Chemical Characterization, Source Identification, and Health Risk Assessment of Atmospheric Fine Particulate Matter in Winter in Hangzhou Bay

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Abstract: PM\(_{2.5}\) is an important pollutant which affects air quality and human health. In this study, chemical components (water-soluble inorganic ions, organic carbons (OC), elemental carbons (EC), and elemental metals) and health effects were analyzed in wintertime in a suburban area in Hangzhou Bay. OC and SNA (sulfate, nitrate, and ammonium) contributed 76.2% to local PM\(_{2.5}\). NH\(_4^+\) existed mainly in the form of \((\text{NH}_4)^2\text{SO}_4\) and NH\(_4\)NO\(_3\). Seven sources were resolved from PMF analysis, namely secondary inorganic aerosol (31.8%), vehicle exhaust (19.5%), industry mixed with coal combustion (16.3%), crustal dust (9.5%), biomass burning (9.4%), sea salt (8.7%), and the leather industry (4.8%). Potential source contribution function (PSCF) and concentration weighted trajectory (CWT) analysis were applied to study regional transport in this region. Secondary inorganic formation was enhanced from the air plume from the northwest, especially from north Jiangsu Province. The results of the health risk assessment of associated metals indicated the higher potential of Cr and Mn to cause noncarcinogenic effects in children. A significant carcinogenic risk was observed for all people of Cr emitted from the leather industry. Our results showed the chemical characterization and sources of PM\(_{2.5}\) in a suburban region, the health effects of which should be addressed in future policies to safeguard public health, especially in the leather industry.

Keywords: PM\(_{2.5}\); source apportionment; PSCF; CWT; heavy metal; health risk

1. Introduction

Recently, China has developed rapidly in its economics and urbanization, leading to associated air pollution. PM\(_{2.5}\) (particles with aerodynamic diameter no more than 2.5 µm) pollution has attracted more focus due to its important influences on haze formation, climate change, human health, and economic loss [1–3]. Thanks to the implementation of the Air Pollution Prevention and Control Action Plan in 2013 and the Blue-Sky Defense War in 2018, in terms of energy construction adjustment and optimization, the national annual PM\(_{2.5}\) concentration declined from 72 µg/m\(^3\) in 2013 to 30 µg/m\(^3\) in 2021 (data from Ministry of Ecology and Environment of the People's Republic of China, https://www.mee.gov.cn/hjzl/shhjzx/) (accessed on 27 May 2014)). However, it is still much higher than the newly published guidelines (5 µg/m\(^3\)) for annual PM\(_{2.5}\) concentration from...
the WHO in 2021 (https://www.who.int/publications/i/item/9789240034433 (accessed on 27 May 2022)).

PM$_{2.5}$ originates from various sources by primary emissions and secondary formation, such as coal combustion, vehicle emissions, crustal dust, industry, and ship emissions [4,5]. With the objective of controlling air pollution, source apportionment is widely performed to resolve the potential sources of air pollutants using the chemical mass balance model (CMB) and positive matrix factorization (PMF) [6–8]. However, limited examples in the literature have investigated the source-associated health risks of elements in PM$_{2.5}$. Toxic heavy metals and organics (e.g., PAHs) have become important contents increasing the health risks of PM$_{2.5}$ [9–11]. Previous studies indicate that PM$_{2.5}$-bound heavy metals can cause oxidative DNA damage [12]. Thus, field campaigns, either long-term or short-term, are performed to study the composition, spatiotemporal variation, and potential emission sources, as well as to evaluate the health risks of PM$_{2.5}$-associated heavy metals [13–16].

The Yangtze River Delta region (YRD) is one of the highest industrialized and urbanized regions in China, while most of the studies on atmospheric chemistry are performed in Shanghai or Jiangsu Province [17–20]. As another fast-developing province in YRD, Zhejiang province attracts less attention than the above provinces, and the campaigns are mainly conducted in urban areas, such as Hangzhou and Ningbo [21–25]. Sources extracted from PMF analysis indicated that secondary formation and vehicle emissions were the top two factors contributing to the local PM$_{2.5}$ pollution [25]. However, with the rapid urbanization and industrialization of the suburban areas and new rural construction, air pollution and its health effects on residents in suburban and rural regions in Zhejiang Province should also receive attention [26,27].

In this study, PM$_{2.5}$ was collected from a suburban area near Hangzhou City, the capital of Zhejiang province in wintertime. The main purposes of this work include: (1) to study the compositions and pollution characteristics of PM$_{2.5}$; (2) to determine the main emission sources and originated regions of PM$_{2.5}$; and (3) to evaluate the noncarcinogenic and carcinogenic health risks of heavy metals and the source-associated health risks.

2. Materials and Methods

2.1. Site Description

The sampling site was chosen at Haining County (30.46°N, 120.51°E), which is located in Jiaxing City, Zhejiang Province (Figure 1). Haining is a satellite city of Hangzhou, the capital of Zhejiang Province. The surroundings near the sampling site included some restaurants, residential districts, and industries. There was a main street about 200 m west of the sampling site, so traffic emissions may be important for this site. Thus, it could represent the characteristics of the PM$_{2.5}$ pollution at Haining County. Due to the relatively heavy PM$_{2.5}$ pollution in wintertime, especially in December (Figures S1 and S2 and Table 1), the field campaign was conducted in winter, from 14 December 2019 to 4 January 2020, across weekdays as well as weekends. The starting sampling time was 0:00, 6:00, 12:00, and 18:00, respectively, and the sampling period lasted 5 h for each sample. A total of 53 samples and 2 blank samples were collected during the campaign.

Table 1. The weather conditions and PM$_{2.5}$ concentrations of sampling site in 2019. Abbreviation: WS for wind speed.

<table>
<thead>
<tr>
<th>Season</th>
<th>PM$_{2.5}$ (µg/m$^3$)</th>
<th>T (°C)</th>
<th>RH (%)</th>
<th>WS (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>44.67</td>
<td>17.69</td>
<td>53.08</td>
<td>2.15</td>
</tr>
<tr>
<td>Summer</td>
<td>23.91</td>
<td>27.84</td>
<td>57.39</td>
<td>2.38</td>
</tr>
<tr>
<td>Autumn</td>
<td>40.60</td>
<td>20.30</td>
<td>54.34</td>
<td>1.91</td>
</tr>
<tr>
<td>Winter</td>
<td>60.36</td>
<td>7.55</td>
<td>59.75</td>
<td>1.81</td>
</tr>
</tbody>
</table>
Figure 1. Sampling site location of the field campaign. (a) Location of Zhejiang Province in China; (b) the sample site location in Zhejiang Province, where the red star represents the sampling site.

2.2. Component Analysis

2.2.1. Weighing Procedure and PM$_{2.5}$ Sampling

The quartz filters were baked in the oven at 450 °C for 4 h to remove the organic residuals on the filters. After pretreatment, the filters were balanced in an automatic constant temperature (25 ± 5 °C) and humidity (50 ± 5%) precision weighing system (CR-E, Weizhizhao Co., Ltd., Hangzhou, China) for 48 h and then weighed by an electronic balance (EX-1025a, Lester Scientific Instruments Co., Ltd., Xiamen, China) with high accuracy (10 µg). Every filter was required to be weighed at least twice to keep the difference smaller than 15 µg. After weighing, all of the filters were stored in a refrigerator at −20 °C.

The PM$_{2.5}$ sampler (PMS-200A, Concentrating Light Technology (Hangzhou) Co., Ltd., Hangzhou, China) was installed on the top of a 5-floor building, which was about 20 m above the ground. The sampling site was 7 km away from the Qiantang River, which flows into the East China Sea. The sampling flow rate for PM$_{2.5}$ was 16.67 L/min. All of the sampled filters were stored in a refrigerator at −20 °C to avoid contamination and volatilization.

2.2.2. OC and EC Analysis

Organic carbon (OC) and elemental carbon (EC) in PM$_{2.5}$ were measured using a thermal/optical carbon analyzer (DRI Model 2001, Atmoslytic Inc., Calabasas, CA, USA) following the IMPROVE (Interagency Monitoring of Protected Visual Environments) protocol. Before the measurement, firstly, the residual organics left in the instrument were cleaned by running the BAKEOVEN procedure. A 0.52 cm$^2$ quartz filter cut from the whole sampled filter was placed in a quartz vessel and proceeded with different temperature programs when measuring OC and EC. Briefly, when detecting OC, the samples were exposed to helium (He) and the temperature was increased to 140 °C, 280 °C, 480 °C, and 580 °C periodically. When it came to EC determination, the carrier gas was He mixed with 2% O$_2$ and the samples were gradually heated from 580 °C to 740 °C, to 840 °C. OC and EC were oxidized to CO$_2$ in a MnO$_2$ oven firstly, and then in the presence of Ni and H$_2$, CO$_2$ was reduced to CH$_4$ in a reduction furnace. The cutting point of OC/EC was determined by measuring the reflectivity and transmittance of the filter using a laser signal at 633 nm wavelength [28]. IMPROVE defined the OC as the OC1 + OC2 + OC3 + OC4 + OPC, and the EC as the EC1 + EC2 + EC3 – OPC. During the analysis, blank samples were tested for removing the interferences. The instrument was calibrated by using sucrose solution before and after the measurement. The detection limit of the OC/EC analyzer was 0.2 µgC/cm$^2$, 0.82 µgC/cm$^2$, and 0.93 µgC/cm$^2$ for TOC (total organic carbon), TEC (total elemental carbon), and TC (total carbon), respectively.
2.2.3. WSIIs Analysis

A quarter of the sampled filters were cut into small pieces by a ceramic scissor for water-soluble inorganic ion (WSII) analysis. The pieces were soaked in 25 mL deionized water (18.2 MΩ cm; Millipore, MA, USA) in a centrifuge tube and extracted for 30 min twice in an ultrasonic bath with ice to keep room temperature. Then, the extracted solutions were filtered by a 0.22 µm microporous membrane to remove impurities and stocked at 4 °C in the refrigerator for further analysis [29]. The concentration of WSIIs in PM$_{2.5}$ samples was determined by ion chromatography (ICS-900, Thermo Fisher, Waltham, MA, USA). Anion species (SO$_{4}^{2-}$, NO$_{3}^{-}$, and Cl$^{-}$) were detected with a Metrosep A5-25 separator column, and cation ions (K$^{+}$, Ca$^{2+}$, Na$^{+}$, Mg$^{2+}$, and NH$_{4}^{+}$) were measured with a Metrosep C2-250 separator column. The mobile phase of the ion chromatography was 20 mmol of methanesulfonic acid (MSA). The detection limit of each inorganic ion was calculated as 3 times the standard deviation of the determination process of low concentration standard sample (Table S1). When conducting the sample testing, a standard sample was added among every 10 samples to check the stability of the instrument.

2.2.4. Heavy Metal Analysis

The heavy metals in PM$_{2.5}$ were detected by an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700, USA). A quarter of the sampled filters were cut into small pieces and stored in the digestion tank for further analysis. The pieces were immersed in 10.0 mL of a HNO$_{3}$-HCl mixture solution and proceeded in an automatic graphite digestion instrument (Thomas Cain, DEENA II, USA) for digestion. The digestion lasted for 15 min at a temperature of 200 °C. After cooling, the extraction was diluted to 50 mL with deionized water [30]. A total of 13 elements (Al, V, Cr, Mn, Fe, Cu, Zn, As, Mo, Cd, Sb, Ba, Pb) were analyzed, since the other elements were under the detection limit of ICP-MS. The detection limit was within the range of 0.1–0.5 ppt and the sensitivity of the instrument was $10^{-7}$–5 $\times 10^{-7}$.

2.3. Data Analysis

2.3.1. PMF

EPA PMF 5.0 was used in this study to resolve the possible emission source in this area. After checking the data (WSIIs, OC, EC, and metals) obtained from the offline instruments, a total of 27 chemical components were input as parameters, including OC (OC1, OC2, OC3, OC4), EC (EC1, EC2), WSIIs (NO$_{3}^{-}$, SO$_{4}^{2-}$, Cl$^{-}$, NH$_{4}^{+}$, K$^{+}$, Mg$^{2+}$, Ca$^{2+}$, Na$^{+}$), and 13 elements (Al, V, Cr, Mn, Fe, Cu, Zn, As, Mo, Cd, Sb, Ba, Pb). The uncertainty calculation in this study follows the equation as follows [31]:

\[
\text{Unc} = \begin{cases} 
5 \times DL, & c < DL \\
\sqrt{(\text{Error Fraction} \times \text{concentration})^2 + (0.5 \times DL)^2}, & c > DL
\end{cases}
\]

Error fraction was 10% in this study, and the DL was the detection limit of each species. Seven reasonable factors were selected after several attempts.

2.3.2. Backward Trajectory and Clustering

The backward trajectory analysis was conducted using Meteoinfo software. In this study, 48 h backward trajectory with 6 h interval was generated. The spatial resolution was 0.5° × 0.5°. The meteorological data were downloaded from the Global Data Assimilation System (GDAS) of the National Center for Environmental Prediction (https://www.ready.noaa.gov/archives.php (accessed on 4 January 2022)). The arrival height of clusters was set to 500 m for the long-range transport study [32,33]. Then, the clustering analysis was conducted based on the trajectories using Meteoinfo software.
2.3.3. PSCF and CWT Analysis

In order to analyze the regional transport of different sources, potential source contribution function (PSCF) and concentration weighted trajectory (CWT) analyses were applied to the potential emission sources resolved from PMF analysis. Briefly, the PSCF and CWT values in the \( i_j \)th cell were defined as below:

\[
PSCF_{ij} = \frac{m_{ij}}{n_{ij}}
\]

\[
CWT_{ij} = \frac{\sum_{l=1}^{M} C_l T_{ijl}}{\sum_{l=1}^{M} T_{ijl}}
\]

where \( n_{ij} \) was the total number of trajectory endpoints which fell into the \( i_j \)th cell and \( m_{ij} \) was the number of polluted trajectory endpoints in the same cell whose concentration was higher than the threshold criterion. \( M \) was the total number of trajectory l. \( C_l \) was the measured concentration of different species of trajectory l. \( T_{ij} \) was the duration that trajectory l stayed in the \( i_j \)th cell. The critical value in this study was set as the mean concentration of each source factor or species. To minimize the uncertainty of values smaller than 3 times \( n_{ij} \), a weight function \( W_{ij} \) was applied to PSCF and CWT analysis, and the calculation equation was as follows [34]:

\[
W_{ij} = \begin{cases} 
1.00 & n_{ij} > 3n_{Ave} \\
0.70 & 3n_{Ave} > n_{ij} > n_{Ave} \\
0.42 & n_{Ave} > n_{ij} > 0.5n_{Ave} \\
0.17 & 0.5n_{Ave} > n_{ij} > 0 
\end{cases}
\]

2.4. Health Risk Assessment Methods

The respiratory health risk assessment of heavy metals (e.g., As, Cr, Mn, Cu, Cd, Pb and Zn) were studied using the hazard quotient (HQ) and the lifetime cancer risk model proposed by the United States National Environmental Protection Agency (US EPA). First, the average daily inhalation exposure doses of each compound were calculated as the following equations:

\[
(L)ADD = \frac{C \times IRi \times EF \times ED}{BW \times AT}
\]

where ADD and LADD represented daily exposure dose of noncarcinogenic and carcinogenic heavy metals (mg kg\(^{-1}\) d\(^{-1}\)), respectively (Table S2). \( C \) was the upper limit of the 95% confidence interval for the mean concentration of heavy metals in PM\(_{2.5}\) (mg/m\(^3\)) [35], which was calculated by SPSS software. The rest of the detailed parameters used in the model are explained in Table 2.

**Table 2.** Calculation parameters and values of daily average respiratory exposure to heavy metals.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Units</th>
<th>Values</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, metal concentration</td>
<td>mg/m(^3)</td>
<td>95%ulc Children, Adult Male, Adult Female</td>
<td>[36]</td>
</tr>
<tr>
<td>IRi, air inhalation</td>
<td>m(^3)/d</td>
<td>5, 19.2, 14.17</td>
<td>[9]</td>
</tr>
<tr>
<td>EF, exposure frequency</td>
<td>d/a</td>
<td>365, 365, 365</td>
<td>[9]</td>
</tr>
<tr>
<td>ED, exposure years</td>
<td>a</td>
<td>6, 30, 30</td>
<td>[9]</td>
</tr>
<tr>
<td>BW, body weight</td>
<td>kg</td>
<td>15, 62.7, 54.4</td>
<td>[9]</td>
</tr>
<tr>
<td>AT, average exposure times (non)</td>
<td>d</td>
<td>2190, 10,950, 10,950</td>
<td>[37]</td>
</tr>
<tr>
<td>AT, average exposure times (carcinogenic)</td>
<td>d</td>
<td>25,550, 25,550, 25,550</td>
<td>[37]</td>
</tr>
</tbody>
</table>
The health risks caused by heavy metals could be divided into noncarcinogens and carcinogens. The noncarcinogenic risk hazard quotient (HQ) and carcinogenic risk (CR) for heavy metals were calculated as the following equations:

\[ HQ = \frac{ADD}{RfD} \quad (5) \]
\[ CR = LADD \times SF \quad (6) \]

where \( RfD \) was the reference dose of each PM_{2.5}-bound heavy metal (Table S3) and SF was the carcinogenic slope factor. If HQ was smaller than 1, it indicated that the noncarcinogenic risk could be negligible; if HQ was above 1, then it meant that there was a noncarcinogenic risk. When CR was larger than \( 10^{-6} \), it implied that there was a carcinogenic risk; if CR was between \( 10^{-6} \) and \( 10^{-4} \), the carcinogenic risk was within the scope (Table S4). It should receive more attention if CR was larger than \( 10^{-4} \) [30].

3. Results and Discussion

3.1. Overview of PM_{2.5}

Time series of PM_{2.5} and related components at Haining are displayed in Figure 2 and Table S4. The PM_{2.5} concentration in this suburban area ranged from 16.8 to 136.8 µg/m^3, and the mean concentration was 67.13 ± 32.76 µg/m^3. Such a level of PM_{2.5} was almost twice as high as the Chinese National Ambient Air Quality Standard (NAAQS) of PM_{2.5} (35 µg/m^3) and more than ten times as the newly established guideline for PM_{2.5} (5 µg/m^3) from the WHO in 2021. Compared with cities nearby and nationwide, it was lower than Jiaxing City (83.13 µg/m^3) [38] and Shanghai (70.92 µg/m^3) [39], but higher than Beijing (55.7 µg/m^3) [40] and Hangzhou (60.1 µg/m^3) [41] in wintertime. Such a phenomenon implied the PM_{2.5} pollution in YRD region still needed more attention.

![Figure 2](image_url). Temporal variations of compositions in PM_{2.5} and the proportions to PM_{2.5}.

The composition distribution and concentration of the main components are shown in Figure 2. The largest contributor was OC (17.73 ± 10.09 µg/m^3), making up ~30% of PM_{2.5}. EC concentration was 3.45 ± 2.65 µg/m^3 with a proportion of 5.4% in PM_{2.5}. The carbonaceous components were regarded as important contributors in PM_{2.5} and the ratio of OC versus EC was often applied to determine the potential sources [42]. Previous studies suggested an existence of secondary organic aerosol (SOA) when the OC/EC ratio was above 2 [38]. The OC/EC ratio at Haining was from 2.27 to 16.47, with an average ratio of 6.10. The higher OC/EC ratio indicated the higher secondary formation due to the stable atmosphere and low temperature in winter [43].

Then, it was followed by water-soluble inorganic compounds SNA (NO_3^-: 15.29 ± 7.44 µg/m^3, NH_4^+: 8.86 ± 5.04 µg/m^3, and SO_4^{2-}: 7.70 ± 2.86 µg/m^3), accounting...
for almost 50% of the total PM$_{2.5}$ mass concentration. The large proportion of SNA indicated that the secondary inorganic formation of anthropogenic pollutants affected the local area intensely. The correlation coefficients of these water-soluble ions were then analyzed for their formation. The correlation coefficient ($R^2$) between NH$_4^+$ and SO$_4^{2-}$ and NO$_3^-$ were 0.76 and 0.80, respectively. For further determination of the substances, the observed data were compared with the calculated data for NH$_4^+$ (Figure 3) [44]. The calculation of NH$_4^+$ was as below:

\[
\text{NH}_4^+ = 0.375 \left( \text{SO}_4^{2-} \right) + 0.29 \left( \text{NO}_3^- \right) \quad (7)
\]

\[
\text{NH}_4^+ = 0.1875 \left( \text{SO}_4^{2-} \right) + 0.29 \left( \text{NO}_3^- \right) \quad (8)
\]

When the NH$_4^+$ was in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$, the estimation followed Equation (7), while if the NH$_4^+$ existed in the form of NH$_4$HSO$_4$ and NH$_4$NO$_3$, the calculation was as in Equation (8). The correlation coefficient between NH$_4^+$ and SO$_4^{2-}$ was higher in the form of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ (0.94) than NH$_4$HSO$_4$ and NH$_4$NO$_3$ (0.91). Moreover, the gradient of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$ was closer to 1. Thus, the NH$_4^+$ during the period mainly existed as (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$.

\[y = 2.2 + 0.58x, \quad R^2 = 0.94\]

\[y = 1.57 + 0.49x, \quad R^2 = 0.91\]

**Figure 3.** Correlation coefficient between calculated and measured NH$_4^+$.  

### 3.2. Sources and Regional Transport of PM$_{2.5}$

#### 3.2.1. Source Apportionment

In order to investigate the potential emission sources of PM$_{2.5}$, PMF 5.0 was applied to perform source apportionment in this study. Finally, seven factors were extracted from the PMF receptor model (Figure 4).

Factor 1 was identified as industry mixed with coal combustion with high loadings of OC, EC, Mn, Fe, Zn, Ba, and Pb. Moreover, heavy metals such as Fe, Mn, Zn, and Pb were regarded as tracers for the iron and steel industry [45,46]. Industry mixed with coal combustion contributed 16.3% to PM$_{2.5}$.

Factor 2 was attributed to the leather industry with a relatively high contribution of Cr (84.5%). Haining is famous for its leather tanning industry. Cr is released during the leather production process [47,48]. The leather industry contributed 4.8% to the total PM$_{2.5}$.

Factor 3 had a higher loading of Na$^+$ (67.2%), which was regarded as sea salt [49,50]. Haining county is located in the estuary of Qiantang River. The sampling site was about 7 km away from Qiantang River. Thus, it could be easily influenced by the air mass from the East China Sea. Na$^+$ is commonly found near the sea, mainly from the sea waves and evaporation [38]. Sea salt had a contribution of 8.7% to PM$_{2.5}$ mass concentration.
Thus, this phenomenon could affect areas nearby via regional transport. From PSCF and CWT analyses, biomass burning was mainly affected by air parcels from western areas, namely south Anhui, south Jiangsu, and north Zhejiang provinces by contributing up to, or more than, 20 μg/m³ of PM$_{2.5}$ (Figure 5). Biomass burning contributed 9.3% to the local PM$_{2.5}$ at Haining.

Figure 5. The potential source region of biomass burning at Haining, Jiaxing city. (a) PSCF analysis and (b) CWT analysis of biomass burning.

Factor 4 was attributed to secondary inorganic aerosols (SIAs) with higher mass contribution of SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$. SIAs were contributed by high loadings of NO$_3^-$, SO$_2^{2-}$ and NH$_4^+$. We discussed the existent form of NH$_4^+$ above. Secondary oxidation of SO$_2$ and NO$_2$ could form SO$_4^{2-}$ and NO$_3^-$ [51]. Secondary inorganic aerosols were the largest contributor by accounting for 31.8% to the PM$_{2.5}$.

Factor 5 was treated as biomass burning with high proportion of K$^+$ and Cl$^-$ [52]. Recently the Chinese government has strictly forbidden biomass burning outdoors, while straw burning is still used for residential cooking in the suburban area at Haining County. Thus, this phenomenon could affect areas nearby via regional transport. From PSCF and CWT analyses, biomass burning was mainly affected by air parcels from western areas, namely south Anhui, south Jiangsu, and north Zhejiang provinces by contributing up to, or more than, 20 μg/m³ of PM$_{2.5}$ (Figure 5). Biomass burning contributed 9.3% to the local PM$_{2.5}$ at Haining.

Figure 4. Seven sources resolved of VOCs from the PMF model.

The back trajectory cluster analysis (Figure 6). Lower PM$_{2.5}$ concentration (75.80 μg/m³) but higher SNA in Cluster 1 (Figure 6b). SIAs were contributed by high loadings of NO$_3^-$, SO$_2^{2-}$, and Cl$^-$, which were regarded as crustal dust (Factor 6). Secondary oxidation of SO$_2$ and NO$_2$ could form SO$_4^{2-}$ and NO$_3^-$ [51]. Secondary inorganic aerosols were the largest contributor by accounting for 31.8% to the PM$_{2.5}$.
Factor 6 was apportioned for crustal dust, which was mainly contributed by Ca\(^{2+}\) (79.1%) and Mg\(^{2+}\) (74.8%). These two ions were regarded as tracers for crustal dust from mixing with loess, floating dust, man-made construction dust, sand dust, and suspended floating dust [53]. In recent years, Zhejiang province has developed rapidly, with its new rural construction leading to the construction dust. Crustal dust contributed 9.5% to the total PM\(_{2.5}\).

Factor 7 was regarded as vehicle emissions with the higher loading of Fe, OC, EC, SO\(_{4}^{2-}\), NO\(_{3}^{-}\), and Cl\(^{-}\). Fe was mainly from the wear of tires and metal parts [54]. Studies have confirmed the large fraction of OC and EC in vehicle exhaust [55,56]. Good correlation (R\(^2\) = 0.78) between OC and EC in factor 7 also indicated that the OC and EC were mainly from the same emission source; (here in this study it was from vehicle emissions) (Figure S3). Vehicle emission was the second dominant source, accounting for 19.5% of the PM\(_{2.5}\).

3.2.2. Back Trajectory Cluster and Regional Transport

Figure 6 shows the backward trajectory clustering result of PM\(_{2.5}\) during the whole field campaign, since the whole period was experiencing heavy pollution. In total, 4 clusters were resolved from clustering (Figure 6a).

Cluster 1 originated from south Jiangsu province, travelled across the East China Sea and Shanghai, and arrived at Haining, which contributed almost fifty percent of all the trajectories. Traffic and industrial activities both contributed highly to SNA and OC in Cluster 1 (Figure 6b). Lower PM\(_{2.5}\) concentration (75.80 µg/m\(^3\)) but higher SNA contribution (53.6%) was tightly related to air masses from Cluster 2. High PSCF and CWT value regions of secondary inorganic aerosols concentrated in eastern Anhui and western Jiangsu province indicated a higher secondary inorganic formation in these areas (Figure 7). A portion of air masses (Cluster 3) travelled from Guangdong and Fujian provinces, containing higher PM\(_{2.5}\) concentration (92.3 µg/m\(^3\)). Cluster 3 contributed 11.11% to the total air trajectories. Long-range transport was resolved as shown in Cluster 4. Cluster 4, which originated from Mongolia, transported across several provinces and sections of the ocean in north and east China. Due to the clean air mass via the China Sea, Cluster 4 had the lowest PM\(_{2.5}\) loading (39.8 µg/m\(^3\)).
3.3. Health Risk Assessment

3.3.1. Health Risk Assessment

The noncarcinogenic risk (HQ) of PM$_{2.5}$-bound heavy metals is described in Figure 8. The HQ of the metals at Haining ranged from $1.8 \times 10^{-4}$ to $7.8 \times 10^{-1}$, $2.1 \times 10^{-4}$ to $9.3 \times 10^{-1}$, and $2.3 \times 10^{-4}$ to 1.0 for adult females, adult males, and children, respectively. The highest contributor was Cr, accounting for 52% of the total HQ, followed by Mn (46%), As, Cd, Pb, Cu, and Zn for different populations. The HQ results from PM$_{2.5}$-bound heavy metals indicated that emission control should receive attention in the local leather industry. Carcinogenic risk (CR) in Figure 8b shows extremely high risk of PM$_{2.5}$ at Haining. The CR values of metals (Cr, Pb, and As) all exceeded 10E-6, and the concentration posed risk to all of the populations. The most toxic metal was Cr, followed by Pb, As, and Cd, respectively. Such an extremely high risk indicated a strict control policy should be raised and implemented in this area to protect human health. For different populations, it seemed that the risk for adult males was the highest, then females and children for all the carcinogenic metals. According to newly published data from the Annual Report of Zhejiang Cancer Registry in 2021, the incidence of cancer was 3.9‰ and 3.5‰ in 2019 in Zhejiang province and Haining county, respectively [57].

3.3.2. Health Risk Associated with Sources

As the components of PM$_{2.5}$ were quite different from every source, so were the health risks caused by each source. Therefore, health risks associated with sources was analyzed to investigate the health risks of each source to the local residents. Industry mixed with coal combustion and the leather industry posed high noncarcinogenic risk to all population...
by a sum proportion of ~90% of the total noncarcinogenic risk (Figure 9a). The leather industry showed a remarkable carcinogenic risk, occupying 61.5% of the total source carcinogenic risk (Figure 9b), and the rest of the other sources had a small contribution. As mentioned above, the leather industry produces Cr during the leather tanning process, which is a human carcinogen. Despite the small contribution of the leather industry (4.8%) to the PM$_{2.5}$ mass concentration, its lifetime carcinogenic risk turned out to be the highest. Such a phenomenon indicated that the emission reduction policy should also consider the health risks of the compounds in different sources. Additionally, the health risks of the air pollution resulted from a combination of sources and the chemical components’ toxicity in each source.

![Figure 9](https://www.mdpi.com/article/10.3390/su141912175/s1)

**Figure 9.** Risk-oriented source apportionment of PM$_{2.5}$-bound metals at Haining: (a) noncarcinogenic risk and (b) carcinogenic risk.

4. Conclusions

In this study, PM$_{2.5}$ and its related chemical components were comprehensively explored at a suburban site in Jiaxing City from December 2019 to January 2020 before the COVID-19 shutdown. Chemical composition analysis indicated the secondary formation of both organics and inorganics were important at the sampling site. Strengthened emission reduction control of major gaseous precursor pollutants such as SO$_2$, NOx and VOCs were of great significance for PM$_{2.5}$ pollution prevention and control in Jiaxing City. PMF analysis was applied to resolve emission sources of PM$_{2.5}$. Seven sources were resolved for PM$_{2.5}$ in this suburban area, namely industry mixed with coal combustion (16.3%), the leather industry (4.8%), sea salt (8.7%), secondary inorganic aerosols (31.8%), biomass burning (9.4%), crustal dust (9.5%) and vehicle emissions (19.5%), respectively. Backward trajectory clustering, PSCE, and CWT results implied the regional joint prevention strategies among provinces should be paying attention to PM$_{2.5}$ reduction. The health risk assessment results showed a higher health risk of PM$_{2.5}$-bound Cr for all the populations from the leather industry. Such a phenomenon indicated that the smaller contributor to PM$_{2.5}$ might be the larger health risk source. The leather industry should be given the most attention to control the health risks of PM$_{2.5}$ in the city.

**Supplementary Materials:** The following supporting information can be downloaded at [https://www.mdpi.com/article/10.3390/su141912175/s1](https://www.mdpi.com/article/10.3390/su141912175/s1), Figure S1: The seasonal variation of PM$_{2.5}$ at Haining from 2019 to 2020; Figure S2: The monthly trends of PM$_{2.5}$ at Haining from 2019 to 2020; Figure S3: The correlation coefficient of OC and EC in PM$_{2.5}$; Table S1: The detection limit (DL) of ICS-900; Table S2: The exposure dose of carcinogenic and non-carcinogenic heavy metals; Table S3: Carcinogenic and non-carcinogenic risk calculation parameters and their values of heavy metals; Table S4: Concentrations of compositions in PM$_{2.5}$; Table S5: The noncarcinogenic risk and carcinogenic risk of PM$_{2.5}$-bound heavy metals with different populations heavy metals.

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