A Modeling Study of a Typical Winter PM$_{2.5}$ Pollution Episode in a City in Eastern China

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ABSTRACT

A PM$_{2.5}$ pollution episode over Hangzhou, China during 8 to 16 December 2011 was simulated using the Models-3 Community Multiscale Air Quality (CMAQ). Relative contributions from local and regional emission sources to the pollution event were also investigated through numerical sensitivity tests. Comparisons between simulations and measurements at six meteorological sites over the Yangtze River Delta Region (YRDR) and four air monitoring stations at Hangzhou were satisfactory. The temporal mean of the PM$_{2.5}$ mass concentration in Hangzhou was lower than those at most areas of Jiangsu province and Shanghai during the episode. Process analysis of the four air monitoring stations at Hangzhou shows that emissions and aerosol processes contributed to the primary and secondary PM$_{2.5}$ concentrations, with the mean accumulated rates of 1.2–25.5 µg/m$^3$/hr and 0.5–1.2 µg/m$^3$/hr, respectively. The process of advection also increased the PM$_{2.5}$ mass concentration (1.2–3.4 µg/m$^3$/hr). Diffusion was the dominant removal process at most air monitoring stations, with the removal rates of 4.1–20.7 µg/m$^3$/hr. The dry (–3.0 to –3.6 µg/m$^3$/hr) and wet deposition and heterogeneous processes (–0.4 to –1.8 µg/m$^3$/hr) contributed to the loss of PM$_{2.5}$. Process analysis also indicates that the maximum concentrations of PM$_{2.5}$ that occurred during 13–14 December were mainly due to ineffective removal through diffusion. Results of the sensitivity tests suggest that non-Hangzhou pollutants made significant contributions to the PM$_{2.5}$ pollution in Hangzhou, reaching up to 70% during the focal episode. Under certain meteorological conditions, pollutants transported from outside of Hangzhou not only increased the PM$_{2.5}$ concentration, but also extended the pollution episode period in Hangzhou by one day. Nevertheless Hangzhou’s local emissions were not negligible, because they had important impacts on PM$_{2.5}$ peak values.

Keywords: Air quality modeling; Atmospheric aerosols; Local and regional emissions; Process analysis.

INTRODUCTION

Tropospheric photochemical smog pollution and secondary fine particle pollution over urban agglomerations have been accompanied with quick economic expansion and urbanization in China (Li et al., 2011; Calvo et al., 2013). Mega urban agglomerations are major sources for aerosols and oxidants (Zhang et al., 2007). The effects of these radiatively active species on air quality and climate on regional to global scales have been widely examined and reported (Intergovernmental Panel on Climate Change (IPCC, 2007). It is necessary to understand the key chemical and physical processes controlling the concentrations of the aerosols and oxidants in the polluted regions (An et al., 2007).

The Yangtze River delta urban agglomeration is one of the rapid economic development regions in China. Hangzhou is a coastal city located in Yangtze River delta region with developing manufacture and transportation industries and growing energy consumption. For example, from the report of Jiao and Hong (2007), the population in Hangzhou reached to more than 4 million people in 2006. And the annual growth rate of gross products in this city has been more than 10 percent for the last 16 years. Industrial coal consumption increased from 8.7 million tons in 2004 to 10.1 million tons in 2006 and the industrial fuel consumption rose from 95 to 163 thousand tons during the
same period. Vehicle population also increased from 0.96 to 1.20 million in this short two-year period. Hangzhou has since been suffering of serious air quality problems like high levels of aerosol particles and poor visibilities (Gao et al., 2011), which have attracted more and more public and government attention. After antipollution measures being taken such as controlling the emissions from heavy polluting enterprises (power plants and steel plants), air quality in Hangzhou has been improved in more recent years, but the concentrations of main contaminants remain high (Zhang et al., 2003a; Hong et al., 2010). This indicates that the pollution issue in Hangzhou cannot be solved thoroughly by only controlling local emissions.

Air pollutants were transported from one city to another and contaminants from different cities influenced each other (Zhang et al., 2004). For example, 20 percent of suspended particulate matter (PM$_{10}$) in Beijing came from surrounding areas (Ren et al., 2004b). The basin-like geophysical feature surrounding by highlands on three sides except for the south of Beijing, and its unique weather system with lower storey structure are determinants of air quality in that city (An et al., 2007). Air pollution transport was quite obvious in the YRDR and air pollutants emitted from southern cities usually imposed a negative effect on the downwind cities in summer (Li et al., 2008). Wang et al. (2008) confirmed that pollutants transported from the northwest to the YRDR at 500 m level in winter. And air pollutants from the YRDR influenced other regions through long-rang transport (Hsu et al., 2006). Hangzhou is hilly in the northwest and southwest and is thus similar to Beijing in the respect of topography feature. It is also a rapidly developed city like Beijing. Air pollution issues over the YRDR usually accompanied by specific weather progress with lower planetary boundary layer (Ren et al., 2004a). In order to improve the air quality in Hangzhou, it is necessary to understand the impacts of both pollutant transports and meteorology conditions (Zhang et al., 2003a). Air quality models are mathematical descriptions of atmospheric transport, diffusion, and chemical reactions of pollutants (Seinfeld, 1988). They can be used to investigate the impacts of transport and meteorological conditions on air quality at specific regions.

U.S. EPA Models-3 Community Multiscale Air Quality (CMAQ) (Dennis et al., 1996; Byun et al., 1999; Binkowski et al., 2003) is one of the many 3-D air quality models which have been developed to simulate the formation of PM$_{2.5}$ on regional scales (Zhang et al., 2009a, b). CMAQ has been widely used in investigating the effect of emission controls and the transformation and transport processes of pollutants (e.g., Unal et al., 2005; Odman et al., 2007, 2009; Zhang et al., 2003b, 2007; Zhang et al., 2009a, b) and air quality problems in China (e.g., An et al., 2005; Chen et al., 2007; Streets et al., 2007; Gao et al., 2010).

Zhang et al. (2009a, b) found that the most influential processes for PM$_{2.5}$ were primary emissions, horizontal transport, aerosol, and cloud process in the United States. Liu et al. (2010a, b) also investigated regional air pollution over China using CMAQ process analysis tools and they found that PM$_{10}$ was mainly produced by primary emissions and aerosol process and removed by horizontal transport. Process analysis was also used to investigate ozone formation over regions in China (Li et al., 2012), but the technique has been rarely used to investigate PM$_{2.5}$ pollution problems over the YRDR.

A previous study (Hong et al., 2010) showed that pollution episodes in Hangzhou generally covered multiple days instead of a single day. And the highest particulate matter concentration also occurred during the multiple-day pollution events in winter. It will provide scientific basis for environment pollution control policies to investigate the typical multiple-day pollution events in winter. In the present study, a heavy PM$_{2.5}$ pollution episode in Hangzhou during 8–16 December 2011 was simulated using CMAQ. The contributions of meteorological and chemical processes were investigated by the process analysis technique. And the relative contributions of local Hangzhou emissions and Non-Hangzhou emissions were quantitatively evaluated by sensitive tests.

**MODEL CONFIGURATIONS**

**Model Setup**

The model system consists of two components, the chemical transport model - CMAQ and the meteorological driver - MM5. The CMAQ version 4.7.1 with the Carbon Bond mechanism V (CB05) chemical mechanism (Yarwood, 2005), the fifth generation of CMAQ aerosol module (AEROS, Binkowski and Rosell, 2003) and the process analysis (Jang, 1995) module was used in this study. The CMAQ default profiles were used for initial (ICON) and boundary conditions (BICON). The meteorological fields were assimilated using Pennsylvania State University/National Center for Atmospheric Research Mesoscale Model (MM5, version 3.6.1) with four dimensional data assimilation (FDDA) (Stauffer and Seaman, 1990). National Centers for Environment Prediction (NCEP) reanalysis data (Grell and Staufer, 1994; Kalnay et al., 1996) was used as input initialization data. The microphysics scheme was the mixed-phase scheme of Reisner et al. (1998). The cumulus parameterization was based on Grell scheme (Grell and Dévényi, 2002). Medium Range Forecast (MRF) scheme (Hong and Pan, 1996) was selected as planetary boundary layer scheme. The Rapid Radiative Transfer Model (RRTM) scheme of Mlawer et al. (1997) was chosen for radiation simulation.

The model domains consisted of a coarse 36-km grid domain that covers the East Asia and a nested fine 12-km domain that covers Shanghai city, most areas of Zhejiang Province, Jiangsu Province and Anhui Province (Fig. 1). The vertical resolution of MM5-CMAQ system includes 30 layers in total from the surface to 100 hPa with the first 15 layers distributed within the lowest 2 km. The simulation period for analysis was from 5 to 16 December 2005, with the first 3 days as spin-up period to minimize the influence of initial conditions.

**Process Analysis**

The process analysis technique was developed and applied
CMAQ uses the fractional time-step method to predict species concentrations based on the species continuity equation; therefore the species concentrations are determined from successive change in concentrations due to the atmospheric processes. In turn changes in concentrations by each process can be accumulated and the contribution of the processes can be determined (Byun and Ching, 1999; Byun and Schere, 2006). This technique does not require additional input variables.

From CMAQ process analysis result, the relative importance of major atmospheric processes such as emissions of primary species, advection (including horizontal and vertical advection, and advection adjustment), diffusion (including horizontal and vertical diffusion), dry deposition, gas-phase chemistry (including photolysis and kinetic reactions), could process, aerosol process (Zhang et al., 2009b) are examined. Cloud process includes the net effect of cloud attenuation of photolysis rates, convective and nonconvective mixing and scavenging by clouds, aqueous-phase chemistry, and wet deposition. And aerosol process represents the net effects of thermodynamic equilibrium of species and dynamic process like homogeneous nucleation, condensation of sulfuric acid and organic carbon on pre-existing particles, evaporation, and coagulation between Aitken and accumulation modes of particulate matters (Liu et al., 2010a, b).

**Emissions**

The emission inventory used in this study consisted of anthropogenic, biogenic and biomass burning emissions. Other sources were not included due to the lack of data.

The anthropogenic emissions were taken from the TRACE-P (Transport and Chemical Evolution over the Pacific) inventory (Streets et al., 2003a, b) with the horizontal resolution of 0.1 degree by 0.1 degree (Woo et al., 2003) and the base year at 2000. It included the following species: SO₂, NOₓ, CO₂, CH₄, NH₃, PM₁₀, PM₂.₅, black carbon (BC), organic carbon (OC) and non-methane volatile organic compounds (NMVOC). There were significant changes in industrial and mobile emissions from 2000 to 2006 (Zhang et al., 2009c) so the industrial and mobile emissions from TRACE-P were replaced by INTEX-B inventory with the resolution of 0.5 degree by 0.5 degree at the base year 2006.

The biogenic emissions of volatile organic compounds (VOCs) were the monthly mean inventories simulated by MEGAN (Model of emission of Gases and Aerosol from Nature) from GEIA (Global Emission Inventory Activity) (www.geiacenter.org/inventories/present.html) (Guenther et al., 2012). The spatial resolution was 0.5 degree by 0.5 degree with the base year at 2002. CO and 13 NMVOC (ethane, propane, ethene, propene, isoprene, monoterpenes, sesquiterpenes, toluene, formaldehyde, acetaldehyde, acetone, othketones, and methanol) were included.

Biomass burning emissions were taken from GFED (Global Fire Emissions Database) with the spatial resolution of 0.5 degree by 0.5 degree at the base year 2006 (Giglio et al., 2010). The following species SO₂, NOₓ, CO, NMVOC, PM₁₀, PM₂.₅, BC and OC were included.

A detailed local source emission database of point, mobile and area sources and population of Hangzhou at the base year 2011 from Hangzhou environmental protection administration was also used in our study to update the area sources of Hangzhou referring to the method used by Wu et al. (2012). Wang et al. (2012) gave the diurnal variation profiles of power, industry, residential and transport emissions. In this study, with the above mentioned information and Asia 2006 sector emissions data (Zhang et al., 2009c), we obtained the diurnal variation of NOₓ, SO₂, CO, NMVOC and particulate matters (Fig. 2). We also added a daily variation for biogenic emission species on the basis of Chang et al. (2012).

**RESULTS**

**Observations and the Pattern of the PM₂.₅ Pollution Episode**

Meteorological variables, including hourly air temperature, pressure, relative humidity (RH), wind speed, precipitation, and visual range (VR), were obtained from China Meteorological Administration (CMA)/National Meteorological Center (www.cdc.cma.gov.cn) for six sites (Fig. 3(a)) in the Yangtze River delta region from 8–16 December 2011. Hourly PM₂.₅ observation data was obtained from the four air quality monitoring stations located within the Hangzhou city (Fig. 3(b)) for the same time period as that for the meteorological data. PM₂.₅ mass concentration...
Fig. 3. Location (denoted by triangles) of the six meteorological observation sites in the YRDR (a) and location of the four PM$_{2.5}$ air quality monitoring sites within the Hangzhou city (b).

was measured by the Tapered Element Oscillating Microbalance (TEOM, Rupprecht & Ratashnick Model 1400a). Calibrations for volumetric flow were performed regularly to guarantee data accuracy. The four air quality monitoring stations were categorized as industrial (Xiasha), residential (Chaohui), scenic (Wolong) and suburban (Xiaoshan) station, respectively, based on their geographic locations for easy discussion.

Fig. 4 shows the time series of the hourly PM$_{2.5}$ mass concentrations at the residential air monitoring station from 8 to 16 December 2011. An obviously high PM$_{2.5}$ pollution episode occurred in Hangzhou with daily mean PM$_{2.5}$ mass concentration exceeding 75 µg/m$^3$ for 5 days from 11 to 15 December and reaching a serious pollution level with a maximum concentration of 198 µg/m$^3$ at 13 December 20:00. And the time in this study is local standard time (LST), which is 8 hour ahead of UTC. Hourly variation of visual range was in a contrary pattern to that of PM$_{2.5}$ with the worse visual range being less than 5 km from 11 to 15 December and the minimum value of 1.2 km at 6:00 14 December 2011. Anticyclones were found from the surface synoptic meteorological charts with the high-pressure center moving between Mongolia and China’s Inner Mongolia Autonomous Region. The Yangtze River Delta region (YRDR) was at the edge of those anticyclones with stable weather patterns and sinking airflow except for 13 December. There was a low-pressure center over the northeast China and its trough situated in the YRDR on 13 December 2011. The surface pressure at the Hangzhou meteorological site changed from high to low and then to high again. Meanwhile, the station experienced the situation of strong wind first, then weak wind, and then strong wind again. There was no intense precipitation from 9 to 16 December 2011.

Model Evaluation

Model performance of MM5 is validated by the mean bias (MB), the mean error (ME) and the correlation coefficient (R) obtained by traditional statistical methods. Table 1 summarizes the statistical performance of MM5 for the hourly pressure, temperature, relative humidity, precipitation and wind speed during the pollution episode. The correlation coefficients are greater than 0.6 between simulated and observed variables except for precipitation at the six sites in the YRDR. The uncertainties in many schemes like convective parameterization (Han et al., 2007; Mei et al., 2009) and initial conditions (Zhang and Hou, 2009) made the prediction of precipitation difficult. Besides, there was not intense rain during the episode and the occurrence and intensity of precipitation were well reproduced although there was a bias for the precipitating time. Pressures were overestimated and the ME ranges are 3.5–9.2 hPa. The reason for the systematic temperature underestimates and wind speed overestimates could be due to the lack of urban canopy module in MM5. The underestimates of temperature (due to the model’s inability of properly describing the heat island effect) might also partly contribute to the overestimates of relative humidity. Overall, MM5 reproduced well most meteorological variables during this episode.

Fig. 5 compares the temporal variations of the simulated hourly PM$_{2.5}$ against available observations at the four air monitoring stations in Hangzhou. Overall, CMAQ reproduced most of the variations and magnitudes of PM$_{2.5}$ at the four stations. The underestimation of PM$_{2.5}$ peak value on 14 December 2011 10:00 may be attributed to the simulated precipitation which did not actually happen. In fact it was foggy over the YRDR in the morning of 14 December 2011, thus the model could overpredict wet scavenging of aerosols. There was some underestimation of PM$_{2.5}$ mass concentration at the industrial station when the concentrations were high during 12–15 December.

The temporal mean of the observed PM$_{2.5}$ mass concentrations were different at different air monitoring stations (Table 2). The highest value was observed at the industrial station, followed by the residential and suburban stations, and the lowest value at the scenic station. In comparison, CMAQ predicted the highest PM$_{2.5}$ at the residential station, the second highest at the industrial station, followed by the suburban station, and the lowest at the scenic stations. This CMAQ simulated PM$_{2.5}$ quantity sequence was consistent with the observations except for...
Fig. 4. Temporal variations of the observed PM$_{2.5}$ mass concentrations at ChaoHui air quality monitoring Station, and visual range, precipitation, pressure, wind speed at the Hangzhou meteorological site from 8 December 2011 00:00 to 16 December 2011 (LST) 23:00.

Table 1. Mean Bias, mean error and correlation coefficient of hourly MM5 predictions of pressure, temperature, relative humidity, precipitation and wind speed from 8 December 2011 00:00 to 16 December 2011 23:00 (LST).

<table>
<thead>
<tr>
<th>Sites</th>
<th>Pressure (hPa)</th>
<th>Temperature (°C)</th>
<th>Relative Humidity</th>
<th>Precipitation (mm)</th>
<th>Wind Speed (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MB</td>
<td>ME</td>
<td>R</td>
<td>MB</td>
<td>ME</td>
</tr>
<tr>
<td>NanTong</td>
<td>3.77</td>
<td>3.83</td>
<td>0.82</td>
<td>-2.28</td>
<td>2.54</td>
</tr>
<tr>
<td>NanJing</td>
<td>8.88</td>
<td>8.88</td>
<td>0.83</td>
<td>-4.66</td>
<td>4.69</td>
</tr>
<tr>
<td>Hefei</td>
<td>7.61</td>
<td>7.61</td>
<td>0.85</td>
<td>-5.43</td>
<td>5.43</td>
</tr>
<tr>
<td>ChangZhou</td>
<td>4.40</td>
<td>4.45</td>
<td>0.82</td>
<td>-3.78</td>
<td>3.94</td>
</tr>
<tr>
<td>Baoshan</td>
<td>4.40</td>
<td>4.48</td>
<td>0.82</td>
<td>-0.21</td>
<td>1.91</td>
</tr>
<tr>
<td>Hangzhou</td>
<td>9.16</td>
<td>9.16</td>
<td>0.83</td>
<td>-3.62</td>
<td>3.67</td>
</tr>
</tbody>
</table>

Mean Bias (MB), mean error (ME) and correlation coefficient (R) defined as

$$MB = \frac{1}{N} \sum_{i=1}^{N} (M_i - O_i)$$

$$ME = \frac{1}{N} \sum_{i=1}^{N} |M_i - O_i|$$

$$R = \left\{ \frac{\sum_{i=1}^{N} (M_i - \bar{M})(O_i - \bar{O})}{\sqrt{\sum_{i=1}^{N} (M_i - \bar{M})^2 \sum_{i=1}^{N} (O_i - \bar{O})^2}} \right\}$$

where $M_i$ and $O_i$ are values of model prediction and observation at time $i$, respectively. $\bar{M}$ and $\bar{O}$ are mean values of model predictions and observations respectively. N is the number of samples ($N = 216$). And the correlation coefficient data accepted the t-test at the confidence level of 0.01 in this study.

The significant underestimation at the industrial station. Under predictions dominated at the industrial, residential and suburban stations which were largely caused by the underestimates of the emissions outside of Hangzhou city, and slight overestimation occurred at the scenic station. The correlation coefficients between the simulated and observed PM$_{2.5}$ mass concentrations exceed 0.61 at the four air monitoring stations, with the largest value of 0.80 at the suburban station. It can be concluded that CMAQ reproduced most of the features of PM$_{2.5}$ and captured major temporal and spatial patterns.

**DISCUSSION**

**Spatial Distribution of Simulated PM$_{2.5}$ over the YRDR**

Spatial distributions of PM$_{2.5}$ mass concentration and wind vector averaged during 8–16 December in the second nested domain (12 km) are shown in Fig. 6. The north and southwest of Jiangsu province were the highest PM$_{2.5}$ regions with the mass concentration exceeding 90 µg/m$^3$. The mean PM$_{2.5}$ mass concentration at Shanghai city was also greater than 80 µg/m$^3$ while it was relatively low at Hangzhou. There was a low PM$_{2.5}$ mass concentration region over the borders of the provinces of Anhui, Zhejiang and Jiangxi. From Fig. 6 we can find that wind direction over land was northwest in the north of the 30°N, but shifted to northeast in the south of the 30°N. Wind direction had important impacts on PM$_{2.5}$ distribution. For example, the high PM$_{2.5}$ mass concentration region extended from the northwest to the southeast in Jiangsu Province. The high PM$_{2.5}$ mass concentration zones, distributing from the northeast toward the southwest in the south part of the YRDR, were along the prevailing wind direction.

**Process Analysis**

Process analysis is a technique used to trace the source(s) of a chemical species within a simulation. Integrated process rate analysis (IPR) was used in this study to determine the
Fig. 5. Time series of observed (open square) and simulated (line) hourly PM$_{2.5}$ mass concentrations ($\mu$g/m$^3$) at the four air monitoring stations in Hangzhou.

Table 2. The temporal mean observed PM$_{2.5}$ mass concentration ($\overline{O}$), temporal mean simulated PM$_{2.5}$ mass concentration ($M$), and the Mean Bias (MB), mean error (ME), correlation coefficient (R) of hourly predictions of PM$_{2.5}$ mass concentration during 8 December 2011 00:00 to 16 December 2011 23:00 (LST) at the four air monitoring stations$^b$.

<table>
<thead>
<tr>
<th>Statistical result</th>
<th>Xiasha-industrial</th>
<th>Chaohui-residential</th>
<th>Wolong-scenic</th>
<th>Xiaoshan-suburban</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\overline{O}$ ($\mu$g/m$^3$)</td>
<td>83.21</td>
<td>74.78</td>
<td>46.50</td>
<td>74.73</td>
</tr>
<tr>
<td>$M$ ($\mu$g/m$^3$)</td>
<td>58.96</td>
<td>64.37</td>
<td>47.93</td>
<td>57.67</td>
</tr>
<tr>
<td>MB ($\mu$g/m$^3$)</td>
<td>$-24.25$</td>
<td>$-10.41$</td>
<td>1.43</td>
<td>$-17.06$</td>
</tr>
<tr>
<td>ME ($\mu$g/m$^3$)</td>
<td>32.19</td>
<td>21.67</td>
<td>17.92</td>
<td>25.16</td>
</tr>
<tr>
<td>R</td>
<td>0.77</td>
<td>0.74</td>
<td>0.61</td>
<td>0.80</td>
</tr>
</tbody>
</table>

$^b$The numbers of PM$_{2.5}$ samples at the industrial, residential, scenic and suburban stations were 210, 216, 207 and 216, respectively.

Fig. 6. Spatial distributions of simulated PM$_{2.5}$ mass concentration and wind field averaged during 8 December 2011 00:00 to 16 December 2011 23:00 over the YRDR (the unit of PM$_{2.5}$ is $\mu$g/m$^3$ and the unit of wind is m/s). Black dot is the location of Hangzhou (30.29°N, 120.157°E).

relative contributions of individual physical and chemical process to the PM$_{2.5}$ components such as ammonium, sulfate, nitrite, organic matter, black carbon and other inorganic aerosols in the surface surface layer. Fig. 7 provides the contributions of the individual process during the PM$_{2.5}$ pollution episode at the four air monitoring stations.

Xiasha is the northernmost station among the four air monitoring stations. Primary particulate matter (PM) emissions were the major contributors at the industrial station with the temporal mean of accumulate rate of 3.7 $\mu$g/m$^3$/hr. Advection process (mainly horizontal transport) also helped significantly to the increase of PM$_{2.5}$ mass concentration (2.7 $\mu$g/m$^3$/hr) during most time of the pollution episode at the station. Because of the under prediction of PM$_{2.5}$ mass concentration, the contribution of advection process might also be underestimated during 12–15 December. Aerosol processes (e.g., gas-to-particle conversion and particle growth) also produced secondary aerosols such as ammonium, sulfate,
nitrite, organic aerosols with a temporal mean accumulation rate of 1.21 µg/m³/hr during the pollution episode. Cloud processes including vertical-convective mixing, scavenging, and wet deposition made important contributions to the loss of PM$_{2.5}$ by a rate of up to −41 µg/m³/hr at 14 December 2011 5:00 (LST). The emission, advection and aerosol processes contributed to the PM$_{2.5}$ production with high accumulation rates during two time periods of 13 December 14:00–23:00 and 14 December 9:00–21:00. Meanwhile, the diffusion and dry deposition processes only made minor contributions to the removal of PM$_{2.5}$. Consequently, there were peak PM$_{2.5}$ mass concentration at the nighttime of 13 and 14 December until the diffusion process provided an important pathway for the PM$_{2.5}$ removal in the morning of 14 and 15 December under the influence of wind speed increase. By design, the gas-phase chemistry process is accounted as part of aerosol process rather than as a direct contribution to PM$_{2.5}$ formation (Zhang et al., 2009b). The pollutants transported from the north of Zhejiang province and Jiangsu province made important contributions to the PM$_{2.5}$ production at the industrial station during the episode.

Chaohui station is located at residential quarters of Hangzhou. Primary PM emissions were the predominant contributor to PM$_{2.5}$ production with a temporal mean accumulation rate of 26 µg/m³/hr at the residential station during the pollution episode. Aerosol processes made subordinate contributions to the PM$_{2.5}$ production with a rate of 0.55 µg/m³/hr. Diffusion, dry deposition, cloud and advection were PM$_{2.5}$ removal processes during the whole pollution episode. The advection process contributed to PM$_{2.5}$ mass concentration with an accumulation rate of 1.3–17.7 µg/m³/hr during 13 December 16:00–23:00. Because high RH conditions favored gas-to-particle conversions, cloud processes contributed to PM$_{2.5}$ production with an accumulation rate of 42 µg/m³/hr at 13 December 22:00. These processes functioned together leading to the occurrence of the peak PM$_{2.5}$ mass concentration of 188 µg/m³ at 14 December 00:00. The diffusion process contributed little to PM$_{2.5}$ removal during 14 December 15:00–21:00. It even increased PM$_{2.5}$ occasionally. Meanwhile, advection process increased PM$_{2.5}$ level and dry deposition played a very minor role in PM$_{2.5}$ removal. These processes led to the occurrence of peak PM$_{2.5}$ mass concentration of 163 µg/m³ at 14 December 21:00. The levels of PM$_{2.5}$ mass concentration did not decrease significantly until the time when advection and dry deposition contributed to PM$_{2.5}$ loss. In conclusion, under stable weather patterns (high surface pressure center, high RH and low surface wind speed), pollutants from primary PM emission and secondary aerosol particle production accumulated and reached heavy pollution levels.
at the residential station.

Wolong station is located in the west side of the West Lake. Primary PM emissions, advection, diffusion and aerosol processes all contributed to PM$_{2.5}$ accumulation at the scenic station. And the processes of dry deposition and cloud contributed to PM$_{2.5}$ removal during the whole pollution episode ((c) in the third panel of Fig. 7). But the magnitudes of both accumulation and removal rates at this site were less than those at the other air monitoring stations. The strengthening aerosol processes provided important production pathways for PM$_{2.5}$ before 13 December 2011. Meanwhile the horizontal transport process contributed to the PM$_{2.5}$ accumulation. Diffusion made important contribution to the PM$_{2.5}$ accumulation during 13 to 14 December which was similar to the situation of the two national parks at the United States where vertical transport dominant to PM$_{2.5}$ accumulation (Zhang et al., 2009b). As local emissions were limited at the scenic station, the dominant contributors to PM$_{2.5}$ production were the transport of particulate matters and their precursors such as SO$_2$ and NO$_2$. And the dry and wet deposition processes were important to PM$_{2.5}$ removal.

Primary PM emissions were the predominate contributors to PM$_{2.5}$ production at the Xiaoshan suburban station with the temporal mean accumulation rate of 10.5 µg/m$^3$/hr. Horizontal advection was also a PM$_{2.5}$ accumulation process with a rate of 3.4 µg/m$^3$/hr since the station is the southernmost among the four air monitoring stations. Aerosol processes had minor contributions to PM$_{2.5}$ production and diffusion, dry deposition and cloud processes decreased PM$_{2.5}$ during the episode (with the temporal mean removal rates of –10.4, –2.8 and –1.3 µg/m$^3$/hr, respectively). The advection process contributed to PM$_{2.5}$ accumulation during most of the time, it however, decreased PM$_{2.5}$ from 13 December 11:00 to 15 December 11:00. The diffusion process reduced PM$_{2.5}$ during most of the time though it occasionally increased PM$_{2.5}$ from 13 December 11:00 to 15 December 11:00. The contributions of advection and diffusion processes to PM$_{2.5}$ gave rise to the PM$_{2.5}$ mass concentration peaks at the nighttime of 13 and 14 December 2011 at the suburban station.

**Sensitivity test results**

From the results of process analysis, it can be found that advection process made contribution to PM$_{2.5}$ mass concentration at both the industrial (northernmost) and the suburban (southernmost) station. It implies that the PM$_{2.5}$ pollutants of Hangzhou can come from the local or the surroundings. Two sensitivity model runs, one with only Hangzhou emissions (OHE) and another with only Non-Hangzhou emissions (NHE) (Fig. 8), were conducted and compared with the base case run including all the emissions (AE).

Table 3 shows the ratios between temporal mean PM$_{2.5}$ mass concentrations simulated with the NHE and that with the AE (NHE/AE). The sum of NHE/AE and OHE/AE at the four stations and spatial mean of Hangzhou is approximately equal to 100%. The nonlinearity uncertainty of Hangzhou was less than 20%, and it was less than 5% in the region outside of Hangzhou from the results we simulated. It implies that the impact of non-Hangzhou emission on PM$_{2.5}$ concentration in Hangzhou is almost linear during the episode. An et al. (2007) gave similar conclusion of non-Beijing sources by comparing the concentration variation patterns under 3 different emission conditions.

The highest NHE/AE of 82% was predicted at the scenic station where the local emission sources were rare, followed by the industrial station, implying the contribution of non-Hangzhou emissions. The residential station had the lowest

![Fig. 8. Spatial distributions of the only Hangzhou emissions (OHE) (a) and Non-Hangzhou emissions (NHE) (b) in the second nested domain with horizontal resolution of 12 km.](image)

**Table 3.** Temporal mean of the simulated PM$_{2.5}$ mass concentrations at the four air monitoring stations and spatial mean of Hangzhou under 3 cases: model run with AE, NHE and OHE, respectively, during 8–16 December 2011.

<table>
<thead>
<tr>
<th>Station</th>
<th>Temporal Mean</th>
<th>AE (µg/m$^3$)</th>
<th>NHE (µg/m$^3$)</th>
<th>NHE/AE (%)</th>
<th>OHE (µg/m$^3$)</th>
<th>OHE/AE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xiasha-industrial</td>
<td>57.95</td>
<td>47.08</td>
<td>81.25</td>
<td>12.98</td>
<td>22.40</td>
<td></td>
</tr>
<tr>
<td>Chaohui-residential</td>
<td>63.30</td>
<td>42.10</td>
<td>66.50</td>
<td>22.44</td>
<td>35.44</td>
<td></td>
</tr>
<tr>
<td>Wolong-scenic</td>
<td>46.63</td>
<td>38.37</td>
<td>82.30</td>
<td>9.65</td>
<td>20.71</td>
<td></td>
</tr>
<tr>
<td>Xiaoshan-suburban</td>
<td>58.45</td>
<td>43.54</td>
<td>74.49</td>
<td>16.66</td>
<td>28.51</td>
<td></td>
</tr>
<tr>
<td>HangZhou Spatial Mean</td>
<td>43.29</td>
<td>30.37</td>
<td>70.15</td>
<td>13.09</td>
<td>30.23</td>
<td></td>
</tr>
</tbody>
</table>
The ratios between temporal mean PM$_{2.5}$ mass concentrations simulated with the OHE and that with the AE (OHE/AE) were also shown in Table 3. The highest OHE/AE was at the residential station (35%) where local emissions was strong, the second highest at the suburban station, and the lowest at the industrial station. The NHE/AE was higher than OHE/AE at all the stations and Hangzhou city. And the predicted temporal mean PM$_{2.5}$ mass concentrations were still greater than 35 µg/m$^3$ at the four stations even without Hangzhou local emissions. This implies that pollutants from outside of Hangzhou made dominant contribution to the PM$_{2.5}$ pollution episode.

The magnitude of hourly PM$_{2.5}$ mass concentration simulated with NHE closed to that simulated with AE at the industrial station during the entire pollution episode (the first panel of Fig. 9). It indicates that the transportation of Non-Hangzhou pollutants made dominant contribution to PM$_{2.5}$ pollution. The runs with either AE or OHE predicted the maximum PM$_{2.5}$ values simultaneously at about 20:00 every day during 8–14 December. This means that the impact of local emissions, while not dominant, was not negligible as they conducd to the occurrence of extreme PM$_{2.5}$ values. The temporal variation patterns of the other stations and Hangzhou spatial mean were similar to the pattern at the industrial station.

CONCLUSIONS

The Models-3/CMAQ coupled with MM5 was applied to investigate the formation process of an aerosol pollution episode occurred during 8 to 16 December 2011 in Hangzhou and the relative contributions of local and surrounding emission sources to the episode. Evaluations between the predicted and observed meteorological variables and PM$_{2.5}$ mass concentrations indicate an overall acceptable

Fig. 10 shows the spatial distribution of PM$_{2.5}$ mass concentration predicted with OHE and NHE. PM$_{2.5}$ mass concentration predicted with NHE continued to accumulate until 13 December over the YRDR. Then it tended to drop under the influence of strengthened wind speed. Hangzhou city also experienced a pollutant accumulation process until 14 December under the scenario of only Hangzhou emissions (OHE). The spatial mean PM$_{2.5}$ mass concentration of Hangzhou predicted with NHE or AE continued to rise until 15 December. But the spatial mean PM$_{2.5}$ mass concentration of Hangzhou simulated with the OHE kept increasing only to 14 December (Fig. 9). This reveals that pollutants transported from outside of Hangzhou not only increased the PM$_{2.5}$ concentration but also extended the pollution time period by an additional day.
performance for the simulation and prediction of PM$_{2.5}$ pollution. The north and southwest of Jiangsu province and Shanghai city were the high PM$_{2.5}$ regions over the YRDR. PM$_{2.5}$ concentration at Hangzhou was relatively low.

The process analysis tool implemented in the CMAQ model was applied to obtain quantitative information about atmospheric processes affecting the PM$_{2.5}$ mass concentration at typical stations of Hangzhou, including the industrial, residential, scenic and suburban station. Primary PM emissions were the dominant contributors to PM$_{2.5}$ concentrations at the four stations. Advection process also significantly increased PM$_{2.5}$ mass concentrations except for the residential station. Aerosol processes produced secondary aerosols which increased the PM$_{2.5}$ mass concentration. Diffusion process increased PM$_{2.5}$ concentration at the scenic station, but decreased PM$_{2.5}$ significantly at the other three stations. The dry deposition, wet deposition and heterogeneous processes contributed to PM$_{2.5}$ loss. Process analysis also indicates that the maximum concentrations of PM$_{2.5}$ occurred during 13–14 December 2011 was due to the ineffective removal through diffusion process and thus caused an accumulation of PM$_{2.5}$ contributed from other processes. The process analysis results may be affected by the biases between the predicted and observed results to some extent. Nevertheless, it provides valuable insights into the governing processes that control PM$_{2.5}$ mass concentrations in this region, which is useful in guiding the PM$_{2.5}$ control measures.

Finally, results of sensitivity tests suggest that the non-Hangzhou pollutants made great contribution to the PM$_{2.5}$ pollution of Hangzhou and the ratio of NHE/AE reached 70% during the episode. But the local Hangzhou emissions are not negligible because they have an important contribution to the PM$_{2.5}$ peak values. And the ratio OHE/AE reached 35% at the residential station. Further understanding of the impact of NHE and OHE on PM$_{2.5}$ and its chemical composition in Hangzhou under various (emission, meteorological) scenarios is critical, and will depend on the further simulation-based investigations.

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