOA factors resolved in previous studies such as ones from Yangzhou (0.45) [37] and Marseille in France (0.54) [50]. The abundances of $C_2H_4O_2^+$ and $C_3H_5O_2^+$ are also in the lower end of previously identified BBOA. This is likely due to that the BBOA contains some aged species (levoglucosan is subjected to degradation thus signal intensities of its AMS fragments decreased), which has been identified before [83,84]. Another probable reason is that we only extracted water-soluble portion of BBOA, and more oxidized organics tended to concentrate in water extract due to their stronger hygroscopicity [85].

The factor with an O/C of 0.47 was regarded as LO-OOA, mainly owing to its good correlation with $C_xH_yO_1^+$ ions (much better than those with BBOA). It had a better correlation with $C_2H_3O^+$ (r^2 of 0.64) than MO-OOA did (r^2 of 0.17), and vice versa, MO-OOA correlated better with CO_2^+ (r^2 of 0.67) than LO-OOA did (r^2 of 0.22). The LO-OOA had significant contribution from $C_xH_y^+$ ions (40.9%), yet contributions from oxygenated ions (especially $C_xH_yO_1^+$ ions) increased remarkably relative to those in HOA. We also found an anti-correlation (r of -0.15) between temporal variations of HOA and LO-OOA, rather than BBOA and LO-OOA (r of 0.04), indicating there was likely a chemical conversion of HOA to LO-OOA, which has been found previously in Nanjing [36] and Beijing [53].

MO-OOA was the factor with the highest O/C of 0.75 and lowest H/C of 1.21. Mass fraction of $C_xH_yO_2^+$ ion family was also the highest (20.6%) among all factors, and correlations between $C_xH_yO_2^+$ ions and MO-OOA were also overall better than those with LO-OOA. The most abundant peak is CO_2^+ , likely a fragment from dicarboxylic acids. All these characteristics demonstrate that MO-OOA was highly aged portion of SOA.

Next, we focus on the ON ions distributed in the four sources. Fractional contributions of ON ions were 10.7%, 7.5%, 4.8% and 11.4% in HOA, BBOA, LO-OOA and MO-OOA, respectively. MO-OOA was the factor that mostly enriched ON ions, and with the highest N/C of 0.082; it also correlated better with ON fragments than other factors did (Figure 11). The corresponding mass spectrometry of WSON factors are depicted in Figure 12, along

with inset bar plots showing relative contributions of two types of ON ion families. It can be seen that, amine-related fragments dominated the mass spectra in all factors, but the contributions in primary factors (HOA_ON, BBOA_ON) were higher (94.2% and 92.9%) than in secondary factors (LO-OOA_ON, MO-OOA_ON) (85.3% and 89.8%). This result is consistent with presence of amino compounds in traffic and biomass burning emissions [17], and further oxidation loss in secondary reactions.

Figure 12. The high-resolution mass spectra of four factors of WSON extracted from PMF-resolved WSOM factors.

Time series of the four WSON factors are shown in Figure 13. Similarly, there might be transformation from HOA_ON rather than BBOA_ON to LO-OOA_ON. Mass concentrations of HOA_ON showed no clear seasonal changes, while BBOA concentrations were relatively high in spring. For the secondary sources, MO-OOA_ON level was clearly high in winter while LO-OOA_ON was relatively abundant in summer.

Mass contributions across the full year and in four seasons of both WSOM and WSON are further illustrated in Figure 14. It should be noted that, the WSON in Figure 14 refers to the sum of concentrations of SP-AMS measured ON fragments, while the WSON in Section 3.2 refers to only the nitrogen mass contained in WSON species. Nevertheless, Figure 14 demonstrates that secondary source dominated both WSOM (64.7%) and WSON (60.5%) in all seasons, in agreement with the correlation analyses for sources of WSOM (Section 3.1) and WSON (Section 3.2.2). On the annual basis, compared to WSOM, MO-OOA_ON contribution to WSON was much higher (40.7% versus 30.0%) and LO-OOA_ON contribution was on the other hand much less (19.8% versus 34.7%). Contribution of MO-OOA_ON (56.9%) even outweighed sum of other three sources in winter, while LO-OOA_ON contribution was highest in summer (40.0%) among all seasons. Previously, some studies have revealed the close links between aqueous-phase oxidation and MO-OOA, and between gas-phase photochemical oxidation and LO-OOA [86,87]. Considering the apparently lower temperature (or solar radiation) in winter than in summer (4.4 °C versus 26.5 °C), and higher RH in winter than in summer (64.7% versus 59.8%), it is very likely that aqueous-phase oxidation dominates secondary WSON formation in winter while photochemical oxidation plays a more important role in summer. For the primary sources, HOA_ON contribution (25.0~29.1%) varied little throughout the year, while BBOA_ON contribution was notably higher in spring (21.3%) than in other seasons (~10%).

Figure 13. Time series of the four WSON factors (HOA_ON, LO-OOA_ON, MO-OOA_ON, BBOA_ON).

Figure 14. Seasonal distribution of average mass contribution of WSOM and WSON factors.

4. Conclusions

In this work, we analyzed the chemical composition $PM_{2.5}$ collected in northern suburban Nanjing with a focus on WSON. On average, inorganic ions, OM, and EC accounted for 83.4% of the total $PM_{2.5}$ mass, and the mass contribution of inorganic ions (58.7%) was more than twice that of OM (22.6%). Inorganic ions were dominated by ammonium, sulfate, and nitrate. The OC/EC-tracer method was used to estimate the mass concentrations of POM and SOM, and the SOM was found to dominate OM mass (68.5%). Correlation analysis showed that SOM was closely related to WSOM, while POM was closely related to WIOM. WSON concentration was on average $2.15 \mu g/m^3$, and presented clear seasonal variations (highest in winter, lowest in summer). WSON correlated much better with SOM/WSOM than POM/WIOM, also inferring a dominance of secondary source to WSON.

An Aerodyne SP-AMS was used to determine the bulk compositions of WSOM as well as WSON. On average, SP-AMS showed that WSON ions occupied ~9% of total WSOM mass. The WSON was composed of $C_xH_yN_p^+$ (91.2%) and $C_xH_yO_zN_p^+$ (8.8%), indicating dominance of amines and presence of other oxygenated ON compounds. PMF analysis resolved four sources of both WSOM and WSON, including two primary sources (traffic, biomass burning) and two secondary sources (a less-oxidized and a more-oxidized factors). Overall, the two secondary sources dominated both WSOM (64.7%) and WSON (60.5%). Contribution of the more-oxidized ON factor was very high in winter, and the less-oxidized

factor was significant in summer, indicating that aqueous-phase processing in winter was more important to secondary WSON formation in winter, while in summer, photochemical oxidation appeared to be more significant in Nanjing. Our work provides useful insights into the chemistry of ON and its effective control in a densely populated region. For example, control of biomass burning activities would be effective as its contribution is relatively high in spring, while during the autumn/winter seasons, strict control of vehicle emissions would be more effective; in addition, different focuses should be placed on elucidating the efficient precursors of secondary WSON species in summer and winter, in order to reduce effectively its mass contribution.

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