Characterization of submicron aerosols and effect on visibility during a severe haze-fog episode in Yangtze River Delta, China

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HIGHLIGHTS

- Particle number size distribution characteristic during haze-fog episode.
- Submicron aerosol influence on light extinction coefficient is evaluated.
- Secondary aerosol formation controlling haze-fog episode.
- The effect of air mass origin on haze-fog formation episode.

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ABSTRACT

Particle size, composition and optical properties were measured at a regional atmosphere background station in the Yangtze River Delta (YRD) to understand the formation and evolution of haze-fog episodes in Jan. 2013. The peak of particle number size distribution was in the size range of 80–100 nm during the measurements. PM1 mass concentration contributed 84% to the total particle mass (PM10). Based on visibility and ambient relative humidity, three types of weather conditions (i.e., clear, haze and fog) were classified in this study. The extinction coefficients of PM1 and PM10 under dry conditions were simulated by the Mie model. Under dry conditions, PM1 was found to contribute approximately 91% to the light extinction coefficient of PM10. However, the PM1 with the assumption of dry state was found to contribute approximately 85% to the ambient extinction coefficient of PM10 during clear conditions, 58% during haze conditions and approximately 41% during fog conditions. The variation of the dry PM1 contribution was related to the water uptake of particles under different relative humidity conditions.

A severe haze-fog event on Jan. 14–17 was discussed in more detail as a case study. Two episodes were chosen to show that nitrate and organics dominated the aerosol component during the severe haze-fog episode and were related to secondary aerosol formation and air mass origin. Nitrate played a more dominant role than sulfate in heavy haze formation in the YRD region, which was different from the North China Plain region.

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1. Introduction

The Yangtze River Delta (YRD), including Shanghai and its neighboring 8 cities in Jiangsu Province and 7 cities in Zhejiang Province, is one of the most densely populated and economically developed regions in China. Complex and regional air pollution, such as high concentrations of ozone, anthropogenic gaseous pollutants (SO2, NOx, NH3 and VOCs) and particulate matter (Wang et al., 2001), has been a severe issue in this region. Haze-fog days caused by fine particles have become the most crucial topic for atmospheric environment research (Zhang et al., 2012). Haze-fog formation is closely related to meteorological conditions and high aerosol mass loading (Wang et al., 2014a), which has a significant impact on the visibility, public health and even the global climate.
Several severe haze-fog periods were observed in the YRD region with major aerosol components, including sulfate, nitrate, ammonium and organic aerosol (Fu et al., 2008). The extinction coefficient in this region is high due to the aerosol mass concentration and is also affected by the aerosol chemical component, particle number size distribution (PNSD), and water vapor in the atmosphere (Pan et al., 2010). The secondary organic aerosol (SOA) played an important role in the haze formation (Zhang et al., 2012). The transformation of SO2 and NO2, which mostly originated from fossil fuel combustion and vehicle emissions (Geng et al., 2009), contributed much to the high concentration of secondary nitrate and sulfate in the YRD (Fu et al., 2008). In Jan. 2013, a large area in China, including the North China Plain (NCP), Central East China (CEC), and part of Southern China, experienced extremely severe and persistent haze pollution. One study in urban cities, including Beijing, Shanghai, Guangzhou and Xi’an, reported that the haze was driven by high aerosol mass concentration, which was contributed to a large extent by secondary aerosol formation (Huang et al., 2014a). It was also found that this severe large area haze episode was accompanied by low visibility, high particle mass loading and aerosol optical depth (Wang et al., 2014b), and also by modification of fog processing on the particle size (Jiang et al., 2014). The field campaign proved that the contribution of secondary species to PM2.5 mass concentration increased to approximately 50% during the haze-fog episode compared with non-haze-fog days in Shanghai, and nitrate mass even exceeded sulfate mass during the episode (Jansen et al., 2014).

In this work, an intensive measurement of submicron aerosol physical and chemical characteristics was performed in Jan. 2013 in YRD region. We focused on the study of PNSD, with auxiliary data including meteorological factors, visibility, reactive gas and aerosol chemical components, as well as the optical model, to illustrate the formation and evolution of the heavy haze-fog episode. We addressed PNSD characteristics under different conditions and tried to estimate the contribution of dry submicron aerosols to the extinction coefficient under dry and ambient conditions. Furthermore, the PNSD evolution processes, as well as the variation of corresponding chemical composition and air mass will be illustrated in detail following a haze-fog episode case study.

2. Experimental methods

2.1. Site description

The measurements were made in Jan. 2013 at the Lin’an regional atmospheric background station (30°17’N, 119°45’E, 138.6 m asl.), which is nearly 50 km west of Hangzhou, the capital of Zhejiang province (Fig. 1). The site is approximately 200 km southwest of Shanghai. Approximately 10 km to the south of the Lin’an station is the Lin’an Township, with a population of approximately 50,000. As one of the regional Global Atmospheric Watch stations in China, the Lin’an station lies on the top of a hill surrounded by patches of pine and bamboo forest. There are very limited local pollution sources nearby; thus, the station can represent the background atmosphere of the economically developed YRD region.

2.2. Instrumentation

Measurements were conducted inside a laboratory with regulated temperature. Sampling air was collected through a PM10 inlet placed on the roof of the room, with a flow rate of 16.7 l/min. The sample air was dried by an auto-regenerated dryer system (Tuch et al., 2009). The dried air then went through the splitter to the TDMPS (Twin Differential Mobility Particle Sizer, TROPOS), APS (Aerodynamic Particle Sizer, TSI 3321), MAAP (Multi-Angle Absorption Photometer, Thermo 5012), AMS (Aerosol Mass Spectrometer, Aerodyne) and a hygroscopicity measurement system based on a wet and a dry nephelometer (TSI, Model 3563).

The TDMPS were used to measure PNSD with electrical mobility diameter in the range of 3–800 nm. The APS measured the particle number size distributions with aerodynamic diameters from 0.5 to 10 μm. The time resolution of the TDMPS and APS was 10 min. We followed the recommended standard inversion routine to derive PNSDs from the measured electrical mobility distribution (Wiedensohler et al., 2012). The PNSDs derived by APS system were converted from aerodynamic to mobility diameters using a particle density of 1.5 g cm⁻³ calculated from the measured chemical components. And the APS data with mobility diameter larger than 800 nm were selected to combine with the TDMPS data.

Scattering coefficients for dry aerosols were measured by an integrating nephelometer at the wavelengths of 450, 550 and 700 nm (Anderson et al., 1996), with a time resolution of 1 min. The MAAP (Multi-Angle Absorption Photometer, Thermo 5012) determined absorption coefficients directly and converted them to mass concentrations of black carbon (BC) with an assumed mass absorption efficiency of 6.6 m² g⁻¹ (Petzold and Schönlinner, 2004).

Online measurement of non-refractory PM1 chemical components, including sulfate, nitrate, ammonium, organic and chloride, was conducted by an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS), which provided high time-resolution (5 min) information to characterize the size-resolved composition of PM1. Details of the AMS have been described in a previous publication (e.g., Canagaratna et al., 2007). More details about AMS set up, calibration protocols and maintenance can be found in Sun et al. (2010).

CO was measured with a gas filter correlation analyzer (TEI, model 48C). NOx, including NO and NO2, was measured with a chemiluminescence analyzer (TEI, model 42C1L), and SO2 was measured by using a pulsed UV fluorescence analyzer (TEI, model 43C1L). The time resolution is 5 min. The maintenance and calibration of the instruments, as well as the correction of the data have been described by Lin et al. (2008).

Meteorological data, including atmospheric temperature (T), relative humidity (RH), precipitation, wind speed and wind direction, were monitored by an automatic weather station (type DZ4, Jiangsu Radio Scientific Institute CO., LTD, China). Visibility was measured by a Vaisala FD12 visibility meter with a time resolution of 15 s. During the measurements, we noticed that the old RH...
sensor had a low bias. To correct this bias, a new RH sensor has been operated in parallel with the old one since July 2014. Details of inter-comparison and correction are given in the supplementary material.

2.3. Modal fitting

Atmospheric aerosol size distributions are often described as the sum of three log-normal distributions (Birmili et al., 2001), which is nucleation mode (3–25 nm), Aitken mode (25–100 nm) and accumulation mode (100–1000 nm) based on Dal Maso et al. (2005):

$$
\frac{dN}{d \log D_p} = \sum_{i=1}^{n} \frac{N_i}{\sqrt{2\pi\log \sigma_i}} \exp\left(-\frac{(\log D_p - \log \bar{D}_{p,i})^2}{2(\log \sigma_i)^2}\right)
$$

(1)

where $N_i$ is the number concentration, $\bar{D}_{p,i}$ is the geometric mean diameter (GMD), and $\sigma_i$ is the standard deviation of the $i$th log-normal mode. In this study, log means log_{10}. In this study we used two modes (Aitken mode and accumulation mode) in the fitting process, as the nucleation mode particle number concentration during the measurement period was usually much lower than the other two modes.

3. Results and discussion

3.1. Meteorological condition and particle number/mass concentration

Mean visibility during the measurement period was 3.4 ± 3.4 km. There were only 5 days with maximum visibility larger than 10 km (Fig. 2a). The worst visibility during the measurement period, lower than 1 km, occurred when it snowed and rained and when RH was larger than 95%. The mean value and standard deviation of RH during the measurement period was 82 ± 17%. From Jan. 14 to 31, large-scale haze-fog phenomena occurred in the CEC, NCP and YRD regions. During this long-lasting period, the surface pressure field showed a uniform pattern, which indicated the wind speed was low and unfavorable for the horizontal and vertical exchange of water vapor and pollutants (Zhang et al., 2014). Based on the surface measurements, wind direction was predominately northeast and southwest. Furthermore, wind speed was normally lower than 4 m s^{-1}. Measurements with precipitation are excluded in the following discussion to segregate the particle scavenging effect by rain or snow, unless specifically mentioned.

The daily mean of PM_{2.5} mass concentration exceeding 75 µg m^{-3}, which was the criterion value of the second grade of air quality (http://www.mep.gov.cn/) in China, was recognized as a polluted condition. Based on this criterion, there were 21 polluted days out of 31 days in Jan. 2013. The mass concentration of PM_1, PM_{2.5} and PM_{10} was calculated based on the measured PNSD, with an estimated particle density of 1.5 g cm^{-3} from the measured chemical components and an assumption of spherical shape. The time series of PM_1, PM_{2.5} and PM_{10} mass concentration with 10 min resolution are given in Fig. 2d. The time series show that PM_1, PM_{2.5} and PM_{10} mass concentration reached 210, 230 and 280 µg m^{-3} under severe polluted conditions (e.g., Jan. 15). On clear days, the PM_{2.5} mass concentration was even less than 35 µg m^{-3}, which was the criterion (daily mean value) of the first grade of the air quality in China. The average and standard deviation of PM_1, PM_{2.5} and PM_{10} mass concentration were 86 ± 36, 94 ± 40 and 104 ± 46 µg m^{-3}, respectively, during the measurement. The mass ratios of PM_1/PM_{10}, PM_1/PM_{2.5} and PM_{2.5}/PM_{10} were 0.84, 0.92 and 0.91, respectively. The mass ratio of PM_1/PM_{10} could be as low as 0.60 when coarse mode particle number concentration increased and also could reach to 0.95 due to the obvious scavenging process.

Fig. 2. The time series of visibility and precipitation (a), evolution of PNSD with the $D_p$ (circles) of the dominant mode (b); particle number concentrations in different modes (c) and the calculated mass concentration of PM_1, PM_{2.5} and PM_{10} (d) during the measurement.
of large particles under fog conditions. Generally speaking, mass of total particles was dominated by submicron particles (PM$_1$) during the entire period.

Fig. 2b shows that PNSD had a large variation from day to day. Particle number concentrations were concentrated below the size of 1 μm, with the $D_p$ of the dominant mode fluctuating approximately 80–100 nm. Aitken mode number concentration ranged from 1000 to 13,000 cm$^{-3}$, with a mean value of 4700 cm$^{-3}$. The accumulation mode number concentration was in the range of 1300–12,000 cm$^{-3}$, with a mean value of 4780 cm$^{-3}$. The nucleation mode number concentration was usually as low as several hundred per cubic centimeter, except when a NPF event occurred. NPF event identification was based on the methods presented in Dal Maso et al. (2005). This method required a sharp increase of nucleation mode particle number concentration, subsequent growth to larger sizes and duration of a few hours. Only one NPF event could be identified during the entire study period, occurring on Jan. 20. The hourly maximum of particle number concentration of nucleation mode increased to a value of approximately $10^6$ cm$^{-3}$, much higher than the mean value during the study period, 490 cm$^{-3}$.

### 3.2. The classification of clear, haze, and fog conditions

The relationship of visibility, RH and PM$_{2.5}$ mass concentration in this study is shown in Fig. 3. In this work, three typical weather conditions, clear, haze, and fog, were considered. The criteria (WMO, 2005) for classifying these conditions were: (1) for the clear condition, visibility $\geq$5 km; (2) for the haze condition, visibility $\leq$5 km and RH $\geq$95%; (3) for the fog condition, visibility $<1$ km and RH $\geq$95%. The classification was based on the meteorological and visibility data with an hour resolution. Theoretically, particle will be activated only at the saturation higher than 100%. However, the RH sensor doesn’t work well at such high RH. Furthermore, it has been revealed that the particles of size 1–10 μm can be activated into cloud droplets with a relative humidity of less than 100% based on the concept of multiphase–multicomponent Köhler theory (Kulmala et al., 1997). Therefore, a threshold value of 95% was chosen as the best choice to identify the fog condition in this study. For the haze condition, PM$_{2.5}$ varied from less than 50 μg m$^{-3}$ to more than 200 μg m$^{-3}$; levels at which aerosols could play major roles in the reduction of visibility. With an elevated RH, the hygroscopic growth of aerosols had a larger impact on visibility due to water uptake (Zhang et al., 2015). As observed from Fig. 3, the PM$_{2.5}$ mass concentration in fog conditions was relatively low, which suggests that some particles could be activated and grow out the range of PM$_{10}$. Therefore, the degradation of visibility was not sensitive to the PM$_{2.5}$ mass concentration.

Classification results for clear, haze, and fog conditions are summarized in Table 1, which also gives the mean PM$_{2.5}$ mass concentration and occurrence frequency during the corresponding conditions. Statistical results were derived based on hourly meteorological data and PM$_{2.5}$ mass concentration. The Table reveals that the haze condition occurred most frequently in Jan. 2013, which also showed the highest mean mass concentration of 115 μg m$^{-3}$ compared with the other conditions. Due to the diurnal variation of RH (normally higher at night and lower during the day), haze could transform to fog and fog to haze. However, this transformation process was not easily and clearly distinguished; thus, this condition is referred to as a haze-fog episode in this study.

### 3.3. Characteristics of particle size distribution on different conditions

The mean PNSD and particle volume size distribution (PVSD) in clear, haze, and fog conditions are given in Fig. 4. The mode fitting results of parameters for PNSD are given in Table 2. PM$_{2.5}$ under clear conditions was dominant in the Aitken mode. For haze and fog days, PNSD was characterized by the accumulation mode, with larger $D_p$ and higher number concentration. $D_p$ of the dominant mode shifted from 78 nm under the clear condition to the larger size of 137 nm under fog condition. Particle growth probably relates to atmospheric aging processes, including oxidation (Ivleva et al., 2007), condensation (Saathoff et al., 2003) and coagulation (Riemer et al., 2004) processes. For PVSD (Fig. 4b), particle volume was dominated by particles of size 300–450 nm under all conditions and was highest under haze conditions, indicating highest particle mass loading under this condition.

### 3.4. The effect of PM$_1$ on visibility

The extinction coefficient of particles could be estimated using the PNSD measurement, particle refractive indices and the Mie model (Bohren and Huffman, 1998; Cheng et al., 2006; Ma et al., 2011, 2012), and then converted to visibility using a modified Koschmieder relation (Schichtel et al., 2001):

$$\text{VIS}_{\text{cal}} = 1.9/\sigma_{\text{ext}}$$

where $\text{VIS}_{\text{cal}}$ is the calculated visibility and $\sigma_{\text{ext}}$ is the extinction coefficient in an ambient state, the sum of scattering and absorption by particles and gases. However, in this work, extinction by gas was not taken into consideration. The standard Koschmieder constant of 3.92 (Seinfeld and Pandis, 1998) is replaced by 1.9 because the real visual targets are not black, are too small in angular size and are located only at quantized distances away from the observer (Carrico et al., 2003; Cheng et al., 2008).

In the Mie calculations, an assumption of internal mixing of all chemical components in the particles was applied. The extinction
gave parameterization results for $f$ values of spring 2013 (Zhang et al., 2015). This study reported the mean wavelength of 550 nm from a wet and a dry nephelometer in $f$ had to be considered. At Lin'an station, the enhancement factor, ambient atmosphere, the hygroscopic characteristics of aerosols respectively, indicating they were in agreement, with the calculated extinction to PM10 extinction under dry conditions, which was underestimated. However, when RH was higher than 85%, that high aerosol volume concentration was responsible for low visibility at RH $< 90%$. In addition, another explanation is that the measurement of PNSD was conducted by using the varied volume fraction of chemical component as the input of the Mie model, with the calculated result showing that the uncertainty induced by the assumption of constant volume fraction input in simulating the optical properties could be 5% higher than an assumption of varied volume fraction. The details of the sensitivity study are given in the supplementary material as well.

Furthermore, if we simulated the optical properties in the ambient atmosphere, the hygroscopic characteristics of aerosols had to be considered. At Lin'an station, the enhancement factor, $f$(RH), was derived based on the scattering coefficient at the wavelength of 550 nm from a wet and a dry nephelometer in spring 2013 (Zhang et al., 2015). This study reported the mean values of $f$(RH) at RH values of 85%, 80%, 70%, 60% and 50%, and gave parameterization results for $f$(RH) based on the equation $f$(RH) = 1 + $a$RH$^b$ (Kotchenruther and Hobbs, 1998). The parameters $a$ and $b$ were given for different polluted cases and were 1.24 and 5.46 for a locally polluted case and 1.20 and 3.90 for a northerly polluted case (Zhang et al., 2015). In this work, the mean value of the two conditions was applied and thus $f$(RH) corresponding to an ambient RH condition could be derived. However, when RH was higher than 85%, $f$(RH) might be underestimated.

The extinction coefficients of PM$_1$ ($\sigma_{ext, 1\mu m, dry, cal}$) and of PM$_{10}$ ($\sigma_{ext, 10\mu m, dry, cal}$) under dry conditions were calculated using the Mie model. Thus we could evaluate the contribution of PM$_1$ extinction to PM$_{10}$ extinction under dry conditions, which was approximately 91 $\pm$ 5% during the measurement, insensitive to the RH. Furthermore, the extinction coefficient of PM$_{10}$ under ambient conditions ($\sigma_{ext, 10\mu m, amb, cal}$) could be derived from $\sigma_{ext, 10\mu m, dry, cal}$ by multiplying the enhancement factor $f$(RH) at ambient RH. Based on the $\sigma_{ext, 10\mu m, amb, cal}$ and the modified Koschmieder relation, the calculated visibility (VIS$_{cal}$) was derived and is shown in Fig. 5b. VIS$_{cal}$ showed a quite similar pattern to the measured visibility (VIS$_{meas}$) except that when the measured visibility was lower than 1 km and the corresponding RH was higher than 95%, the calculated visibility was always higher than the measured visibility. Under this condition, the VIS$_{cal}$ was approximately a factor of 2–20 higher than the VIS$_{meas}$, which indicated that the visibility was overestimated.

Once activated, particles may grow freely and cause a significant enhancement in extinction coefficient. The ambient extinction coefficient in fog therefore cannot be simulated with $f$(RH) because $f$(RH) is based on hygroscopic growth. Furthermore, the contribution by snow or rain droplets was not estimated, which was the larger contributor to reducing visibility during precipitation. Another explanation is that the measurement of PNSD was underestimated, especially for the accumulation mode particles. During fog conditions, there could be many particles being activated as fog droplets, which have been removed by the PM$_{10}$ impactor.

The mean ratio of $\sigma_{ext, 1\mu m, dry, cal}$ to $\sigma_{ext}$, and the standard deviation of contribution of PM$_1$ (PM$_{1, contrib}$) was 85 $\pm$ 11% under clear conditions, 58 $\pm$ 18% under haze conditions and 41 $\pm$ 1% under fog conditions, as shown in Fig. 5c. This ratio could reflect the contribution of PM$_1$ with the assumption of dry state to the extinction of aerosols at ambient RH conditions, which mixed the optical contribution of dry PM$_1$ and the influence of RH. And the influence of hygroscopic growth of particles on light extinction under haze and fog conditions could be inferred based on the difference of $\sigma_{ext, 1\mu m, dry, cal}$ to $\sigma_{ext}$, amb between clear condition. It could be roughly estimated that the contribution of the hygroscopic growth of PM$_1$ particles to the light extinction was 27% under haze condition and 44% under fog condition, respectively. Because the contribution of PM$_1$ extinction to PM$_{10}$ extinction under dry condition had been evaluated (~90%), the ratio of $\sigma_{ext, 1\mu m, dry, cal}$ to $\sigma_{ext}$, amb could be regarded as an indicator of the influence of RH. The result was comparable with the study conducted in the NCP region that high aerosol volume concentration was responsible for low visibility at RH $< 90%$ and that for RH $> 90%$ low visibility was usually caused by the increase of RH (Chen et al., 2012). In addition, we used the available nephelometer measurement data (Jan. 16–25) and corresponding MAAP data to calculate the single scattering albedo at the wavelength of 550 nm, which was 0.84 $\pm$ 0.08 during these days.

<table>
<thead>
<tr>
<th>Type</th>
<th>Number size distribution</th>
<th>$N_1$</th>
<th>$\bar{D}_{N, 1}$</th>
<th>$\sigma_{N, 1}$</th>
<th>$N_2$</th>
<th>$\bar{D}_{N, 2}$</th>
<th>$\sigma_{N, 2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear</td>
<td></td>
<td>2770</td>
<td>17</td>
<td>1.8</td>
<td>11,000</td>
<td>78</td>
<td>1.9</td>
</tr>
<tr>
<td>Haze</td>
<td></td>
<td>1800</td>
<td>31</td>
<td>1.6</td>
<td>14,500</td>
<td>125</td>
<td>1.9</td>
</tr>
<tr>
<td>Fog</td>
<td></td>
<td>1010</td>
<td>33</td>
<td>1.5</td>
<td>12,800</td>
<td>137</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Fig. 4. The mean PNSD and PVSD under different conditions.

Table 2: Characteristic parameters to represent PNSD belong to different conditions. The symbols mean: geometric mean diameters $\bar{D}_{N, i}$(nm), particle number concentration $N$ (cm$^{-3}$), and geometric standard deviation $\sigma_N$. The subscript of $n$ indicated the mode fitting parameters for number size distribution, respectively. The number of 1 and 2 in the subscript indicated there two modes fitted base on the PNSD data.
3.5. Case study of a severe haze-fog period

In Jan. 2013, extensive and long-lasting haze-fog phenomena occurred due to poor meteorological conditions and accumulating pollutants. Two major heavy haze-fog episodes were observed, occurring on Jan. 7–17, and Jan. 23–28, respectively. From Fig. 2, it can be observed that there were cycles of a few days when the mass concentration of aerosols built up gradually until the pollution was removed by strong wind or precipitation. In the following discussion, we chose Jan. 14–17 as a representative case to discuss the haze-fog formation and evolution in more detail.

The evolution of PNSD, GMD of the dominated mode \(D_p\), surface and volume concentration, as well as the meteorological conditions during this severe haze-fog period is shown in Fig. 6. There were two episodes, marked with P1 and P2, when haze occurred during daytime and transformed into fog during the night. During these episodes, the visibility decreased significantly and the surface and volume concentration built up under haze conditions. The time period was chosen as 16:00 on Jan. 14 to 06:00 on Jan. 15 for the P1 episode and 13:00 on Jan. 15 to 09:00 on Jan. 16 for the P2 episode, respectively. During the P1 episode, \(D_p\) showed a continuous increase from about 100 nm to 150 nm, with a growth rate of 6.8 nm h\(^{-1}\) from 18:00 to 23:00 on Jan. 14. During the P2 period, \(D_p\) also showed a growth trend, with a growth rate of 6.1 nm h\(^{-1}\) from 18:00 on Jan. 15 to 02:00 on Jan. 16. The wind vector showed dominant wind directions of northeast and southwest, with occasional calms.

The particle surface and volume concentration were derived based on the PNSD measurements, with the assumption of spherical particles. The surface and volume concentration could be enhanced significantly by a factor of ~2 and ~3 during these two episodes. The increased surface concentration not only enhanced the light extinction ability of particles; it also provided a larger surface area for heterogeneous reactions. The high volume concentration indicates increased aerosol mass loading.

72 h backward trajectories were calculated using the HYSPLIT 4 model (Draxler and Rolph, 2003) on Jan. 14–17 at 08:00, 14:00 and 20:00 LT, with a terminal height of 500 m above the ground level. It showed that most of the back trajectories on Jan. 14–16 traveled at the low height and affected by the mixing layer. Model results (Fig. 7) on Jan. 14 confirmed that the air mass originated from the Shanghai metropolitan area (by a prevailing northeasterly air mass), traveled a relatively short distance and crossed the boundary area between Jiangsu and Zhejiang, which contained high mass loading of anthropogenic emissions. On Jan. 15, an air mass coming from the East Sea also passed over the same area, but turned to the south and circled around Hangzhou Bay before arriving at the station. The air mass on Jan. 15 could favor more local pollutants being entrained and taken to the station. The areas along the banks of the Yangtze River and Hangzhou Bay have many industrial zones for manufacturing, steel production and chemical production, which were the main contributors of air pollutants (Huang et al., 2011). On Jan. 16 and 17, the air mass advected from the north of the station. On Jan. 17, an air mass originated from Mongolia, traveling a longer distance, which resulted in improvement of visibility in the afternoon. As discussed above, the particles in this study period built up under stagnant meteorological conditions over the course of several days followed by quick removal associated with the air mass from a clean region.

Gaseous pollutants (SO\(_2\) and NO\(_x\)) and chemical components of non-refractory PM\(_1\) (NH\(_4^+\), NO\(_3^-\), SO\(_4^{2-}\) and Organics) are shown in Fig. 8. However, chemical component data were not available after 18:00 on Jan. 16. To segregate possible physical effects, such as evolution of boundary layer and transport, the gaseous pollutants and aerosol chemical components were normalized to the mass concentration of CO (Su et al., 2008). If the normalized values were
dramatically changed, this would indicate that the air masses could be different. Elevated concentrations of SO$_2$ and NO$_x$ were observed in the P1 and P2 episodes, indicating that emissions of SO$_2$ and NO$_x$ were much more abundant in haze-fog episodes. The P1 and P2 episodes had higher nighttime concentrations, presumably due to continuous emissions at night, slower photochemical reaction processes, and weaker vertical mixing. Excluding the vertical mixing effect, peaks of SO$_2$ and NO$_x$ were observed approximately 18:00–20:00 on Jan. 14 and 15, respectively.

In the P1 episode, the maximum mass concentration of each chemical composition, NH$_4^+$, NO$_3^-$, SO$_4^{2-}$ and Organics, was 23, 48, 20 and 39 mg m$^{-3}$, respectively, appearing at approximately 22:00 on Jan. 14. At the start time of the P1 episode (16:00 on Jan. 14), organics were the dominant species, with their contribution to the sum of the non-refractory components being 40%. During the evolution of the heavy P1 episode, the contribution by the organics decreased from 50% to 30%, and the contribution by NO$_3^-$ was enhanced, with the fraction changing from 18% to 37%. While the contribution of SO$_4^{2-}$ decreased, NH$_4^+$ changed only slightly. The results suggested that the nitrate and organics contributed most significantly during the P1 haze-fog episode. They also revealed that the mass concentration of major secondary aerosol compounds increased to a different extent in the P1 episode. The normalized mass concentration of all of the species increased from 18:00 to 24:00 on Jan. 14. This variation indicated that secondary aerosol formation, including inorganic and organic aerosol, contributed to the high mass loading and the particle growth.

In the P2 episode, the PM$_1$ mass concentration reached an even higher value, approximately 200 mg m$^{-3}$. It can be observed that during this episode the contribution of organics was even higher. At the beginning of the P2 episode, approximately 14:00, the decrease in the mass concentration ratio of [organics]/[CO] and [SO$_4^{2-}$]/[CO] occurred, indicating an air mass change, which is consistent with the back trajectory analysis results. It is probable that the air mass circling around Hangzhou and the nearby cities could enhance the air pollution. The analysis above showed that different haze periods could be formed due to different types of aerosols and their formation processes. For the P2 episode, the contribution by organics aerosols was more dominant.

The result in the YRD region was different from that in the NCP region, where secondary sulfate played a more important role than nitrate under polluted conditions (Wiedensohler et al., 2009) and haze episodes (Wang et al., 2014b). The difference might be caused by the various emissions sources in the YRD and the NCP. Especially in the cold season, coal burning for heating would be a major SO$_2$ emitter in the NCP region. In the YRD region, nitrate from industrial and traffic emissions would probably be a larger contributor to the fine particles.

4. Conclusion

A consecutive series of haze-fog episodes occurred in a large area in the Yangtze River Delta in Jan. 2013. During this period, PM$_1$, PM$_{2.5}$ and PM$_{10}$ mass concentrations reached levels of over 200 mg m$^{-3}$ under severe pollution conditions. In general, PM$_1$ could contribute 84% to the mass concentration of PM$_{10}$ during the period. Three types of conditions were classified based on visibility and RH: clear, haze and fog days. The particle number size distribution on haze and fog days shifted to a larger size than on clear days. The largest number and volume concentrations occurred...
during haze conditions. The extinction coefficient of PM$_1$/PM$_{10}$ under dry conditions was derived based on the Mie model, which revealed that PM$_1$ could contribute approximately 90% to PM$_{10}$ extinction under dry conditions. Thus, the contribution of PM$_1$ with the assumption of dry state to the ambient extinction coefficient due to water uptake was evaluated as 85% during clear conditions, 58% during haze conditions and 41% during fog conditions.

A typical heavy haze-fog event, occurring on Jan. 14 to 17, was
selected to illustrate the aerosol characteristics during formation and evolution of haze-fog. There were two separate episodes, marked with P1 and P2, showing significant decrease of visibility and increase of particle mass loading. During these two episodes, the geometric mean diameter of particle number size distribution increased, with a growth rate of approximately 6.1 and 6.8 nm h⁻¹, respectively. The study also revealed that the growth process was mainly due to the nitrate and organics components, driven by the processes of secondary aerosol formation and air mass origin. Nitrate was found to play a more important role in haze formation in the YRD region, which is different from the NCP region where sulfate was a larger contributor. The difference suggests that the dominant emission source should be different between the YRD and the NCP regions. Thus, a better understanding of the relationship between secondary aerosol formation and haze-fog pollution is crucial to the control of regional air quality for different regions in China.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.09.011.

References


