

# Pollution Characteristics of PM<sub>2.5</sub> during a Typical Haze Episode in Xiamen, China

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## ABSTRACT

In this study, mass concentrations and chemical compositions of fine particles, mass concentrations of coarse particles, light extinction, and meteorological parameters in the atmosphere of Xiamen were presented and analyzed to study the chemical and optical characteristics of a typical haze episode from Dec 25, 2010 to Jan 1, 2011. The major chemical compositions of PM<sub>2.5</sub>, such as water soluble inorganic ions (WSIIs), carbonaceous fractions (mainly composed of organic carbon (OC) and elemental carbon (EC)), and elements were determined. The results showed that with the typical haze episode process, the concentrations of PM<sub>2.5</sub> mass, WSIIs, OC, EC, and TE first increased and then decreased. The average concentrations of PM<sub>2.5</sub> mass in the stages of Before Haze, During Haze, and After Haze were (88.80 ± 19.97), (135.41 ± 36.20), and (96.35 ± 36.26) μg/m<sup>3</sup>, respectively. The corresponding average concentrations of secondary organic carbon (SOC) were 6.72, 8.18, and 10.39 μg/m<sup>3</sup>, accounting for 46.5%, 27.0%, and 61.0% of OC, respectively. SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and NH<sub>4</sub><sup>+</sup> were three major WSIIs species, accounting for 31.4%, 26.0%, and 12.1% of total WSIIs. The major elements in PM<sub>2.5</sub> were S, K, Fe, Zn, Pb, Ti, and Mn, covering 97.9% of the total elements, while the percentage of the other ten elements was only 2.1%. The average value of light extinction coefficients ( $b_{\text{ext}}$ ) was 371.0 ± 147.1 Mm<sup>-1</sup> during the typical haze episode. The average percentage contributions to  $b_{\text{ext}}$  were 39.3% for organic mass, 19.9% for elemental carbon, 16.0% for ammonium sulfate, 13.0% for coarse mass, and 11.8% for ammonium nitrate.

**Keywords:** Fine Particles; Haze; Water Soluble Inorganic Ions; Organic Carbon; Elemental Carbon; Elements; Light Extinction Coefficients; Xiamen

## 1. Introduction

Haze is defined by China Meteorological Administration as the phenomenon which leads to atmospheric visibility less than 10 km due to the suspended particles, smoke, and vapor in the atmosphere [1]. Closely related to chemical compositions and meteorological conditions, haze has adverse effects on air quality, human health, visibility, cloud formation and even global climate [2-4]. As a worldwide phenomenon, haze has been given much attention in many countries. Previous studies have been carried out for the investigation of characteristics and source apportionment of atmospheric particulate matter during haze episodes [5-9].

Fine particles (aerodynamic diameter less than 2.5 μm, PM<sub>2.5</sub>) play an important role on the formation of haze [10]. The major chemical compositions in PM<sub>2.5</sub>, such as

water soluble inorganic ions (WSIIs), carbonaceous fractions, mainly composed of organic carbon (OC) and elemental carbon (EC), and elements also have been found to be widely associated with health problems [11-15].

The atmospheric condition is relatively more stable during haze episodes, which results in worse accumulation of atmospheric particulate and light extinction. Visibility degradation is primarily attributed to light scattering and light absorption caused by particulate pollutants and gas pollutants in the atmosphere [16,17]. The impacts of aerosol on solar radiation include light scattering and light absorption, in general called light extinction. It is believed that the degradation of visibility is mainly attributed to the scattering and absorption of visible light by PM<sub>2.5</sub> [18]. Therefore, it is very crucial to investigate chemical characteristics and light extinction coefficients of particulate matter, especially the fine particles during haze episodes.

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Xiamen is a subtropical climate city located in the coastal line of southeastern China, with an area of 1565.1 km<sup>2</sup> and a population of approximately 3.5 million. With rapid industrialization and urbanization, like many other cities in China [8,19-21], Xiamen also suffers from air pollution problems, and the haze problems in Xiamen were increasingly severe during the last few years. The rapid increase of traffic vehicles and coal consumptions in Xiamen have been regarded as the main reasons for the deterioration of air quality in urban area [22]. However, there were very few reports available devoted to determining the effects of chemical composition to visibility (light extinction) during haze episodes in Xiamen, especially during a typical haze episode.

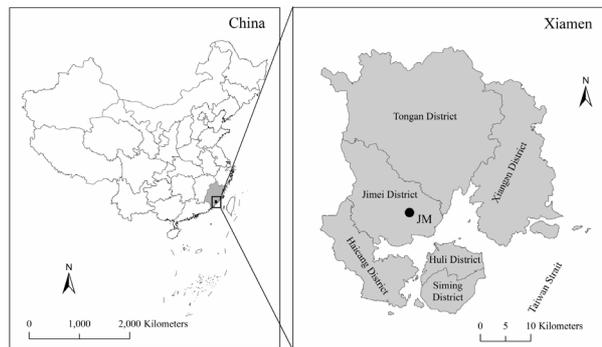
In this study, particle mass and chemical compositions of PM<sub>2.5</sub>, light extinction, and meteorology in the atmosphere of Xiamen from Dec 25, 2010 to Jan 1, 2011 were analyzed to study the pollution characteristics of a typical haze episode. The objectives of this paper are 1) to present the characteristics and source apportionments of particle mass, water soluble inorganic ions, carbonaceous fractions, and elements in PM<sub>2.5</sub>; 2) to estimate the contributions of light extinction coefficients in atmospheric aerosol by IMPROVE algorithm; 3) to investigate the relationships between visibility degradations and chemical compositions in the atmosphere during a typical haze episode.

## 2. Methodology

### 2.1. Site and Sampling

Aerosol samples were collected at a laboratory building rooftop of Institute of Urban Environment, Chinese Academy of Sciences, about 30 m above the ground. The sampling site is located in Jimei District of Xiamen (JM) with rapid urbanization during the last few years, which is surrounded by highway, schools, residential buildings and railway station within two kilometers, as illustrated in **Figure 1**.

Daytime samples (from 7:00 to 19:00, local time) and nighttime samples (from 19:00 to next day 7:00, local time) were collected from Dec 25, 2010 to Jan 1, 2011 during a typical haze episode, based on the historical meteorological data and weather forecast of Xiamen. A middle volume sampler (TH-150C III, Tianhong, China) was employed for collecting samples at a flow rate of 100 L/min. Then 16 sets of samples were obtained in this study. Each set of sample contained fine particle and coarse particle samples. The particulate was retained on quartz fiber filters (QFFs Ø75/Ø90 mm, Whatman, UK). QFFs were previously annealed for 5 h at 450°C in a furnace to remove residual pollutants for the analysis of particulate mass concentration, WSIs, OC, EC and TE. Then all the filters were kept in baked aluminum foil-



**Figure 1.** Location of the sampling site.

within sealed polyethylene plastic bags. During sampling period the meteorological parameters, including visibility, ambient temperature, relative humidity, and wind speed, were also supplied by the Institute of Meteorological Science of Fujian Province, China.

### 2.2. PM<sub>2.5</sub> Mass Analysis

The particulate mass concentrations of fine particle and coarse particle were determined gravimetrically. Each QFF was weighted before and after exposure with an analytical microbalance (T-114, Denver Instrument, USA) after being stabilized under constant temperature (25°C) and relative humidity (52%) in chamber (HWS-080, Jinghong, China) for 24 hr. Typical uncertainty for gravimetric measurements is  $\pm 20 \mu\text{g}$ , which represents less than  $\pm 5\%$  of total aerosol mass of field samples.

### 2.3. Chemical Compositions Analysis

#### 2.3.1. WSIs Analysis

Water soluble inorganic ions in PM<sub>2.5</sub> ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) were analyzed by Ion chromatography system (ICS3000, Dionex, USA). The details were given elsewhere [23]. Field blank values were subtracted from sample concentrations. The detection limits were about 0.05  $\mu\text{g}/\text{mL}$  for anions and cations, based on three times the standard deviation of measurement blank.

#### 2.3.2. OC and EC Analysis

The PM<sub>2.5</sub> samples were measured for OC and EC with carbon analyzer (Model-4, Sunset Lab, USA) by the thermal optical transmission method following the National Institute for Occupational Safety and Health protocol. The detailed analysis procedures were described in literature [23,24]. Field blanks were collected and determined to examine the operational contamination of the field during measured periods. Generally, the concentrations of OC and EC of field blanks were less than 1% of the sample batches, and were not subtracted from the samples. The detection limit for EC and OC was 0.1  $\mu\text{g}$

$C/cm^2$ .

### 2.3.3. Element Analysis

The samples were cut into strips (width  $\times$  length =  $6 \times 20$  mm<sup>2</sup>) and stuck parallel on a frame. The elements in PM<sub>2.5</sub> were analyzed by proton induced X-ray emission (PIXE) in the Institute Low Energy Nuclear Physics of Beijing Normal University. The PIXE analysis was carried out at the 1.7 MV tandem accelerator with a 2.5 MeV proton beam, and the X-rays were collected by a Si/Li detector [25]. 17 elements were determined in this study including S, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, and Pb. The detection limits ranged from  $3.0 \times 10^{-4}$  to  $5.4 \times 10^{-2}$   $\mu\text{g}/\text{cm}^2$  for 17 elements, based on three times the standard deviation of measurement blank. All the values of sample were corrected by blank filters.

### 2.3.4. Extinction Analysis

Equations developed by Interagency Monitoring of Protected Visual Environments (IMPROVE) program are used to estimate total light extinction coefficients ( $b_{\text{ext}}$ ) via multiplying the concentrations of each major chemical composition of atmospheric aerosol by composition-specific light extinction efficiency, and summed over all species. Equation (1) is the IMPROVE algorithm used to reconstruct  $b_{\text{ext}}$  [26,27].

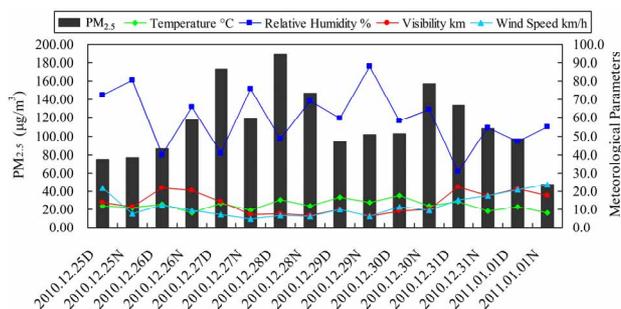
$$\begin{aligned}
 b_{\text{ext}} = & 3f(RH)\{[\text{Ammonium Sulfate}] \\
 & + [\text{Ammonium Nitrate}]\} \\
 & + 4[\text{Organic Mass}] + 10[\text{Elemental Carbon}] \quad (1) \\
 & + [\text{Fine Soil}] + 0.6[\text{Coarse Mass}] \\
 & + 0.161[\text{Nitrogen Dioxide}] + 10
 \end{aligned}$$

where  $f(RH)$  is relative humidity (RH) dependent adjustment factor which illustrates the relationships between RH and scattering efficiencies for sulfates and nitrates; and Equation (1) includes a constant  $10 \text{ Mm}^{-1}$  for the Rayleigh scattering of clear air. The light extinction coefficients of atmospheric aerosol are in unit of  $\text{Mm}^{-1}$ ; chemical composition concentrations shown in brackets are in unit of  $\mu\text{g}/\text{m}^3$ ; dry efficiency terms are in unit of  $\text{m}^2/\text{g}$ ; and the hygroscopic growth terms,  $f(RH)$ , are unitless. **Table 1** summarizes different  $f(RH)$  values in selected relative humidity ranges [28].

## 3. Results and Discussion

### 3.1. Concentrations and Variations of PM<sub>2.5</sub> with Meteorological Conditions

The correlations between PM<sub>2.5</sub> mass and meteorological parameters during the typical haze episode are illustrated in **Figure 2**. Haze is closely related to atmosphere qual-



**Figure 2.** Concentration levels and temporal variations of PM<sub>2.5</sub> during the typical haze episode with meteorological parameters (D: day time, N: night time).

ity, for which visibility is one of the most effective indicators. However, fog could also reduce visibility in addition to haze. When relative humidity is greater than 90%, fog is the major factor that reduces visibility, whereas when relative humidity is less than 90%, haze plays a major role. In order to distinguish haze from fog, relative humidity was also analyzed in this study (**Figure 2**). All the values of relative humidity were less than 90% during the sampling. According to the definition of haze defined by China Meteorological Administration, the 8-day haze episode could be divided into three stages: Before Haze (Dec 25-26, 2010), During Haze (Dec 27-30, 2010), and After Haze (Dec 31, 2010-Jan 1, 2011).

The average PM<sub>2.5</sub> concentrations in the stages of Before Haze, During Haze, and After Haze were  $(88.80 \pm 19.97)$ ,  $(135.41 \pm 36.20)$ , and  $(96.35 \pm 36.26)$   $\mu\text{g}/\text{m}^3$ , respectively, which far exceeded the 24-hour limit of Ambient Air Quality Standard (AAQS) for PM<sub>2.5</sub> ( $75 \mu\text{g}/\text{m}^3$ ) [29]. In particular, the average concentration of PM<sub>2.5</sub> in the stage of During Haze reached as much as 1.8 times of the AAQS standard. The results indicated that there were serious fine particle pollutions in Xiamen during haze episodes.

The 12-hour concentrations of PM<sub>2.5</sub> were in the range of  $47.37 - 188.30 \mu\text{g}/\text{m}^3$ , with mean and standard deviation of  $113.99 \pm 38.09 \mu\text{g}/\text{m}^3$ , which showed significant temporal variation during the typical haze episode (**Figure 2**). With the typical haze process, the PM<sub>2.5</sub> concentration first increased and then decreased, except for a little reduction during Dec 29-30, 2010. As there was a negative correlation between PM<sub>2.5</sub> mass and relative humidity in this study ( $r = -0.3$ ), lower concentrations of PM<sub>2.5</sub> were mainly caused by higher relative humidity during Dec 29-30, 2010. As shown in **Figure 2**, the variation of wind speed was opposite to PM<sub>2.5</sub> mass but consistent with visibility. Low wind speed is not conducive to the diffusion of PM<sub>2.5</sub>, which plays an important role on the formation of haze [10]. Moreover, there was no apparent correlation between PM<sub>2.5</sub> and temperature.

In this study, the vertical variations of meteorological soundings in the atmosphere of Xiamen were also ob-

served by the soundings system of University of Wyoming during the haze episode. The vertical variations during Dec 26-28, 2010 are illustrated in **Figure 3**. As shown in **Figure 3**, there were temperature inversions in the surface atmosphere from Dec 26 night to Dec 28 day, especially at Dec 27 night. Although the temperature inversions disappeared on Dec 28 day, whereas the haze phenomenon still existed due to the hysteresis effects of atmospheric process. Overall, vertical temperature inversion phenomenon led to stable atmospheric conditions in haze days, which promoted the accumulation of pollutants.

Dew point is generally associated with relative humidity. The higher the relative humidity, the closer the dew point is to the ambient temperature. Two main results could be deduced from **Figure 3**: one was that the vertical variation of relative humidity was obvious during the haze episode; the other was that the relative humidity of surface atmosphere on day was lower than that at corresponding night, which was consistent with **Figure 2**.

### 3.2. Chemical Compositions and Source Apportionments of PM<sub>2.5</sub>

**Table 2** summarizes the concentrations of chemical-

**Table 1. Statistical summary of mean  $f(\text{RH})$  values in selected relative humidity (%) ranges.**

RH	30 - 35	35 - 40	40 - 45	45 - 50	50 - 55	55 - 60	60 - 65	65 - 70	70 - 75	75 - 80	80 - 85	85 - 90
$f(\text{RH})$	1.16	1.21	1.22	1.27	1.33	1.38	1.45	1.55	1.65	1.83	2.10	2.46

**Table 2. Concentrations of chemical compositions in PM<sub>2.5</sub> during the haze episode: OC, EC, WSIs, and elements ( $\mu\text{g}/\text{m}^3$ ).**

	Before Haze				During Haze								After Haze			
	Dec 25		Dec 26		Dec 27		Dec 28		Dec 29		Dec 30		Dec 31		Jan 1	
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
OC	11.47	14.93	12.97	17.59	30.10	26.52	41.68	35.19	22.80	21.48	24.44	25.31	18.13	23.15	17.30	11.24
EC	3.86	4.82	1.99	7.07	7.32	12.55	11.01	18.14	7.03	14.96	10.23	11.62	2.83	7.92	3.14	2.46
Na <sup>+</sup>	0.64	1.60	1.27	1.84	1.35	2.27	1.88	1.92	1.45	2.86	2.17	2.17	3.46	2.32	1.86	2.28
NH <sub>4</sub> <sup>+</sup>	0.19	3.97	2.75	6.72	3.78	6.63	3.90	5.11	3.82	8.48	3.82	3.76	0.73	3.84	1.51	1.74
K <sup>+</sup>	0.13	0.46	0.45	0.96	0.78	1.01	0.89	1.30	0.78	1.17	1.02	0.91	0.75	1.23	0.90	0.69
Mg <sup>2+</sup>	0.02	0.01	0.07	0.10	0.13	0.07	0.11	0.12	0.07	0.05	0.08	0.13	0.13	0.16	0.13	0.05
Ca <sup>2+</sup>	1.98	1.16	2.26	2.28	4.52	2.27	3.81	3.28	2.03	1.37	2.10	3.67	3.83	3.22	3.20	1.66
F <sup>-</sup>	ND	ND	ND	ND	0.01	ND	ND	ND	ND	ND	ND	0.01	ND	0.01	ND	ND
Cl <sup>-</sup>	0.90	4.71	0.66	6.56	2.30	6.22	2.01	6.41	1.19	6.61	1.56	4.69	1.11	4.02	1.21	1.06
NO <sub>3</sub> <sup>-</sup>	2.63	3.76	4.53	4.35	9.94	9.48	15.16	9.46	6.89	10.18	6.97	6.41	5.31	8.58	8.97	7.42
SO <sub>2</sub> <sup>-</sup>	3.27	6.49	8.88	11.27	10.21	10.53	11.45	9.68	10.48	13.75	13.00	10.79	6.77	8.32	7.04	3.66
S	1.17	1.72	2.59	3.00	4.20	2.42	4.91	3.21	3.66	3.04	3.95	4.25	2.73	2.59	0.95	1.86
K	0.48	0.50	0.77	1.15	1.73	0.88	1.82	1.95	1.18	0.99	1.32	1.71	1.66	1.72	0.75	0.88
Ti	0.07	0.06	0.06	0.11	0.23	0.06	0.31	0.17	0.11	0.03	0.06	0.15	0.17	0.15	0.03	0.07
V	0.01	0.01	0.01	0.01	0.01	ND	0.01	0.01	ND	ND	ND	0.01	0.01	0.01	0.01	0.01
Cr	0.01	ND	ND	0.01	ND	0.01	0.02	0.01	0.01	0.02	ND	0.01	0.01	0.01	ND	ND
Mn	0.04	0.07	0.07	0.08	0.12	0.08	0.22	0.11	0.10	0.21	0.17	0.12	0.12	0.07	0.04	0.05
Fe	0.69	0.42	0.78	0.92	2.11	0.84	3.33	1.78	1.11	0.99	0.90	1.49	1.64	1.42	0.49	0.70
Ni	ND	ND	ND	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.02	ND	ND	0.01	0.01	0.01
Cu	0.02	0.01	ND	0.01	0.02	ND	0.04	0.01	0.04	0.02	0.03	0.02	0.02	0.02	0.04	0.02
Zn	0.17	0.30	0.14	0.19	0.47	0.33	1.26	0.70	0.41	0.55	0.55	0.45	0.52	0.35	0.42	0.21
As	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	ND	0.03	ND	0.01	0.01	0.01
Se	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.01	ND	0.01	0.01	0.01	0.01	0.01	0.01
Br	0.01	0.03	0.01	0.01	0.01	0.02	0.04	0.02	0.01	0.02	0.06	0.02	ND	0.03	0.01	ND
Rb	0.03	0.01	0.01	0.01	0.02	ND	0.06	0.02	0.04	0.02	0.01	0.01	0.01	0.03	0.02	0.01
Sr	0.01	0.01	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.02	0.01	0.02	ND	0.02	0.02	0.02
Zr	0.01	0.03	0.01	ND	0.01	0.03	0.04	ND	0.02	0.03	0.01	0.01	0.02	0.01	0.01	0.02
Pb	0.02	0.03	0.12	0.17	0.07	0.06	0.22	0.12	0.05	0.10	0.16	0.46	0.14	0.10	0.07	0.05

ND: not detected.

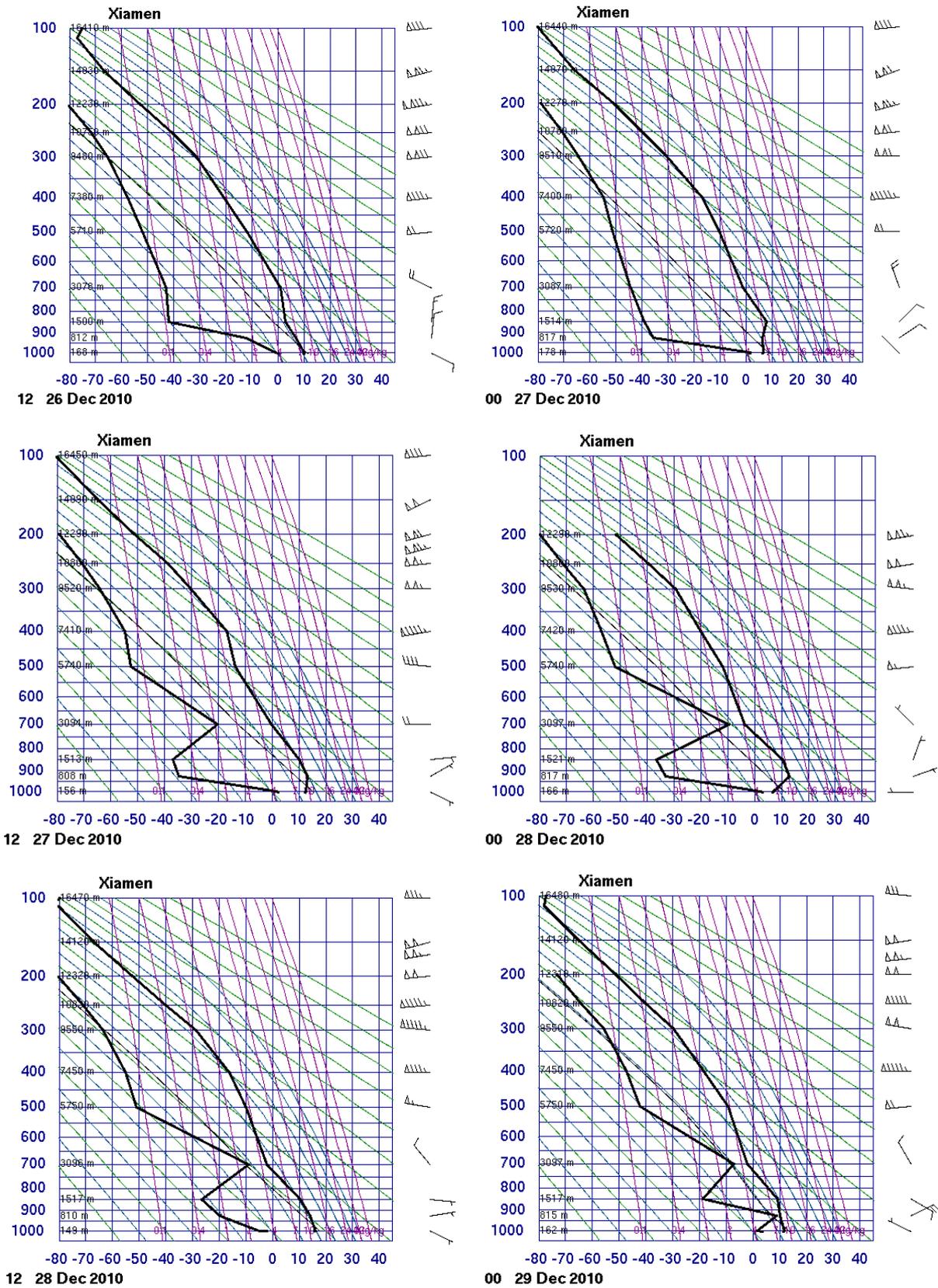


Figure 3. Vertical variations of meteorological soundings in the atmosphere of Xiamen during Dec 26-28, 2010 (left curve: dew point, right curve: ambient temperature, ordinate axis: pressure/Pa, abscissa axis: temperature/°C).

compositions in  $PM_{2.5}$  including OC, EC, WSIs ( $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $NH_4^+$ ,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ), and elements (S, K, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, and Pb) detected during the haze episode. The temporal variations of major chemical compositions in  $PM_{2.5}$  exhibited a similar change trend as  $PM_{2.5}$  mass during the typical haze episode (Figure 2). The high concentrations of pollutant in Xiamen during haze episodes mainly resulted from the local sources emission and the long distance transport of polluted air mass, which might deteriorate the air quality of Xiamen in some degree.

In this study Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model developed by the National Oceanic and Atmospheric Administration was also used to investigate potential source regions and transport pathways of air mass during the sampling period. The back trajectories were calculated for three different arrival altitudes (100, 500, 1000 m above the ground level, AGL) during the period of Dec 24–31, 2010.

The 168-hour back trajectory is presented in Figure 4. During sampling period the air mass originated from northwestern China, even Russia and other European countries (Figure 4), would carry polluted air mass on

travelling pathways then invaded into Xiamen. Consequently, both the local source emission and the long distance transport of pollutants from northwest would have important contribution to  $PM_{2.5}$  in Xiamen, which promoted the occurrence of haze.

In addition, the backward trajectory of air mass in Xiamen also showed that the 500-meter AGL air mass moved slower than the 100-meter AGL and 1000-meter AGL air mass (Figure 4). The result indicated that there was an inversion at 500-meter AGL, which was consistent with the vertical variations of atmosphere soundings in Xiamen (Figure 3).

### 3.3. Organic Carbon and Elemental Carbon in $PM_{2.5}$

Carbonaceous fractions is significant composition of  $PM_{2.5}$  in the urban atmosphere [30], which is usually classified into organic carbon (OC) and elemental carbon (EC). EC, as a primary pollutant, derives from incomplete combustion of carbon containing materials, while OC can be either released directly (primary organic carbon, POC) or produced from gas-to-particle reactions (secondary organic carbon, SOC) in the atmosphere [31, 32].

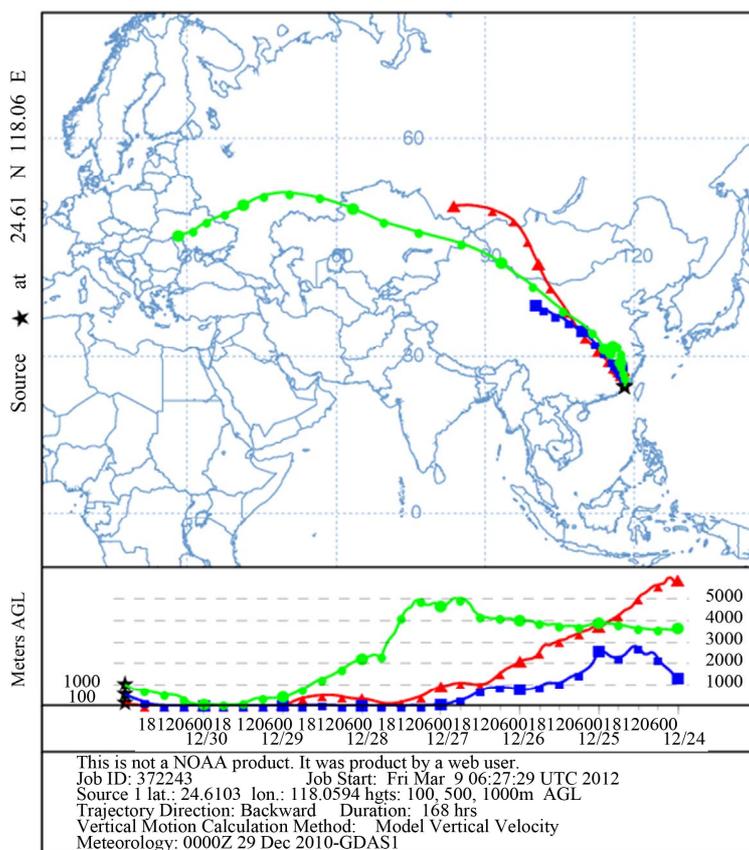


Figure 4. HYSPLIT backward trajectory of air mass during the haze episode in Xiamen.

The concentrations of OC and EC in PM<sub>2.5</sub> during the sampling period are listed in **Table 2**, which showed similar trend as PM<sub>2.5</sub> mass. The average concentrations of OC and EC were (14.24 and 4.43), (28.44 and 11.61), and (17.46 and 4.09)  $\mu\text{g}/\text{m}^3$  in the stages of Before Haze, During Haze, and After Haze, respectively. Total carbon (TC, sum of OC and EC) constituted up to 21.2%, 30.5%, and 23.7% of PM<sub>2.5</sub>, correspondingly. Therefore, either concentration or contribution of carbonaceous fractions were higher in haze days, which indicated that carbonaceous fractions were more enriched in PM<sub>2.5</sub> mass during haze episodes.

Generally, the correlation between OC and EC can reflect the origin of carbonaceous fractions [33]. If OC and EC were emitted from a primary source, the correlation between OC and EC should be strong, because the correlated emission rates of EC and OC would be proportional to each other [34]. In this study strong correlations between OC and EC were found in the stages of Before Haze ( $r = 0.8$ ) and After Haze ( $r = 0.8$ ), whereas weak correlation between OC and EC was observed in the stages of During Haze ( $r = 0.2$ ). The results showed that the sources of carbonaceous fractions were complex in haze days, and there were comprehensive reactions of secondary formations, such as SOC.

The direct quantification of POC and SOC are difficult, although there are many methods for quantification of total organic carbon (TOC). Nowadays, the minimum OC/EC ratio method has been widely used to estimate the SOC formation [32,35]. The approach suggests that samples with lowest OC/EC ratio contain almost exclusively POC. Then, the concentration of SOC can be estimated by the following Equations (2) and (3):

$$\text{SOC} = \text{TOC} - \text{POC} \quad (2)$$

$$\text{POC} = \text{EC} \times (\text{OC}/\text{EC})_{\min} \quad (3)$$

where  $(\text{OC}/\text{EC})_{\min}$  is the value of lowest OC/EC ratio, which were 2.3 and 1.4 in daytime and nighttime in this study.

Based on Equations (2) and (3), it could be estimated that the average concentrations of SOC were 6.72, 8.18, and 10.39  $\mu\text{g}/\text{m}^3$  in the stages of Before Haze, During Haze, and After Haze, which accounted for 46.5%, 27.0%, and 61.0% of OC, respectively. It was an interesting finding that the contribution of SOC in the stage of During Haze was lower than in the other two stages, while the concentration of OC in the stage of During Haze was the highest. The reasons might be as follows: First, there might be a threshold for OC generating SOC. When the concentration of SOC reaches a numerical value in a certain time, the reaction process would not continue with the increase of OC. Secondly, the reaction of OC generating SOC needs certain time, which will not complete immediately. Compared to haze weather, there

is a time lag for the formation of SOC. Therefore, both concentration and contribution of SOC reached the highest values in the stage of After Haze.

The OC/EC ratios have been widely used to identify the formation of SOC when the value exceeds 2.0 [33]. In this study the average OC/EC ratios of daytime and nighttime were (4.7 and 2.8), (3.4 and 1.9), and (6.0 and 3.8) in the stages of Before Haze, During Haze, and After Haze, respectively, which implied the existence of intense secondary transformation in Xiamen, especially in daytime of After Haze. The OC/EC ratios are also used to distinguish the origin and transport characteristics of carbonaceous fractions [36]. Generally, the typical sources of carbonaceous fractions include vehicle exhaust (OC/EC = 2.5 – 5.0) [37], coal combustion (OC/EC = 2.5 – 10.5) [38], biomass burning (OC/EC = 3.8 – 13.2) [39], and kitchen emissions (OC/EC = 4.3 – 7.7) [40], etc. Overall, the OC/EC ratios in this study varied from 1.4 to 7.4 with an average value of 3.5, which suggested that vehicle exhaust, coal combustion, biomass burning and kitchen emissions were the mainly sources of carbonaceous fractions in Xiamen during haze episodes.

### 3.4. Water Soluble Inorganic Ions in PM<sub>2.5</sub>

The validity of WSIs measurement could be verified through anions (A) and cations (C) balances [41]. The equivalent molar ratio ( $\mu\text{eq}/\text{m}^3$ ) of anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ) to cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) (A/C) ranged from 0.63 to 1.04 with average and standard deviation of  $0.87 \pm 0.10$  during sampling period, showing that the analysis results were reliable and the main ions species in PM<sub>2.5</sub> were identified.

The concentrations of each WSIs during the haze episode are listed in **Table 2**. All WSIs exhibited similar trend as PM<sub>2.5</sub> mass (**Figure 2**). The concentrations of total WSIs in the stage of During Haze ( $35.31 \pm 5.62 \mu\text{g}/\text{m}^3$ ) were higher than those in the stages of Before Haze ( $21.72 \pm 9.94 \mu\text{g}/\text{m}^3$ ) and After Haze ( $24.29 \pm 5.56 \mu\text{g}/\text{m}^3$ ), verifying that WSIs were enhanced in haze days in Xiamen. In this study, total WSIs accounted for 23.8, 27.6, and 27.7% of PM<sub>2.5</sub> mass in the stages of Before Haze, During Haze, and After Haze, respectively. Previous studies showed that WSIs accounted for about one-third of PM<sub>2.5</sub> mass in Chinese urban aerosols [42–44].  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  were three major WSIs species, accounting for 31.4%, 26.0%, and 12.1% of total WSIs during sampling period, while minor WSIs species (the other WSIs species except for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$ ) accounted for 30.5%.

The examination of scatter analysis of  $(2 \times [\text{SO}_4^{2-}] + [\text{NO}_3^-])$  versus  $[\text{NH}_4^+]$  (in moles) can be used to judge if the measured  $\text{NH}_4^+$  is sufficient or not to fully neutralize  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . It is clear that

$\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are fully neutralized by  $\text{NH}_4^+$  when the slope of  $(2 \times [\text{SO}_4^{2-}] + [\text{NO}_3^-])$  versus  $[\text{NH}_4^+]$  is greater than or equal to 1. In this study, the slope of  $(2 \times [\text{SO}_4^{2-}] + [\text{NO}_3^-])$  versus  $[\text{NH}_4^+]$  was 0.86 during sampling period in Xiamen. The result indicated that  $\text{NH}_4^+$  was not sufficient to fully neutralize  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  during the haze episode, and the existing chemical forms of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  were  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{HSO}_4$ , and  $\text{NH}_4\text{NO}_3$  during sampling period.

Coal is the main energy of Xiamen with rapid development of economy.  $\text{Cl}^-$  is usually considered from coal combustion [42].  $\text{Cl}^-$  was accumulated during the sampling period in this study. The crustal WSIs ( $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) are mainly from ground dust and construction dust, which were also accumulated during the haze episode. Therefore, WSIs from both anthropogenic sources and natural sources were enriched in haze days.

$\text{NO}_2$  emission from vehicle exhaust is an important contribution to  $\text{NO}_3^-$  in the atmosphere, while  $\text{SO}_2$  released from coal combustion converts into  $\text{SO}_4^{2-}$ . Therefore, the mass  $\text{NO}_3^-/\text{SO}_4^{2-}$  ratio is used to evaluate the influences of mobile sources versus stationary sources of sulfur and nitrogen in the atmosphere. A previous study indicated that high  $\text{NO}_3^-/\text{SO}_4^{2-}$  ratios occurred when the influences of vehicle emissions exceeded those of coal combustion [45]. The  $\text{NO}_3^-/\text{SO}_4^{2-}$  ratio during measured period was  $0.88 \pm 0.41$ , which was higher than those of normal day in Xiamen (0.52) [23]. The results suggested that the accumulation of pollutant from mobile sources (vehicle exhaust) was more severe than from stationary sources (coal combustion) during haze episodes, although the stationary sources were still dominant sources of pollutants in the atmosphere in Xiamen.

Previous studies indicated that nitrogen oxidation ratio (defined as  $\text{NOR} = \text{NO}_3^- / (\text{NO}_3^- + \text{NO}_2)$ ) (in mole) and sulfur oxidation ratio (defined as  $\text{SOR} = \text{SO}_4^{2-} / (\text{SO}_4^{2-} + \text{SO}_2)$ ) (in mole) could be used to estimate the secondary transformation processes from  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  and  $\text{NO}_2$  to  $\text{NO}_3^-$  [46]. Generally, NOR values are lower than SOR values. In this study, the average NOR and SOR were (0.10 and 0.24), (0.09 and 0.14), and (0.15 and 0.13) in the stages of Before Haze, During Haze, and After Haze, respectively. As shown in Equation (4), the values of NOR did not increase with the increase of  $\text{NO}_2$  due to the depletion of hydroxyl radical ( $\text{OH}\cdot$ ) [47].



In this study, the concentrations of  $\text{NO}_2$  exceeded those of  $\text{SO}_2$  during the haze episode. In the case of high  $\text{NO}_2$  concentrations, the concentrations of  $\text{OH}\cdot$  were reduced, and further decreased the possibility of  $\text{SO}_2$  generating  $\text{SO}_4^{2-}$  [8]. As a result, the values of SOR also did not increase with the increase of  $\text{SO}_2$  during the haze

episodes.

For primary pollutants the value of SOR is usually lower than 0.10 [48]. When SOR value is higher than 0.10, the photochemical oxidation of  $\text{SO}_2$  occurs in the atmosphere [49]. The SOR values of  $\text{PM}_{2.5}$  aerosols in Xiamen were higher than 0.10 during the haze episode, which indicated that the formation of secondary pollutants from  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  occurred during sampling period due to the subtropical climate.

### 3.5. Elements in $\text{PM}_{2.5}$

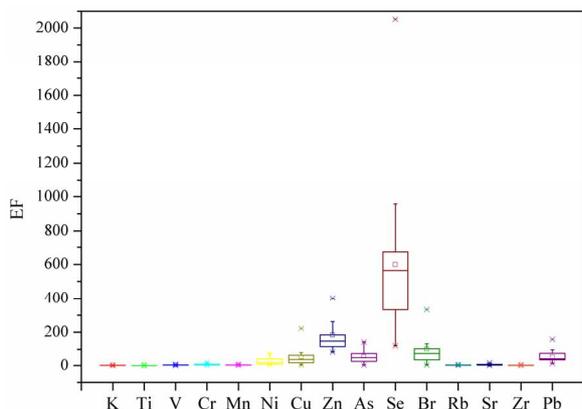
The 12-hour concentrations of elements during the haze episode in Xiamen are given in **Table 2**. The average concentrations of total elements were  $(4.07 \pm 1.35 \mu\text{g}/\text{m}^3)$ ,  $(7.90 \pm 2.27 \mu\text{g}/\text{m}^3)$ , and  $(5.11 \pm 2.02 \mu\text{g}/\text{m}^3)$  in the stages of Before Haze, During Haze, and After Haze, respectively. All element concentrations first increased and then decreased exhibiting similar trend as  $\text{PM}_{2.5}$  mass during the haze episode, and all elements were easily accumulated in haze days when the atmospheric condition was stable. The major elements in  $\text{PM}_{2.5}$  were S, K, Fe, Zn, Pb, Ti, and Mn, with average concentrations of 2.89, 1.25, 1.23, 0.44, 0.12, 0.11, and  $0.10 \mu\text{g}/\text{m}^3$ , respectively. Seven major elements in  $\text{PM}_{2.5}$  accounted for 97.9% of the total elements, while the percentage of the other ten elements was only 2.1%.

In order to identify the sources and evaluate the degree of anthropogenic influences of elements in Xiamen aerosol during the haze episode, the enrichment factors (EF) for the measured elements were calculated. The EF is defined as Equation (5):

$$EF = \frac{(C_X/C_R)_{\text{aerosol}}}{(C_X/C_R)_{\text{crust}}} \quad (5)$$

where  $C_X$  is the concentration of investigated element and  $C_R$  is the concentration of reference element. The subscripts of aerosol and crust refer to the particles in aerosol samples and crustal materials. The crustal source is primary source of crustal elements (such as Si, Al, and Fe), which are stable in the atmosphere and are usually selected as reference elements to calculate the EF of aerosol. In this study, Fe was selected as the reference element and crustal compositions were given by the background values of soil elements in China [50].

**Figure 5** illustrates the EF values of measured elements except for Fe in  $\text{PM}_{2.5}$  aerosol during the sampling period. As shown in **Figure 5**, different elements in  $\text{PM}_{2.5}$  had different value of EF according to the EF analysis results. Based on the EF values of different elements, a preliminary four-category system was proposed in this study: slightly enriched ( $1 < EF \leq 5$ ), moderately enriched ( $5 < EF \leq 20$ ), substantially enriched ( $20 < EF \leq 50$ ), and extremely enriched ( $EF > 50$ ). Among the 17



**Figure 5.** Enrichment factors ( $EF$ ) of elements with Fe as the reference element during the sampling period.

elements except for S and Ti, Fe, K, Zr, Rb, V, and Mn were slightly enriched during the haze episode, which indicated that they originated from natural source; Sr and Cr were moderately enriched, so that they partly originated from natural and anthropogenic sources; Ni was substantially enriched, whereas, Cu, Pb, As, Br, Zn, and Se were extremely enriched, so that they originated from anthropogenic sources. Overall, Ni, Cu, Pb, As, Br, Zn, and Se were strongly enriched in haze days, especially Br, Zn, and Se, with EF of 101.8, 184.5, and 599.8, respectively.

Previous studies showed that: Ni is regarded as an indicator of emission from fossil fuel combustion and vehicle exhaust [51,52]; Cu, Pb, Br, and Zn are often considered as markers associated with vehicle exhausts [53-55], while Cu and Zn are also derived from industrial emissions [56]; As and Se are known as the elements derived from coal combustion [57]. Overall, coal combustion, vehicle exhausts, and industrial emissions might be the important contributors of enriched elements in  $PM_{2.5}$  during haze episodes.

### 3.6. Extinction Effects of Chemical Compositions and Visibility Degradation

In this study, we mainly studied the extinction effects of major chemical composition in atmospheric particles causing visibility degradation and we excluded the contributions of fine soil and nitrogen dioxide in  $b_{ext}$  estimation, which only accounted for a small fraction of aerosol. Then, the modified IMPROVE algorithm is presented in Equation (6):

$$b_{ext} \approx 3f(RH) \{ [\text{Ammonium Sulfate}] + [\text{Ammonium Nitrate}] + 4[\text{Organic Mass}] + 10[\text{Elemental Carbon}] + 0.6[\text{Coarse Mass}] \} \quad (6)$$

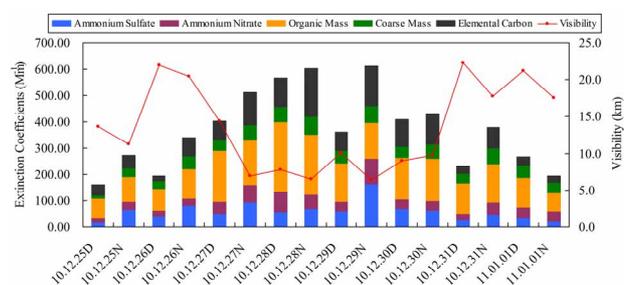
where  $[\text{Ammonium Sulfate}] = 0.944[\text{NH}_4^+] + 1.02[\text{SO}_4^{2-}]$  and  $[\text{Ammonium Nitrate}] = 1.29[\text{NO}_3^-]$ , when  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are not fully neutralized by  $\text{NH}_4^+$  in the atmosphere [28,58]; organic mass (OM) is estimated to be 1.6 times of OC [32]; coarse mass (CM) means particles covering a range between 2.5  $\mu\text{m}$  and 10  $\mu\text{m}$  in aerodynamic diameter.

**Figure 6** shows the variations of light extinction coefficients of chemical compositions in the atmosphere and visibility in Xiamen during the haze episode. On the whole, the 12-hour extinction coefficients of aerosol peaked in haze days, while the corresponding visibility of aerosol showed a contrary change, which touched bottom during the haze episode. The trend of extinction coefficients was negatively correlated with visibility ( $r = -0.8$ ). The  $b_{ext}$  is inverse proportional to visibility. Hence, higher value of  $b_{ext}$  represents poorer visibility [58,59].

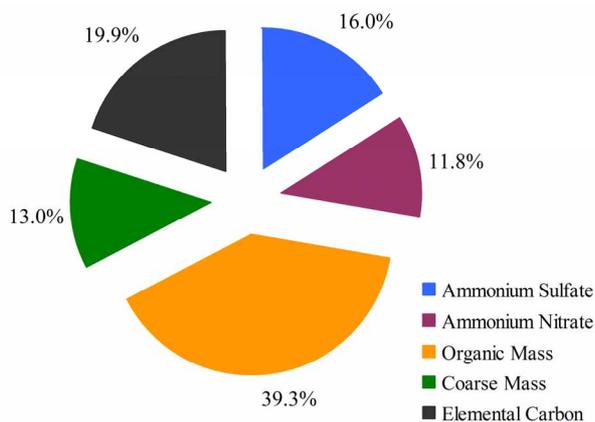
The average value of light extinction coefficients was  $371.0 \pm 147.1 \text{ Mm}^{-1}$  during the typical haze episode. Compared with the annual average value of  $b_{ext}$  ( $214.3 \pm 78.9 \text{ Mm}^{-1}$ ) on normal days in Xiamen [23], the  $b_{ext}$  was higher during the haze episode suggesting that more serious atmospheric pollution resulted in poorer visibility in haze days. The highest value of extinction coefficient occurred at the nighttime of Dec 29, 2010 with value of  $611.5 \text{ Mm}^{-1}$ . Although the concentrations of chemical compositions in the atmosphere at the nighttime of Dec 29, 2010 were not the highest, the corresponding relative humidity presented the highest value ( $88.3\% \pm 8.3\%$ ). Consequently, the extinction coefficient occurred at the nighttime of Dec 29, 2010 was still the highest.

As shown in **Figure 7**, organic mass provided the largest contribution to  $b_{ext}$  accounting for  $39.3\% \pm 6.8\%$  of the light extinction coefficients in the atmosphere, followed by elemental carbon ( $19.9\% \pm 5.9\%$ ), ammonium sulfate ( $16.0\% \pm 5.5\%$ ), coarse mass ( $13.0\% \pm 2.9\%$ ), and ammonium nitrate ( $11.8\% \pm 3.2\%$ ).

According to the results of IMPROVE algorithm, visibility degradation in Xiamen during the haze episode was mainly caused by higher organics mass concentration. The reason might be that OC abundances were high in



**Figure 6.** Temporal variations in extinction coefficients of chemical compositions in the atmosphere and visibility during the haze episode.



**Figure 7. Relative contribution to light extinction coefficients of chemical compositions in the atmosphere during the haze episode.**

Xiamen [60] not only affected by accumulation of local pollutants, but also impacted by subtropical climate (high temperature, strong sunlight, and high photochemical activity). Compared with the contributions of chemical compositions to  $b_{\text{ext}}$  on normal days in Xiamen [23], elemental carbon was the second largest contributor to  $b_{\text{ext}}$  during the haze episode suggesting that the primary accumulation of pollutants were serious then resulted in poor visibility in haze days. Moreover, ammonium sulfate and ammonium nitrate also played an important role in visibility degradation, which accounted for 27.8% of  $b_{\text{ext}}$ . Generally, ammonium sulfate and ammonium nitrate in the atmosphere are mainly derived from the secondary formation of  $\text{SO}_2$  and  $\text{NO}_2$ . Therefore, the primary accumulation and the secondary formation of pollutants were the main factors in the haze formation progress. The reduction of carbonaceous fractions released into aerosol could effectively improve the visibility of atmosphere in Xiamen during haze episodes.

#### 4. Conclusions

12-hour concentrations of fine particles and coarse particles, chemical compositions of fine particles, light extinction, and meteorology in the atmosphere of Xiamen were presented and analyzed during a typical haze episode from Dec 25, 2010 to Jan 1, 2011.

With the typical haze episode process, the concentrations of  $\text{PM}_{2.5}$  mass, WSIs, OC, EC, and TE were in the trend of that first increased and then decreased, which suggested the serious air pollution in haze days. The high concentrations of pollutant in Xiamen during haze episodes mainly resulted from the local sources emission and the long distance transport of air pollutants, which could be illustrated by the backward trajectory of HYSPLIT model. Moreover, the results of meteorological soundings showed that there was a vertical tempera-

ture inversion which led to stable atmospheric condition during the haze episode, which promoted the accumulation of pollutants.

Both primary species (EC) and secondary species ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ ) were accumulated during the haze episode. However, the accumulation of secondary species was not obviously stronger than that of primary species, which indicated that there might be thresholds for precursors generating secondary species. In this study, it was found that SOC,  $\text{NO}_3^-/\text{SO}_4^{2-}$ , and  $\text{SO}_4^{2-}$  did not increase with the increase of OC,  $\text{NO}_2$ , and  $\text{SO}_2$ , respectively, during the haze episode.

High  $\text{NO}_2$  concentrations resulted in the reduction of OH, and further decreased the possibility of  $\text{SO}_2$  generating  $\text{SO}_4^{2-}$ . Therefore, the values of NOR and SOR did not increase with the increase of  $\text{NO}_2$  and  $\text{SO}_2$  during the haze episode. The value of  $\text{NO}_3^-/\text{SO}_4^{2-}$  ratio during measured period (0.88) was higher than that of normal days (0.52), which suggested that the accumulation of pollutants from vehicle exhaust was more severe than that from coal combustion during haze episodes.

The EF analysis showed that Ni was substantially enriched ( $20 < \text{EF} \leq 50$ ), whereas, Cu, Pb, As, Br, Zn, and Se were extremely enriched ( $\text{EF} > 50$ ), so that they originated from anthropogenic sources. The OC/EC ratios in this study suggested that vehicular exhausts, coal combustions, biomass burning and kitchen emissions were the main sources of carbonaceous fractions in Xiamen during haze episodes.

The average percentage contributions to  $b_{\text{ext}}$  were 39.3% for organic mass, 19.9% for elemental carbon, 16.0% for ammonium sulfate, 13.0% for coarse mass, and 11.8% for ammonium nitrate during the haze episode. Compared to normal days, elemental carbon was the second largest contributor to  $b_{\text{ext}}$  during the haze episode. The primary accumulation and the secondary formation of pollutants were the main factors in the haze formation process. The reduction of carbonaceous fractions released into aerosol could effectively improve the atmospheric visibility of Xiamen during haze episodes.

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