Modeling diurnal variation of surface PM$_{2.5}$ concentration over East China with WRF-Chem: Impacts from boundary layer mixing and anthropogenic emission

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Key points:
1. Planetary boundary layer (PBL) mixing is the determinant factor in modeling the diurnal cycle of surface PM$_{2.5}$ concentration over East China
2. PBL mixing coefficient instead of PBL height is the key factor controlling the simulated diurnal cycle of surface PM$_{2.5}$ concentration in WRF-Chem
3. The PBL mixing during the night over East China may be underestimated by WRF-Chem; Increase of PBL mixing during the night can significantly reduce the modeling biases of surface PM$_{2.5}$ concentration and also the modeling sensitivity to the PBL configuration
4. The diurnal cycle and injection height of anthropogenic emission have impacts on simulating diurnal cycle of surface PM$_{2.5}$ concentration but smaller than that from PBL mixing
Abstract

Diurnal variation of surface PM$_{2.5}$ concentration (diurnal PM$_{2.5}$) could dramatically affect aerosol radiative and healthy impact, and can also well reflect the physical and chemical mechanisms of air pollution formation and evolution. So far, diurnal PM$_{2.5}$ and its modeling capability over East China have not been investigated, and therefore, are examined in this study. Based on the observations, the normalized diurnal amplitude of surface PM$_{2.5}$ concentrations averaged over East China is the weakest (~1.2) in winter, and reaches ~1.5 in other seasons. The diurnal PM$_{2.5}$ shows the peak concentration during the night in spring and fall and during the daytime in summer. The simulated diurnal PM$_{2.5}$ with WRF-Chem and its contributions from multiple physical and chemical processes are examined in the four seasons. The simulated diurnal PM$_{2.5}$ with WRF-Chem is primarily controlled by planetary boundary layer (PBL) mixing and emission variations, and significantly overestimates the observations during the night. This modeling bias is likely primarily due to the inefficient PBL mixing of primary PM$_{2.5}$ during the night. The simulated diurnal PM$_{2.5}$ is sensitive to the PBL schemes and vertical layer configurations with WRF-Chem. The PBL mixing coefficient instead of PBL height is found as the critical factor determining the PBL mixing of pollutants in WRF-Chem. The increase of lower limit of PBL mixing coefficient during the night can significantly reduce the modeling biases in diurnal PM$_{2.5}$ and also the mean concentrations, particularly at the major cities of East China. It can also reduce the modeling sensitivity to the PBL vertical layer configurations. The diurnal variation and injection height of anthropogenic emissions also play roles on simulating diurnal PM$_{2.5}$, but the impact is relatively smaller than that from the PBL mixing. This study underscores that more efforts are needed to improve the boundary mixing process of pollutants in models with observations of PBL structure and mixing fluxes in addition to PBL height, in order to simulate reasonably the diurnal PM$_{2.5}$ over East China. The diurnal variation and injection height of anthropogenic emissions are also necessary to be included to simulate the diurnal PM$_{2.5}$ over East China.
1. Introduction

The Yangtze River Delta (YRD) region of East China hosts the economic engine and a major portion of the Chinese population. During the past two decades, the rapid economic growth has resulted in significant elevated surface air pollutants over East China, especially particulate matter (PM), also called aerosols. Previous studies have indicated that exposure to the high concentrations of PM$_{2.5}$ (fine particulate matter with aerodynamic diameter less than 2.5 μm) can cause many health issues such as lung cancer (LC), ischemic heart disease (IHD), asthma, and nervous system breakdown (e.g., Seaton A et al., 1995; Davidson C I et al., 2005; Pope III C A et al., 2006; Ho et al., 2018; Li T et al., 2018; Liu T et al., 2018). It has become the fourth risk factor of deaths in China and 11.1% of all deaths are attributable to the ambient elevated concentration of particulate matter (Gakidou et al., 2017). Besides the health impacts, atmospheric aerosol can also influence the radiative energy budget of the Earth’s system through interacting with radiation, and serving as cloud condensation nuclei (CCN) and ice nuclei (IN) and hence modifying cloud microphysics (e.g., Ackerman T P., 1977; Dickerson R R et al., 1997; Jacobson M. Z., 1998).

Many studies have investigated spatial and temporal variations of atmospheric aerosol over China in last decades. The PM$_{2.5}$ concentrations are higher in North China than in South China. The highest surface PM$_{2.5}$ concentrations appear in winter and the lowest in summer, and the highest and lowest surface PM$_{2.5}$ concentration of a day often occurs in the evening and afternoon, respectively (e.g., Gong et al., 2007; Fu et al., 2008; Hu et al., 2014; Wang ZF et al., 2014; Wang YG et al., 2014; Wang YJ et al., 2014; Geng et al., 2015; Xie et al., 2015; Zhang and Cao, 2015; Zhang H et al., 2015). Moreover, modeling analysis can help understand the chemical and physical processes affecting aerosol formation and evolution (e.g., Ying et al., 2009; Zhang et al., 2010; Liao et al., 2014; Wang YX et al., 2014; Wang YJ et al., 2014; Hu et al., 2016; Li et al., 2016; Yang et al., 2016; Hu et al., 2017; Zhao B et al., 2017). Yang et al. (2016) reproduced an increasing trend of winter PM$_{2.5}$ concentrations averaged over East China for 1985-2005 with the GEOS-Chem model, and found that the variations in anthropogenic emissions dominated the increase of winter surface PM$_{2.5}$ concentrations over East China and the variations in meteorological fields also played an important role in influencing the decadal increase in winter PM$_{2.5}$ concentrations over East China. Hu et al., (2017) investigated the spatial and temporal distribution of secondary organic aerosol (SOA) in China in 2013 with the WRF-CAMQ model and found that the formation of SOA from biogenic emissions was significantly enhanced due to anthropogenic emissions.
Most of previous modeling studies focused on understanding the mechanisms driving PM variation on daily or seasonal scales or/and evaluating the simulation of daily and monthly mean PM concentrations over East China. Few studies evaluated the model performance in simulating diurnal cycle of surface PM concentration and investigated the mechanisms underneath. However, the model capability of capturing diurnal cycle of surface PM concentration is critical for revealing mechanisms of PM formation and evolution and may also affect simulating mean concentration. Some studies also found that diurnal variation of surface PM concentration can affect the daily average radiative forcing (e.g., Arola A et al., 2013; Kassianov E et al., 2013; Kuang Y et al., 2015; Wang Z et al., 2015; Song et al., 2018). Based on the ground-based data collected in Hefei from 2007 to 2013, Wang Z et al. (2015) demonstrated that using daily averaged aerosol properties to retrieve the 24-h average direct aerosol radiative forcing can have positive biases of up to 7.5 W m\(^{-2}\) for the cases. Arola et al. (2013) found that the aerosol optical depth (AOD) diurnal cycles have significant impacts on the daily mean aerosol radiative forcing.

Previous studies have observed evident diurnal variations of surface PM over East China (e.g., Gong et al., 2007; Gu et al., 2010; Pathak R K et al., 2011; Feng et al., 2014; Hu et al., 2014; Huang et al., 2014; Ma et al., 2014; Zhang and Cao, 2015; Chen et al., 2016; Tao et al., 2016; Zhao et al., 2016; Chen et al., 2017; Jia et al., 2017; Guo H et al., 2017; Guo J et al., 2017). Zhang and Cao (2015) used a long-term dataset of surface PM\(_{2.5}\) concentration measured at 190 cities of China, and found that the diurnal variation of the PM\(_{2.5}\)-to-CO ratio consistently displayed a pronounced peak during the afternoon, reflecting a significant contribution of secondary PM formation. Guo H et al. (2017) investigated the diurnal cycle of PM\(_{2.5}\) in China with the observations obtained at 226 sites of China during the period of January of 2013 to December of 2015 and found the surface PM\(_{2.5}\) concentration reached the maximum in the morning over the YRD region.

Diurnal variation of surface PM concentration can be controlled by many factors including emissions, chemical reactions, and meteorology (e.g., Wang et al., 2006; Huang et al., 2010; Wang et al., 2010; Menut et al., 2012; Qi et al., 2012; Quan et al., 2013; Tiwari et al., 2013; Li et al., 2014; Pal et al., 2014; Sun et al., 2015; Zhang and Cao, 2015; RR Rodelas et al., 2019; Xu et al., 2019). Wang et al. (2010) found that simulations with hourly emission inventory can reproduce the diurnal variation patterns and magnitude of AOD better than simulations with daily emission inventory. Xu et al. (2019) compared the diurnal cycles of aerosol species between 2014 and 2016 observed by Aerodyne high-resolution aerosol mass spectrometer in...
Beijing and found that the increase of secondary inorganic nitrate, sulfate, and ammonium throughout the day in 2016 were mainly caused by the enhanced photochemical production. With the dataset of PBL height derived from the space-borne and ground-based lidar, Su et al. (2018) investigated the relationship between PBL height and surface PM concentrations across China and found nonlinearly negative responses of PM to PBL height evolution over polluted regions, especially when the PBL height is shallow and PM concentration is high.

Since very few studies evaluated the modeling performance of diurnal cycle of surface PM concentration over East China and investigated the mechanisms underneath, this study investigates the WRF-Chem (Weather Research and Forecasting model coupled with Chemistry) simulation of diurnal variation of PM$_{2.5}$ over East China. WRF-Chem (Grell et al., 2005) is an online-coupled meteorology and chemistry model that simulates meteorological fields and air pollutant concentrations simultaneously. It has been widely used for studying the temporal and spatial variation of aerosols (e.g., Jiang et al., 2012; Zhou et al., 2014; Bei et al., 2016; Wang et al., 2016; Zhang et al., 2016; Zhong et al., 2016; Li et al., 2017; Zhao et al., 2017; Zhou et al., 2017; Liu S et al., 2018; Ni et al., 2018) and their meteorological and climatic impacts over East China (e.g., Gong et al., 2007; Ding et al., 2013; Wu et al., 2013; Gao et al., 2014; Chen et al., 2014; Zhao et al., 2014; Zhang B et al., 2015; Zhang L et al., 2015; Huang et al., 2016; Liu et al., 2016; Petäjä et al., 2016; Zhao B et al., 2017). Most of the previous modeling studies with WRF-Chem over China investigated the influencing factors on spatial distribution and monthly or seasonal variation of PM. None of them focused on the performance of simulating diurnal variation of PM with WRF-Chem.

The study will examine the observed characteristics of diurnal variation of surface PM$_{2.5}$ concentration over the YRD region of East China in four seasons of 2018. The WRF-Chem simulations are conducted for one month of each season over East China as shown in Fig 1a, and the simulated diurnal cycle of surface PM$_{2.5}$ concentration will be evaluated through comparing with hourly observations of surface PM$_{2.5}$ concentration released by the Ministry of Environmental Protection (MEP) of China for 190 stations over the YRD region of East China in 2018. The model is also used to investigate the mechanisms driving the diurnal cycle of surface PM$_{2.5}$. This study will focus on the impacts from meteorology and anthropogenic emissions on the diurnal variation of surface PM$_{2.5}$ concentration. For meteorology, we will focus on the PBL mixing process that has been found largely controlling the diurnal variation of surface pollutant concentrations (Liu M et al., 2018). For emissions, based on the findings of Wang et al. (2010) and Yang et al. (2019), the diurnal variation and injection height of emission will be investigated. The rest of the paper is organized as follows. The detailed
introduction of WRF-Chem model and numerical experiments, anthropogenic emissions, and
observations will be presented in Section 2. The examination of simulated diurnal variation of
surface PM$_{2.5}$ concentrations and the impacts of PBL mixing and emission will be discussed in
Section 3. The conclusions can be found in Section 4.

2. Methodology

2.1 Models and experiments

2.1.1 WRF-Chem

In this study, the version of WRF-Chem updated by University of Science and Technology
of China (USTC version of WRF-Chem) is used. This USTC version of WRF-Chem includes
some additional capabilities such as the diagnosis of radiative forcing of aerosol species, land
surface coupled biogenic VOC emission, aerosol-snow interaction compared with the
publically released version (Zhao et al., 2013a,b, 2014, 2016; Hu et al., 2019). Particularly, in
order to understand the modeling mechanisms driving the diurnal variations of surface PM$_{2.5}$
concentration over East China, this study updates the USTC version of WRF-Chem to include
the diagnosis of contribution to surface PM$_{2.5}$ concentration from individual process including
transport, emission, dry and wet deposition, PBL mixing, and chemical production/loss through
estimating the difference of surface PM$_{2.5}$ concentration before and after individual process
during the simulation.

The Model for Simulating Aerosol Interactions and Chemistry (MOSAIC, Zaveri and
Peter, 1999; Zaveri et al., 2008) and the CBM-Z (carbon bond mechanism) photochemical
mechanism (Zaveri and Peters, 1999) are used. The MOSAIC aerosol scheme includes physical
and chemical processes of nucleation, condensation, coagulation, aqueous phase chemistry,
and water uptake by aerosols. All major aerosol components including sulfate, nitrate,
ammonium, black carbon, organic matter, sea salt, mineral dust, and other inorganics (OIN)
are simulated in the model. Aerosol size distributions are represented by eight discrete size bins
through the bin approach (Fast et al., 2006). Dry deposition of aerosol mass and number is
simulated following the approach of Binkowski and Shankar (1995), which includes both
particle diffusion and gravitational effects. Wet removal of aerosols by grid resolved stratiform
clouds/precipitation includes in-cloud removal (rainout) and below-cloud removal (washout)
by impaction and interception, following Easter et al. (2004) and Chapman et al. (2009). In this
study, cloud-ice-borne aerosols are not explicitly treated in the model but the removal of
aerosols by the droplet freezing process is considered. Convective transport and wet removal
of aerosols by cumulus clouds follow Zhao et al. (2013a). Aerosol radiative feedback is coupled with the Rapid Radiative Transfer Model (RRTMG) (Mlawer et al., 1997; Lacono et al., 2000) for both SW and LW radiation as implemented by Zhao et al. (2011). The optical properties and direct radiative forcing of individual aerosol species in the atmosphere are diagnosed following the methodology described in Zhao et al. (2013b). A detailed description of the computation of aerosol optical properties in WRF-Chem can be found in Fast et al. (2006) and Barnard et al. (2010). Aerosol-cloud interactions were included in the model by Gustafson et al. (2007) for calculating the activation and re-suspension between dry aerosols and cloud droplets.

2.1.2 Numerical experiments

In this study, WRF-Chem is conducted with two nested domains (one-way nesting) in one month of each season of 2018 (i.e., January, April, July, October of 2018). The outer quasi-global domain with 360x145 grid cells (180°W~180°E, 67.5°S~77.5°N) at the 1°x1° horizontal resolution is used to provide the chemical boundary to the inner domain with 112x105 grid cells (109.0°E~124.9°E, 24.0°N~38.9°N) at the horizontal resolution of 15 km over East China covering the entire YRD region as shown in Figure 1a. More details about the quasi-global WRF-Chem simulation can be found in Zhao et al. (2013a) and Hu et al. (2016). To better resolve the PBL structure and mixing and examine the modeling sensitivity to vertical configuration within PBL, two experiments (CTL1 and CTL2, Table 1) are configured with 40 vertical layers but have different distributions (as shown Fig. 1b). One configuration (L1) has roughly 20 layers below 2 km above the ground, and the other has about 10 layers below 2 km (Fig. 1b). In both CTL1 and CTL2, MYNN2 PBL scheme (Nakanishi and Niino, 2006) is used. To demonstrate the modeling sensitivity to PBL parameterizations, the experiment CTL3 is conducted as the way similar to CTL2 but with the YSU PBL scheme (Hong et al., 2006). Two additional sensitivity experiments (EXP1 and EXP2, Table 1) are also conducted corresponding to the experiments CTL1 and CTL2, respectively, except that the PBL mixing coefficient is modified (see details in Section 3.2.2). All these WRF-Chem experiments use the Morrison two-moment cloud microphysics (Morrison et al., 2009), Kain-Fritsch convective scheme (Kain et al., 2004), CLM land surface scheme, and RRTMG longwave and shortwave radiation schemes. The meteorological initial and lateral boundary conditions are derived from the NCEP Final reanalysis data with 1°x1° degree resolution and 6-hour temporal resolution. The modeled u component and v component wind and atmospheric temperature are nudged...
towards the reanalysis data only to the layers above the PBL with nudging coefficients of $3 \times 10^{-231} \text{s}^{-1}$ with a nudging timescale of 6-hour (Stauffer and Seaman, 1990; Seaman et al., 1995).

2.1.3 Emissions

Anthropogenic emissions for the outer quasi-global simulation are obtained from the Hemispheric Transport of Air Pollution version-2 (HTAPv2) at 0.1°×0.1° horizontal resolution and a monthly temporal resolution for year 2010 (Janssens-Maenhout et al., 2015), except that emissions over China within the domains are from the Multi-resolution Emission Inventory for China (MEIC) at 0.1°×0.1° horizontal resolution for 2015 (Li M et al., 2017), which is also used for the inner domain simulation over East China. Figure 1a shows the spatial distributions of emissions of primary PM$_{2.5}$, NO$_x$, and SO$_2$ over East China. The default anthropogenic emission inventories assume no diurnal variation of emissions and that all emissions are near the surface (e.g., first model layer). Since diurnal variation of emissions and injection height of power plant emissions may have impacts on diurnal variation of surface pollutants, the experiments discussed above apply the diurnal profiles of anthropogenic emissions from five individual sector (i.e., agriculture, industry, transport, energy, and residential) following Olivier et al. (2003) and Wang et al. (2005) as shown in Fig. 1c and vertical distributions of anthropogenic power plant emissions following Wang et al. (2010) as shown in Table 2. As shown in Fig. 1c, emissions from all sectors show peak values during the daytime, and the diurnal variations from agriculture, residential, and transportation are much stronger than those from industry and power plant. The emissions from power plant are distributed from the bottom to a height of ~900 m with more than 90% below 500 m. Two sensitivity experiments, EXP1_E1 and EXP1_E2, are conducted as the way similar to EXP1 except that EXP1_E1 assumes no diurnal variation of anthropogenic emissions and EXP1_E2 assumes all power plant emissions are placed near the surface (i.e., the first model layer). Comparing EXP1 with EXP1_E1 and EXP1_E2 can examine the impact of diurnal variation and injection height of anthropogenic emissions on diurnal cycle of surface PM$_{2.5}$, respectively. All these experiments are summarized in Table 1. Biomass burning emissions are obtained from the Fire Inventory from NCAR (FINN) with hourly temporal resolution and 1 km horizontal resolution (Wiedinmyer et al., 2011), and are vertically distributed following the injection heights suggested by Dentener et al. (2006) from the Aerosol Comparison between Observations and Models (AeroCom) project. Sea-salt emission follows Zhao et al. (2013a), which includes correction of particles with radius less than 0.2 μm (Gong, 2003) and dependence of sea-salt
emission on sea surface temperature (Jaeglé et al., 2011). The vertical dust fluxes are calculated with the GOCART dust emission scheme (Ginoux et al., 2001), and the emitted dust particles are distributed into the MOSAIC aerosol size bins following a theoretical expression based on the physics of scale-invariant fragmentation of brittle materials derived by Kok (2011). More details about the dust emission scheme coupled with MOSAIC aerosol scheme in WRF-Chem can be found in Zhao et al. (2010, 2013a).

2.2 Observations

The ground observations of hourly surface PM$_{2.5}$ mass concentration in January, April, July, and October of 2018 are obtained from the website of the Ministry of Environmental Protection of China (MEP of China). Since this study focuses on the YRD region of East China, 190 stations over East China are selected for analysis. The locations of these 190 stations are shown in Fig. 1a within the black box (116.0°E–122.5°E, 29.0°N–33.0°N). Besides regional average analysis, four cities (Fig. 1a) as the Center (Shanghai, 121.45°E and 31.21°N; Hefei, 117.25°E and 31.85°N; Hangzhou, 120.08°E and 30.21°N) of the YRD city cluster are also selected for further analysis at urban areas.

3. Results

3.1 Modeling diurnal cycle of surface PM$_{2.5}$ concentration

In order to investigate the diurnal cycle of surface PM$_{2.5}$ concentration, this study defines an index to better show the diurnal variation. The diurnal index (DI) is defined as the value of each hour divided by the minimum value within 24-hour on monthly average. The peak DI within 24-hour represents the amplitude of diurnal variation. Figure 2 shows the diurnal index of surface PM$_{2.5}$ concentration within 24-hour averaged over the YRD region of East China (as shown as the black box in Fig. 1a) for January, April, July, October of 2018 from the WRF-Chem experiments and observations. The experiment CTL1 uses the MYNN PBL scheme and finer boundary layer configuration (L1 in Fig. 1b). The simulation results are 3-hourly and sampled at the observational sites as shown in Fig. 1a. On regional average, the observed variation of DI is the weakest in winter with the peak value around 1.2 among the four seasons. The observed DI reaches the maximum of 1.5 in autumn. In spring and autumn, the observed diurnal variation of DI is similar, showing two peaks in the morning and night, respectively, and reaching the minimum in the afternoon, which is consistent with previous findings with observations over East China (e.g., Zhang and Cao., 2015; Liu et al., 2016; Guo et al., 2017).
summer, different from other seasons, the observed diurnal variation of DI shows the single peak around 1.4 near the noon time. The CTL1 experiment can generally reproduce two peaks in spring and autumn, however, the CTL1 simulation overestimates the observed peak DI in the two seasons, particularly in autumn. The experiment generally captures the seasonality of DI of surface PM$_{2.5}$ concentration that is higher DI in spring and autumn and the weakest DI in winter, except that in summer the experiment significantly overestimates the DI during the night and produces opposite diurnal pattern with the minimum DI near the noon time. The spatial distributions of DI over East China are also generally consistent between observations and simulations and show similar seasonality (Figure S1 in the supporting material). The area with higher surface PM$_{2.5}$ concentration generally has higher DI (Figure S2 in the supporting material), particularly from the simulation.

Therefore, the DI distribution at the four cities as the Center (Shanghai) and sub-Center (Nanjing, Hefei, Hangzhou) of the YRD city cluster in East China (as shown in Fig. 1a) are further analyzed. Figure 3 shows the diurnal index of surface PM$_{2.5}$ concentration within 24-hour averaged over the four cities for January, April, July, October of 2018 from the WRF-Chem experiments and observations. The observed diurnal variation of DI in these four cities are consistent with that on regional average of East China. The diurnal variation of DI is more evident in the two inland cities (Hefei and Nanjing) than the two coastal cities (Hangzhou and Shanghai). Consistent with the results based on regional average, the CTL1 experiment can generally capture the diurnal variation of DI of surface PM$_{2.5}$ in the four cities, but overestimates the DI in the night, particularly in spring and autumn. In summer, again, the CTL1 significantly overestimates the DI during the night and produces the opposite diurnal pattern compared to observations. In general, the CTL1 produces even higher DI during the night in the four cities than regional average, which results in larger diurnal amplitudes in the four cities than regional average. The CTL1 can generally simulate stronger diurnal variation in the two inland cities than in the two coastal cities.

The analysis above for both regional average and city average indicates that the CTL1 simulation has high positive biases of DI during the night. In order to understand the modeling biases and the mechanisms driving the simulated diurnal variations of surface PM$_{2.5}$ concentration over East China, the contribution to diurnal variation of surface PM$_{2.5}$ concentration from individual process including transport, emission, dry and wet deposition, mixing, and chemical production/loss is estimated. The contribution is calculated as the difference of surface PM$_{2.5}$ concentration before and after individual process during the simulation. Figure 4 shows the contribution of individual process to the variation of surface
PM$_{2.5}$ concentration every 3-hour in Hefei from the WRF-Chem experiments averaged for January, April, July, and October of 2018. The 3-hourly tendency of surface PM$_{2.5}$ concentration is also shown. The contributions and tendencies are divided by monthly mean surface PM$_{2.5}$ concentration for each month. The results for the other three cities (Nanjing, Hangzhou, Shanghai) are similar to that of Hefei and are shown in the supporting material (Figure S3a-c). Process contribution analysis is verified by comparing the variations of surface PM$_{2.5}$ concentration with the sum of the contribution from each individual process. As shown in Figure S4, the sum contributions of all processes are consistent with the variations in surface PM$_{2.5}$ concentration following the principle of mass balance.

In Fig. 4, positive value denotes relative increase of surface PM$_{2.5}$ concentration and negative value denotes relative decrease. From the CTL1 experiment, the contributions from emission and chemistry are positive through the day, while the contributions from transport, PBL mixing, wet and dry deposition are negative through the day. The CTL1 simulates the largest variation of tendency in summer and the smallest variation in winter. The tendency is negative from the morning to the afternoon, resulting the simulated minimum surface PM$_{2.5}$ concentration in the afternoon in all seasons, which is consistent with the result shown in Fig. 3. It is evident that emission, PBL mixing, and transport are the three main processes controlling the diurnal variation of surface PM$_{2.5}$ concentration, and emission and PBL mixing are the dominant two. Emission increases the surface PM$_{2.5}$ concentration and reaches the maximum near the noon time, while PBL mixing reduces the surface PM$_{2.5}$ concentration and also reaches the maximum reduction near the noon time. The combined effect of emission and PBL mixing is reflected as the overall tendency. Therefore, PBL mixing is the determinant process leading to the simulated minimum DI near the noon time and higher DI during the night. To further demonstrate the contribution of each PM$_{2.5}$ composition to the diurnal variation of surface PM$_{2.5}$ concentration, Figure 5 shows the diurnal variation of surface concentration of each PM$_{2.5}$ composition in Hefei from the WRF-Chem experiments averaged for January, April, July, and October of 2018. The diurnal variations of surface concentrations of OM, BC, and OIN are larger than other components of PM$_{2.5}$, showing evident higher concentration during the night and minimum near the noon time in all seasons except winter. The sum of OM and OIN contribute to more than half of surface PM$_{2.5}$ concentration. Therefore, it suggests that the PBL mixing of the primary PM$_{2.5}$ determines the simulated diurnal variation of surface PM$_{2.5}$ concentration. The results for the other three cities (Nanjing, Hangzhou, Shanghai) are similar to that of Hefei and are shown in the supporting material (Figure S5a-c).
3.2 Sensitivity to PBL mixing

3.2.1 Sensitivity to the PBL configuration

As discussed above, the PBL mixing is very important for modeling diurnal variation of surface PM$_{2.5}$ concentration, and it may be affected by PBL parameterizations and vertical layer configuration within the PBL. Therefore, two experiments, CTL2 and CTL3, are conducted to examine the sensitivity of simulated diurnal variation of surface PM$_{2.5}$ concentration to different PBL configurations. The CTL2 uses the MYNN PBL scheme as the CTL1 but is configured with different vertical layer distribution (L2) as shown in Fig. 1b, in which less vertical layers are put within the PBL as described in Section 2.2. The CTL3 uses the YSU PBL scheme and is configured with the L2 vertical layer distribution as the CTL2. As shown in Fig. 2, on regional average, the CTL2 and CTL3 generally simulate similar diurnal and seasonal patterns as that by the CTL1 with the minimum DI near the noon time and the peak DI during the night. The CTL2 simulates lower DI than the CTL1 during the night in all seasons. This indicates that the model with finer vertical resolution within the PBL, which is supposed to better resolve the PBL structure, produces higher positive biases of DI. The CTL3 simulates similar diurnal variation of DI as the CTL2 but overestimate the DI during the night to some extent, particularly in summer, which indicates the model with the YSU PBL scheme produces higher positive biases of DI during the night compared to the one with the MYNN PBL scheme. In the four cities as shown in Fig. 3, the CTL2 and CTL3 also simulate similar diurnal and seasonal patterns as that by the CTL1. It is also interesting to note that the difference of DI between CTL2 and CTL1 are larger than that between CTL3 and CTL2, which indicate that the modeling sensitivity of DI to the vertical layer configuration within the PBL is even greater than that to the PBL scheme. Overall, all these three WRF-Chem experiments produce similar positive biases of DI during the night compared to the observations in all seasons over the YRD region of East China, particularly in cities. This is consistent with previous findings about the simulated positive biases of diurnal variation of surface PM$_{2.5}$ concentration over East China (e.g., Liu M et al., 2018). The changes of PBL schemes and vertical configurations within the PBL can affect the simulated DI but cannot improve the simulations to reproduce the observations.

In order to better understand the modeling sensitivity of DI to the PBL configuration, Fig. 4 and 5 also shows the simulated results for the city of Hefei from the CTL2 and CTL3. Similar as CTL1, the results from CTL2 and CTL3 also show that emission, PBL mixing, and transport are the three main processes controlling the diurnal variation of surface PM$_{2.5}$ concentration, and emission and PBL mixing are the dominant two (Fig. 4). Since the number
of vertical layer within the PBL in CTL2 and CTL3 is much less than that in CTL1, the thickness of first model layer in CTL2 and CTL3 is about a factor 2 of that in CTL1. With the same emission flux, CTL2 and CTL3 simulate much smaller contribution from emission to the surface PM$_{2.5}$ concentration than does CTL1. Correspondingly, the contribution from PBL mixing to the surface PM$_{2.5}$ concentration in CTL2 and CTL3 is also lower than that in CTL1. The combined effect of emission and PBL mixing results in weaker diurnal variation of surface PM$_{2.5}$ concentration in CTL2 and CTL3 than that in CTL1, as shown by the diurnal variation of overall tendency of surface PM$_{2.5}$ concentration. CTL3 with the YSU PBL scheme simulates stronger diurnal variation of surface PM$_{2.5}$ concentration than does the CTL2 with the MYNN PBL scheme, primarily due to its larger diurnal variation of PBL mixing. With less contribution from emission to the surface PM$_{2.5}$ concentration, CTL2 and CTL3 simulate less primary PM$_{2.5}$ (OIN, OM, BC) than does CTL1 (Fig. 5), particularly during the night when the PBL mixing is weak. This leads to the weaker diurnal variation of total surface PM$_{2.5}$ concentration in CTL2 and CTL3 as discussed above. The higher DI during the night in CTL3 than CTL2 can also be explained by the higher primary PM$_{2.5}$ during the night due to weaker PBL mixing.

3.2.2 Sensitivity to the PBL mixing coefficient

The results discussed above suggest that, the WRF-Chem simulated diurnal variation of surface PM$_{2.5}$ concentration over East China is largely controlled by the PBL mixing process, and is sensitive to the PBL scheme and vertical layer configuration within the PBL. However, the increase of number of vertical layer within the PBL and use of different PBL schemes cannot reduce the modeling biases in diurnal variation of surface PM$_{2.5}$ concentration. Many previous studies investigated the PBL mixing of pollutants through establishing the relationship between surface pollutant concentration and PBL height. However, it is noteworthy that in most atmospheric models, the mixing of pollutants within the PBL is treated either as full mixing within the PBL height (i.e., uniformly distributed within the PBL height) or as calculated based on the mixing coefficient diagnosed from the PBL scheme. The former method represents the strongest PBL mixing and the surface concentration can be largely influenced by the PBL height. However, the latter one means that the pollutant mixing does not depend explicitly on PBL height.

In WRF-Chem, the PBL mixing of pollutants is treated with the second approach. In order to further examine the simulated PBL mixing process in this study, Figure 6 shows the diurnal variation of PBL heights and PBL mixing coefficients below PBL height in Hefei in January, April, July, and October of 2018 from the WRF-Chem experiments CTL1, CTL2, and CTL3.
The black line represents the PBL height while the contour shading represents the PBL mixing coefficients within the PBL height. First of all, the PBL heights simulated from the three experiments all show evident diurnal variation with the maximum in the daytime and the minimum during the night. The simulated PBL heights from CTL1 and CTL2 with the same PBL scheme (MYNN) show very similar diurnal pattern, indicating the vertical layer configuration has small impact on modeling PBL height. Both experiments simulate the largest diurnal variation of PBL height in summer with a changing factor of ~10 from ~2 km in the afternoon to ~200 m in the early morning, and the smallest diurnal variation of PBL height in winter with a changing factor of 2 from ~700 m in the afternoon to ~350 m in the early morning.

It should be noted that the PBL mixing coefficients within the PBL also exhibit evident diurnal variation with a changing factor of ~1000 and ~50 in summer and winter, respectively, which is much larger than that of the PBL height in all seasons. The CTL3 simulation with the YSU PBL scheme also show that the diurnal variation of PBL mixing coefficient is much larger than that of PBL height. The difference between CTL2 and CTL3 is consistent with the analysis about the simulated diurnal variation of surface PM$_{2.5}$ concentration, further demonstrating that the WRF-Chem simulated diurnal variation of surface PM$_{2.5}$ concentration is determined by the PBL mixing coefficient instead of PBL height. For example, in autumn the PBL height during the night is lower in CTL3 than in CTL2, while the DI during the night is lower in CTL3 than in CTL2 (Fig. 3) due to the higher PBL mixing coefficient during the night in CTL3 than in CTL2. More WRF experiments with different PBL schemes are conducted and all show similar results that the diurnal variation of PBL mixing coefficient is much stronger than that of PBL height (not shown).

With relatively large values of PBL mixing coefficient during the daytime, the emitted pollutants can be mixed up roughly reaching the layer of PBL height. However, weak PBL mixing coefficient during the night results in that the emitted PM$_{2.5}$ and its precursors will stay near the surface (i.e., within the first layer of model) during the night and cannot be mixed up reaching the PBL height (Fig. S6 in the supporting material). This leads to the large difference of DI between CTL1 and CTL2 with different thickness of first model layer during the night although they simulate similar PBL height. The comparison between simulations and observations (Fig. 2 and 3) suggests the positive modeling biases of DI during the night may be partly due to the underestimation of the PBL mixing during the night. To examine the sensitivity of simulated DI to the PBL mixing coefficient, the sensitivity experiments, EXP1 and EXP2, are conducted corresponding to CTL1 and CTL2, respectively, through setting the lower limit of PBL mixing coefficient from 0.1 m$^2$/s (default in the publically released version...
of WRF-Chem) to 5 m$^2$/s within the PBL. Figure 7 shows the simulated PBL height and mixing coefficients from the two sensitivity experiments, EXP1 and EXP2, in January, April, July, and October of 2018 in Hefei. It shows that the PBL mixing coefficient increases during the night within the PBL compared to the results shown in Fig. 6, while the values during the daytime remain almost the same. The difference of simulated surface PM$_{2.5}$ between CTL1 and EXP1 is relatively small during the daytime, but significant during the night, which is due to that EXP1 can mix up the surface PM$_{2.5}$ to the PBL height during the night (Fig. S6). It is noteworthy that the lower limit parameter of 5 m$^2$/s is entirely empirical. It is selected to represent the moderate mixing strength between the full PBL mixing and no PBL mixing. A few other values such as 1 m$^2$/s and 10 m$^2$/s are also tested. The results do not change the conclusion found in this study and therefore are not shown.

The change of PBL mixing coefficient during the night can significantly affect the diurnal variation of PBL mixing. Figure 8 shows the contribution of individual process to the variation of surface PM$_{2.5}$ concentration every 3-hour in Hefei simulated by EXP1 and EXP2 averaged for January, April, July, and October of 2018. The 3-hourly tendency of surface PM$_{2.5}$ concentration is also shown. Same as Fig. 4, the contributions and tendencies are divided by monthly mean surface PM$_{2.5}$ concentration for each month. The results for the other three cities (Nanjing, Hangzhou, Shanghai) are similar to that of Hefei and are shown in the supporting material (Figure S7a-c). Compared to the results from CTL1 and CTL2 shown in Fig. 4, it is evident that the diurnal variation of tendency of surface PM$_{2.5}$ concentration is significantly reduced in all seasons. This is mainly resulted from the significantly reduced diurnal variation of PBL mixing contribution. Specifically, the PBL mixing contribution during the night is increased. Figure 9 shows the diurnal variation of surface concentration of each PM$_{2.5}$ composition in Hefei simulated by the EXP1 and EXP2 averaged for January, April, July, and October of 2018. The diurnal variations of surface concentrations of OM, BC, and OIN are significantly reduced primarily due to their reduced concentration during the night in EXP1 and EXP2, compared to CTL1 and CTL2 (Fig. 5). The results for the other three cities (Nanjing, Hangzhou, Shanghai) are similar to that of Hefei and are shown in the supporting material (Figure S8a-c).

The change of PBL mixing and diurnal variation of primary PM$_{2.5}$ near the surface turn out different DI. Figure 10 shows the diurnal variation of DI of surface PM$_{2.5}$ averaged over the YRD region of East China for January, April, July, and October of 2018 from the observations and the experiments CTL1, CTL2, EXP1, and EXP2. In general, the simulated DI are reduced significantly during the night in EXP1 and EXP2 much more consistent with
the observations compared to the ones in CTL1 and CTL2. In spring, the EXP1 and EXP2 slightly underestimate DI during night. Figure 11 shows the diurnal variation of DI averaged over the four cities for January, April, July, October of 2018 from the observations and the experiments CTL1, CTL2, EXP1, and EXP2. As discussed above the diurnal variation of DI is much stronger in cities with relatively more emissions. The simulated DI is also more sensitive to the change of PBL mixing coefficient in these four cities compared to that on regional average. The EXP1 and EXP2 produce much more consistent DI with the observations in the four cities than do CTL1 and CTL2 in all seasons. It is also noteworthy that the difference between EXP1 and EXP2 and that between CTL1 and CTL2 is reduced both on city average and regional average, which indicates that the enhanced PBL exchange coefficient during the night help reduce the modeling sensitivity to the vertical layer configuration. The analysis above suggests that the simulated PBL mixing during the night in the publically-released WRF-Chem may be too weak.

Comparing the simulated surface concentrations of PM$_{2.5}$ components between CTL1 (Fig. 5) and EXP1 (Fig. 9), it can be found that the daily average surface PM$_{2.5}$ mass concentration should also be reduced when the diurnal variation is reduced due to the reduction of nighttime surface PM$_{2.5}$ concentration. Figure 12 shows the comparison of monthly mean surface PM$_{2.5}$ concentration between the observations and the simulations from CTL1 and EXP1 at each observation site over the YRD region of East China for January, April, July, and October of 2018. In all seasons, the CTL1 significantly overestimates the observed surface PM$_{2.5}$ concentration with the normalized mean biases (NMB) of 22% (winter) - 109% (summer) on regional average. The EXP1 reduces the NMB to 7% (winter) - 38% (summer) on regional average. In CTL1, the NMB of simulation exceeds 50% at 20%, 35%, 65%, and 60% of observational sites over the YRD region of East China in January, April, July, and October, respectively, which reduces to 0%, 10%, 35%, and 20% of all sites in EXP1. In addition, the EXP1 also increases the spatial correlation between observations and simulated results in all seasons (Fig. 12), although with the improvement of modeling diurnal variation the EXP1 still cannot fully capture the observed spatial variability of surface PM$_{2.5}$ concentration among the observational sites. This may be related to the biases in spatial distributions of emission and model processes contributed to the spatial variability of surface PM$_{2.5}$ concentration, which deserves further investigation in future.

3.3 Impacts from emission distributions

3.3.1 Impacts from emission diurnal variability
Besides the meteorology such as PBL mixing as discussed above, the diurnal variation of emissions may also play an important role in determining the DI of surface PM$_{2.5}$ concentration. One sensitivity experiment, EXP1_E1, without diurnal variation of anthropogenic emissions (Fig. 1b) is conducted. Figure 13 shows the spatial distribution of the difference in maximum DI between EXP1 and EXP1_E1 over East China. As removing diurnal variation of emissions will lead to more emissions during the night and thus increase the DI during the night over polluted area, which generally results in larger maximum DI. Therefore, EXP1 has lower maximum DI than EXP1_E1 over most regions of East China in seasons other than winter. EXP1 could have slightly larger maximum DI in winter when the diurnal variation of DI is relatively small (Fig. 2 and 3) and over the relatively clean region (Fig. 1a) in summer. Figure 14 shows the diurnal index of surface PM$_{2.5}$ concentration within 24-hour averaged over the four cities for January, April, July, and October of 2018 from observations and the EXP1 and EXP1_E1 experiments. In general, EXP1 shows lower DI than EXP1_E1 during the night, and therefore has smaller diurnal variation of DI in four cities. The largest difference between EXP1 and EXP1_E1 in four cities exists in summer and the smallest is in winter. Comparing to the impacts from PBL mixing as shown in Fig. 11, the reduction of diurnal variation of DI by adding diurnal variation of anthropogenic emissions is much smaller.

Fig. 13 shows that EXP1 with diurnal variation of emissions could simulate slightly larger diurnal variation of DI over the relatively clean region than EXP1_E1 in winter and summer. The higher DI in EXP1 than EXP1_E1 is primarily in the afternoon and evening (Fig. S9 in the supporting material). One grid over south Anhui is selected for analysis of contributions from different processes in the model to the diurnal variation of surface PM$_{2.5}$ concentration from the experiments EXP1 and EXP1_E1 (Fig. 15). Different from the process contributions over the relatively polluted region (Fig. 8), the contribution from direct local emission to the surface PM$_{2.5}$ concentration is relatively small over the clean region. Instead, the contributions from chemistry, dry deposition, PBL mixing, and transport dominate the diurnal variation of surface PM$_{2.5}$ concentration. The PBL mixing could increase the surface PM$_{2.5}$ concentration during the daytime because of mixing down the pollutants transported from polluted regions above the surface. The diurnal change of surface PM$_{2.5}$ concentration between EXP1 and EXP1_E1 is very similar with slightly difference that results in their slight difference in DI in the afternoon and night.
Previous studies suggested that the injection height of emissions from power plants may also affect the diurnal cycle of surface pollutant concentration, particularly for SO$_2$ (e.g., Wang et al., 2010; Lin et al., 2012; Qi et al., 2012; Xu et al., 2014). Therefore, one sensitivity experiment, EXP1_E2, is conducted with setting the anthropogenic emissions placed only in the first layer of model. Figure 16 shows the spatial distribution of the difference in maximum DI between EXP1 and EXP1_E2 over East China. Over most areas of East China, EXP1 simulates lower maximum DI than EXP1_E2, and the difference is primarily in spring and summer. The impact of injection height is negligible in winter. The distribution of impacts correlates highly with the distribution of power plant locations. The reduction of DI of surface SO$_2$ concentration in EXP1 compared to EXP1_E2 is mainly due to more emissions are placed above the PBL during the night (Fig. S10 in the supporting material). As shown in Table 2, most of power plant emissions are placed below 500 m in EXP1. The larger impact in summer than in winter is mainly due to the higher PBL height during the night in winter (Fig. 7).

Therefore, emissions are still placed within the PBL even with the injection height, which results in the small difference of DI of surface SO$_2$ concentration between EXP1 and EXP1_E2. For surface PM$_{2.5}$ concentration, the impact of emission injection height is even smaller and only distinguishable in summer (Fig. S11 in the supporting material). Overall, impact from the injection height of emission on the diurnal variation of surface PM$_{2.5}$ concentration is much smaller than that from PBL mixing.

4. Summary and discussion

In this study, the observed characteristics of diurnal variation of surface PM$_{2.5}$ concentration over the YRD region of East China in four seasons of 2018 is examined based on the hourly surface observations at 190 stations of the region. On regional average, the observed diurnal variation is the weakest in winter and the strongest in autumn. In spring and autumn, the observed patterns of diurnal variation are similar, showing the minimum surface PM$_{2.5}$ concentration in the afternoon, consistent with previous studies (e.g., Zhang and Cao et al., 2015; Liu et al., 2016; Guo et al., 2017). In summer, different from other seasons, the observed diurnal variation shows the maximum surface PM$_{2.5}$ concentration near the noon time.

The WRF-Chem experiments are conducted over East China and the simulated diurnal variations of surface PM$_{2.5}$ concentration are compared with the observations. The model generally captures the observed seasonality of diurnal variation of surface PM$_{2.5}$ concentration, except that in summer the model significantly overestimates the diurnal peak during the night.
and produces opposite diurnal pattern with the minimum concentration near the noon time. The model can generally reproduce the patterns with the minimum noontime concentration in spring and autumn, but overestimates the observed nighttime peaks, particularly in autumn. The modeling biases and the mechanisms driving the diurnal variation of surface PM$_{2.5}$ concentration in four seasons are further investigated. Emission and PBL mixing are found to be the two dominant processes controlling the diurnal variation of surface PM$_{2.5}$ concentration over the polluted areas, and the PBL mixing leads to the simulated diurnal pattern of surface PM$_{2.5}$ concentration. More specifically, the simulations suggest that the PBL mixing of the primary PM$_{2.5}$ determines the modelled diurnal variation of surface PM$_{2.5}$ concentration. Although the observation of PM$_{2.5}$ components is not available to evaluate the diurnal variation of primary PM$_{2.5}$, the diurnal variation of surface mixing ratio of CO that is normally used to represent the primary pollutant supports the findings (Fig. S12 in the supporting material).

The modeling results are found sensitive to the PBL schemes and the vertical configuration (i.e., the number of model layers within PBL) of simulations. However, none of the PBL schemes in WRF-Chem can reduce the modeling biases in diurnal variation of surface PM$_{2.5}$ concentration. Contrary to the intuition, more model layers within PBL worsen the model performance, which is mainly due to that more layers within PBL makes the first model layer thinner and enlarges the contribution from emission if PBL mixing is not efficient. The analysis indicates that the PBL mixing coefficient instead of the PBL height controls the PBL mixing in WRF-Chem, particularly during the night. Increasing the lower limit of PBL mixing coefficient within the PBL can significantly reduce the modeling biases in diurnal variation of surface PM$_{2.5}$ concentration, primarily during the night. In addition, it can also reduce the modeling sensitivity to the model vertical configuration. The model performance of daily mean surface PM$_{2.5}$ concentration is also largely improved when the biases of diurnal variation are reduced. The diurnal variation of anthropogenic emissions and injection height of power plant emissions can affect the diurnal cycle of surface PM$_{2.5}$ concentration to some extent, but the impact is much smaller than that of PBL mixing.

This study highlights the importance of modeling PBL mixing coefficient within PBL in models like WRF-Chem that simulates the PBL mixing process based on the mixing coefficient instead of PBL height. Some studies found that other models also overestimated the diurnal variation of observed surface PM$_{2.5}$ concentration over East China (e.g., Cai et al., 2011; Liu M et al., 2018). Our finding suggests that those models may also have the problems in modeling PBL mixing during the night. Many of previous modeling and observation studies focus on investigating the variation of PBL height and its interaction...
with aerosol concentration (e.g., Sawyer et al., 2015; Ding et al, 2016; Li et al, 2017; Song et al., 2018; Su et al., 2018). However, this study reveals that the PBL mixing flux is more critical than PBL height in terms of understanding the mixing of pollutants within PBL, particularly during the night, which can not only significantly affect the diurnal variation but also the daily mean of surface pollutant concentration. The increase of PBL mixing during the night reduces the modeling biases, which may suggest that the simulated PBL mixing during the night in WRF-Chem is too weak. One possible reason may be due to urban heat island effect that is not accounted in this study, because the observation sites are mostly at urban or sub-urban areas. The test simulations with the current version of WRF-Chem using Noah land surface model with urban effect can increase the nighttime PBL mixing coefficient from 0.1 m²/s to 1-10 m²/s during some cases at urban areas, but the results are sensitive to the urban schemes (not shown), which deserves investigation in future. Another suggestion is that the PBL mixing of pollutants may not be able to follow directly the mixing coefficient diagnosed by PBL parameterization for meteorology, which deserves further investigation. The improvement of modeling PBL height is not enough for understanding the PBL mixing of pollutants. This suggests that the understanding of PBL structure and detailed mixing process are needed. Besides the observation or retrieval of PBL height, observations of PBL characteristics are needed.

Although the sensitivity adjustment of PBL mixing coefficient during the night can largely reduce the modeling biases in diurnal variation of surface PM$_{2.5}$ concentration, one evident deficiency is that the model produces opposite diurnal pattern compared with observations in summer. It needs to be noted that the WRF-Chem simulations conducted in this study do not consider the SOA production that still has large uncertainties in mechanisms. One sensitivity experiment with the SOA production shows that the model can better represent the observed diurnal pattern of surface PM$_{2.5}$ concentration in summer showing the maximum concentration in the daytime (Fig. S13 in the supporting material). This indicates that the SOA production may be important for modeling the diurnal variation of surface PM$_{2.5}$ concentration in summer over East China, which suggests more detailed analysis of impact of SOA production on diurnal cycle of surface PM$_{2.5}$ concentration is needed with observations. It is also noteworthy that the impact of SOA production on diurnal variation of surface PM$_{2.5}$ concentration is only significant in summer, likely due to the strong photochemistry activity in summer. Another uncertainty of the results in this study may be related to emissions. Although the diurnal variation and injection height of emission do not contribute significantly to the night time positive biases of surface PM$_{2.5}$
concentration, the emission uncertainties of primary PM may influence the diurnal cycle of surface PM$_{2.5}$. For example, overestimation of primary PM emission can increase the diurnal variation. Therefore, this study suggests that the long-term measurements of PM$_{2.5}$ components at more stations are needed to further investigate the characteristics of diurnal variation of PM$_{2.5}$, which can improve our understanding of the impacts of multiple processes, such as chemical production, emissions, and meteorology, on the formation and evolution of air pollution.

Data availability

The release version of WRF-Chem can be download from http://www2.mmm.ucar.edu/wrf/users/download/get_source.html. The updated USTC version of WRF-Chem can be downloaded from http://aemol.ustc.edu.cn/product/list/ or contact chunzhao@ustc.edu.cn. Also, the code modifications will be incorporated the release version of WRF-Chem in future.

Author contributions

Qiuyan Du and Chun Zhao designed the experiments, conducted and analyzed the simulations. All authors contributed to the discussion and final version of the paper.

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Table 1 Numerical experiments conducted in this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>PBL scheme</th>
<th>Vertical structure</th>
<th>PBL mixing coefficient (m$^2$/s)</th>
<th>Emission diurnal cycle</th>
<th>Emission injection height</th>
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<td>MYNN</td>
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<td>Yes</td>
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<tr>
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<td>layer2</td>
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<td>Yes</td>
</tr>
<tr>
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<tr>
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<td>No</td>
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</tbody>
</table>

Table 2 Vertical distributions of power plant emissions: percentage of each species allocated to the height of the vertical layers in the WRF-Chem model.

<table>
<thead>
<tr>
<th>Species</th>
<th>Height of Emission Layers (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-76</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>5</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>5</td>
</tr>
<tr>
<td>CO</td>
<td>5</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>5</td>
</tr>
<tr>
<td>NMVOC</td>
<td>5</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
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</tr>
<tr>
<td>PM$_{10}$</td>
<td>5</td>
</tr>
<tr>
<td>OC</td>
<td>5</td>
</tr>
<tr>
<td>BC</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure 1a. MEIC China emission of SO$_2$, NO$_2$, PM$_{2.5}$ over the simulation domain (109.0°E~124.9°E, 24.0°N~38.9°N) with black boxes showing the analyzed domain (116.0°E~122.5°E, 29.0°N~33.0°N), overlaid with observational sites and four cities as the Center (Shanghai, 121.45°E and 31.21°N) and sub-Center (Nanjing, 118.78°E and 32.06°N; Hefei, 117.25°E and 31.85°N; Hangzhou, 120.08°E and 30.21°N) of the YRD city cluster.

Figure 1b. Vertical profiles of the layer thickness from L1 and L2 layer configuration.
Figure 1c. Diurnal profiles of emissions from five individual sector (agriculture, industry, transport, energy, and residential).
Figure 2. Diurnal index of surface PM$_{2.5}$ concentration within 24-hour averaged over the YRD region of East China (within black box of Fig. 1a) for January, April, July, and October of 2018 from the experiments CTL1, CTL2, CTL3, and observations. The simulated results are from 3-hourly output and sampled at the observational sites.
Figure 3. Diurnal index of surface PM$_{2.5}$ concentration within 24-hour averaged over four cities (Hefei, Nanjing, Hangzhou, Shanghai) for January, April, July, and October of 2018 from the experiments CTL1, CTL2, CTL3, and observations.
Figure 4. Contribution to surface PM$_{2.5}$ concentration every 3-hour from individual process (transport, emission, dry and wet deposition, PBL mixing, chemical production/loss) averaged over Hefei for January, April, July, and October of 2018 from the experiments CTL1, CTL2, and CTL3. The 3-hourly tendency of surface PM$_{2.5}$ concentration is also shown.
Figure 5. Diurnal variation of surface concentration of each PM$_{2.5}$ composition (Dust, OC, EC, Sea Salt, NH$_4^+$, SO$_4^{2-}$, NO$_3^-$, and other inorganics) averaged over Hefei for January, April, July, and October of 2018 from the experiments CTL1, CTL2, and CTL3.
Figure 6. Diurnal variation of PBLH and PBL mixing coefficient below PBLH averaged over Hefei for January, April, July, and October of 2018 from the experiments CTL1, CTL2, and CTL3.
Figure 7. Diurnal variation of PBLH and PBL mixing coefficient below PBLH averaged over Hefei for January, April, July, and October of 2018 from the experiments EXP1 and EXP2.
Figure 8. Contribution to surface PM$_{2.5}$ concentration every 3-hour from individual processes (transport, emission, dry and wet deposition, PBL mixing, and chemical production/loss) averaged over Hefei for January, April, July, and October of 2018 from the experiments EXP1 and EXP2.
Figure 9. Diurnal cycle of surface PM$_{2.5}$ compositions concentration (Dust, OC, EC, Sea Salt, NH$_4$$^+$, SO$_4$$^{2-}$, NO$_3$$^-$, and other inorganics) averaged over Hefei for January, April, July, and October of 2018 from the experiments EXP1 and EXP2.
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Figure 12. Comparison of monthly mean surface PM$_{2.5}$ concentration between the observations and the simulations from the experiments CTL1 and EXP1 at each observation site over the YRD region of East China for January, April, July, and October of 2018.
Figure 13. Spatial distribution of the difference in daily maximum diurnal index of surface PM$_{2.5}$ between the experiments EXP1 and EXP1_E1 over East China in January, April, July, and October of 2018.
Figure 14. Diurnal index of surface PM$_{2.5}$ concentration within 24-hour averaged over four cities (Hefei, Nanjing, Hangzhou, Shanghai) for January, April, July, and October of 2018 from the experiments EXP1_E1, EXP1, and observations.
Figure 15. Contribution to diurnal variation of surface PM$_{2.5}$ concentration from individual processes (transport, emission, dry and wet deposition, PBL mixing, and chemical production/loss) averaged over South Anhui for January, April, July, and October of 2018 from the experiments EXP1_E1 and EXP1.
Figure 16. Spatial distribution of the difference in daily maximum diurnal index of surface SO$_2$ between the experiments EXP1_E2 and EXP1 over East China in January, April, July, and October of 2018.