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An integrated process rate analysis of a regional fine particulate matter episode over Yangtze River Delta in 2010

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HIGHLIGHTS

- A high $PM_{2.5}$ episode over the YRD was simulated using the CMAQ modeling system.
- Integrated process rate was applied to study the formation mechanism of $PM_{2.5}$.
- Contributions of different atmospheric processes to $PM_{2.5}$ were analyzed.

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ABSTRACT

A high $PM_{2.5}$ pollution episode was detected in Shanghai in November 2010. The integrated process rate method, an advanced diagnostic tool, was applied to account for the contribution of different atmospheric processes during the high pollution episode in the Yangtze River Delta region (YRD). The $PM_{2.5}$ process analysis indicates that the emission of fine particles is the dominant source of high surface $PM_{2.5}$ concentrations in the major cities of the YRD like Shanghai, Nanjing, and Hangzhou, following horizontal transportation and aerosols. The $PM_{2.5}$ concentration could be reduced due to vertical advection and diffusion from lower levels to the upper air. The aerosols process such as homogeneous nucleation and condensation producing $PM_{2.5}$ occurs throughout the PBL layer in urban areas, causing vertical transport from upper levels down to the surface layer. The aerosols process is much more significant in a downwind rural and coastal site like Zhoushan than in the urban areas. The $PM_{2.5}$ change initiated by both horizontal transport and vertical transport is much stronger at 40–2000 m height than in the surface layer, while the $PM_{2.5}$ change caused by horizontal diffusion is very small. Dry deposition can significantly reduce concentration of the particulates in the surface level of the atmosphere, and wet deposition can remove the particles in the planetary boundary layer (PBL). The cloud processes can either increase $PM_{2.5}$ due to the aqueous-phase oxidation of SO_2 and NO_2 or remove $PM_{2.5}$ due to cloud scavenging. Solar radiation and humidity are more important to secondary pollution, and they are the significant external factors affecting the chemical reactions among sulfur dioxide, nitrogen oxides, ammonia, volatile compounds and fine particles.

1. Introduction

Pollution caused by fine particulate matter with aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) has attracted much interest and more attention in recent years in the Yangtze River Delta, one of the most important city-clusters of China (Chang et al., 2009; Gao et al., 2011; Wang and Hao, 2012; Xiao et al., 2011) due to its great impact on regional haze, human health and global climate change (Ge et al., 2011; IPCC, 2007; Yang et al., 2007). To reduce the $PM_{2.5}$ concentrations and improve the air quality, China published its new National Ambient Air Quality Standards (NAAQS) in February 29, 2012 (http://kjs.mep.gov.cn/hjbhbz/bzwb/dqhjbh/dqhjzlbz/201203/t20120302_224165.htm)

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to protect public health. Within China's new NAAQS, the $PM_{2.5}$ standard was firstly established, with the annual average concentration standard of 35 μg m^{-3} and the daily average of 75 μg m^{-3}. However, most of the cities in the YRD region exceed the $PM_{2.5}$ standards (Van et al., 2010; Wang et al., 2013), especially the $PM_{2.5}$ concentration are usually very high in the winter season (Chan and Yao, 2008; Gao et al., 2011), thus the regional haze occurs frequently (Fu et al., 2008). A lot of researches have been recently conducted to examine the $PM_{2.5}$ pollution characteristics over the YRD with both measurement and modeling methods. Some studies are focused on the chemical compositions and secondary formation of $PM_{2.5}$ (Feng et al., 2009; Huang et al., 2013), some on the extinction effect of $PM_{2.5}$ (Cheng et al., 2013), and others are related to the sources of the components in $PM_{2.5}$ (Feng et al., 2013; Zhang et al., 2012). These studies provided insightful information about the chemical species, size distribution, the light extinction effect, and source apportionment of fine particles. However, very limited information is available regarding to the formation process of high concentrations of $PM_{2.5}$ in winter in the Yangtze River Delta (YRD). In this study, we investigate what are the governing chemical and physical processes contributing to the change of $PM_{2.5}$ in a high pollution episode occurred in winter over the YRD during November 19–21, 2010, with the application of the integrated process rate analysis method coupled within the CMAQ modeling system.

2. Overview of the high $PM_{2.5}$ pollution episode

2.1. Weather conditions

During the period of November 19–21, 2010, a subtropical high pressure system started to move toward the sea over the YRD area. Shanghai was at the northwest edge of the subtropical high pressure system. Both the pressure field and the southwest wind were very weak. From the afternoon of Nov. 19, the air became stable, and heavy fog formed in Shanghai and the surrounding area (http://traditionalchinese.wunderground.com). A ground-level inversion occurred during the night of Nov. 19 and in the morning of Nov. 20 (http://weather.uwyo.edu/upperair/sounding.html). During this period, surface meteorological data show that the average surface temperature was around 14.1 °C, the average relative humidity was 69.4%, and the average wind speed was only 1.3 m/s. The maximum relative humidity reached 91.8% (on Nov. 21) and the lowest wind speed was only 0.4 m/s. These conditions were very favorable for the accumulation of air pollutants. Fig. 1 shows the surface weather patterns over eastern Asia at 8:00 a.m., Nov. 19 and 20, 2010, respectively.

2.2. Air pollution observation

Under these weather conditions, the concentration of PM increased greatly, and a large-scale regional haze occurred, which is confirmed by MODIS satellite images as shown in Fig. 2. Observational data show that the highest daily concentration of PM_{10} reached 210 μg m^{-3} in Shanghai, 146 μg m^{-3} in Nanjing, 170 μg m^{-3} in Suzhou, 164 μg m^{-3} in Hangzhou, and 170 μg m^{-3} in Ningbo (MEP, 2010). The maximum hourly concentrations of PM_{10} and $PM_{2.5}$ observed at the Shanghai Academy of Environmental Sciences (SAES) site reached 317 and 193 μg m^{-3}, respectively.

(http://rapidfire.sci.gsfc.nasa.gov/subsets/?subset=FAS_China4.20101120.aqua.1km.jpg&vectors=fires+coast+borders http://rapidfire.sci.gsfc.nasa.gov/subsets/?subset=FAS_China4.20101120.terra.1km.jpg&vectors=fires+coast+borders).

The measurements are collected simultaneously at the surface site of SAES. The continuous PM_{10} and $PM_{2.5}$ concentrations were measured by Thermo Fisher commercial instruments β-ray particulate monitor. The water soluble ions were measured by a model ADI 2080 online analyzer for monitoring of aerosols, and the organic carbon and elemental carbon were measured by the carbon analyzer provided by Sunset laboratory Inc.

The daily average concentration of PM_{10} increased from 97 μg m^{-3} on Nov. 18 to 243 μg m^{-3} on Nov. 20, while $PM_{2.5}$ increased from 57 μg m^{-3} to 158 μg m^{-3}. The $PM_{2.5}/PM_{10}$ ratio increased from 58.8% to 65.0%. During Nov. 19–21, the average concentrations of PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ were 192 ± 67 μg m^{-3}, 123 ± 48 μg m^{-3} and 75 ± 31 μg m^{-3}, and the maximum hourly concentrations of PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ reached 317, 193 and 157 μg m^{-3} respectively. The average $PM_{1.0}/PM_{2.5}$, $PM_{1.0}/PM_{10}$ and $PM_{2.5}/PM_{10}$ ratios were 61.0%, 39.1% and 64.1%, respectively. The total period with visibility less than 5.0 km lasted for 44 h, as shown in Figs. 3 and 4.

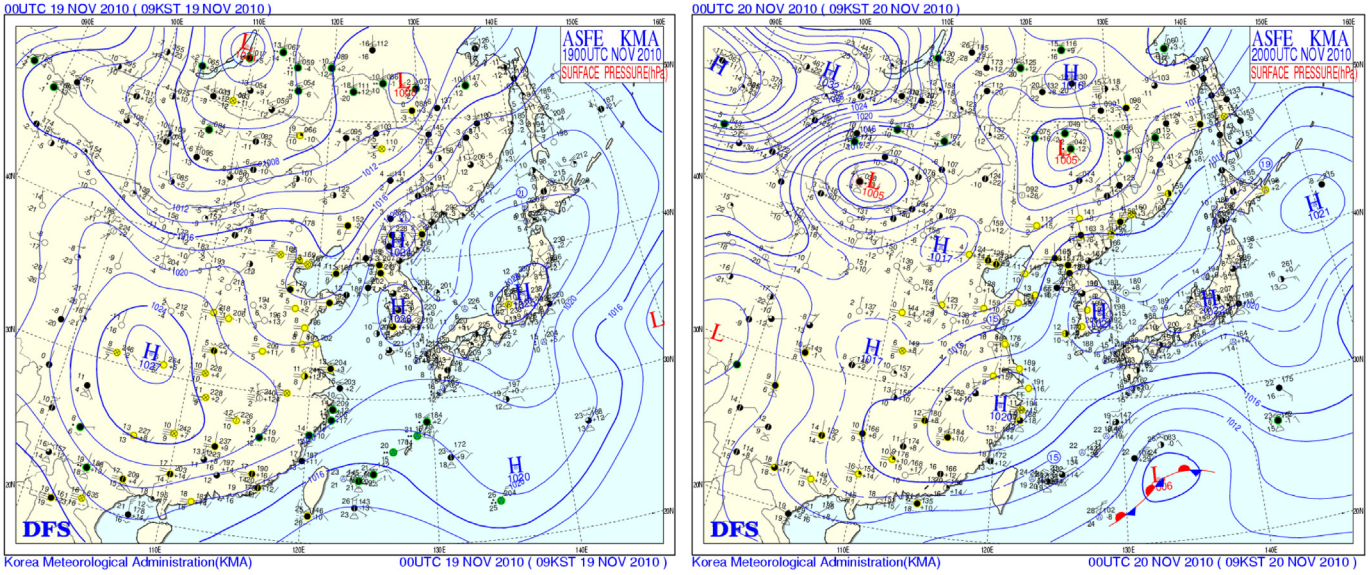

Fig. 1. Surface weather patterns over the eastern Asia at 8:00 a.m. on November 19 (left) and 20 (right), 2010 (from Korea Meteorological Administration).

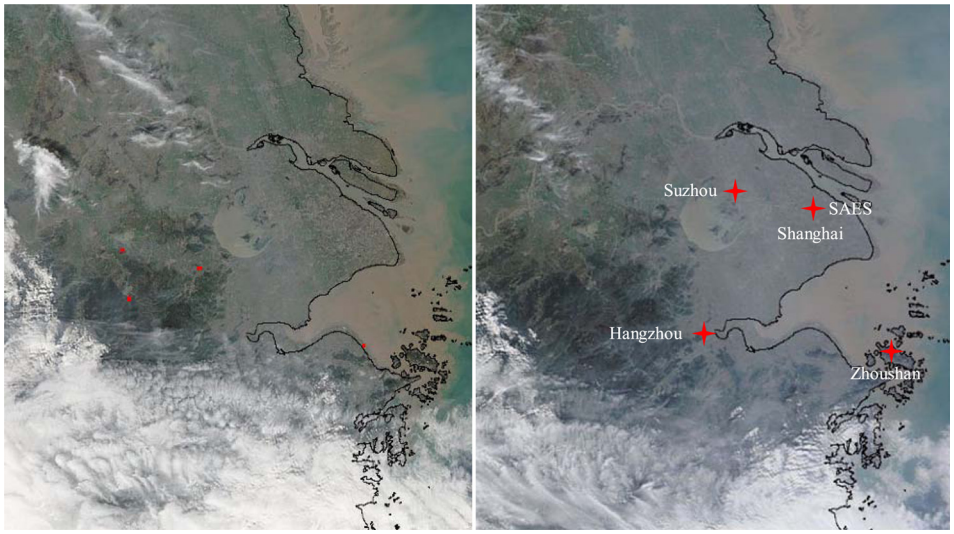

Fig. 2. Satellite image on 20 November 2010: Aqua (left), Terra (right) and the locations selected to do $PM_{2.5}$ process analysis in the YRD (right).

During the pollution episode, the concentrations of total water soluble inorganic ions (TWSII) and the total of sulfate, nitrate and ammonia (SNA) were 72.96 ± 24.21 and 63.85 ± 23.24 μg m^{-3}, accounting for 59.3% and 51.9% of the total $PM_{2.5}$. SNA comprised 87.5% of the TWSII. The percentages of sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonia (NH_4^+), potassium (K^+), sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), organic carbon (OC), element carbon (EC) and others to $PM_{2.5}$ were 17.7%, 21.4%, 12.9%, 2.1%, 0.5%, 0.4%, 0.0%, 4.4%, 23.9%, 5.6%, and 11.0%, respectively. The accumulation speed was greater for NO_3^- than for SO_4^{2-}. Fig. 5 shows the chemical composition of $PM_{2.5}$ at the SAES site during the pollution episode.

3. Methodology

3.1. Modeling system

The Community Multi-scale Air Quality Modeling System (CMAQ Version 4.6) (Byun and Schere, 2006; Foley et al., 2010) with the Carbon Bond 05 (CB05) chemical mechanism and aero4 aerosol portion was used to reproduce the high $PM_{2.5}$ pollution case, and an integrated process rate analysis (IPR) method, implemented within CMAQ, was applied to analyze the formation process of $PM_{2.5}$ at typical sites in the YRD. This is undertaken to identify the dominant processes contributing to the $PM_{2.5}$ formation and to determine the characteristics of the aerosol system at different locations or at a given location on different days. IPR analysis can provide contributions from vertical advection (ZADV), vertical diffusion (VDIF), horizontal advection (HADV), horizontal diffusion (HDIF), dry deposition (DDEP), cloud process (CLD), aerosol process (AERO) and emission (EMIS) to $PM_{2.5}$ concentrations at each grid cell. The aerosol module of CMAQ is designed to be an efficient and economical depiction of aerosol dynamics in the atmosphere. The approach taken represents the particle size distribution as the superposition of three lognormal sub-distributions. The processes of particle coagulation, particle growth by the addition of new mass, new particle formation by binary homogeneous nucleation in a sulfuric acid/water vapor system, and the production of an organic aerosol component from gas-phase precursors are included (Byun and Schere, 2006). The module includes estimates of the primary emissions of elemental and organic carbon, dust, water soluble ions and secondary organic aerosols. Secondary species considered are sulfate, nitrate, ammonium, water and organic species from precursors of anthropogenic and biogenic origin (Byun and Schere, 2006). In the IPR analysis method, aerosol process (AERO) refers to the effects of aerosol module, which includes processes of nucleation, condensation and coagulation, and equilibrium thermodynamics. Wet deposition is included in the cloud process. Effects of aerosol gaseous precursors, such as H_2SO_4 and HNO_3,

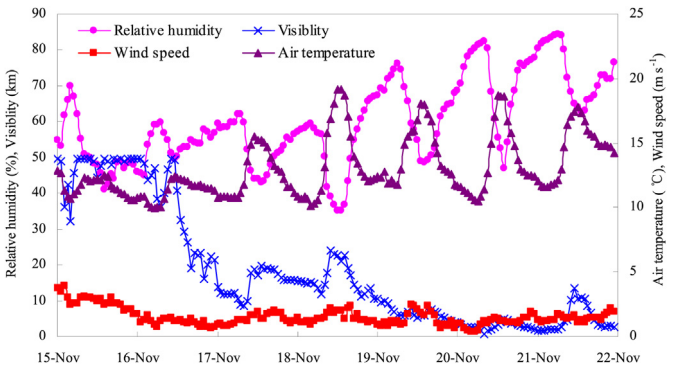

Fig. 3. Hourly variation of meteorological variables at SAES site during Nov. 19–21, 2010.

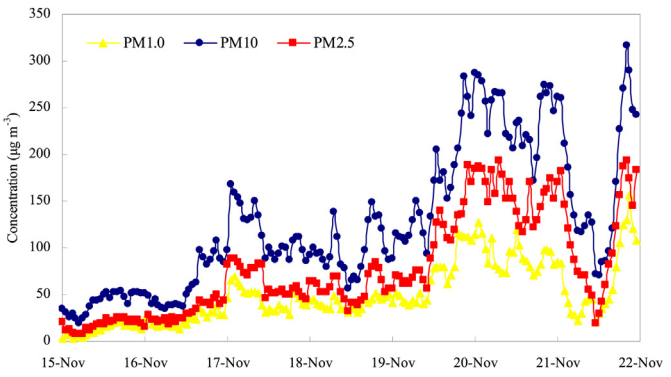

Fig. 4. The hourly concentrations of $PM_{10}/PM_{2.5}/PM_{1.0}$ at SAES from 15 to 23 November 2010.

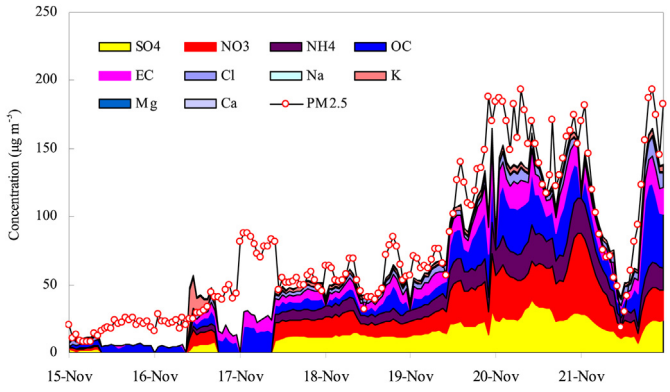

Fig. 5. The hourly chemical composition of the $PM_{2.5}$ at the SAES site during Nov.15–23, 2010.

generated by the gas-phase chemistry on the formation of aerosol particles are included in the aerosol process.

For the IPR analysis, we first assess the roles of various atmospheric processes in $PM_{2.5}$ formation at the supersite located in Shanghai Academy of Environmental Sciences (SAES), which is a representative site in urban Shanghai with large amounts of traffic emissions. We then investigate the influences of different processes on the formation and evolution of regional $PM_{2.5}$ pollution at three other sites over the YRD region, Hangzhou, Suzhou and Zhoushan. Locations of the sites selected to do $PM_{2.5}$ process analysis in this study are shown in Fig. 2.

The CMAQ model domain is based on a Lambert Conformal map projection, using a one-way nested mode with grid resolutions of 81 km, 27 km, 9 km and 3 km that covers an area of most of the YRD. In an accompanying paper (Li et al., 2012), we described the model configurations, evaluation protocols, input data, and the process analysis method in detail. Predicted meteorological parameters including wind speed, wind direction, temperature and humidity, $PM_{2.5}$ and its species concentrations are compared with the available hourly observations. The model performance is judged by statistical measures, including the root mean square error (RMSE), gross error, mean bias (MB), the normalized mean error (NME), the normalized mean bias (NMB) and the index of agreement (I).

3.2. Emission inventory

We have developed an emission inventory of major anthropogenic air pollutants for the Yangtze River Delta region for the year 2004 (Li et al., 2011) and 2007 (Huang et al., 2011) respectively. In this study, we updated the regional emission inventory to the year 2010, using the "bottom-up" methodology, which is the same as what we used in previous studies. The emission sectors include industry, transport, residential and agriculture. The industry sector mainly includes emissions from fuel combustion in power plants, boilers, kilns, and emissions directly from the industrial processes like iron and steel production, oil refining, cement production, industrial coating and printing. Transport sector include vehicle exhaust, oil evaporation, and road dust. The residential sector includes fuel combustion, domestic paint and solvent use, and gas evaporation. The agriculture sector mainly includes emissions from livestock feeding, fertilizer application and biomass burning. The emission source data are from the update of pollution source survey and the statistical data in 2010. The pollutants included in this study are SO_2, NO_x, CO, PM_{10}, $PM_{2.5}$, VOCs and NH_3.

To study the photochemical reactions of particulate matters, the VOC and $PM_{2.5}$ emissions are speciated into its chemical species according to the CB05 mechanism based on both literature survey and on-site measurement on typical emission sources. For the $PM_{2.5}$ chemical species, we have added emissions of primary elemental carbon (PEC) and primary organic carbon (POC). The PEC and POC emission profiles from combustion in power plants and boilers, heavy diesel trucks, road dust and biomass burning are based on the on-site measurement in the Yangtze River Delta (Tang et al., 2014). Other related studies will be published soon. PEC and POC emission factors are based on related researches (Zhi et al., 2008). The $PM_{2.5}$ source profiles for industrial process like iron & steel production, cement production are from the SPECIATE database. The VOC source profiles are based on the SPECIATE database, but we updated the profiles of vehicle exhaust, coking, solvent and biomass burning based on on-site measurement (Qiao et al., 2012; Wang et al., 2014a, 2014b).

Fig. 6 shows the comparisons between the updated 2010 YRD emission inventory and the 2007 one. In 2010, the total emissions of SO_2, NO_x, CO, PM_{10}, $PM_{2.5}$, VOCs, NH_3, PEC and POC are 1276 kt, 1697 kt, 8000 kt, 1569 kt, 764 kt, 2208 kt, 546 kt, 51 kt and 87 kt, respectively. Compared with the anthropogenic emissions in 2007, emissions of most pollutants have decreased except CO. The major reason is that we have updated the activity data and emission factors. The decrease of SO_2 is mainly because the percent of combustion equipment with flue-gas desulfurization in power plants and boilers has changed. For NO_x emissions, the activity data has changed, and we also revised the emission factors based on on-site measurement. The decrease of PM_{10} and $PM_{2.5}$ are mainly due to update of the activity data for cities in the YRD region. The emission differences among the four cities are shown in Fig. 7. Emissions in Shanghai, Hangzhou, and Suzhou are relatively high, whereas emissions in Zhoushan are low. In winter, the major wind direction is northwest (NW), thus Zhoushan is located at the downwind of the YRD region.

4. Results and discussion

4.1. Model performance on meteorological predictions

MM5 model performance is evaluated by using the metstat statistical analysis package (Emery et al., 2001), including the root mean square error, bias, gross error and index of agreement. Table 1 summarizes the performance statistics for surface temperature, wind speed, wind direction and relative humidity during the period of November 15–23, 2010 at four surface stations in Shanghai, Baoshan (BS), Jinshan (JS), Nanhui (NH) and Qingpu (QP). As shown in Table 1, MM5 reproduces the diurnal change of surface temperature quite well at all sites. It predicts well the maximum temperature at JS and NH sites, but under predicts those on some days at BS and QP. The model tends to over predict the minimum temperature on all sites. For relative humidity, MM5 can also reproduce

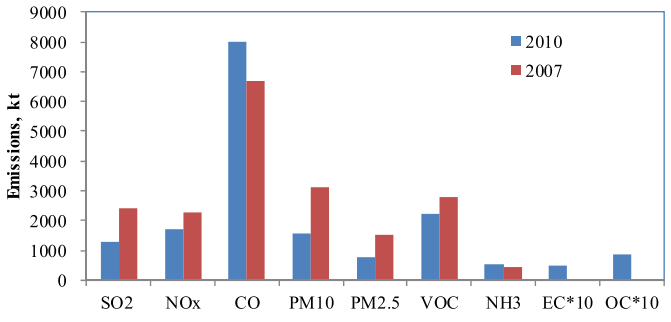

Fig. 6. Comparisons between the 2007 and the updated 2010 YRD emission inventory.

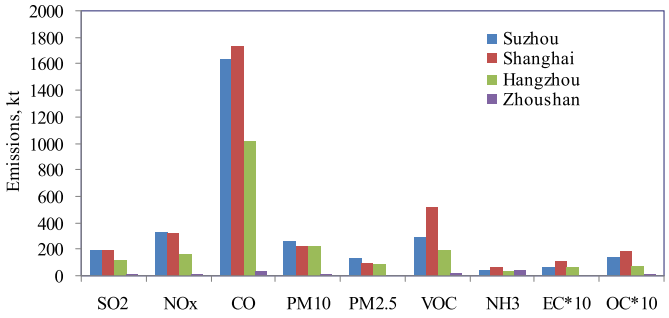

Fig. 7. Emissions in Suzhou, Shanghai, Hangzhou, and Zhoushan in the year of 2010.

its diurnal variation very well. For wind speed and direction, MM5 predictions agree well with the observations in terms of daily change and magnitude, but certain discrepancies exist on some days in the simulation of wind direction.

4.2. Model performance on PM predictions

Fig. 8 shows the time series of observed and predicted data for $PM_{2.5}$, sulfate, nitrate, ammonia, elemental carbon and organic carbon with aerodynamic diameter less than 2.5 μm ($SO_{42.5}$, $NO_{32.5}$, $NH_{42.5}$, $EC_{2.5}$ and $OC_{2.5}$). Results show that CMAQ can reproduce the variation trends of the $PM_{2.5}$, with a correlation coefficient of 0.83, NMB of −26.96%, NME of 35.0%, and Index of Agreement of 0.85. Comparisons of $PM_{2.5}$ chemical compositions including $SO_{42.5}$, $NO_{32.5}$, $NH_{42.5}$, $EC_{2.5}$ and $OC_{2.5}$ at the monitoring site further demonstrate that the $PM_{2.5}$ formation is captured reasonably well over the domain and throughout the period. The indexes of agreement for $SO_{42.5}$, $NO_{32.5}$, and $NH_{42.5}$ are 0.66, 0.87, and 0.86 respectively, as shown in Table 2. However, Fig. 8 indicates that the $SO_{42.5}$, $OC_{2.5}$ and $EC_{2.5}$ are generally underestimated compared with the observed data. Table 2 shows that the overall trend of the predicted $SO_{42.5}$ agrees well with measurement, with the correlation efficient of 0.81, better than $OC_{2.5}$. Relative modeling studies found that winter underestimation of sulfate is a common issue detected with CMAQ over Europe (Matthias, 2008), which may be explained by a lack of model calculated oxidants or missing reactions (Kasibhatla et al., 1997). The results of the carbonaceous aerosol (including $OC_{2.5}$ and $EC_{2.5}$) are far from being representative. The biases of $EC_{2.5}$ can be attributed to the probable underestimation of primary carbonaceous emission (Bond et al., 2004; Tsyro, 2005; Monks et al., 2009). Some researches have found the feature of SOA underestimation in most current models. For example, Volkamer et al. (2006) showed underestimation of SOA by a factor of 6. Basart et al. (2012) reported that the observed values are approximately a factor of 4 higher than the modeled values. The large uncertainties are mainly due to the state-of-the-science concerning SOA formation pathways (Appel et al., 2008; Eder and Yu, 2006; Edney et al., 2007; Foley et al., 2010). Overall, these statistics are generally consistent with or even better than the current performance reported for most air quality models (Wang et al., 2010; Zhang et al., 2006).

Table 1
Statistical results between MM5 model and observation data at surface stations in Shanghai.

		BS	JS	NH	QP	Average
Wind speed	RMSE (m/s)	1.03	0.92	1.4	0.97	1.08
	Bias (m/s)	0.47	0.13	−0.45	0.32	0.12
	IOA	0.8	0.78	0.58	0.72	0.72
Wind direction	Gross error (deg.)	30.5	40	31.4	35.8	34.43
	Bias (deg.)	−14.7	5.1	−0.99	9.4	−0.30
Temperature	Gross error (K)	1.07	1.3	2.1	1.65	1.53
	Bias (K)	−0.23	−0.02	1.44	0.25	0.36
	IOA	0.87	0.85	0.82	0.81	0.84
Relative humidity	Gross error (g/kg)	1.1	0.93	1.05	1.19	1.07
	Bias (g/kg)	0.6	−0.04	−0.38	0.45	0.16
	IOA	0.75	0.99	0.77	0.99	0.88

4.3. Atmospheric process contribution to $PM_{2.5}$ formation in the YRD region

The CMAQ modeling results on the hourly contributions of different atmospheric processes to the evolution of $PM_{2.5}$ at the four sites at the surface layer from Nov. 19 to 21, 2010 are shown in Fig. 9. In the surface layer, the primary emission (EMIS) is the dominant contributor to high $PM_{2.5}$ concentrations in Shanghai, Hangzhou and Suzhou, with the contribution rates of 21.87 ± 10.87, 27.00 ± 13.42 and 9.50 ± 4.72 μg m^{-3} h^{-1}, accounting for 31.0%, 32.6% and 13.7% of the average net $PM_{2.5}$ change, respectively. This indicates that primary emissions of fine particles are still a major source of high $PM_{2.5}$ concentrations in the urban areas of YRD. The primary PM emissions mainly consist of black carbon emissions from vehicle exhaust, fuel combustion, power plants, iron & steel process, plus process of mineral product in the YRD region. As the primary particle emissions are highly correlated with the anthropogenic activities, the contribution to ambient $PM_{2.5}$ shows an obvious diurnal change, with high contributions during daytime and low contributions at night. The contributions of primary particulate emissions (EMIS) to $PM_{2.5}$ in Zhoushan were very small (1.84 ± 0.79 μg m^{-3} h^{-1}), which is mainly because the local emissions in Zhoushan area are much lower than other urban cities, with the annual primary $PM_{2.5}$ emissions of only 4.4 kt (Fig. 7).

The hourly contributions of vertical advection (ZADV) to the surface $PM_{2.5}$ in Shanghai were 12.20 ± 65.25 μg m^{-3} h^{-1}, accounting for 17.3% of the net $PM_{2.5}$ change on average. Vertical diffusion (VDIF) and vertical advection (ZADV) were the two major dynamic processes to remove surface $PM_{2.5}$ in Hangzhou and Suzhou. The hourly contributions of ZADV to surface $PM_{2.5}$ is the second largest contributor to net $PM_{2.5}$ change in Zhoushan, showing that the vertical transport is important for this area.

Since the surface wind speed in Shanghai was very low during this episode (1.3 m s^{-1}, on average), the average $PM_{2.5}$ destruction rate contributed by HADV was only −3.51 ± 61.25 μg m^{-3} h^{-1}, accounting for −5.0% of the net $PM_{2.5}$ change, which was not beneficial to reducing surface $PM_{2.5}$. However, the hourly contributions of HADV to the surface $PM_{2.5}$ were 11.34 ± 22.90 μg m^{-3} h^{-1} in Hangzhou and 20.76 ± 29.22 μg m^{-3} h^{-1} in Suzhou, accounting for 13.70% and 30.0% of the net $PM_{2.5}$ change on average, respectively. This means that the regional transport is quite significant in this region. The vertical diffusion (VDIF) reduced $PM_{2.5}$ concentrations in the surface layer by transporting fine particles to the upper air. The average $PM_{2.5}$ destruction rate contributed by VDIF was −28.63 ± 18.18 μg m^{-3} h^{-1}, accounting for −40.6% of the net $PM_{2.5}$ change in Shanghai. The dry deposition (DDEP) process could also remove some of the surface $PM_{2.5}$ at four sites, accounting for −1.4% to −3.2% of the net surface $PM_{2.5}$ change in the YRD region.

Aerosols process (AERO) mainly includes aerosol dynamics, new particle production by nucleation and the smaller mode growing into the larger mode and partially merging with it. During the simulation period, the hourly contributions of AERO to surface $PM_{2.5}$ in Shanghai were very small. The net $PM_{2.5}$ increase contributed by AERO process in Shanghai and Suzhou mainly occurs at night, while it acts as a sink during daytime. This is possible because ammonium nitrate (NH_4NO_3) dominated the inorganic aerosol fraction and showed a distinct diurnal signature

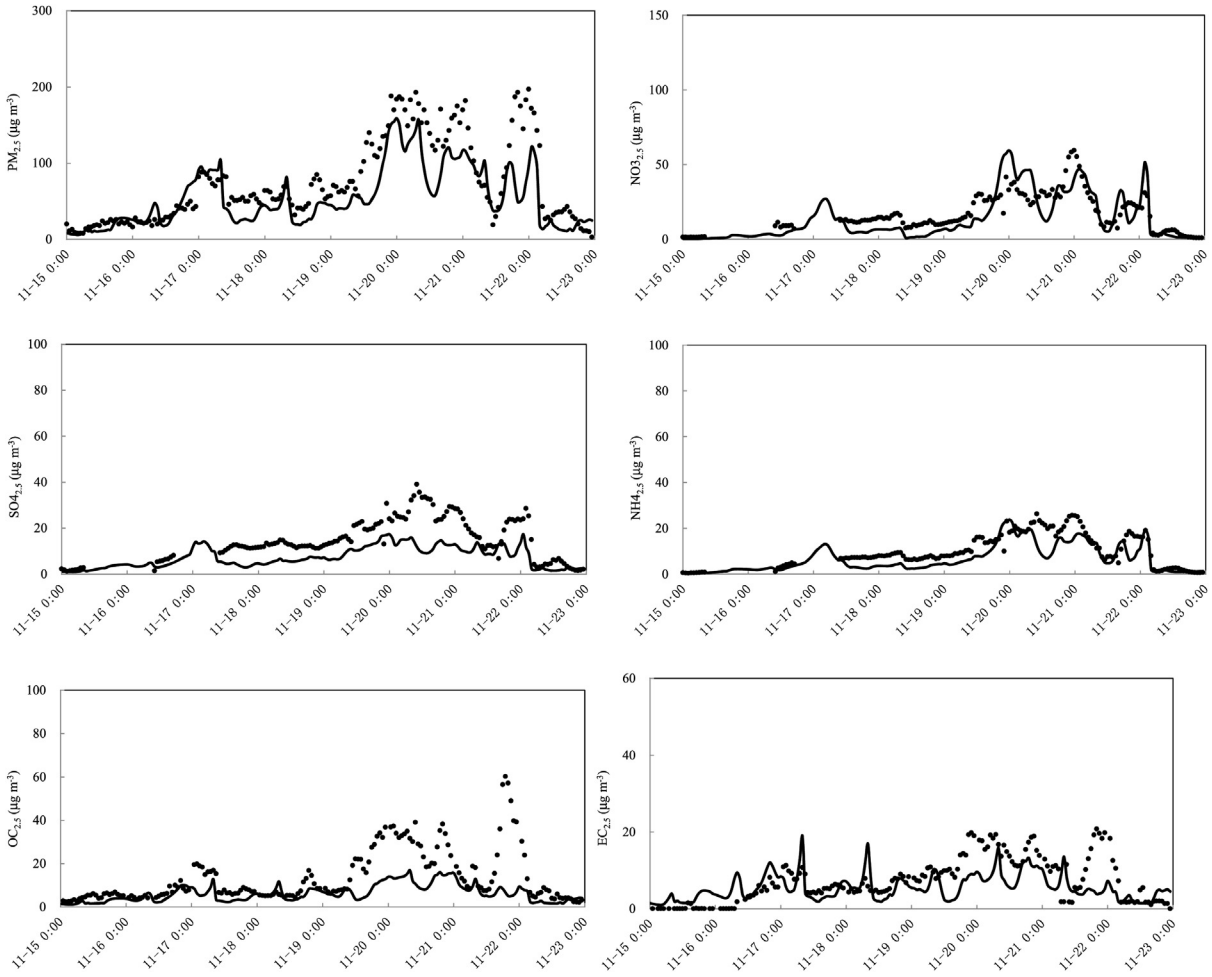

Fig. 8. Time series of observed and predicted surface $PM_{2.5}$, sulfate, nitrate, ammonium, organic carbon and elemental carbon with aerodynamic diameters less than 2.5 μm ($SO_{42.5}$, $NO_{32.5}$, $NH_{42.5}$, $OC_{2.5}$ and $EC_{2.5}$) at the SAES site during November 15–23, 2010.

characterized by rapid morning production and a rapid mid-day concentration decrease (Hennigan et al., 2008). A significant fraction (40%) of the nitrate loss was due to particle evaporation, and the volatilization did have a meaningful impact (25%) on the decrease of water soluble organic compounds (Hennigan et al., 2008). As indicated in Fig. 2, Zhoushan is located in the southeastern corner of the YRD. In winter, Zhoushan is in the downwind area of the region. The water content in the atmosphere is much higher there than in the other cities of the YRD. CMAQ modeling results show that the major contributor to $PM_{2.5}$ change in Zhoushan was aerosols (AERO). During the simulation period, the hourly positive contributions of aerosols to $PM_{2.5}$ in Zhoushan were 28.04 ± 42.24 μg m^{-3} h^{-1}, accounting for 36.4% of the net $PM_{2.5}$ change on average. The AERO process producing $PM_{2.5}$ in Zhoushan occurs during the whole day, but is more obvious during night time. The high humidity is beneficial for gaseous precursors like NO_2 and SO_2 to form particles through heterogeneous reaction, which accelerates the formation of fine particles (Guo et al., 2010; Seinfeld and Pandis, 2006; Tang et al., 2006). The relationship between the humidity and nitrate has been reported quite lot (Zhang et al., 2005; Zheng et al., 2008). The higher the relative humidity, the more nitrate in particles. The formation of sulfate is mainly formed through oxidation of SO_2, thus, its concentration is usually high at noon. Therefore, the gaseous precursors like NO_x, SO_2, and VOCs are transported from upwind region to Zhoushan, and form secondary particles under the more favorable met conditions, which is a major reason for the positive contribution of AERO to $PM_{2.5}$ at Zhoushan site.

Table 2
Statistical results of CMAQ model performance.

Species	R	MB	NMB	NME	I
$PM_{2.5}$	0.83	−19.98	−26.96%	35.0%	0.85
$NO_{32.5}$	0.80	−2.23	−12.85%	43.8%	0.87
$SO_{42.5}$	0.81	−7.41	−49.12%	50.5%	0.66
$NH_{42.5}$	0.83	−3.11	−30.03%	36.2%	0.86
$OC_{2.5}$	0.65	−7.44	−54.76%	56.9%	0.56
$EC_{2.5}$	0.50	−1.85	−25.12%	55.5%	0.64

As shown in Fig. 10, during the IPR analysis period, the $PM_{2.5}$ change initiated by both horizontal transport (HADV) and vertical transport (ZADV) was much stronger at the 40–2000 m height than in the surface layer in Shanghai, Hangzhou, Suzhou and Zhoushan. From 40 to 2000 m height, the $PM_{2.5}$ formation rates contributed by HADV account for −50.1% to 8.3% of net $PM_{2.5}$ change on average in the various layers in Shanghai. The $PM_{2.5}$ formation rates contributed by ZADV account for −8.6% to 46.1%. Compared with advection processes, the $PM_{2.5}$ changes caused by diffusion at high layers were much smaller, especially the horizontal diffusion (HDIF), which is almost negligible in the YRD region. At 100–2000 m height, cloud processes (CLDS) can slightly remove $PM_{2.5}$ in Shanghai, Hangzhou, Suzhou and Zhoushan. The positive contribution to $PM_{2.5}$ from aerosols (AERO) mainly occurred throughout

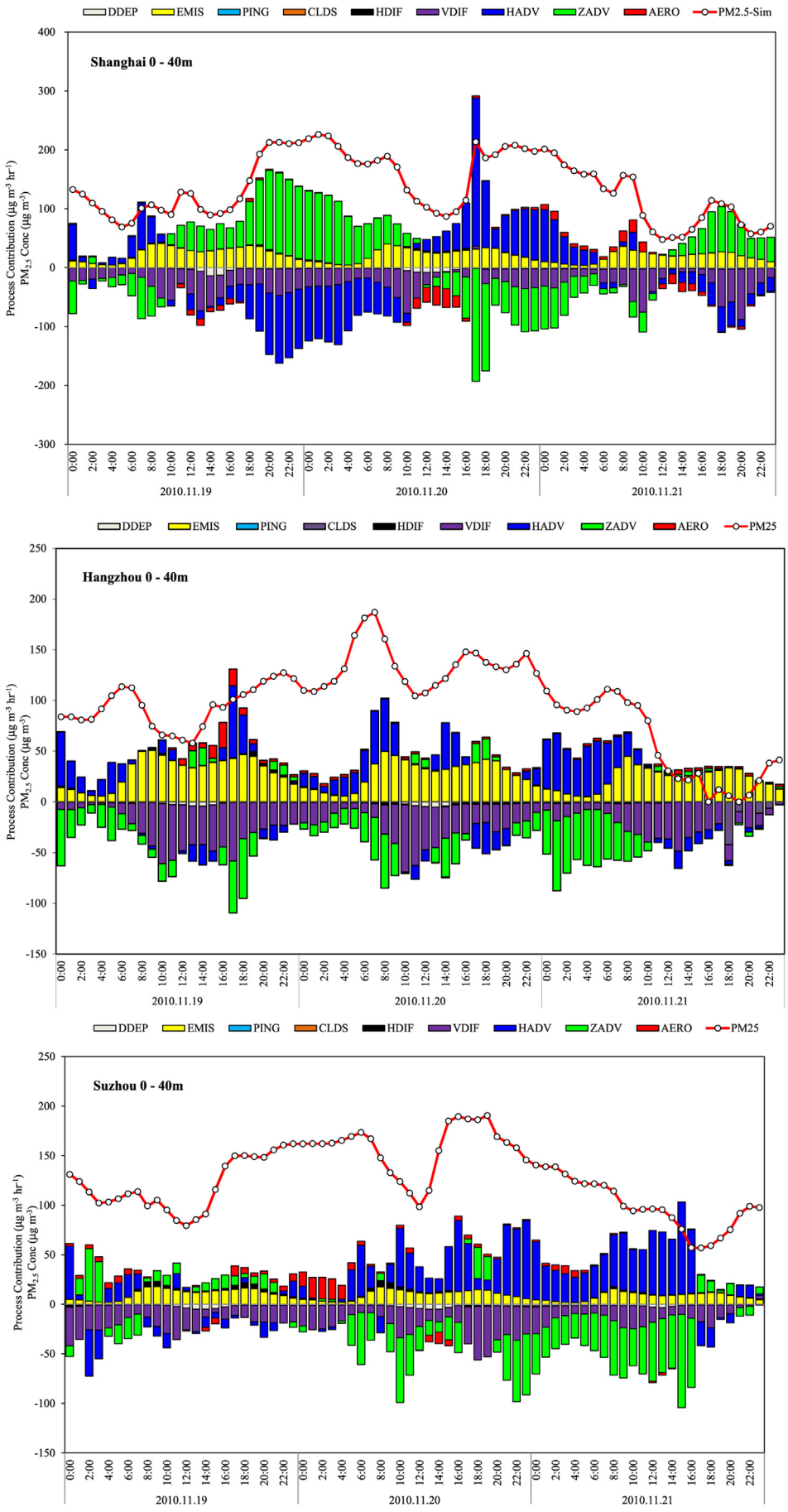

Fig. 9. Atmospheric processes contribution to net surface $PM_{2.5}$ at the surface layer at SAES site during November 19–21, 2010.

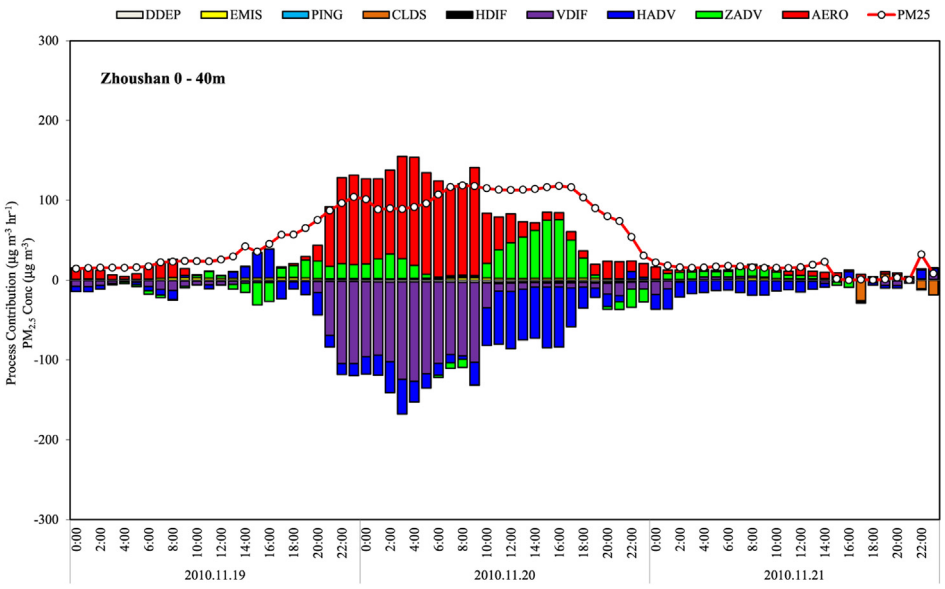

Fig. 9. (*continued*).

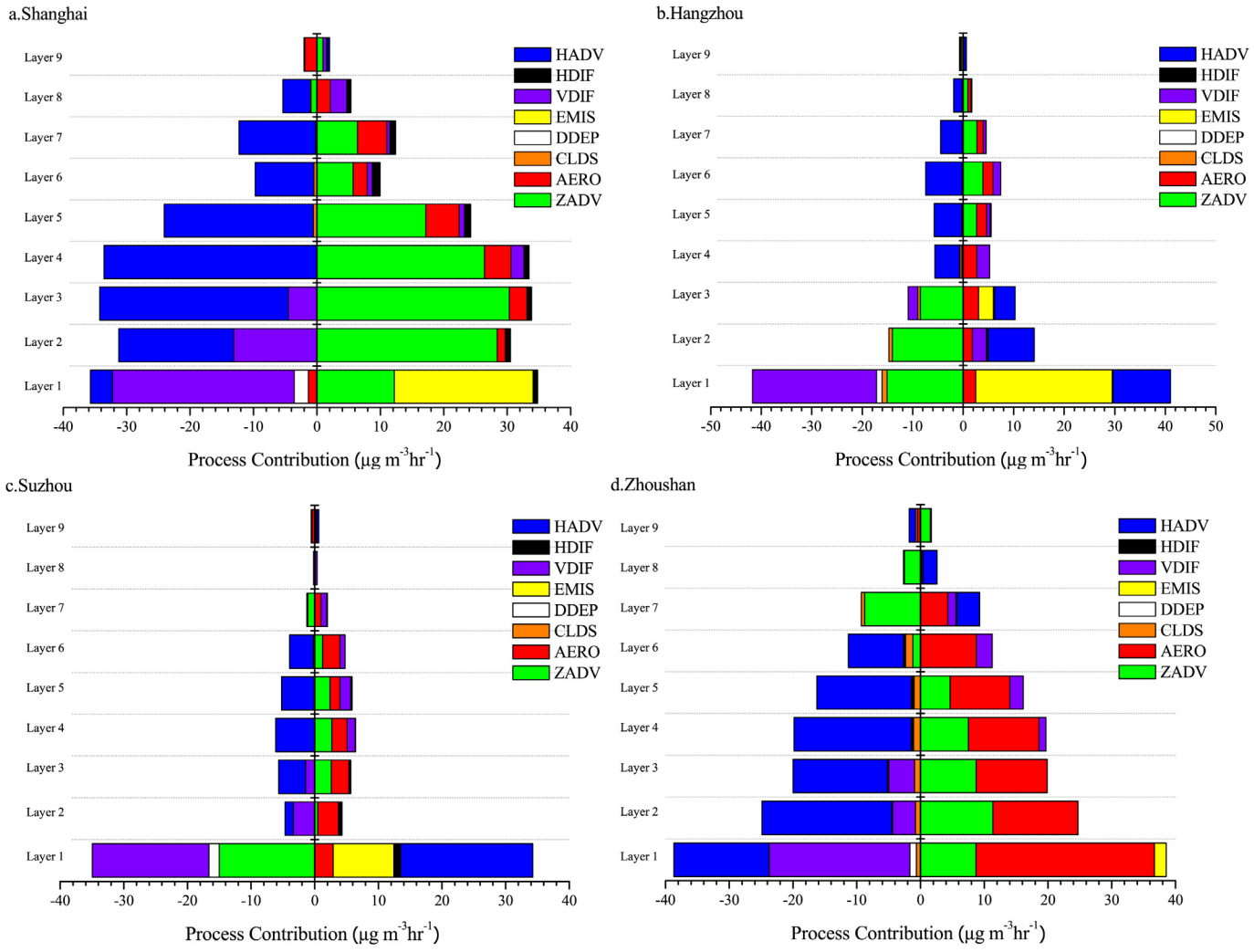

Fig. 10. Atmospheric processes contribution to net $PM_{2.5}$ at the vertical heights during November 19–21, 2010.

the PBL layer, causing vertical $PM_{2.5}$ transport from upper levels to the surface layer. This is mainly because the air temperature in the upper air is lower than at the surface, and there are more clouds in the upper layer, which is beneficial for the formation of secondary organic aerosol. This indicates that the strong vertical $PM_{2.5}$ import to the surface layer is initiated by the urban plume arrival. From layer1 to layer8, the $PM_{2.5}$ formation rates contributed by AERO ranges from 2.0% to 19.6% of net contribution. At 240–2000 m height, the cloud processes (CLDS) can either increase $PM_{2.5}$ due to the aqueous-phase oxidation of SO_2 and NO_2 or remove $PM_{2.5}$ due to cloud scavenging. The aerosol behavior in clouds that is considered in the model includes two components: the Aitken mode forms interstitial aerosol which is scavenged by the cloud droplets, and the accumulation mode forms cloud nuclei and thus is distributed as aerosol within the cloud water.

The modeled maximum $PM_{2.5}$ concentration approached 226 $\mu g\ m^{-3}$ in Shanghai at 01:00 LST on Nov 20, 2010. At this time, the vertical advective transport into the area constituted the major positive contribution to net $PM_{2.5}$, with a formation rate of 114.8 $\mu g\ m^{-3}\ h^{-1}$, accounting for 46.3% of net surface $PM_{2.5}$ change; local primary PM emissions were the second largest contributor, with a $PM_{2.5}$ formation rate of 9.9 $\mu g\ m^{-3}\ h^{-1}$ and 4.0% of positive contribution. There was also a certain amount of $PM_{2.5}$ formed through aerosols, with a production rate of 0.79 $\mu g\ m^{-3}\ h^{-1}$ and 0.3% of positive contribution on average. At this time, the horizontal advection, vertical diffusion and dry deposition were the three major processes removing surface $PM_{2.5}$ in Shanghai. If we look at the vertical profile, we find that the aerosols process played a positive role in the $PM_{2.5}$ change under 1400 m, with a contribution of 50.43 $\mu g\ m^{-3}\ h^{-1}$ through the surface layer to 1400 m height.

The predicted maximum $PM_{2.5}$ concentration in Hangzhou approached 186 $\mu g\ m^{-3}$ at 07:00 LST on November 20, 2010. At this time, the horizontal advective transport into the area constitutes the major positive contribution to net $PM_{2.5}$, with the formation rate of 52.1 $\mu g\ m^{-3}\ h^{-1}$, accounting for 35.3% of net surface $PM_{2.5}$ production; local primary PM emission is the second largest contributor, with the $PM_{2.5}$ formation rate of 37.4 $\mu g\ m^{-3}\ h^{-1}$ and 25.4% of positive contribution. The modeled maximum $PM_{2.5}$ concentration in Suzhou approached 190 $\mu g\ m^{-3}$ at 19:00 LST on November 20, 2010. At this time, the vertical advective transport into the area constitutes the major positive contribution to net $PM_{2.5}$, with the formation rate of 23.6 $\mu g\ m^{-3}\ h^{-1}$, accounting for 22.8% of net surface $PM_{2.5}$ production; local primary PM emission is the second largest contributor, with the $PM_{2.5}$ formation rate of 14.2 $\mu g\ m^{-3}\ h^{-1}$ and 13.7% of positive contribution; horizontal advection ranks the third. The maximum $PM_{2.5}$ concentration in Zhoushan was 118 $\mu g\ m^{-3}$ at 08:00 LST on November 20, 2010. At this time, the aerosols process constitutes the major positive contribution to net $PM_{2.5}$, with the formation rate of 114.2 $\mu g\ m^{-3}\ h^{-1}$, accounting for 98.8% of net surface $PM_{2.5}$ production.

These process analysis results show that the $PM_{2.5}$ formation processes differ with locations, heights and the time development of the episode. Local primary emissions or emissions from upwind areas are the dominant contributor to $PM_{2.5}$ mass concentrations in urban sites like Shanghai, Suzhou and Hangzhou. In contrast, aerosols process is the major contributor to $PM_{2.5}$ in rural region like Zhoushan. Cloud processes can increase $PM_{2.5}$ formation due to the aqueous-phase oxidation of SO_2 and NO_x during the episode, and they can also reduce $PM_{2.5}$ at some time due to a dominance of cloud scavenging. Horizontal transport and vertical transport may either serve as a sink or a source for $PM_{2.5}$ accumulation. Secondary aerosols are an important contributor to regional haze in the Yangtze River Delta. The secondary particles are mainly formed through the oxidization reactions among the gaseous precursors. The less volatile substances will be formed by these reactions, and then form aerosols directly or condense on the existing aerosols to become secondary particles. Major secondary particles include sulfate, nitrate, ammonia and secondary organic aerosols. The predicted $PM_{2.5}$ concentrations in urban regions like Shanghai and Suzhou sites are very high, with the max hourly $PM_{2.5}$ concentrations larger than 200 $\mu g/m^3$. The IPR analysis shows that the AERO process mainly plays a positive role during night time but negative in daytime. This is possibly due to the formation mechanism of nitration in $PM_{2.5}$. Gaseous HNO_3 and N_2O_5 (NO_3) are major precursors of nitrate (Atkinson, 2000). The gaseous HNO_3 are mainly formed through the oxidization reactions between NO_2 and OH, which is formed through photochemical reactions (Atkinson, 2000) in daytime. During night time, NO_2 can be oxidized to NO_3 by O_3, and the NO_3 can be further oxidized with NO_2 to form N_2O_5. Since the NO_3 is easily to be photolyzed under the sunlight, thus these reactions mainly occur at night. The hydrolysis of NO_3 and N_2O_5 are the major ways of particle nitrate formation at night time. In major regions of the north hemisphere, more than half of the nitrate comes from these reactions. In the urban polluted area, the contributions of N_2O_5 and NO_3 hydrolysis to nitrate are larger (Atkinson et al., 1986; Heintz et al., 1996). In daytime, the photolysis of NO_3 and N_2O_5 are very quickly, and the decrease of the humidity will reduce the water content of particles, therefore, the particle nitrate will evaporate to become gases. In general, as a major form of particulate nitrate, the formation of NH_4NO_3 is favored by high RH and low temperature (Wang et al., 2009).

5. Conclusions

The Integrated Process Rate methodology implemented in the CMAQ model was used to obtain quantitative information about the different atmospheric processes affecting fine particle formation in four typical cities located in the Yangtze River Delta area: Shanghai, Hangzhou, Suzhou and Zhoushan. A representative wintertime particulate pollution episode (Nov 19–21, 2010) was selected. Applying the Integrated Process Rate tool to the surface layer provides information about the time-development of surface concentrations of PM. In order to obtain a deeper understanding of the contributions of the main atmospheric processes leading to surface concentrations of $PM_{2.5}$, the vertical $PM_{2.5}$ production and loss mechanisms from Layer2 (40–100 m) to Layer9 (1400–2000 m) were also examined. Although the results cannot be verified because of lack of vertical observations, this study do provides insights into the formation mechanism of high $PM_{2.5}$ pollution episode.

The PM model performance is generally acceptable although some bias in the simulation of both $PM_{2.5}$ and its chemical components exist. The $PM_{2.5}$ process analysis indicates that primary fine particle emissions are the dominant sources of high surface $PM_{2.5}$ concentrations in three of the cities, Shanghai, Hangzhou and Suzhou. Horizontal transportation can also increase the surface $PM_{2.5}$ mass concentrations in Hangzhou and Suzhou, which means that the regional transport is also quite obvious in the YRD region. Aerosol process is the most important process leading to high $PM_{2.5}$ concentrations in Zhoushan, due to the downwind location and its beneficial meteorology conditions for SOA formation like high humidity there. $PM_{2.5}$ could be reduced due to the vertical advection and diffusion from lower level to upper air in the urban cites. The aerosols process producing $PM_{2.5}$ in the urban areas occurs throughout the PBL layer, causing vertical transport from upper levels to the surface layer. Particulate matter in the atmosphere can either be primary or secondary. Primary particulate matter is emitted directly into the atmosphere from natural or anthropogenic emissions via the physical process “EMIS”. However,

secondary particulate matter is formed in the atmosphere either from precursors, as a result of chemical reactions, or from condensation or deposition onto primary particles that are already present in the atmosphere, these processes are included in the model as the aerosols process (AERO). The chemical species treated in the aerosol component include sulfates, nitrates, ammonium, water, anthropogenic and biogenic organic carbon, elemental carbon, and other unspecified material of anthropogenic origin. The secondary species sulfate is produced by chemical reaction of hydroxyl radical on sulfur dioxide to produce sulfuric acid that may condense on existing particles or nucleate to form new particles. Precursors of anthropogenic organic aerosol (such as alkanes, alkenes, and aromatics) react with hydroxyl radicals, ozone, and nitrate radicals to produce condensable material. Monoterpenes react in a similar manner to produce biogenic organic aerosol species. The $PM_{2.5}$ change initiated by both horizontal transport and vertical transport is much stronger at 40–2000 m height than in the surface layer, while the $PM_{2.5}$ change caused by horizontal diffusion is very small. At 240–2000 m height, the cloud processes can either increase $PM_{2.5}$ due to the aqueous-phase oxidation of SO_2 and NO_2 or remove $PM_{2.5}$ due to cloud scavenging. Dry deposition can significantly reduce the particulates in the surface level, and wet deposition can reduce particles below the planetary boundary layer in the YRD region. The model biases may affect process analysis results to some extent. For example, the under-prediction of $OC_{2.5}$ may indicate that the contribution of aerosols to $PM_{2.5}$ may be underestimated to some extent. However, the analysis can provide valuable insights into the governing processes that control $PM_{2.5}$ concentrations, which is helpful in understanding the sources and transport of $PM_{2.5}$.

This analysis shows that the formation of complex regional air pollution in the YRD is not only related to primary air pollutant emissions, but also is significantly influenced by the local meteorological conditions like wind direction, wind speed and atmospheric stability. Solar radiation and humidity are also important for the formation of secondary pollutants, and they are the significant external factors affecting the chemical reactions among sulfur dioxide, nitrogen oxides, ammonia, volatile compounds and fine particles. Therefore, more stringent and consistent controls are needed to further improve the regional complex air quality in the YRD area.

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