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

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Abstract: Chemical characterization of fine atmospheric particles ($PM_{2.5}$) is important for effective reduction of air pollution. This work analyzed $PM_{2.5}$ samples collected in Yangzhou, China, during 2016. Ionic species, organic matter (OM), elemental carbon (EC), and trace metals were determined, and an Aerodyne soot-particle aerosol mass spectrometer (SP-AMS) was introduced to determine the OM mass, rather than only organic carbon mass. We found that inorganic ionic species was dominant (~52%), organics occupied about 1/4, while trace metals (~1%) and EC (~2.1%) contributed insignificantly to the total $PM_{2.5}$ mass. Water-soluble OM appeared to link closely with secondary OM, while water-insoluble OM correlated well with primary OM. The $PM_{2.5}$ concentrations were relatively low during summertime, while its compositions varied little among different months. Seasonal variations of water-soluble organic nitrogen (WSON) concentrations were not significant, while the mass contributions of WSON to total nitrogen were remarkably high during summer and autumn. WSON was found to associate better with secondary sources based on both correlation analyses and principle component analyses. Analyses of potential source contributions to WSON showed that regional emissions were dominant during autumn and winter, while the ocean became relatively important during spring and summer.

Keywords: PM_{2.5}; organic aerosol; water-soluble ions; organic nitrogen; aerosol mass spectrometry

1. Introduction

In recent years, particular matter (PM) pollution has gained wide attention from both government and the public due to its impacts on air quality, human health, and climate change [1–3]. In particular, much effort has been devoted to the study of fine particles with an aerodynamic diameter less than 2.5 μ m (PM_{2.5}) due to its adverse health effects. Along with rapid economic growth, PM_{2.5} pollution events ('haze') have occurred frequently in China, and many studies have been carried out to elucidate the properties of PM_{2.5}, especially in densely populated regions [4–9]. However, the chemical composition of PM_{2.5} is highly complex, possibly containing a wide variety of components, including inorganic salts (nitrate, sulfate, and ammonium), trace metals, elemental carbon, and a large number of organic species. Moreover, the relative contributions of different components may change significantly under different atmospheric environments [10,11]. Local PM_{2.5} properties have been shown to be governed by many factors, such as meteorological conditions, emission sources,



boundary layer heights, and atmospheric transportation [12–14]. Therefore, comprehensive chemical analysis of $PM_{2.5}$, with a focus on particular geographic locations is necessary and essential for a better understanding of aerosol chemistry and its impacts.

Among various PM_{2.5} components, the water-soluble organic nitrogen (WSON) species is an important group of compounds [15–17]. The mass fraction of WSON can account for ~10% to 68% of total aerosol nitrogen from continental to oceanic sites, highlighting the importance of organic nitrogen (ON) in atmospheric aerosols [18–21]. Some certain ON species, for example, amino compounds [22], have been shown to be very important for atmospheric new particle formation [23], secondary organic aerosol formation [24], aerosol hygroscopicity [25,26], and toxicity [27]. However, investigations on ON characteristics in China are scarce [28]. To the best of our knowledge, only one study, conducted in Changzhou [29], has reported on the WSON concentrations in the Yangtze River Delta (YRD) region.

In this study, we conducted filter sampling and chemical characterization of the $PM_{2.5}$ samples collected in urban Yangzhou during 2016. Yangzhou is located in the northern YRD region and is a major city with a population of ~4.6 million and an area of 6634 km². The city is a few hundred kilometers from Shanghai, and although it is a famous tourist city, it has also suffered recently from serious air pollution. Moreover, as an inland city, its air quality is influenced by multiple sources, including the transportation of air pollutants from nearby regions. However, even with these ongoing issues and concerns, chemical characterizations of the fine particles that are present in Yangzhou are quite scarce. In this paper, we applied a suite of analytical tools to achieve a relatively comprehensive analysis of the PM_{2.5} components. Our analysis included a study of the following: Organic matter, elemental carbon, inorganic ions, and trace metals. In particular, we determined the mass concentration of the WSON. As part of our discussion, we highlight our analysis of the concentration of the WSON, with a particular focus on its seasonal variations, sources, and potential source areas. Our findings are a valuable contribution to the effort to reduce air pollution in Yangzhou and advance our understanding of aerosol properties in eastern China.

2. Experiments

2.1. Sampling Site and PM_{2.5} Collection

The sampling site is located in urban Yangzhou (119.40° N, 32.38° E), next to the Yangtze Road (~300 m) and the Slender West Lake (~1 km) (Figure 1). The site is surrounded by residential areas, not directly influenced by industrial emissions. Samples for $PM_{2.5}$ analyses were collected from 6 April 2016 to 2 November 2016 by using a high volume (flow rate of 1.05 m³ min⁻¹) sampler (Jinshida Ltd., Qingdao, China, model KB-1000) from 9.00 a.m. to 7.00 a.m. of the next day. This timeframe ensured a duration for each sample of 22 h. All particles were collected on 8 × 10-inch quartz fiber filters (Pallflex, Ann Arbor, MI, USA), which were prebaked at 450 °C in a muffle furnace for 4 h. A total of 128 samples were collected (no samples on precipitation days). Note, $PM_{2.5}$ samples during 13 November 2015–5 April 2016 were analyzed previously [30], and the results of that study were directly used in our study for comparison. For WSON analyses, samples across a whole year (232 samples) were used.

The PM_{2.5} mass concentrations were determined gravimetrically by using a digital balance (OHAUS DV215CD, precision 0.01 mg) at 45% relative humidity (RH) and room temperature. Two filed blanks were treated in the same way as for the samples. All filters were wrapped in aluminum foil and stored in a freezer at -18 °C until analyzed. Hourly meteorological parameters were also recorded at the same site.



Figure 1. Sampling site and its surrounding areas.

2.2. Chemical Analyses

Ionic species. 1/4 filter was extracted with 100 mL ultrapure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) for 45 min ultrasonication in an ice-water bath. The solution was then filtered through a 0.45 µm syringe filter (Spartan, Whatman). An ion chromatograph (IC, Dionex ICS-600 for anions and ICS-1500 for cations) was used to measure the concentrations of water-soluble inorganic ions (WSIIs, including Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, and F⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻) in the aqueous extract. The operational details and method detection limits of these ionic species are the same as those described in Ye et al. [29].

Water-soluble organic carbon (WSOC) and total nitrogen (WSTN). A quarter of each filter was pre-treated in the same way as for ionic species. Following this, the WSOC concentrations were determined by a TOC-VCPH analyzer (Shimazu, Japan) using a thermo-catalytic oxidation approach. TN contents were determined by the TNM-1 unit of the analyzer. Instrument details and analysis procedures can be found in Ge et al. [31].

Organic carbon (OC) and elemental carbon (EC). A round piece with a diameter of 17 mm was cut from each filter and analyzed for total OC and EC contents by the thermal-optical OC/EC analyzer (Sunset Laboratory, Hillsborough, NC, USA) following the IMPROVE TOR protocol described in Chow et al. [32].

Trace elements. To measure the concentrations of trace metals, a MARS6 Xpress CEM corporation Microwave Digestion System was used to digest the PM_{2.5} samples. About 2 cm² of each filter was cut into pieces and put into the polytetrafluoroethylene (PTFE) pressure digestion tank with 1 mL 49% hydrofluoric acid (HF) and 5 mL 69% nitric acid (HNO₃). The digest tank processed 8 samples in a batch. A Thermo Fisher X2 Series Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was then used to determine the concentrations of 14 trace elements, including Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Ba, and Pb. More details and detection limits of the elements can be found in Qi et al. [33].

Water-soluble organic matter (WSOM). Moreover, we introduced an Aerodyne soot-particle aerosol mass spectrometer [34] to obtain the composition of WSOM. Recently, this technique has been used for PM_{2.5} samples in China [29,30,35–38]. Briefly, the water extracts were nebulized with argon by using a constant output atomizer (TSI Model 3076) and then dehumidified by a diffusion dryer filled with silica-gel. The dried particles were sent to the soot particle aerosol mass spectrometer (SP-AMS) for analysis. This instrument can output 70 ev electron impact ionization mass spectrum, and elemental ratios of the WSOM can be calculated based on the mass spectrum. More operational details can be found in our previous work [29,30].

2.3. Data Analyses

WSOM and water-insoluble OM (WIOM) estimations. The SP-AMS data were processed with the Igor-based ToF-AMS Analysis Toolkit (SQUIRREL v.1.57A and Pika v.1.16A) [39]. CO⁺ was directly determined as we used pure argon as a carrier gas. Therefore, the CO⁺ signal was not influenced by the N₂⁺ signal and was easily quantified. For the organic CO₂⁺ signal, since it can be influenced by carbonates [40] and nitrate [41], we set it equal to CO⁺, similar to Aiken et al. [42]. The signals

of H_2O^+ , HO^+ and O^+ were scaled to CO_2^+ according to Aiken et al. [42]: $H_2O^+ = 0.225 \times CO_2^+$, $HO^+ = 0.05625 \times CO_2^+$, and $O^+ = 0.009 \times CO_2^+$. After determining WSOM mass spectrum, the oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios were calculated based on the method of Canagaratna et al. [43], while nitrogen-to-carbon (N/C) ratio was calculated based on Aiken et al. [42]. The organic mass-to-organic carbon (OM/OC) ratio was then calculated. Therefore, in a different approach from the traditional method, which often assumes a fixed OM/OC ratio (for example, 1.6 [44]), we are able to determine the OM/OC ratio for each sample by using the SP-AMS. However, it should be noted that these estimates were still empirical and are subject to uncertainties.

The SP-AMS directly-measured WSOM concentrations were affected by the concentrations of aqueous extracts and flow rates of the carrier gas, etc., Therefore, they cannot represent the original WSOM ambient mass loadings. As a result of this, we used the OM/OC ratios and TOC concentrations to calculate the WSOM concentrations:

$$WSOM = WSOC \times OM / OC_{WSOM}$$
(1)

The WIOM concentrations can be determined by the following equation:

$$WIOM = (OC - WSOC) \times 1.3$$
⁽²⁾

The difference between total OC determined by the OC/EC analyzer and the WSOC, is water-insoluble OC (WIOC). The factor of 1.3 is used to convert WIOC to WIOM [45].

Primary (POM) and secondary OM (SOM) estimations. The OC and EC concentrations measured by the OC/EC analyzer can be used to infer the primary and secondary origins of OC by the EC-tracer method [46], as follows:

$$POC = EC \times (OC/EC)_{pri}$$
(3)

$$SOC = OC - POC$$
 (4)

The $(OC/EC)_{pri}$ in Equation (3) refers to the value of primary OC (POC), which is typically the minimum value among all samples (1.92 in this study). The OC/EC ratios can vary among different sources and some primary organic aerosols, such as those from coal combustion and biomass burning may also have large OC/EC ratios. However, the uncertainty of POC and SOC estimations should be small according to Wu and Yu [47]. We can further estimate the POM and SOM concentrations [30]:

$$POM = POC \times 1.2 \tag{5}$$

$$SOM = (WSOM + WIOM) - POM$$
 (6)

WSON estimations. The WSON concentrations can be calculated by the following equation:

$$WSON = WSTN - WSIN$$
(7)

In this study, concentrations of WSTN came from the TOC analyzer, while the concentrations of water-soluble inorganic nitrogen (WSIN) were the mass concentrations of nitrogen from NH_4^+ , NO_3^- , and NO_2^- measured by the IC. Negative values (20 out of 232 samples) were not included.

Air mass trajectory and potential source contribution analyses of WSON. 72 h back trajectories of the air masses (at 500 m height) were obtained by using the Hybrid Single-particle Lagrangian Integrated Trajectory (HYSPLIT) model [48], based on the meteorological data downloaded from the National Oceanic and Atmospheric Administration (NOAA) Global Data Assimilation System (GDAS). The potential source contribution function (PSCF) analysis was performed to explore the air mass origins, and to identify potential source areas of WSON. Details of the PSCF analyses are described in Ge et al. [30].

3. Results and Discussion

3.1. General Characteristics of PM_{2.5} Components

In our previous work [30], we focused on the characteristics of $PM_{2.5}$ in relatively polluted periods of autumn and winter; while this work presents results of less polluted periods, mainly spring and summer. Therefore, we were able to compare the $PM_{2.5}$ chemical characteristics between polluted and less polluted periods in a one-year span in Yangzhou. During the sampling period, wind speeds varied from 0.2 m/s to 5.2 m/s with an average of 1.6 m/s. RH had a mean value of 70%, which was on average higher than 62% during autumn–winter [30]. Average temperature was 24.2 °C (0 to 39.9 °C), being much higher than the 9.2 °C during autumn–winter [30]. The higher RH and temperature can influence the aerosol formation and gas-particle partitioning. Therefore, the aerosol properties could be different. Average precipitation was 2.63 mm, more than that during November 2015 to April 2016 [30], and most of the rainfall events occurred in June and July.

Figure 2a shows the time series of each major PM_{2.5} component, and the reconstructed and weighted PM_{2.5} mass concentrations. The average PM_{2.5} concentration was 60.9 (±32.0) μ g/m³, ranging from 10.1 to 178.5 μ g/m³. This concentration was much lower than the mean value of 104 μ g/m⁻³ during autumn–winter [30]. This result can be expected air pollution during autumn–winter is typically heavy [11] due to unfavorable meteorological conditions and increased primary emissions, such as coal combustion, etc. The summed mass concentrations of all measured components, including OM (=WSOM + WIOM), EC, ionic species and trace metals, were found to be correlated well with the gravimetrically determined PM_{2.5} concentrations (Pearson's *r* = 0.94) (Figure 2b). However, the slope was only 0.80 (±0.02), indicating ~20% PM_{2.5} mass was unidentified. This unknown fraction may include some unmeasured species, such as crustal materials, carbonate, and particle-bonded water, etc. In particular, organosulfates, recently recognized as a possible important component in PM_{2.5} [49–51], may also contribute to this unknown portion. Sampling loss, analysis artifacts, and measurement uncertainties of various instruments may also add to this unknown portion. A previous similar study [38] also included an unidentified portion, sometimes up to 35.5% (results for PM_{2.5} during January 2013 in Xi'an, China).



Figure 2. (a) Time series of total particular matter ($PM_{2.5}$) and major components, and (b) scatter plot of the reconstructed versus measured $PM_{2.5}$ mass concentrations (colored by time).

As shown in Figure 3, on average, the WSIIs (=Na⁺ + NH₄⁺ + K⁺ + Mg²⁺ + Ca²⁺ + F⁻ + Cl⁻ + NO₂⁻ + NO₃⁻ + SO₄²⁻) occupied the largest proportion (51.8%) of PM_{2.5} mass; OM took up 24.6%, EC occupied 2.1%, and trace metals occupied only ~1%. The structure of PM_{2.5} composition, and the relative abundances of these components, were similar to those observed during the autumn–winter period [30], revealing the general and consistent behavior of PM_{2.5} in Yangzhou. Among WSIIs, sulfate was the most abundant component (36.4% of WSIIs), followed by nitrate (27.6%), and ammonium

(21.4%). The sum of sulfate, nitrate, and ammonium (SNA) was 85.4% of WSIIs mass, which was similar to 80.6% for the WSIIs during autumn–winter [30]. However, on the contrary, nitrate was more abundant than sulfate during autumn-winter. This result is consistent with previous findings in Changzhou [29] and other cities [52], since ammonium nitrate tends to evaporate into a gas phase at warm temperatures. Chloride fraction (3.2%) was also lower than that of autumn–winter [30], likely due to enhanced primary emissions of chloride, such as coal combustion. In Figure 4, we further presented the monthly averaged PM_{2.5} chemical compositions during the sampling period. First, it can be seen that the $PM_{2.5}$ concentrations were low during summer (June–August). The relative contributions of different components varied, especially during June, the mass portion of WSIIs occupied ~70% PM_{2.5} mass. EC and metal contributions were a bit larger during September and October than in other months. However, the average chemical composition of the most polluted month (April) was almost the same as that of the cleanest month (August), again indicating the consistent PM_{2.5} characteristics in Yangzhou. It is important to note that daily samples were unable to capture the fast-chemical changes during pollution episodes. These samples are more likely to be representative of the average aerosol properties. Detailed characterization of aerosol properties during specific episodes can be investigated by highly time-resolved measurements, such as online AMS measurements [53–55].

Besides SNA, another relatively rich ionic species was calcium, which took up ~8.2% WSIIs mass, followed by minor contributions from Mg^{2+} (0.3%), K⁺ (1.0%), and Na⁺ (1.2%) (Figure 3). Other trace metals together, only occupied ~1% of total PM_{2.5} mass, which was lower than those reported in Changzhou (2.7% and 5.0%) [29], etc., but similar to that found in Nanjing (1%) [33]. Zn, Al, Pb, and Mn were relatively rich (together 75.4%), and the other 10 elements only occupied ~1/4 mass of the trace elements. It is important to note that during autumn–winter [30], Zn, Al, Pb, and Mn were also the top four abundant trace elements, but the relative contributions were very different, indicating different sources at different seasons for the trace metals in Yangzhou.



Figure 3. Average chemical compositions of total PM_{2.5}, organic matter, ionic species, and trace metals (2016.4.6~2016.11.2).



Figure 4. Monthly averaged chemical compositions and mass concentrations of $PM_{2.5}$ (**a**), and mass contributions of different components to $PM_{2.5}$ (**b**).

By using the OC/EC-tracer based method and the SP-AMS measured results, we can separate OM mass into POM and SOM, as well as WSOM and WIOM. SOM dominated over POM, and WSOM dominated the OM (Figure 3), both were similar to the results during autumn–winter [30]. Tight correlations were observed between WSOM and SOM (*r* of 0.96 and slope of 0.81) (Figure 5a), and between WIOM and POM (*r* of 0.80 and slope of 1.37) (Figure 5b). A possible reason for this, is that the process generally involved in the generation of SOM from POM is oxidation, which increases polarity (e.g., generation of carboxylates). The parent compounds (POM) might generally be expected to be non-polar (e.g., polycyclic aromatic compounds and long-chain hydrocarbons) and so would be expected to correlate well with WIOM. This result links POM and SOM with their hygroscopicities, and demonstrates that SOM is likely hygroscopic, while POM is probably hydrophobic. Of course, higher SOM fraction than WSOM fraction (69.1% vs. 57.2%) indicates that a portion of SOM can be water-insoluble.



Figure 5. Scatter plots of water-soluble organic matter (WSOM) versus secondary OM (SOM) (**a**), and water-insoluble OM (WIOM) versus primary OM (POM) (**b**) (colored by time).

In ambient air, ammonia is typically the major basic compound to neutralize sulfuric, nitric, and hydrochloric acids. In this work, the equivalent molar ratios of ammonium to the sum of sulfate, nitrate and chloride, was on average 0.95 and the correlation was also good (r of 0.92) (Figure 6a). This result manifests that sulfate, nitrate, and chloride are dominantly bonded with ammonium. The fitted slope of 0.95 (±0.03), less than 1, likely indicates a slight deficiency of ammonium, and suggests a small portion of sulfate, etc., may bond with other cations, such as Ca²⁺, according to Figure 3.

Considering all measured ionic species, the ionic balance can be calculated by using the molar equivalent ratios of cations (CE) to anions (AE), as follows:

$$CE = \frac{[Na^+]}{23} + \frac{[NH_4^+]}{18} + \frac{[K^+]}{39} + \frac{[Ca^{2+}]}{40} \times 2 + \frac{[Mg^{2+}]}{24} \times 2$$
(8)

$$AE = \frac{[SO_4^{2-}]}{96} \times 2 + \frac{[NO_3^{-}]}{62} + \frac{[Cl^{-}]}{35.5} + \frac{[F^{-}]}{19}$$
(9)

It is important to note that NO_2^- concentration was below the detection limit and was, therefore, not included in Equation (9). The scatter plot between CE and AE is presented in Figure 6b. The correlation was very tight (*r* of 0.95), and the slope of was 1.06 (±0.03), a bit larger than 1. The result shows that measured cations are able to neutralize all measured anions, and also suggests the possible existence of some other undetected anions (probably carbonate and organic anions).



Figure 6. Scatter plots of molar ratios of ammonium versus sum of sulfate, nitrate, and chloride (**a**), and cations versus anions (**b**) (colored by time).

3.2. Seasonal Properties and Sources of WSON

By using the method provided in Section 2.3, we calculated the WSON concentrations for all samples across a full year. The annual mean WSON concentration was determined to $1.71 (\pm 1.08) \mu g/m^{-3}$. Table 1 compares our results with a number of previous studies conducted in China and a few other locations. It can be seen that, the WSON level in Yangzhou was much higher than those in Japan, Greece, and Florida, USA. It was also higher than ON in PM₁ in Beijing, but this was likely due to the fact that ON in supermicronmeter aerosols was not included in that study. This argument is furthered by another study on PM_{2.5} in Beijing, which showed a much higher WSON concentration. The WSON concentration in Yangzhou was also much lower than those in Xi'an and Guangzhou, but similar to that observed in Changzhou. However, the annual average mass percentage of WSON in WSTN was 18.7%, which is relatively high among the studies listed in Table 1 (except Beijing and Xi'an), indicating an important role of WSON in Yangzhou PM_{2.5}.

Location	Samples	Period	WSON (µg/m ³)	WSON/WSTN (%)	Ref.
Beijing, China	PM _{2.5}	1998.11-1999.2	3.17	30	[56]
Xi'an, China	PM _{2.5}	2008-2009	4.20	45	[21]
Guangzhou, China	PM _{2.5}	2014	4.78	12.2	[16]
Changzhou, China	PM _{2.5}	2015.7-2016.4	1.16	7.7	[29]
Beijing, China *	PM_1	2013.12.16-2014.12.15	0.26~0.59	7-10	[28]
East China Seas	TSP (Sea fog)	2014.3.17-2014.4.22	2.06 ± 2.39	10 ± 6	[57]
Rishiri Island, Japan	PM_{10}	2010.4.16-2012.11.8	0.077	13	[58]
Kofu, Japan	PM_{10}	2016.4.16-2016.10.13	0.071	10	[59]
Crete, Greece	PM _{1.3}	2005.1-2003.12	0.83 ± 1.0	13	[17]
Florida, USA	PM _{2.5}	2005.7-2005.9	0.36 ± 0.21	8.9 ± 5.8	[60]
Yangzhou, China	PM _{2.5}	2015.11.12-2016.11.2	1.71 ± 1.08	18.7	This work

Table 1. Mass concentrations of water-soluble organic nitrogen (WSON) measured in different sites.

* Online measurement of ON in PM1. It may include both water-soluble and water-insoluble ON.

We present the seasonal average WSON concentrations in Figure 7a and the corresponding monthly averages in Figure 8a. The average concentrations were 1.87, 1.55, 1.66, and 1.70 μ g/m⁻³ in winter, spring, summer, and autumn, respectively. Winter had a slightly higher WSON concentration than in other seasons, but overall the seasonal or monthly differences of WSON concentrations were not significant except a higher concentration during December and a lower concentration during August. Furthermore, we illustrate the seasonal average nitrogen concentrations in ammonium $(NH_4^+_N)$ and nitrate (NO₃⁻_N) together with WSON in Figure 7b. In all seasons, NH_4^+ _N was the most dominant N-containing species but displayed a decreasing trend from winter to autumn. NO₃⁻_N concentration was second to NH₄⁺_N and showed a similar trend with an exception in summer. During summer, WSON concentration was even higher than NO₃⁻_N concentration, which is again attributed to the thermodynamic dissociation of NH₄NO₃ under summertime high temperatures. Overall, different from insignificant seasonal variations of WSON concentrations shown in Figure 7a, the mass contributions of WSON to WSTN were remarkably higher in summer (24.9%) and autumn (24.5%) than in winter (11.4%) and spring (12.6%). Monthly data, as can be seen in Figure 8b, further shows that the average mass percentages of WSON/WSTN were nearly 40% in August and September. This result underscores the importance of WSON in summer and autumn in Yangzhou, despite the total PM_{2.5} concentrations were relatively low in these two seasons.



Figure 7. Seasonal average concentrations of WSON (**a**), and average concentrations of WSON, nitrogen in ammonium (NH_4^+ _N) and nitrate (NO_3^- _N), and WSON/water-soluble total nitrogen (WSTN) (%) (**b**).



Figure 8. Monthly average concentrations of WSON (a), and WSON/WSTN (%) (b).

To explore the sources of WSON, we first investigated the correlations between WSON and SOM (also POM), as shown in Figure 9. The correlation of WSON with SOM (*r* of 0.49) was better than it was with POM (*r* of 0.26), indicating that WSON was more likely associated with secondary formation processes than with primary emissions in Yangzhou. However, the correlation coefficient (0.49) was only moderate, demonstrating that WSON sources were, in fact, complex. Therefore, we further used principle components analyses (PCA) to identify the possible sources of WSON (as well as PM_{2.5}). Twelve variables including OC, EC, WSOC, WSON, and major ionic species of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺ were chosen as input parameters.



Figure 9. Scatter plots of WSON versus POM (a), and WSON versus SOM (b) (colored by time).

The PCA resolved four principle factors (or sources) with eigenvalues larger than 1, together accounting for 82.41% of the total variance of original data matrix. The factor profiles, representing the correlation coefficients between the input variables with the factor, are given in Table 2. Component 1 (PC1), which explained 53.1% of the variance, was very likely from biomass and fossil fuel combustions, as it associated closely with K⁺ (biomass burning marker ion), OC, EC, and Cl⁻ (possible species from fossil fuel and or coal combustion). PC2 explained 11.77% of the total variance and the species with high loadings are SNA (SO₄²⁻, NO₃⁻, NH₄⁺) and WSON. SNA are known to be generated from secondary reactions, therefore PC2 represents the secondary source. The third component (PC3, 9.34% variance) had high loadings of Mg²⁺ and Ca²⁺, likely indicating dust origin (from soil and construction activities, etc.). For the fourth component (PC4, 8.21% variance), only Na⁺ had a high loading (0.97), suggesting a sea salt source. Generally, for WSON, obviously higher loading in the secondary source (PC2) than in other primary sources was observed, strongly indicating that WSON was mainly from a secondary source, consistent with the correlation analysis results in Figure 8. Nevertheless, further molecular characterizations and quantifications of the WSON species and other source markers, combined with source apportionment techniques are still needed to provide more insights into the sources of WSON.

Components	PC1	PC2	PC3	PC4
EC	0.94	0.02	0.11	0.09
OC	0.79	0.36	0.21	-0.02
Cl ⁻	0.88	0.03	0.10	0.12
NO_3^-	0.79	0.50	-0.03	-0.11
SO_4^{2-}	0.42	0.78	0.02	-0.07
NH_4^+	0.79	0.51	-0.07	-0.04
Ca ²⁺	0.29	-0.02	0.74	0.17
Mg ²⁺	-0.03	0.06	0.90	-0.18
Na ⁺	0.04	0.06	-0.03	0.97
K ⁺	0.93	0.15	0.14	0.03
WSOC	0.82	0.42	0.11	-0.01
WSON	0.09	0.79	0.03	0.13
Initial Eigenvalue	6.37	1.41	1.12	1.00
Variance Explained	53.10	11.77	9.34	8.21
Cumulative Variance Explained	53.10	64.86	74.20	82.41
NH_4^+ Ca^{2+} Mg^{2+} Na^+ K^+ WSOC WSON Initial Eigenvalue Variance Explained Cumulative Variance Explained	0.79 0.29 -0.03 0.04 0.93 0.82 0.09 6.37 53.10 53.10	0.51 -0.02 0.06 0.06 0.15 0.42 0.79 1.41 11.77 64.86	-0.07 0.74 0.90 -0.03 0.14 0.11 0.03 1.12 9.34 74.20	$\begin{array}{c} -0.04 \\ 0.17 \\ -0.18 \\ 0.97 \\ 0.03 \\ -0.01 \\ 0.13 \\ 1.00 \\ 8.21 \\ 82.41 \end{array}$

Table 2. Principle components analyses (PCA) analysis results of PM_{2.5} and WSON (numbers in bold highlight the components with significances).

The potential source areas (PSCs) of WSON and clusters of air mass trajectories in four seasons are displayed in Figures 10 and 11, respectively. Five clusters were identified during winter, while other seasons only had three clusters. During winter, the WSON PSCs were mainly distributed within the YRD region (Figure 10a), indicating the dominance of regional emissions. But a few hotspots were also found in Shandong province and, correspondingly, two clusters, one originating from Beijing (42.86% of total trajectories) and one initiated from Mongolia (25.40% of total trajectories), both travelled across Shandong Province. Although the WSON PSCs during winter could trace back far beyond the YRD region and Shandong province, other areas contributed relatively insignificantly (correspondingly clusters 2, 4, and 5 together occupied ~30% of all trajectories in Figure 11a). No obvious source from the ocean was found during winter.

For spring, the WSON PSCs mainly distributed in the YRD region and Jiangxi province, rather than in Shandong Province (Figure 10b). Interestingly, there was a potentially large source in the Yellow sea close to Korea, and consistently a relatively short cluster starting from Bohai sea, crossing over Shandong Peninsula and the Yellow Sea, occupied the majority of air mass (62.75%) (Figure 11b).

The WSON PSCs during summer concentrated mainly in Jiangsu and Zhejiang provinces. There were also some WSON likely from the ocean, including the Yellow Sea and the East China Sea (Figure 10c). The trajectories during summer were also unique: It had one cluster (41.3%), which originated from the east Pacific Ocean, and another one (19.57%) crossed over Bohai Sea and Yellow Sea. There was only one inland cluster (41.3%), which started from Guangdong Province (Figure 11c).

During autumn, the WSON PSCs were predominantly located in Jiangsu Province and Shanghai, with less contributions from Shandong Province and the Yellow Sea. Consistently, a short cluster across the Yellow Sea, Shanghai, and Jiangsu Province, was the major one (55.88%). The area of WSON potential sources during autumn appeared to be the smallest among all seasons.



Figure 10. The potential source contributions to WSON during (**a**) winter, (**b**) spring, (**c**) summer, and (**d**) autumn (colored by the potential source contribution function (PSCF) values).



Figure 11. Clusters of the 72-h back trajectories during (a) winter, (b) spring, (c) summer, and (d) autumn.

4. Conclusions

In this work, we analyzed the chemical compostions of $PM_{2.5}$ samples collected in urban Yangzhou, China during spring and summer of 2016. Ionic species, OM, EC, and trace metals, on average. occupied ~80% of total $PM_{2.5}$ mass. Mass contribution of ionic species (~52%) was twice that of the OM (~25%), while EC and trace metals together contributed little (~3%). Sulfate, nitrate, and ammonium dominated the ionic species. The Aerodyne SP-AMS was used to determine the mass spectra of WSOM, and derived the OM/OC ratio, and was therefore the WSOM and WIOM mass

concentrations. An EC-tracer based method was used to estimate SOM and POM mass concentrations. Correlation analyses showed that SOM linked closely with WSOM, while POM correlated well with WIOM. In particular, this work measured the WSON concentrations in one year-long PM_{2.5} samples. Different from the monthly variations of PM_{2.5} concentrations, WSON concentrations had no significant seasonal and monthly differences. However, seasonal and monthly differences of mass contributions of WSON to total nitrogen were significant, which were much higher in summer and autumn than in winter and spring. Temporal variation of WSON concentrations was found to correlate better with that of SOM than with POM, indicating secondary formation is important for the WSON in Yangzhou, which was also supported by the PCA results. PSCF analyses of WSON demonstrated that regional sources were dominant during autumn and winter, while oceans became relatively important for the WSON during spring and summer.

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