Dominant Contributions of Secondary Aerosols and Vehicle Emissions to Water-Soluble Inorganic Ions of PM$_{2.5}$ in an Urban Site in the Metropolitan Hangzhou, China

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Abstract: Water soluble inorganic ions (WSIs) are important components in PM$_{2.5}$ and could strongly affect the acidity and hygroscopicity of PM$_{2.5}$. In order to achieve the seasonal characteristics and determine the potential sources of WSIs in PM$_{2.5}$ in Hangzhou, online systems were used to measure hourly mass concentrations of WSIs (SO$_4^{2−}$, NO$_3^{−}$, NH$_4^{+}$, Cl$^{−}$, Na$^{+}$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$) as well as PM$_{2.5}$, NO$_x$ and SO$_2$ at an urban site for one month each season (May, August, October, December) in 2017. Results showed that the hourly mass concentrations of PM$_{2.5}$ during the whole campaign varied from 1 to 292 μg m$^{-3}$ with the mean of 56.03 μg m$^{-3}$. The mean mass concentration of WSIs was 26.49 ± 20.78 μg m$^{-3}$, which contributed 48.28% to averaged PM$_{2.5}$ mass. SNA (SO$_4^{2−}$, NO$_3^{−}$ and NH$_4^{+}$) were the most abundant ions in PM$_{2.5}$ and on average, they comprised 41.57% of PM$_{2.5}$ mass. PM$_{2.5}$, NO$_x$, SO$_2$ and WSIs showed higher mass concentrations in December, possibly due to higher energy consumption emissions, unfavorable meteorological factors (e.g., lower wind speed and temperature) and regional transport. Results from PCA models showed that secondary aerosols and vehicle emissions were the dominant sources of WSIs in the observations. Our findings highlight the importance of stronger controls on precursor (e.g., SO$_2$ and NO$_x$) emissions in Hangzhou, and show that industrial areas should be controlled at local and regional scales in the future.

Keywords: secondary aerosols; vehicle emissions; water-soluble inorganic ions; HYSPLIT model; Hangzhou

1. Introduction

Due to rapid urbanization and industrialization during the decades, Chinese metropolitan cities suffered from heavy air pollution that was mainly caused by high PM$_{2.5}$ concentrations [1–4]. PM$_{2.5}$ (particulate matters less than 2.5 μm in aerodynamic diameter), originating from both direct emissions and secondary transformations, could strongly affect physical health [5–7], air quality [8,9] and radiative forcing [10,11]. For sustainable developments, reducing PM$_{2.5}$ concentration levels had become one of the most urgent issues in China. In order to alleviate air pollution, the Chinese government released a series of strong and rigorous regulations since 2013 (e.g., “Air Pollution Prevention and Control Action Plan”) and PM$_{2.5}$ levels in many polluted cities were reported to decrease...
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2. Experiment

2.1. Instruments

Hourly average concentrations of NO₂, SO₂, and PM₂.₅ were measured with a model 42i NO₂ analyzer, model 43i SO₂ analyzer and TEOM 1405F-FDMS (Thermo Fisher Scientific, Co., Ltd., Waltham, MA, USA), respectively. These instruments underwent external calibration four times a year. Meteorological factors (relative humid, temperature, wind speed, wind direction, rainfall) were measured by automatic weather station (Vaisala WXT520).

WSIIs were measured by Monitoring of AeRosols and GAses (MARGA 1S, Applikon Analytical B. V. Corp., Schiedam, Netherlands) with hourly time resolution. The MARGA 1S system comprises a sampling box and an analytic box. Ambient air is first drawn through a PM₂.₅ size selecting inlet (flow rate: 1 m³·h⁻¹) by an air pump controlled by a Mass Flow Controller (MFC). After that, air flows pass through a Wet Rotating De-nuder (WRD) and the trace gases can be removed by 0.0035% H₂O₉ liquid film in WRD. Particles can directly pass the WRD with air flow and then grow by a deliquescent progress and be captured in a Steam Jet Aerosol Collector (SJAC), within which a supersaturated environment was created by a streamer (120 °C–140 °C). After degassing progresses and mixing with internal standard solutions (LiBr, Li⁺ was the internal standard for cations’ analyses and Br⁻ was the internal standard for anions’ analyses), the WRD sample considerably [12,13]. Nonetheless, PM₂.₅ concentrations still exceeded the corresponding Chinese National Ambient Air Quality Standard (CNAAQS) in many cities [14–18].

PM₂.₅ comprises a variety of components such as water-soluble inorganic ions (WSIIs). WSIIs accounted for more than one-third of PM₂.₅ mass [19] and can significantly affect the characteristics of PM₂.₅ [20] by existing in specific forms. For example, NH₄NO₃ and (NH₄)₂SO₄ were found to be two important forms in PM₂.₅ and higher mass fractions of which could make PM₂.₅ more hygroscopic in the atmosphere, thus leading to degradation of visibility [21,22]. Moreover, WSIIs can also affect the acidity of PM₂.₅, and heterogeneous chemical reactions on surfaces of fine particles [23,24].

Hangzhou is the capital city of the Zhejiang province and it is located in east of the YRD area. Cities surrounding Hangzhou include the megacity of Shanghai in the northeast and highly industrialized cities such as Suzhou, Wuxi, and Changzhou in the north and Ningbo in the southeast. Hangzhou belongs to the subtropical zone with a humid monsoon climate, characterized by a prevailing southeasterly wind in summer and northerly wind in winter [25]. The Gross Domestic Product in Hangzhou was 1255.6 billion in 2017, increasing by 50.50% from 2013 [26]. However, with the rapid growth, Hangzhou suffered from severe air pollution. For example, during the heavy haze period in the winter of 2013, most of PM₂.₅ hourly concentrations were higher than 200 μg·m⁻³ with the highest concentration of 588 μg·m⁻³, largely exceeding the CNAAQS [22].

While there were many observations of WSIIs in Hangzhou [27–33], most studies focused on pollution episodes in one or two seasons [30–32] and seasonal observations in Hangzhou were rare. Moreover, many long-term studies of WSIIs employing offline analytical methods with filter-based sampling may have the drawbacks of low time resolution and mass losses owing to semi-volatile aerosol evaporation [34,35]. Thus, in this study, we used on-line Monitoring of AeRosols and GAses (MARGA 1S, Applikon Analytical B. V. Corp., Netherlands) to measure hourly concentrations of WSIIs during one month for each season at an urban site in Hangzhou. Simultaneously, hourly concentrations of PM₂.₅, NO₂, and SO₂ were also measured to analyze ionic reactions. Here, we first give detailed descriptions of the levels of PM₂.₅ and WSIIs during observation. Then, we use back trajectory analyses, cluster analyses and principal component analyses (PCA) to determine sources of WSIIs during four months of sampling. The object of the study is to give scientific insights into seasonal variations and potential sources of WSIIs of PM₂.₅, providing scientific basis for air pollution controls in Hangzhou.
liquid will be transported by syringes and finally analyzed by Ion Chromatographic (IC). The MARGA IS system has the capability of measuring hourly averaged aerosol concentrations of major WSII (SO\(_2^2\), NO\(_2\), NH\(_3\), Cl\(^-\), Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\)). The detection limits of the MARGA IS system were 0.001 µg m\(^{-3}\) for Cl\(^-\), 0.005 µg m\(^{-3}\) for NO\(_2\), 0.004 µg m\(^{-3}\) for SO\(_2^2\), 0.005 µg m\(^{-3}\) for NH\(_3\), 0.005 µg m\(^{-3}\) for Na\(^+\), 0.009 µg m\(^{-3}\) for K\(^+\), 0.006 µg m\(^{-3}\) for Mg\(^{2+}\), 0.009 µg m\(^{-3}\) for Ca\(^{2+}\). More details of the MARGA IS system can be found elsewhere [36].

2.2. Site

The observation site was located in Zijingang Campus of Zhejiang University in Hangzhou, China (30.31°N, 120.08°E); MARGA IS system, model 42i NO\(_2\) analyzer, model 43i SO\(_2\) analyzer and TEOM 1405F-FDMS were located in a measurement container, within which the temperature was maintained at ~25 °C. Sample Inlets of the MARGA IS system, model 42i NO\(_2\) analyzer, model 43i SO\(_2\) analyzer and TEOM 1405F-FDMS were located at the roof of the container. Around 700 m in the north side away from the sample site was a main road. Student dormitories were around 500 m away from the site on the east side. Construction areas were around 400 m from the site to the west and north. The observation site was influenced by a combination of traffic, residences, and construction and thus could well represent the urban area [37]. PM\(_{2.5}\), SO\(_2\), NO\(_2\) and WSII were measured during one month per season in 2017: May in spring, August in summer, October in autumn and December in winter.

2.3. Methods

2.3.1. Back Trajectory and Clusters Analysis

Based on the National Ocean and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://ready.arl.noaa.gov/HYSPLIT.php accessed on 29 July, 2021), an open source software (TrajStat, Version 1.2.2.6) was used to calculate the backward air mass trajectories arriving at our site to determine the regional transport of pollutants [38,39]. Inputs were Global Data Assimilation System (GDAS) meteorological data at a grid resolution of 1° × 1° [22].

In this study, 72 h back trajectories run 4 times a day (i.e., with ending time at 0:00, 6:00, 12:00, 18:00, local time) ending at the arrival level of 100 m from the measured site. The concentrations of pollutants (e.g., PM\(_{2.5}\)) were associated with the corresponding trajectory [40]. By using a K-means clustering algorithm, air mass trajectories were assigned in different clusters [39,40].

2.3.2. Principal Component Analysis

Principal component analysis (PCA) method can reduce the dimensionality of a data set effectively [41]. In this study, the PCA model was used to determine sources of WSII during four months of sampling. When assuming linear relationships between the contributions of each source and concentrations of pollutants, a pollutant data matrix \(\{C_{ij}\}\) can convert to dimensionless standardized form \(\{S_{ij}\}\) using the following formula [42]:

\[
\{C_{ij}\} = \begin{bmatrix} c_{11} & \cdots & c_{1n} \\ \vdots & \ddots & \vdots \\ c_{m1} & \cdots & c_{mn} \end{bmatrix}
\]

\[
\{S_{ij}\} = \frac{c_{ij} - d_i}{\sigma_j}
\]

where \(m\) and \(n\) are number of total hours (i.e., lines of \(\{C_{ij}\}\)) of the input observation data and total number of pollutants’ species (i.e., columns of \(\{C_{ij}\}\)), respectively. \(C_{ij}\) represents concentration of hour \(i\) and pollutant \(j\). \(\sigma_j\) and \(d_i\) are the standard deviation and mathe-
matic average value of pollutant, \( j \), respectively. Then, the covariance matrix of standardized \( \{S_{ij}\} \) and the corresponding eigenvalues and eigenvectors of the covariance matrix were calculated by applying eigenvector decomposition. The eigenvector with higher corresponding eigenvalue could account for the larger proportion of variability and cover more information of original \( \{C_{ij}\} \) [41]. After performing the above procedures, \( C\{S_{ij}\} \) could finally be expressed as the equation below:

\[
\{S_{ij}\} = \left( \sum_{i=1}^{k} a_{ik} b_{kj} \right)
\]

where \( k \) is the number of total sources and \( l = 1, 2, \ldots, k \). \( a_{ik} \) and \( b_{kj} \) are the factor loadings and scores [42], respectively.

In this study, all species of WSIs in four seasons observed by MARGA were used in the PCA calculations performed by SPSS software (version 23.0, corportion of IBM).

2.4. Quality Assurance/Quality Control

The MARGA 15 system was well calibrated twice a year with external blank and at least 4 individual standard solutions with different concentrations. The concentration ranges of WSIs for calibrations were 6 ppb–600 ppb for \( \text{Cl}^{-} \), 20 ppb–400 ppb for \( \text{Br}^{-} \), 20 ppb–2000 ppb for \( \text{NO}_{3}^{-} \), 30 ppb–3000 ppb for \( \text{SO}_{2}^{2-} \), 20 ppb–400 ppb for \( \text{Li}^{+} \), 20 ppb–400 ppb for \( \text{Na}^{+} \), 25 ppb–500 ppb for \( \text{NH}_{4}^{+} \), 50 ppb–1000 ppb for \( \text{K}^{+} \), 25 ppb–500 ppb for \( \text{Mg}^{2+} \) and 50 ppb–1000 ppb for \( \text{Ca}^{2+} \). The correlation coefficients (R²) of calibration curves were all above 0.98. Outliers and concentrations of WSIs that below minimum detection limit were removed before the PCA analysis. The percentages of valid data of all WSIs were above 90% except for \( \text{Mg}^{2+} \) which was above 85%.

The concentrations of internal standard solutions (\( \text{Br}^{-} \) and \( \text{Li}^{+} \)) were varied within mean concentration ±3*standard deviations during the whole observations, ensuring the stability and accuracy of data for the whole observations.

3. Results and Discussions

3.1. \( \text{SO}_{2}, \text{NO}_{2} \) and \( \text{PM}_{2.5} \) Levels

Table 1 shows the mean concentrations of \( \text{SO}_{2} \), \( \text{NO}_{2} \) and \( \text{PM}_{2.5} \) in Hangzhou as well as other cities in China. The concentrations of \( \text{SO}_{2} \) in Hangzhou varied from 2 to 39 \( \mu\text{g} \cdot \text{m}^{-3} \) with the mean of 7.95 \( \mu\text{g} \cdot \text{m}^{-3} \), which was notably lower than those in Handan (37.2 \( \mu\text{g} \cdot \text{m}^{-3} \)) in 2017. Higher energy consumptions and higher emission industries in Handan than those in Hangzhou may be the main cause [14]. The mean concentration of \( \text{SO}_{2} \) in our study was slightly higher than that in Shanghai (7 \( \mu\text{g} \cdot \text{m}^{-3} \)) in 2013–2014, partly due to better diffusional conditions in the coastal cities (e.g., Shanghai). The concentrations of \( \text{NO}_{2} \) in 2017 in Hangzhou varied from 3 to 120 \( \mu\text{g} \cdot \text{m}^{-3} \) with the mean of 36.49 \( \mu\text{g} \cdot \text{m}^{-3} \), which was largely higher than those in Hangzhou (23 \( \mu\text{g} \cdot \text{m}^{-3} \)) in 2013–2014. The car ownership was around 2.79 million in 2017 and 2.54 million in 2013 [26] in Hangzhou, respectively, thus the increasing trend of \( \text{NO}_{2} \) annual concentration could be attributed to the growth of automobile population in Hangzhou.

The concentrations of \( \text{PM}_{2.5} \) in the field ranged from 1 to 292 \( \mu\text{g} \cdot \text{m}^{-3} \) with a mean of 56.03 \( \mu\text{g} \cdot \text{m}^{-3} \), which exceeded Chinese National Ambient Air Quality Standard grade II (35 \( \mu\text{g} \cdot \text{m}^{-3} \)). The mean concentration in this study was lower than those in Handan (85.7 \( \mu\text{g} \cdot \text{m}^{-3} \)), Chengdu (65 \( \mu\text{g} \cdot \text{m}^{-3} \)), Wuhan (89.6 \( \mu\text{g} \cdot \text{m}^{-3} \)), Zhengzhou (70.5 \( \mu\text{g} \cdot \text{m}^{-3} \)) and Xinxiang (69.0 \( \mu\text{g} \cdot \text{m}^{-3} \)), similar to that in Shanghai (56 \( \mu\text{g} \cdot \text{m}^{-3} \)), but higher than those in Nanning (36 \( \mu\text{g} \cdot \text{m}^{-3} \)) and Guangzhou (31.59 \( \mu\text{g} \cdot \text{m}^{-3} \)) (Table 1). As shown in Table 1, \( \text{PM}_{2.5} \) mean concentration dropped from 2013–2014 to 2017 in Hangzhou. This could be attributed to the implementation of stringent emission control measures during the period 2013–2017 in China [14]. However, the annual \( \text{PM}_{2.5} \) concentrations were still 1.60 times the Chinese National Ambient Air Quality Standard of \( \text{PM}_{2.5} \) (35 \( \mu\text{g} \cdot \text{m}^{-3} \)), indicating that air pollution was still severe in Hangzhou.
Table 1. The mean concentrations of SO\(_2\), NO\(_2\) and PM\(_{2.5}\) in Hangzhou and other cities.

| City     | Time                | Mean Concentration (μg·m\(^{-3}\)) | Reference |
|----------|---------------------|-------------------------------------|-----------|
|          |                     | SO\(_2\) | NO\(_2\) | PM\(_{2.5}\) |          |
| Handan   | 2017                | 37.2     | 51.7     | 85.7        | [14]     |
| Nanning  | 2017/09–2018/08     | 11       | 36       | 36          | [43]     |
| Chengdu  | 2016                | 16       | 43       | 65          | [44]     |
| Guangzhou| 2017                | 10.11    | 52.27    | 31.59       | [45]     |
| Wuhan    | 2013/03–2014/02     | 32.4     | 54.9     | 89.6        | [46]     |
| Zhengzhou| 2017–2018           | 20.5     | 51.6     | 70.5        | [16]     |
| Xinxian  | 2017–2018           | 23.8     | 51.4     | 69.0        | [16]     |
| Shanghai | 2013/03–2014/02     | 7        | 20       | 56          | [47]     |
| Hangzhou | 2013/03–2014/02     | 9        | 23       | 64          | [47]     |
| Hangzhou | 2017/05,08,10,12    | 7.95     | 36.49    | 56.03       | This study|

As shown in Table 2, PM\(_{2.5}\) showed obvious variations in Hangzhou in four months. PM\(_{2.5}\) mean concentrations were the highest in December (89.35 ± 40.21 μg·m\(^{-3}\)), followed by May (58.39 ± 26.00 μg·m\(^{-3}\)), October (47.26 ± 26.05 μg·m\(^{-3}\)) and August (26.30 ± 13.55 μg·m\(^{-3}\)). The lowest PM\(_{2.5}\) concentrations, in August, were due to the highest wind speed (1.45 ± 0.71 m·s\(^{-1}\)) and temperature (30.14 ± 3.76 °C), which were favorable factors for the diffusion of pollutants. The highest concentrations of precursors SO\(_2\) (12.57 ± 5.37 μg·m\(^{-3}\)) and NO\(_2\) (50.20 ± 17.35 μg·m\(^{-3}\)) also occurred in the December, indicating more energy consumption and pollutant emissions. Additionally, the lowest wind speeds and temperatures also occurred in December, resulting in the accumulation of pollutants.

Table 2. The mean (mean ± standard deviation) of meteorological factors, concentrations of gases and WSIIs.

|          | May       | August    | October   | December  | Mean       |
|----------|-----------|-----------|-----------|-----------|------------|
| RH (%)   | 70.58 ± 22.00 | 71.95 ± 17.06 | 76.82 ± 17.32 | 71.17 ± 23.34 | 72.62 ± 20.26 |
| T\(^{\circ}\) (°C) | 22.73 ± 4.73    | 30.14 ± 3.76    | 18.82 ± 4.58    | 6.77 ± 4.14    | 19.62 ± 9.49    |
| WS\(^{b}\)(m·s\(^{-1}\)) | 1.40 ± 0.75     | 1.45 ± 0.71     | 1.36 ± 0.70     | 1.04 ± 0.64    | 1.31 ± 0.72    |
| SO\(_2\) | 7.70 ± 3.37     | 4.59 ± 1.58     | 6.98 ± 3.37     | 12.57 ± 5.37   | 7.95 ± 4.67    |
| NO\(_2\) | 39.55 ± 17.99   | 20.23 ± 10.38   | 36.13 ± 15.96   | 50.20 ± 17.35  | 36.49 ± 19.02  |
| PM\(_{2.5}\) | 58.39 ± 26.00   | 26.30 ± 13.55   | 47.26 ± 26.05   | 89.35 ± 40.21  | 56.03 ± 36.35  |
| Cl\(^{-}\) | 0.68 ± 0.69     | 0.32 ± 0.21     | 0.98 ± 0.60     | 2.65 ± 1.43    | 1.07 ± 1.33    |
| NO\(_3\) | 8.38 ± 6.93     | 2.12 ± 1.92     | 10.26 ± 8.44    | 20.62 ± 12.15  | 9.86 ± 10.75   |
| SO\(_4\) | 9.22 ± 3.94     | 5.48 ± 3.98     | 7.35 ± 5.05     | 9.36 ± 5.93    | 7.57 ± 4.99    |
| NH\(_4\) | 5.80 ± 3.10     | 2.76 ± 1.85     | 5.54 ± 4.18     | 10.50 ± 6.43   | 5.86 ± 4.91    |
| Na\(^{+}\) | 0.19 ± 0.11     | 0.17 ± 0.10     | 0.23 ± 0.16     | 0.37 ± 0.18    | 0.23 ± 0.16    |
| K\(^{+}\) | 0.75 ± 0.61     | 0.23 ± 0.11     | 0.40 ± 0.24     | 0.94 ± 0.54    | 0.45 ± 0.47    |
| Ca\(^{2+}\) | 0.32 ± 0.35     | 0.16 ± 0.08     | 0.19 ± 0.17     | 0.61 ± 0.47    | 0.27 ± 0.30    |
| Mg\(^{2+}\) | 0.06 ± 0.04     | 0.05 ± 0.03     | 0.08 ± 0.04     | 0.09 ± 0.08    | 0.08 ± 0.10    |

Calculations

- Mean ± SD
- Sum\(^{c}\)(μg·m\(^{-3}\))
- Percentage\(^{d}\)(%)

\(^{a}\) Temperature. \(^{b}\) Wind speed. \(^{c}\) sum of WSIIs. \(^{d}\) mean value of sum of WSIIs divided by mean concentration of PM\(_{2.5}\).
3.2. WSIIIs in PM$_{2.5}$

As shown in Table 2, the mean WSIIIs concentration in PM$_{2.5}$ was 26.49 $\pm$ 20.78 $\mu$g·m$^{-3}$, which contributed 48.28 $\pm$ 15.33% to PM$_{2.5}$ concentrations. The contribution was notably higher than that in Taiyuan (32.86%) [48], but lower than that in Nanning (51.65%) [43]. The concentrations of WSIIIs in PM$_{2.5}$ from high to low were NO$_3^-$ (9.86 $\pm$ 10.75 $\mu$g·m$^{-3}$), SO$_4^{2-}$ (7.57 $\pm$ 4.99 $\mu$g·m$^{-3}$), NH$_4^+$ (5.86 $\pm$ 4.91 $\mu$g·m$^{-3}$), Cl$^-$ (1.07 $\pm$ 1.33 $\mu$g·m$^{-3}$), K$^+$ (0.45 $\pm$ 0.47 $\mu$g·m$^{-3}$), Ca$^{2+}$ (0.27 $\pm$ 0.30 $\mu$g·m$^{-3}$), Na$^+$ (0.23 $\pm$ 0.16 $\mu$g·m$^{-3}$), and Mg$^{2+}$ (0.08 $\pm$ 0.10 $\mu$g·m$^{-3}$). On average, the SNA (SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) concentrations were 23.29 $\mu$g·m$^{-3}$ in sum, contributing 91.73% and 41.57% to WSIIIs and PM$_{2.5}$, respectively. The mean concentration of SNA was lower than that in Zhengzhou (28.4 $\mu$g·m$^{-3}$) and in Xinxian (29.6 $\mu$g·m$^{-3}$) in 2017–2018 [16]. However, the mean contribution of SNA to PM$_{2.5}$ concentrations in Hangzhou were notably higher than that in Zhengzhou (23.8%) and in Xinxian (23.0%) [16]. This may due to the higher RH in Hangzhou (72.62%) than those in Zhengzhou (62.6%) and in Xinxian (60.9%) as the higher RH could enlarge the sizes of particle matters, thus facilitating the absorption of NO$_2$ and SO$_2$ on the aerosol surfaces through heterogeneous formations of nitrates and sulfates [14].

Figure 1 shows the mean variations of PM$_{2.5}$, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ in this study, as well as previous studies in Hangzhou [27,28], as well as comparing these with measurements at Handan, a typical polluted city in the North China Plain, during similar a period [14]. As shown in Figure 1, annual concentrations of PM$_{2.5}$ decreased by $\sim$26.06% from the periods of April 2004–March 2005 (108.2 $\mu$g·m$^{-3}$) to December 2014–November 2015 (80.0 $\mu$g·m$^{-3}$) and then continuously decreased by $\sim$35.43% to 2017 (56.03 $\mu$g·m$^{-3}$) (this study). Annual concentrations of SO$_4^{2-}$ and NH$_4^+$ also showed a decreasing trend. Such remarkable reductions could be attributed to the implementation of stringent emission control measures, especially on emissions of combustions of traditional fossil fuel [17,49]. NO$_3^-$ showed a different trend, rising from 8.3 $\mu$g·m$^{-3}$ (April 2004–March 2005) to 14.2 $\mu$g·m$^{-3}$ (December 2014–November 2015) and then decreasing to 9.86 $\mu$g·m$^{-3}$ in 2017. This may due to the increasing automobile population. The automobile population was 0.41 million in the year of 2004, and it notably increased to 2.54 million in 2013 [26], resulting in higher annual NO$_3^-$ concentrations in December 2014–November 2015. Though the automobile population was 2.79 million in 2017 and was higher than that of 2013 [26], the implementation of stringent emission control measures since 2013 could be the main cause of the reduction in NO$_3^-$.
Figure 1. Comparisons of concentrations of PM$_{2.5}$ and WSIIs with previous results in the cities of Hangzhou and Handan.

The average SNA/PM$_{2.5}$ value was 32.0% during April 2004–March 2005 (calculated by SNA and PM$_{2.5}$ average concentrations in [28]). Notably, it increased 1.39-fold to 44.5% in 2014–2015 [27] and then generally stayed stable in 2017 (41.57%) (this study), indicating the increase contributions of secondary reactions to PM$_{2.5}$ in Hangzhou. SNA/PM$_{2.5}$ ratios in Handan were 40.4%, lower than those in this study, representing a lower contribution of secondary transformations to PM$_{2.5}$ in Handan. As discussed above, this is partly due to higher RH on average in Hangzhou than in Handan because higher RH could promote liquid and heterogeneous reactions, resulting in the increased formations of SNA [14].

WSIIs values showed obvious variations during the four sampling months in Hangzhou. As shown in Table 2, the mean concentrations of Cl$^-$ in December were the highest, being 8.28 times higher than those in August because of enhanced emissions from coal combustion in winter. The concentrations of K$^+$ were higher in December and May. This can be attributed to biomass burning in May and December, since K$^+$ is a dominant ion from biomass burning [50]. This differed from Beijing, where concentrations of K$^+$ were found to be the highest in autumn [19]. SO$_4^{2-}$ is commonly believed to be a crucial ion in WSIIs and is mainly produced by photochemical oxidations of sulfur-containing precursors [51]. In this study, SO$_4^{2-}$ showed low concentration levels and minor changes in four sampling months. On the other hand, NO$_3^-$ indicated strong variations, with the mean concentrations in December being 9.73 times higher than those in August. Strong volatility of nitrate (e.g., NH$_4$NO$_3$) under high temperature conditions can be a possible reason for low concentrations of NO$_3^-$ in August, whereas the high NO$_3^-$ concentration in December may intensify the production of NO$_3^-$. NH$_4^+$ could result from fertilizers and conversion from NH$_3$ and be affected by aerosol acidity, temperature and water availability [52]. In this study, the variation order of NH$_4^+$ from low to high is December > October > May > August. Ca$^{2+}$, as an important indicator of dust, showed very low concentrations in the observation.
3.3. Acidity

We used ion balance calculations to investigate the PM$_{2.5}$ acidities, which can be strongly influenced by the equivalence of WSIIs. Here, two equations (Anion Equivalence and Cation Equivalence) were used for calculating the balance between anions and cations as follows:

(1) Cation Equivalence (CE) = $[\text{NH}_4^+] + [\text{Na}^+] + [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}]$

(2) Anion Equivalence (AE) = $2[\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{Cl}^-]$

where the concentrations of WSIIs ($\mu$g·m$^{-3}$) were converted into micro-equivalents ($\mu$mol·m$^{-3}$) in the above two equations.

As illustrated by the scatter plots in Figure 2, strong correlations existed between CE vs. AE. The slopes of correlation equations in May (Figure 2a), August (Figure 2b), October (Figure 2c), and December (Figure 2d) were 1.00, 1.03, 1.01, and 1.11, respectively, revealing a slightly basic trend and a deficiency in anions (CE/AE > 1) in the PM$_{2.5}$ samples. Good correlations existed between $[\text{NH}_4^+]$ vs. $([\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{Cl}^-])$ with the slopes of 0.96 (May), 1.00 (August), 0.99 (October), and 1.08 (December), revealing that anions could be fully neutralized by $\text{NH}_4^+$ except in May; that is, other cations might affect the neutralization in May in addition to $\text{NH}_4^+$. Thus, we calculated the correlations between $([\text{NH}_4^+] + [\text{K}^+])$ and $([\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + [\text{Cl}^-])$ in May, and found that the slope was 1.00, suggesting that $\text{K}^+$ was another cation that could strongly influence the neutralization of anions in PM$_{2.5}$. Comparatively, the result differed from that of Ningbo, where $\text{Ca}^{2+}$ was found to be another cation affecting the neutralization [27].

Figure 2. Scatter plots of cations equivalents (CE) versus anions equivalents (AE) in May (a), August (b), October (c) and (d) December.
3.4. Formations of Secondary Aerosols

Sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) had been frequently used in previous studies to measure the degrees of oxidation of sulfur and nitrogen [27,35,52]. Higher SOR and NOR values could indicate a larger proportion of sulfate and nitrate formed by the secondary chemical reactions [53]. Thus, we calculated the values of the sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) in four seasons for further investigating the transformation of SO$_2$ to sulfate and NO$_2$ to nitrate, respectively [53]:

\[
(1) \quad \text{SOR} = \frac{[\text{SO}_2^{2-}]}{[\text{SO}_2^{2-}] + [\text{SO}_3^{2-}] + [\text{NO}_2^+] + [\text{NO}_3^-]}
\]

\[
(2) \quad \text{NOR} = \frac{[\text{NO}_2^+] + [\text{NO}_3^-]}{[\text{NH}_4^+] + [\text{H}_2\text{O}^+] + [\text{H}_3\text{O}^+] + [\text{H}_4\text{O}^+]} + [\text{NO}_2^+] + [\text{NO}_3^-]
\]

Secondary transformations of SO$_2$ and NO$_2$ were dominant sources of sulfate and nitrate, respectively, when the values of SOR and NOR were > 0.1 [54]. During the study period, the average values of SOR and NOR were 0.39 ± 0.13 and 0.15 ± 0.10, with the highest values of 0.87 and 0.65, respectively. Mean values of SOR were 0.45 in May, 0.41 in August, 0.39 in October and 0.32 in December. Lower values of SOR in December may be due to lower temperature, since low temperature was an unfavorable factor for transformations of SO$_2$ to SO$_2^{2-}$ [51]. Higher values of SOR in May and August were a result of higher solar radiation and temperature, which could enhance the reactions of SO$_2$ with OH radicals [27]. Mean values of NOR were 0.14 in May, 0.07 in August, 0.16 in October and 0.22 in December. NOR values showed the lowest value in August, although solar radiation was more favorable for the conversion of NO$_2$ to nitrate [54]. This may be due to the fact that nitrates (e.g., NH$_4$NO$_3$) can decompose into gaseous NH$_3$ and HNO$_3$ under higher temperatures in summer time [51].

3.5. Back Trajectory and Clusters Analysis

As shown in Figure 3 and Table 3, in May (Figure 3a), cluster 1 accounted for 9.70% of total air masses, mainly through the East China Sea and the southern part of Zhejiang province, carrying the highest concentrations of sulfate and PM$_{2.5}$. Industrial areas in the southern part of Zhejiang province (e.g., Ningbo) may have contributed to cluster 2 [55]. Cluster 2 accounted mostly for total air masses (41.08%) through the East China Sea and Zhejiang province, carrying the lowest PM$_{2.5}$ concentrations among the four clusters. 35.46% of air masses (cluster 3) came through Shandong and Jiangsu provinces, carrying the highest SNA before approaching Hangzhou. Cluster 3 passed through polluted and coastal areas, so moisture coming from the sea may have facilitated the secondary reactions of SO$_2$ and NO$_2$ [29]. Cluster 4 carried the lowest SNA concentrations through Hubei and Jiangxi provinces.

In August (Figure 3b), cluster 1 accounted for 24.53% of total air masses mainly through Jiangxi, Anhui provinces, carrying the highest concentrations of SNA and PM$_{2.5}$. Cluster 2 and cluster 3 accounted for 23.13% and 19.76% of total air masses which mainly passed the Yellow Sea and the South China Sea. Cluster 4 accounted for 32.56% of total air masses which mainly passed the South China Sea, Guangdong province and Fujian province, carrying the lowest concentrations of SNA and PM$_{2.5}$. In October (Figure 3c), the air masses of cluster 1 (50.30%)—which originated from the Liaoning province passed through the Yellow Sea and Jiangsu province to reach the site—were dominated by the lower concentrations of PM$_{2.5}$ and SNA. Cluster 3, passing through the Yellow Sea and the Bohai Sea, accounted for 31.04% of total air masses. Air masses passing through Henan and Anhui provinces (cluster 2) and the southern region of Zhejiang province (cluster 4) carried the high concentrations of PM$_{2.5}$ and SNA and they accounted for a low percentage (18.68%) of the total air masses. In December (Figure 3d), the air masses originated from the northwest and southwest. Air masses of cluster 1 originated from the Inner Mongolia region, passing through Hebei and Shandong provinces with the lowest concentrations of SNA and PM$_{2.5}$. This
was because cluster 1 mainly passed through the clean sea areas which caused the low PM$_{2.5}$ level. Cluster 2, which came from Bohai Sea through the middle areas of Jiangsu province, carried the highest concentrations of SNA (45.16 μg·m$^{-3}$). Central areas of Jiangsu province were also found to be one of important potential sources areas for the winter haze event because of their high emissions [29,31,55]. Cluster 3 through Shanxi, Henan and Anhui provinces accounted for 46.02% of total air masses and carried the highest PM$_{2.5}$ concentrations (100.14 μg·m$^{-3}$). Cluster 3 carried lower SNA concentrations than cluster 2 did, and this could be explained by the inland pathways of cluster 3 (i.e., less moisture than coastal pathway of cluster 2) [29].

![Figure 3](image)

**Figure 3.** Clusters from 72 h backward trajectory analyses in May (a), August (b), October (c) and December (d) in 2017.

**Table 3.** Percentages of trajectories, mean concentrations of PM$_{2.5}$, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ for each trajectory cluster in May, August, October and December (see Figure 3).

| Seasons | Cluster | Percent  | PM$_{2.5}$ | SNA  | NO$_3^-$ | SO$_4^{2-}$ | NH$_4^+$ | Main Area Passed by Air Masses |
|---------|---------|----------|------------|------|----------|-------------|----------|--------------------------------|
| May     | 1       | 9.70%    | 65.17 ± 19.92 | 22.24 ± 4.81 | 5.49 ± 1.77 | 11.03 ± 2.62 | 5.72 ± 1.26 | Zhejiang province              |
|         | 2       | 41.08%   | 53.91 ± 23.39 | 22.23 ± 10.62 | 8.63 ± 3.40 | 8.11 ± 5.60 | 5.49 ± 2.68 | East China Sea, Zhejiang province |
|         | 3       | 35.46%   | 64.65 ± 31.06 | 29.43 ± 16.68 | 11.85 ± 6.98 | 10.35 ± 7.79 | 7.23 ± 4.07 | Shandong, Jiangsu provinces    |
|         | 4       | 13.71%   | 57.75 ± 23.21 | 18.77 ± 8.55 | 4.28 ± 1.53 | 9.78 ± 3.92 | 4.71 ± 2.22 | Hubei, Jiangxi provinces       |
| August  | 1       | 24.53%   | 39.27 ± 12.69 | 19.16 ± 9.32 | 4.87 ± 1.58 | 9.21 ± 4.12 | 5.08 ± 2.44 | Jiangxi, Anhui provinces       |
|         | 2       | 23.13%   | 32.74 ± 10.47 | 17.11 ± 4.62 | 5.64 ± 3.02 | 7.18 ± 2.77 | 4.29 ± 1.18 | Yellow Sea                     |
|         | 3       | 19.76%   | 34.28 ± 7.63  | 9.96 ± 5.48  | 2.59 ± 0.96 | 4.72 ± 4.26 | 2.65 ± 1.52 | South China Sea                |
3.6. PCA Analysis

PCA results are shown in Table 4. In May, the WSIIs were mainly the result of two principal sources which constituted 56.55% of total variances. Component 1 accounted for 37.17% of total variance with very high loadings of SNA and K⁺, revealing that vehicle emissions, biomass burning, and secondary inorganic aerosols made significant contributions to PM$_{2.5}$ in May. Component 2 accounted for 19.38% of total variance with high loadings of Na⁺, Ca⁺, and Mg²⁺, suggesting possible main contributions from sea salts and construction dusts.

In August, three principal components identified explain 70.14% of the total variance. Component 1 accounted for 40.83% of variance with high loadings of SNA and K⁺, revealing that the sources of secondary aerosols, vehicle emissions and biomass burning contributed notably in August. Component 2 with high loadings of Na⁺ and Mg²⁺ could be attributed to sea salts. Component 3 accounted for 13.06% of total variance with a high loading of Ca²⁺ contributed from dusts of constructions.

In October, three main factors were obtained from the PCA model calculation. Component 1 accounted for 41.05% of total variance with high loadings of SNA and Cl⁻, indicating major contributions from fossil fuel combustions, vehicle emissions and secondary aerosols. Component 2 accounted for 18.59% of total variance with high loadings of Na⁺ and Mg²⁺ probably resulted from sea salt sources. Component 3 covered 11.36% of total variance with high loadings of K⁺ and Ca²⁺ probably contributed by biomass burning and dusts.

In December, there were two major components which accounted for 69.31% of total variance. Component 1 accounting for 45.56% of total variance comprised SNA, Na⁺ and Cl⁻, suggesting the contributions from secondary aerosols, vehicle emissions and coal combustions. Component 2, accounting for 23.75% of variance with high loading of K⁺ and Ca²⁺, could be explained by contributions from biomass burning and dust from constructions.
Table 4. Results of the principal component analysis for WSIIs in PM$_{2.5}$ in Hangzhou.

| Season | May | August | October | December |
|--------|-----|--------|---------|----------|
|        | Component 1 | Component 2 | Component 3 | Component 1 | Component 2 | Component 3 | Component 1 | Component 2 | Component 3 |
| NO$_3^-$ | 0.88 | -0.01 | 0.86 | -0.08 | -0.18 | 0.93 | -0.14 | -0.18 | 0.90 | -0.23 |
| SO$_4^{2-}$ | 0.65 | -0.30 | 0.92 | -0.08 | 0.01 | 0.79 | -0.45 | 0.07 | 0.82 | -0.45 |
| NH$_4^+$ | 0.92 | -0.13 | 0.98 | -0.11 | -0.05 | 0.95 | -0.25 | -0.12 | 0.91 | -0.37 |
| Cl$^-$ | 0.20 | -0.04 | -0.11 | -0.66 | 0.25 | 0.71 | 0.31 | -0.18 | 0.65 | 0.16 |
| K$^+$ | 0.69 | 0.38 | 0.82 | 0.07 | 0.24 | 0.04 | -0.48 | 0.77 | 0.57 | 0.60 |
| Na$^+$ | 0.55 | 0.59 | 0.07 | 0.69 | -0.32 | 0.30 | 0.71 | 0.30 | 0.72 | 0.48 |
| Ca$^{2+}$ | -0.32 | 0.68 | 0.04 | 0.36 | 0.89 | 0.29 | 0.14 | 0.50 | 0.05 | 0.83 |
| Mg$^{2+}$ | -0.05 | 0.69 | 0.13 | 0.48 | 0.05 | 0.45 | 0.59 | 0.20 | 0.21 | 0.40 |
| variance (%) | 37.17 | 19.38 | 40.83 | 16.25 | 13.06 | 41.05 | 18.59 | 11.36 | 45.56 | 23.75 |
| Cumulative (%) | 37.17 | 56.55 | 40.83 | 57.08 | 70.14 | 41.05 | 59.64 | 71.00 | 45.56 | 69.31 |

Note: values in bold indicate loading factors discussed in this study.

4. Conclusions

To investigate potential sources and provide scientific insights into seasonal variations in the chemistry of WSIIs (SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Cl$^-$, Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$) of PM$_{2.5}$ in Hangzhou, hourly concentrations of WSIIs, as well as PM$_{2.5}$, NO$_2$ and SO$_2$ were measured online at an urban site during four months (May, August, October and December) in 2017. The hourly concentrations of PM$_{2.5}$ during the whole campaign varied from 1 to 292 μg·m$^{-3}$ with the mean of 56.03 μg·m$^{-3}$, which exceeded Chinese National Ambient Air Quality Standard grade II (35 μg·m$^{-3}$). The average concentration of WSIIs was 26.49 ± 20.78 μg·m$^{-3}$, which contributed 48.28% to PM$_{2.5}$ mass. SNA (SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) were the most abundant ions in PM$_{2.5}$ and averagely comprised 41.57% of PM$_{2.5}$ during the observation. PM$_{2.5}$, NO$_2$, SO$_2$ and all WSIIs showed higher concentrations in December among four sampling months, possibly due to higher emissions and unfavorable meteorological factors (e.g., lower wind speed and temperature). SOR and NOR were, on average, 0.39 ± 0.13 and 0.15 ± 0.10, respectively, revealing that secondary transformations of SO$_2$ and NO$_2$ were dominant sources of sulfate and nitrate. Secondary aerosols and vehicle emissions were dominant sources of WSIIs in Hangzhou based on the PCA analysis and regional transports of aerosols cannot be neglected. Thus, in the future, further controls on emissions of precursors of SNA (e.g., SO$_2$ and NO$_2$) should be implemented in Hangzhou. Moreover, emissions of industrial areas should be controlled at local and regional scales.

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