WRF-Chem Simulation of a Severe Haze Episode in the Yangtze River Delta, China

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ABSTRACT

WRF-Chem was used to study a severe haze episode that occurred over the Yangtze River Delta (YRD), China, in November 2013. This episode was characterized by a high PM$_{2.5}$ concentration (> 400 µg m$^{-3}$), high relative humidity (> 80%) and low visibility (< 900 m). Regional average results showed that PM$_{2.5}$ concentration peaks corresponded closely with a low wind speed and a low planetary boundary layer (PBL) height, and the maximal PM$_{2.5}$/PM$_{10}$ ratio of 0.89 indicated fine particle dominance. Horizontal dispersion analysis showed that the ventilation coefficient (VC) dropped from above 3000 m$^2$ s$^{-1}$ (clean days) to below 1500 m$^2$ s$^{-1}$ (polluted days), and the average VC for December for the period of 2008–2012 was 2119 m$^2$ s$^{-1}$; horizontal transport flux showed central and northwest YRD mainly outputted pollutants in this episode. Vertically, because of the influence of the PBL and nocturnal inversion, the region of high PM$_{2.5}$ concentration (> 125 µg m$^{-3}$) extended to 1 km height during daytime, but was confined to below 200 m at night. However, near-surface inversion was observed even on clean days. Therefore, we concluded that poor horizontal dispersion ability played a dominant role in the haze formation, and weak vertical dispersion ability, together with high relative humidity, aggravated the pollution. Chemical analysis showed that, compared with PM$_{2.5}$ in the northwest part of the YRD, PM$_{2.5}$ in the central YRD contained a higher proportion of nitrate and a lower proportion of black carbon and organic carbon. The observed NO$_3^-$/SO$_4^{2-}$ ratio was 1.54 for this episode, and the monthly average dropped to 1.40 for December 2013. We concluded that mobile sources contributed considerably to the episode. Moreover, in winter, higher NO$_3^-$/SO$_4^{2-}$ and nitrate being the main component (29%) in PM$_{2.5}$ made central YRD different from the Beijing-Tianjin-Hebei region.

Keywords: Haze; Yangtze River Delta; Dispersion ability; PM$_{2.5}$ chemical characteristics; WRF-Chem.

INTRODUCTION

The Yangtze River Delta (YRD), located on the eastern coast of China, has an area of 99,600 km$^2$ and a population of 108.6 million. It includes the Shanghai municipality, eight cities of Jiangsu Province, and seven cities of Zhejiang Province and has become one of the fastest growing economic regions in China in recent decades. Despite the wealth brought by fast economic growth, severe haze events are increasing because of increasing energy consumption (e.g., industrial activity, residential heating, busy traffic). YRD has become one of the four heaviest haze regions in China, with the other three being the Pearl River Delta (PRD), Beijing–Tianjin–Hebei (BTH) region, and Chongqing.

Haze is a pollution phenomenon with poor horizontal visibility of less than 10 km caused by fine particles suspended in the atmosphere, which is defined in the observation standard released by the China Meteorological Administration (CMA) (CMA, 2003). Recently, haze has drawn considerable attention because of its impact on human health, visibility, and the climate (Tie and Cao, 2009; Ma et al., 2012). Numerous studies have been conducted on haze in the PRD and BTH region, and many of the haze characteristics and the formation mechanism have been discovered (Wu et al., 2005; Wu et al., 2011; Zhao et al., 2013; Tao et al., 2014; Zhang et al., 2015).

Among the studies on haze in the YRD, the study of Fu et al. (2008) analyzed a haze episode of 2007 based on observation and found that stagnant dispersion conditions played a predominant role in the haze formation. Ding et al. (2013a) analyzed observation data for the PM$_{2.5}$ concentration in Nanjing for the period of 2011–2012 by using a Lagrangian dispersion model and found that subregional transport (within the YRD) and cross-boundary transport (from the BTH region to the YRD) substantially influenced the air quality in the YRD. Chemical analysis has shown heavy amounts of secondary aerosols during haze episodes in the YRD, and the main inorganic components have been identified as nitrate, sulfate, and ammonia (Huang et al., 2012; Zhang et al., 2012). Although previous studies have

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discovered many characteristics and the formation mechanism of haze in the YRD, systematic process studies on haze episodes, based on high-resolution data covering the entire YRD region, are insufficient.

Numerical models are useful tools for studying haze events because they can reproduce high-resolution meteorological and chemical fields that can help compensate for the lack of high-resolution observations. In this study, an online-coupled meteorology and chemistry model—the Weather Research and Forecasting (WRF) model with chemistry (WRF-Chem)—was used to simulate a heavy haze episode that occurred in the YRD from November 28 to December 11, 2013. This prolonged episode, with the maximal observed PM$_{2.5}$ concentration exceeding 590 μg m$^{-3}$, resulted in the government taking drastic measures such as closing a highway and suspending classes in primary and secondary schools; the episode affected the health and daily life of residents considerably and underscored the need for haze control in the YRD. Therefore, with the objective of discovering the characteristics and formation mechanism of haze episodes occurring in recent years and offering an appropriate haze control method, we studied this severe episode by using high-resolution model results for the entire YRD region.

The paper is organized as follows: Section 2 describes the model configurations and data used in this study. Section 3 briefly describes the characteristics of the haze episode. In Section 4, first, we present simulation results and their evaluation against observation data. Next, spatial distributions of meteorological and chemical fields, as well as regional average results are analyzed. This is followed by a discussion of the horizontal and vertical dispersion ability of the atmosphere. Finally, detailed chemical composition analysis of PM$_{2.5}$ is conducted in a rural site of Nanjing, and the chemical composition in different regions of YRD are compared. Section 5 summarizes the major findings of this study.

**METHODOLOGY AND DATA**

**Model Configuration**

WRF-Chem (Version 3.5.1; Grell et al., 2005) was used in the simulation performed in this study. The major physics options selected included the Rapid Radiative Transfer Model (RRTM) longwave radiation scheme (Mlawer et al., 1997), the Goddard shortwave radiation scheme, the Fast-J photolysis scheme (Wild et al., 2000), the Yonsei University (YSU) planetary boundary layer scheme (Hong et al., 2006), the Noah land-surface module (Chen and Dudhia, 2001), WRF Single Column 5-Class (WSM5) Cloud Microphysics (Hong et al., 2004), and Grell 3D cumulus parameterization. The gas-phase chemistry was based on the Regional Acid Deposition Model, version 2 (RADM2) (Chang et al., 1989) and the aerosol module was Modal Aerosol Dynamics Model for Europe and Secondary Organic Aerosol Model (MADE/SORGAM) (Ackermann et al., 1998; Schell et al., 2001). The Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006) was used for biogenic emissions calculation, and the land-use data was the 1-km Moderate Resolution Imaging Spectroradiometer (MODIS) data (Friedl et al., 2002). The initial and boundary meteorological conditions were obtained from the National Center for Environmental Prediction (NCEP) Final Analysis (FNL) data, available every 6 h at a grid spacing resolution of 1° × 1°. The chemical initial and boundary conditions were constrained from simulations of the Model for Ozone and related chemical Tracers, version 4 (MOZART-4) at 1.9 × 2.5° (Emmons et al., 2010).

The WRF-Chem model was configured with three nested domains (shown in Fig. 1): the outer domain (D01), the medium domain (D02), and the inner domain (D03) with grid spacings of 27 km × 27 km, 9 km × 9 km, and 3 km × 3 km, respectively. D03 had grid point dimensions of 241 × 265 and covered the entire YRD region. The vertical resolution included 25 layers with a fixed model top pressure of 50 hPa. The simulation started from 00:00 (UTC) on November 27, 2013, and ended at 00:00 (UTC) on December 12, 2013, and the output was obtained on an hourly basis. The simulation results for the first 24 hours were discarded as spin-up time. Therefore, simulation results analyzed were for a duration of 14 days.

**Anthropogenic Emissions**

The anthropogenic emission inventory used in this study was obtained from the Multi-resolution Emission Inventory for China (MEIC, http://www.meicmodel.org; He, 2012) for the base year 2010 and allocated vertically in the model by following the method of Wang et al. (2010). MEIC is a new emission inventory for China available at a horizon resolution of 0.25° × 0.25°, and it contains emission information on black carbon (BC), CO, CO$_2$, NH$_3$, NO$_x$, organic carbon (OC), PM$_{2.5}$, PM$_{10}$, SO$_2$, and nonmethane volatile organic compounds for five sectors (power, industrial, residential, transportation, and agriculture sectors). It was developed by improving and updating the bottom-up emission inventories developed by the same group at Tsinghua University, China (Zhang et al., 2009; Li et al., 2014; Zheng et al., 2014). The inventory is available for 2008, 2010, and 2012. The MEIC has been previously used to simulate PM$_{2.5}$ and PM$_{10}$ in a severe haze event that occurred in January 2013 over eastern and northern China, and it was found to provide reasonable estimations of emissions (Wang et al., 2014).

**Observation Data**

PM$_{2.5}$ concentrations for Nanjing (NJ), Changzhou (CZ), Suzhou (SZ), Hangzhou (HZ), Suqian (SQ), and Shanghai (SH) were obtained from the Ministry of Environmental Protection database for evaluating the model performance. Meteorological data (i.e., 10-m wind speed, 2-m temperature, 2-m relative humidity, and visibility) for SZ, CZ, and SH used in this study were obtained from the Chinese National Meteorological Center (CNMC). Air quality observation data were available for 00:00, 03:00, 06:00, 09:00, 12:00, 18:00, and 21:00 (UTC) and meteorological data were available at 00:00, 03:00, 06:00, 09:00, 12:00, 15:00, 18:00, and 21:00 (UTC) on each day.

The PM$_{2.5}$ chemical composition was evaluated using the observation data (hourly PM$_{2.5}$, nitrate, sulfate, ammonium,
Fig. 1. (a) Domain configuration of the WRF-Chem simulation and (b) the inner domain showing the terrain height and monitoring site location (red stars).

and BC concentrations) from the Station for Observing Regional Processes of the Earth System (SORPES), which is located on the Xianlin Campus of Nanjing University in a suburban area northeast of NJ (118°57′10″E, 32°07′14″N), approximately 20 km from the downtown area (Ding et al., 2013a).

The locations of the aforementioned monitoring sites are shown in Fig. 1(b).

Calculation of Visibility

The recommended Meteorological Observation Range defined by the World Meteorological Organization is based on Koschmieder’s law (Koschmieder, 1924). For an assumed brightness contrast threshold (ε) of 0.05, the visibility (ν) is given as

\[ \nu = \frac{2.996}{B_{\text{ext}}} \]

where \( B_{\text{ext}} \) (km\(^{-1}\)) is the light extinction coefficient and is used as an indicator of visibility. It is calculated from the following expression described by Chow et al. (2002):

\[ B_{\text{ext}} = 0.003 \times f(\text{RH}) \times \left[ [\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{NH}_4^+] \right] + 0.004 \times [\text{OM}] + 0.01 \times [\text{BC}] + 0.0006 \times [\text{Coarse}] + 0.001 \times [\text{Soil}] + A \]

where [SO\(_4^{2-}\)], [NO\(_3^-\)], [NH\(_4^+\)], [OM], [BC], [Coarse], and [Soil] are the concentrations (µg m\(^{-3}\)) of sulfate, nitrate, ammonia, organic matter, black carbon, coarse particles (PM\(_{2.5-10}\)), and soil-derived aerosols. The constant A (= 0.01) represents the scattering of clean air, and \( f(\text{RH}) \) is a dimensionless adjustment factor for relative humidity.

CHARACTERISTICS OF THE HAZE EPISODE

According to observation data, the continuous haze episode was divided into three periods: Phases (1), (2), and (3), corresponding to the pre-pollution period (November 28, 00:00–November 30, 23:00), severely polluted period (1 December 00:00 to 8 December 23:00), and post-pollution period (December 9, 00:00–December 11, 23:00).

In Phase (1), particulate matter concentrations were relatively low. As shown in Table 1, the average PM\(_{2.5}\) concentrations were 68.5, 70.4, 69.8, 50.4, 49.5, and 124.3 µg m\(^{-3}\) for NJ, CZ, SZ, HZ, SQ, and SH, respectively. In Phase (2), the values increased to 173.9—266.4 µg m\(^{-3}\) for the six sites, 1.8—3.9 times those in Phase (1). The hourly PM\(_{2.5}\) concentration reached 599 µg m\(^{-3}\) in NJ on 4 December, and 480 µg m\(^{-3}\) in SZ on 8 December. In this phase, the visibility was poor, below 500 m, in SH and the surrounding area, indicating heavy particulate matter pollution. In Phase (3), the concentration started to decrease and the air quality finally returned to a well level.

During Phase (2), 500 hPa large-scale circulation was

<table>
<thead>
<tr>
<th>Site</th>
<th>Phase 1</th>
<th>Phase 2</th>
<th>Phase 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NJ</td>
<td>68.5</td>
<td>258.8</td>
<td>108.8</td>
</tr>
<tr>
<td>CZ</td>
<td>70.4</td>
<td>266.4</td>
<td>109.7</td>
</tr>
<tr>
<td>SZ</td>
<td>69.8</td>
<td>246.9</td>
<td>111.3</td>
</tr>
<tr>
<td>HZ</td>
<td>50.4</td>
<td>195.2</td>
<td>95.3</td>
</tr>
<tr>
<td>SQ</td>
<td>49.5</td>
<td>173.9</td>
<td>104.1</td>
</tr>
<tr>
<td>SH</td>
<td>124.3</td>
<td>226.5</td>
<td>166.4</td>
</tr>
</tbody>
</table>
stable, and weak high-pressure systems or uniform pressure fields were present in the YRD in surface weather patterns, leading to stagnant weather conditions. A detailed description of synoptic weather charts can be referred to Wang et al. (2015).

RESULTS AND DISCUSSION

Meteorological Variable Verification

The comparative results for meteorological variables at three sites are shown in Fig. 2. The correlation coefficient ($R$), mean bias (MB), and root mean square error (RMSE) were calculated for evaluating the model performance (Table 2). Note that all the data analyzed next were from the innermost domain. The simulated 2-m temperature ($T_2$), 2-m relative humidity ($RH_2$), and 10-m wind speed ($WS_{10}$) corresponded closely with the observation for almost all sites. For SH and SZ, the simulated $T_2$ was higher than the observed value during December 6–7, resulting in the MBs reaching 1.02 and 1.33°C, respectively. $RH_2$ was underestimated at SH site (with an MB of –17.90%) as the model has the deficiency of simulating coastal wind direction, which is closely related to $RH_2$ in that area. An acceptable overestimation of $WS_{10}$ by the model was observed for CZ and SH, and the MBs were 1.39 and 1.51 m s$^{-1}$, respectively. For visibility, the model reproduced the sharp variation during the transition of different phases, and the results for all the sites matched closely with the observation during Phases (1) and (3). In Phase (2), the model successfully reproduced the daily minimum visibility in CZ and SZ, but a large overestimation was noticed for SH, resulting in an MB of 7.25 km.

Fig. 3 shows a comparison of the vertical temperature profiles obtained from sounding data and model results. Overall, the simulation results corresponded closely with the observations, but the model tended to underestimate the height of the temperature inversion, particularly for December 8.

Chemical Species Verification

The simulated and measured PM$_{2.5}$ at each of the six sites, together with the corresponding statistical analysis (Table 2), are compared in Fig. 4 for evaluating the model performance. For all the sites, the PM$_{2.5}$ concentrations in Phase (2) were higher than those in the other two phases, indicating that the model successfully reproduced the haze...
Table 2. Statistical analysis of the simulated and observed variables.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Site</th>
<th>R</th>
<th>MB</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2, °C</td>
<td>CZ</td>
<td>0.88</td>
<td>0.87</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td>SZ</td>
<td>0.80</td>
<td>1.33</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>SH</td>
<td>0.86</td>
<td>1.02</td>
<td>2.53</td>
</tr>
<tr>
<td>RH2, %</td>
<td>CZ</td>
<td>0.77</td>
<td>-15.24</td>
<td>19.88</td>
</tr>
<tr>
<td></td>
<td>SZ</td>
<td>0.74</td>
<td>-9.50</td>
<td>17.18</td>
</tr>
<tr>
<td></td>
<td>SH</td>
<td>0.75</td>
<td>-17.90</td>
<td>23.40</td>
</tr>
<tr>
<td>WS10, m s⁻¹</td>
<td>CZ</td>
<td>0.63</td>
<td>1.39</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>SZ</td>
<td>0.61</td>
<td>1.06</td>
<td>2.10</td>
</tr>
<tr>
<td></td>
<td>SH</td>
<td>0.69</td>
<td>1.51</td>
<td>2.06</td>
</tr>
<tr>
<td>VIS, km</td>
<td>CZ</td>
<td>0.70</td>
<td>3.18</td>
<td>5.08</td>
</tr>
<tr>
<td></td>
<td>SZ</td>
<td>0.79</td>
<td>5.86</td>
<td>7.30</td>
</tr>
<tr>
<td></td>
<td>SH</td>
<td>0.62</td>
<td>7.25</td>
<td>8.57</td>
</tr>
<tr>
<td></td>
<td>NJ</td>
<td>0.44</td>
<td>-44.41</td>
<td>131.76</td>
</tr>
<tr>
<td>PM₂.₅, µg m⁻³</td>
<td>CZ</td>
<td>0.52</td>
<td>-24.60</td>
<td>112.43</td>
</tr>
<tr>
<td></td>
<td>SZ</td>
<td>0.56</td>
<td>-26.35</td>
<td>101.49</td>
</tr>
<tr>
<td></td>
<td>HZ</td>
<td>0.50</td>
<td>-32.63</td>
<td>90.90</td>
</tr>
<tr>
<td></td>
<td>SQ</td>
<td>0.49</td>
<td>-31.39</td>
<td>82.53</td>
</tr>
<tr>
<td></td>
<td>SH</td>
<td>0.17</td>
<td>-39.31</td>
<td>146.55</td>
</tr>
</tbody>
</table>

Fig. 3. Comparison of simulated (solid lines) and observed (dashed lines) vertical temperature profiles for the Nanjing (NJ) site. The sounding data were obtained from: http://weather.uwyo.edu/upperair/sounding.html.
episode. The RMSEs ranged from 82.53 to 146.55, and the $R$ values were 0.44, 0.52, 0.56, 0.50, 0.49, and 0.17 for NJ, CZ, SZ, HZ, SQ, and SH, respectively. The model results were quite well, except for the SH site, where $R$ was only 0.17 because the model failed to capture the variation in the PM$_{2.5}$ concentration during December 2–7. Large underestimations of the peak values were observed on December 5–6 in SH, and the other sites also showed a negative bias on December 6. A likely reason is that because the YRD is located near the coastline and sea–land air exchange is frequent in the area, clean air from the sea strongly affected the pollutant concentration. Hence, the model’s performance of the pollutant concentration is strongly related to the accuracy of the simulated wind field. During December 5–6, the observed wind direction in SH was northwest or southwest, but the simulated wind direction was northeast, and therefore, clean air from the sea incorrectly reduced the pollution near coastline cities in the YRD and caused the underestimation. Furthermore, in SH, around 00:00 (UTC) on December 4, the bias in the wind direction caused the model to overestimate the particulate matter concentration. Thus, it is clear that for SH and other coastal cities, the main factor influencing the accurate reproduction of the pollutant concentration by the model for the severe haze episode is the wind direction. Noted that though with the underestimation of the RH$_2$, the model performance was well in SQ and CZ during December 3–6. This implied that the wind speed and height of the temperature inversion, which have been well simulated by the model, may be more important for PM$_{2.5}$ concentration model performance than the RH$_2$ during this episode.

Overall, the model captured the key feature of the haze event with an acceptable bias. This provided a solid foundation for the subsequent analysis.

**Spatial Distribution of PM$_{2.5}$ Concentration, Wind Field, Relative Humidity, and Visibility**

The simulated PM$_{2.5}$ concentration and near-surface wind fields (Fig. 5), together with the surface relative humidity and visibility (Fig. 6), at 00:00 (UTC) on November 28–December 11 were analyzed. Note that in the following
Fig. 5. Distribution of the simulated PM$_{2.5}$ concentration (µg m$^{-3}$) and wind field (m s$^{-1}$) at 00:00 (UTC) from November 28 to December 11. In (f), Regions A and B are marked by white rectangles.

Fig. 6. Distribution of simulated visibility (km) and surface relative humidity (% , dashed lines) at 00:00 (UTC) from November 28 to December 11.
paragraph, T2, RH2 and WS10 were selected for representing the surface condition. Moreover, we labelled the northwest part of the YRD as Region A and the NJ–SZ–SH region in the central YRD as Region B; the two regions are marked by white rectangles in Fig. 5(f).

In Phase (1), which was the prepollution period, northwest or southwest wind prevailed in YRD region and the PM$_{2.5}$ concentration was relatively low (Figs. 5(a) and 5(b)). The relative humidity was approximately 50% and visibility in most of the YRD varied above 10 km (Figs. 6(a) and 6(b)). The PM$_{2.5}$ concentration of some large cities in Region B has already exceeded 180 µg m$^{-3}$, and the visibility consequently dropped below 7 km.

In Phase (2) (Figs. 5(c)–5(f) and Figs. 6(c)–6(f)), the near-surface wind weakened and the air quality rapidly deteriorated. On December 4 and 6, the wind speed in most of the area varied below 3 m s$^{-1}$, and in Region B, it dropped below 1 m s$^{-1}$. Moreover, December 4 corresponded to the time when the PM$_{2.5}$ concentration reached the first peak. The central YRD (Region B) with a dense population was threatened by severe particulate matter pollution (PM$_{2.5}$ concentration $> 400$ µg m$^{-3}$) at that time, and a high relative humidity center ($> 80\%$) was also located there. Because of the high relative humidity and PM$_{2.5}$ concentration, the visibility dropped below 4 km in Region B.

In the morning of December 6, the wind direction changed to northeast and brought clean air from the sea to the YRD region, mitigating the air pollution near the coastline for a short time (Fig. 5(e)). Although the PM$_{2.5}$ concentration dropped, visibility hardly increased or even decreased (i.e., to the north of Anhui Province), likely because of the increase in the relative humidity ($> 80\%$) as a result of wet sea air.

When the prevailing wind direction returned to northwest or southwest and the wind speed dropped to the minimum, pollutants accumulated rapidly again and the PM$_{2.5}$ concentration reached the second peak. At 00:00 (UTC) on December 7, most of the YRD showed a high PM$_{2.5}$ concentration, with that in Region B exceeding 400 µg m$^{-3}$ and that in Region A exceeded 300 µg m$^{-3}$. Simultaneously, the high relative humidity center ($> 80\%$) expanded to the northwest. As a result, the visibility varied below 4 km in most of the YRD, and some cities such as CZ even had a visibility below 900 m.

In the morning of December 9, strong and dry northwest wind ($> 6$ m s$^{-1}$) prevailed, and the PM$_{2.5}$ concentration started to drop from north to south. At 00:00 (UTC) on December 11, the haze completely dissipated with the PM$_{2.5}$ concentration to be below 100 µg m$^{-3}$ and the visibility returning to above 14 km.

We conclude that this episode was characterized by a high relative humidity and PM$_{2.5}$ concentration, weak near-surface wind, and poor visibility. The central YRD was most severely affected by the particulate matter pollution and showed the highest PM$_{2.5}$ concentration. The prevailing wind direction during the high-pollution period was northwest or southwest, and it prevented clean ocean air from dissipating the pollutants near the coastline. This may be one reason for the higher frequency of haze in winter than in summer (when southeast wind prevails).

**Regional Average Results**

The regional average results are shown in Fig. 7. The land area northward of 29°30′N was selected for calculation because it was the area most severely affected by the haze episode.

The PM$_{2.5}$ concentration increased rapidly before December 8 and reached peak values of 179.9 and 201.2 µg m$^{-3}$ on the morning of December 4 and 7, respectively. The variation trend of the PM$_{2.5}$/PM$_{10}$ ratio was consistent with that of the PM$_{2.5}$ concentration, and the ratio reached 0.88 and 0.89 at the first and second peaks of the PM$_{2.5}$ concentration, which indicated that the formation and accumulation of fine particles dominated the formation of the episode.

The planetary boundary layer height (PBLH) and horizontal wind speed are key factors determining the horizontal and vertical dispersion ability of the atmosphere. The wind speed directly affects the horizontal dispersion ability of the atmosphere, and it also influences the evolution of the PBLH, thereby indirectly influencing the vertical aspect. As shown in Fig. 7(b), both variables maintained a low value from November 29 to December 8, which was the time when the PM$_{2.5}$ concentration increased gradually. The nocturnal PBLH was decreasing before December 7, and it reached the lowest value of 49 m on the night of December 6, causing the second peak in the PM$_{2.5}$ concentration to be higher than the first peak. We can therefore infer that a low nocturnal PBLH is critical for pollutants to accumulate and, therefore, it promotes the occurrence of severe pollution events at night.

The surface temperature was higher on heavily polluted days (Phase (2)) both in the model simulation and observation results (Figs. 2 and 7(c)), but it was not contrary to previous studies reporting the cooling effect of aerosols (Ding et al., 2013b). The higher temperature in this period may have resulted from the heating effect of air subsidence caused by weak high-pressure systems that warmed the lower atmosphere in Phase (2), as well as the cooling effect of cold air masses from the north in Phase (3). The relative humidity was also higher in Phase (2), and it promoted gas-to-particle transformation and aggravated the pollution through particle formation, as reflected by the high PM$_{2.5}$/PM$_{10}$ ratio.

Because of the increase in the PM$_{2.5}$ concentration and relative humidity, the visibility deteriorated rapidly. The maximum visibility on December 7 dropped below 9 km, and the minimum visibility on that day was only 4.7 km.

On December 8, the PBLH and surface wind speed increased sharply, indicating improved vertical and horizontal dispersion ability of the atmosphere. Under these conditions, the PM$_{2.5}$ concentration dropped sharply below 100 µg m$^{-3}$ and the visibility returned to above 10 km.

**Dispersion Ability Analysis**

To quantitatively analyze the dispersion ability of the atmosphere, we introduced the ventilation coefficient (VC) in this study. The VC is the product of the PBLH and the horizontal wind speed. It is an indicator of the ability of the
The higher the coefficient is, the more efficient the disposal of the pollutants is and the higher the air quality is (Krishnan and Kunhikrishnan, 2004; Ashrafi et al., 2009; Iyer and Raj, 2013). On the basis of the aforementioned studies, the VC \( \text{m}^2 \text{s}^{-1} \) in this study was defined as follows:

\[
\text{VC} = \sum_{i=1}^{n} V_h(i) \times h_i
\]

where \( V_h \) represents the horizontal wind speed at the \( i \)th level of the model, \( h_i \) is the depth of that level, and \( n \) is the total number of model levels under the PBLH.

Fig. 8 shows the average VC of the three phases of the haze episode. Clearly, the VC of the central YRD varied above 3000 m^2 s^−1 in Phases (1) and (3) (Figs. 8(a) and 8(c)), and it dropped below 1500 m^2 s^−1 on heavily polluted days (Fig. 8(b)). NCEP FNL data were used to calculate the 5-year regional average VC for December for the period of 2008–2012 and the value of the land area in D03 was 2119 m^2 s^−1.

Regarding spatial distribution, the VC was much lower in the south than in the central and northern YRD, likely because of the hills and mountains in that area (Fig. 1(b)) that blocked air flow and resulted in a lower wind speed, as shown in Fig. 5. Although the flat terrain in the central and northern YRD led to a higher VC and thus more efficient dispersing ability, the pollutant concentrations in those areas were still higher than in the south, mainly because of the higher pollutant emission rate of the megacity clusters there.

SH is a coastal city with VC much higher than the surrounding area, which probably resulted from higher PBLH near coastline in winter. However, pollution in SH was severe because of the high pollutant emission rate.

We also compared the time variation of the VC and PM\(_{2.5}\) concentration during the episode (Fig. 9). In Phase (2), the minimum VC of all four sites dropped below 1000 m^2 s^−1 and the troughs of the VC corresponded closely with the peaks of the PM\(_{2.5}\) concentration. The correlation coefficients between the VC and the PM\(_{2.5}\) concentration were −0.54, −0.61, −0.57, and −0.61 (Statistically significant at the 95% confidence level) for NJ, SZ, SH, and CZ, respectively.

Daily PM\(_{2.5}\) horizontal transport flux was also presented to discuss the net effect of the inflow and outflow across the borders of Region A and Region B (Fig. 10). The flux was defined as the product of PM\(_{2.5}\) concentration, wind speed and cross-sectional area on the border. The height of the cross-section was the PBLH outputted by the model. All the four borders of one region were selected for calculation and then added together. If the flux is negative, the outflow of PM\(_{2.5}\) is dominant, and vice versa.
For the whole simulation period, the net flux values of the two regions were mainly negative. This showed that Region A and Region B mainly outputted PM$_{2.5}$ during this episode, aggravating the level of pollution in surrounding regions. When compared with Phases (1) and (3), the output flux of Phase (2) weakened significantly in both Region A and B. The period average flux values of Region A were $-831$ and $-1268$ ton day$^{-1}$ for Phases (1) and (3), and it dropped to $-226$ ton day$^{-1}$ for Phase (2). That was similar with Region B, with the values of $-3820$, $-1985$ and $-5213$ ton day$^{-1}$ for Phase (1), (2) and (3), respectively. Moreover, the transport of PM$_{2.5}$ was stronger in Region A than Region B, though the total border length of the former is about 1.3 times as large as the latter.

From the analysis above, we conclude that the variation of horizontal dispersion ability and the resulting transport flux played the key role in the formation and dissipation of this haze episode.

To analyze the vertical distribution of pollutants and determine the vertical dispersion ability, we selected the NJ site for the single-station analysis (Fig. 11). Because the PBLH is determined using a critical bulk Richardson number of 0 in the YSU planetary boundary layer scheme, which may not be applicable for typical simulations at night.
Fig. 10. PM$_{2.5}$ horizontal transport flux (ton day$^{-1}$) for Region A and Region B.

Fig. 11. Time series of the vertical profile of the PM$_{2.5}$ concentration (µg m$^{-3}$) and PBLH (m, solid line) at Nanjing. Note that the nocturnal PBLH is defined as the height of the top of the inversion layer.

where the Richardson number is equal to 0 at the surface, we used the height of the top of the inversion layer as the nocturnal PBLH.

Compared with Phase (1) and (3), the PM$_{2.5}$ concentration in Phase (2) increased considerably. At night during December 3–8, a high concentration of PM$_{2.5}$ (> 125 µg m$^{-3}$) was trapped below 200 m, which was due to the strong inversion layer at that height. In the daytime, because of the lifting of the PBLH, vertical mixing and convection were enhanced and the pollutants were diluted and dispersed to the upper level. For example, a high PM$_{2.5}$ concentration (> 125 µg m$^{-3}$) was observed above 1 km on December 7.

The major peaks in the PM$_{2.5}$ concentration matched closely with the relatively low value of nocturnal PBLH (i.e., on December 4 and 8). However, on November 28 and December 9, when the nocturnal PBLH was even lower, the near-surface pollution was considerably low. This indicates that a low PBLH is a crucial factor in aggravating near-surface pollution when the horizontal dispersion ability is already weak, but it does not play a dominant role in haze formation.

**Chemical Composition Analysis**

Detailed PM$_{2.5}$ chemical composition of the simulation results was compared with SORPES observation data. As shown in Fig. 12, the model performance was well in Phases (1) and (3), but the inorganic salt concentration was underestimated in the daily PM$_{2.5}$ concentration modeled in Phase (2), which was mainly caused by the bias of sulfate. One possible cause is the different base years in the MEIC inventory (2010) and simulation (2013). From 2010 to 2013, pollution emission in Xianlin, a rural site of NJ, increased considerably because of rapid development and urbanization. For example, although numerous buildings have been constructed in Xianlin in recent years, the MEIC inventory does not consider this information, which causes the underestimation of emission. A similar bias was found in Beijing when a severe haze episode that occurred in
January 2013 was simulated using the same inventory; the bias was due to the exit of industrial manufacturers from urban areas in recent years (Wang et al., 2014). Nevertheless, the model well captured the growth of nitrate concentration, which was the largest inorganic component of PM$_{2.5}$ during the haze episode of the current study. The BC concentration was also well simulated by the model.

Sulfate aerosols mainly originate from coal combustion, thus both residential heating in many relatively small towns and cities and industrial activities are the main sources of the high sulfate concentration in China. For nitrate, nitrogen oxide is a crucial precursor that originates mainly from the combustion of fossil fuel, and coal-based power plants and motor vehicle emissions contribute approximately 22% and 41% of nitrogen oxide released by fossil fuel combustion (Zhang et al., 2012). In this study, we used the concentration ratio of nitrate to sulfate (NO$_3^-$/SO$_4^{2-}$) in PM$_{2.5}$ to evaluate their relative size. If the NO$_3^-$/SO$_4^{2-}$ ratio is greater than 1, mobile sources contribute more to SO$_2$, NOx, and particulate matter in the atmosphere. When the ratio is smaller than 1, stationary sources dominate (Huebert et al., 1988; Novakov and Penner, 1993). Numerous studies have focused on the NO$_3^-$/SO$_4^{2-}$ ratio. Huang et al. (2006) studied the chemical composition of PM$_{2.5}$ in NJ in 2005 and found that the average NO$_3^-$/SO$_4^{2-}$ ratio was 0.29 in winter. Wei et al. (2009) studied the PM$_{2.5}$ chemical composition during 2007–2008 in NJ and found that the average NO$_3^-$/SO$_4^{2-}$ ratio was 0.94 on normal days (free of fog and haze) and 0.80 on haze days in winter. During a long-lasting haze episode in NJ in October 2009, this ratio was 1.05 in PM$_{10}$ (Kang et al., 2013). Apparently, an increasing trend was observed for the NO$_3^-$/SO$_4^{2-}$ ratio in winter for the period from 2005 to 2009 in NJ. A similar trend of 0.40–0.75 for the period from 2005 to 2009 was also observed in SH, the biggest mega-city of the YRD (Yao et al., 2002; Wang et al., 2006; Huang et al., 2012).

In the haze episode that occurred in the winter of 2013, the average NO$_3^-$/SO$_4^{2-}$ ratios in Phase (2), obtained from observations and simulation were 1.54 and 2.36 for Xianlin; both values exceeded 1.0. The observed average value for the month of December 2013, excluding Phase (2), was 1.40, which indicates that the NO$_3^-$/SO$_4^{2-}$ ratio was higher on heavily polluted days. However, in 2007–2008, the situation was the exact opposite. Therefore, we can infer that compared with previous haze episodes, the increase in the nitrate concentration played a more critical role in the formation of the haze episode of the current study.

We have also analyzed the SO$_2$ and NOx emission of different sources based on the 2006 INTEX-B emission inventory (Zhang et al., 2009) and the 2010 MEIC inventory. As important precursors of nitrate and sulfate aerosols, SO$_2$ and NOx greatly determined the level of particle pollution in this episode. The results showed that in D03, the transportation sector accounted for 25% and 1% of the total NOx and SO$_2$ emission in 2010. From 2006 to 2010, the total NOx emission increased from 4809 Gg year$^{-1}$ to 5894 Gg year$^{-1}$ (+23%). NOx from the transportation sector was 1099 Gg year$^{-1}$ and 1494 Gg year$^{-1}$ in 2006 and 2010, having increased by 36%. That was 19% for the total emission of the other sectors (i.e., industry, residential and power), increasing from 3709 Gg year$^{-1}$ to 4400 Gg year$^{-1}$. The increase of NOx emission was probably caused by the development of industries and the growth in motor vehicle number. Furthermore, with the innovation of denitrification technology in industries and the rising motor vehicle numbers, NOx from the transportation sector may account for a larger proportion of the total emission in 2013. For SO$_2$, as a result of the desulphurization of industries, the emission decreased from 6065 Gg year$^{-1}$ to 3959 Gg year$^{-1}$ (−35%), while SO$_2$ from the transportation sector still increased by 21 Gg year$^{-1}$ (+ 75%). From the analysis above, it is clear that transportation sources contributed considerably to this episode, which was also revealed by the high NO$_3^-$/SO$_4^{2-}$ ratio.

To analyze the chemical composition distribution in the
YRD, the northwest part of the YRD (Region A) and central YRD (Region B) were compared (Fig. 13). Region B includes large cities such as SH, NJ, and SZ, and, therefore, it has a denser population, more developed industry and busier traffic than Region A. Both Regions A and B witnessed a remarkable increase in soluble inorganic ions during Phase (2), which indicated that inorganic secondary aerosols played a key role in the formation of the haze episode in both regions. On December 7, when the PM$_{2.5}$ concentration reached the maximum, nitrate accounted for 29% of PM$_{2.5}$ in Region B, much higher than that of Region A (15%). This showed that nitrate accounted for a larger proportion of PM$_{2.5}$ in the central YRD because of higher traffic and industry emission. By contrast, BC and OC in Region A were much higher than those in Region B. This may have been due to coal combustion for heating purposes in northern China in winter (Li et al., 2015); such coal combustion would generate a huge amount of carbonaceous aerosols. In the haze episode, OC was the main PM$_{2.5}$ component in Region A, whereas nitrate was the main component in Region B.

The YRD and BTH regions are the two major severe haze regions in China, and from the analysis presented earlier in this paper, we can conclude that the chemical characteristics of the two regions are different in winter. First, compared with the YRD, the NO$_3^-$/SO$_4^{2-}$ ratio in the BTH region is lower. Wang et al. (2005) analyzed daily PM$_{2.5}$ samples for the period of 2001–2003 for Beijing and found that the average NO$_3^-$/SO$_4^{2-}$ ratio in winter was 0.49. Gao et al. (2015) found that the ratio was 0.90 on severely polluted days in January 2013 in Beijing. Because of the policy on sulfur emission control and the increase in the number of motor vehicles, the NO$_3^-$/SO$_4^{2-}$ ratio has increased in both the YRD and BTH regions in recent years. However, the ratio exceeded 1.40 in the YRD and continued to vary below 1.0 in the BTH region. Second, OC was the main component of PM$_{2.5}$ in winter in Beijing (Zhang et al., 2013; Zheng et al., 2015), whereas, for the central YRD (Region B), nitrate was the main component in the episode.

CONCLUSION

In this study, the WRF-Chem model was used for investigating the formation mechanism and characteristics of a severe haze episode that occurred in the YRD from November 28 to December 11, 2013. The model results were compared with ground-based measurements and soundings data obtained from the the CNMC, Air Quality Network, and SORPES, and they showed acceptable accuracy. The WS10 and T2 data were well simulated by the model, but the RH2 data were underestimated. The model also captured the time evolution of the near-surface inversion height effectively. In this study, the MEIC was shown to provide a reasonable estimation of emission conditions. The PM$_{2.5}$ concentration corresponded closely with the urban monitoring site data, but large underestimations existed in a rural site of NJ, which was likely due to the difference in the base year between the simulation and the emission inventory. A larger bias in visibility was found on heavily polluted days because it was calculated from the output pollutant concentration and relative humidity, which were underestimated by the model.

During the haze episode, weather conditions were stable. The PM$_{2.5}$ concentration once exceeded 400 µg m$^{-3}$ in the central YRD, which includes the cities SH, NJ, and SZ, and 300 µg m$^{-3}$ in the northwest part of the YRD. In these regions, the high PM$_{2.5}$ concentration was accompanied by high relative humidity (> 80%), resulting in low visibility (< 4 km). Some severely polluted cities, such as CZ, had a visibility below 900 m. Weak northwest or southwest winds (< 3 m s$^{-1}$), together with a low PBLH, trapped pollutants during heavily polluted days. The wind direction also prevented clean ocean air from dissipating and diluting pollutants in the YRD, which may be one reason for the higher frequency of haze events in winter than in summer. A high PM$_{2.5}$/PM$_{10}$ ratio with a peak value of 0.89 indicated
fine particle dominance of particulate matter, possibly caused by enhanced gas-to-particle transformation associated with high relative humidity.

The VC was calculated to determine the horizontal dispersion ability of the atmosphere. From the clean period to the heavily polluted period, the period average VC showed a sharp decrease (from above 3000 m² s⁻¹ to below 1500 m² s⁻¹), and the 5-year average value for 2008–2012 was 2119 m² s⁻¹. Time series of the PM₂.₅ concentration and VC showed an inverse relationship at NJ, SZ, SH, and CZ. Analysis of PM₂.₅ transport flux showed that Region A and Region B mainly acted as pollutant sources, and PM₂.₅ output of the latter was stronger than the former; PM₂.₅ output weakened significantly for both regions during Phase (2). The vertical profile of the PM₂.₅ concentration in NJ showed that during daytime on December 7, the region of high PM₂.₅ concentration (> 125 µg m⁻³) extended to a height of 1 km because of an increase in the PBLH; when there was heavy pollution at night (e.g., December 3–8), the region of high PM₂.₅ concentration was confined to below 200 m because of the presence of the inversion layer at that height. Nevertheless, in Phases (1) and (3), when the air quality was reasonably high, the inversion layer continued to exist. We conclude that poor horizontal dispersion ability with the resulting weakened transport flux was the main cause of the severe haze episode, and the accompanied strong nocturnal inversion aggravated the pollution, causing extremely high nocturnal PM₂.₅ concentration on December 4 and 7.

The PM₂.₅ chemical composition of the central YRD differed from that of the northwest part of the YRD. Nitrate was higher in the central YRD, whereas BC and OC were higher in the northwest part of the YRD. These differences may mainly due to higher traffic and industry emission in the central YRD and the larger amount of carbonaceous aerosols emitted for the purpose of heating in winter in the northwest part of the YRD.

The NO₃⁻/SO₄²⁻ has been increasing in recent years in the YRD. During the haze episode, the observed ratio on heavily polluted days was 1.54 and the average value for December was 1.40, higher than the ratios in BTH region (varying below 1.0). Nitrate was the main component (29%) of PM₂.₅ in the central YRD during this episode, and OC was the main component in the BTH region in winter. These differences reflect that mobile sources are more important for haze formation in the YRD than in BTH region.

On the basis of the analysis, we suggest that the control of mobile sources (i.e., traffic emission) and the resulting nitrate pollution should be given due weightage for devising a haze control strategy, particularly for the central YRD.

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