Enhanced atmospheric oxidizing capacity in simulating air quality with updated emission inventories for power plants especially for haze periods over East China

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Abstract. Air pollutant emissions play a determinant role in deteriorating air quality. However, an uncertainty in emission inventories is still the key problem for modeling air pollution. In this study, an updated emission inventory of coal-fired power plants (UEIPP) based on online monitoring data in Jiangsu province of East China for the year of 2012 was implemented in the widely used Multi-resolution Emission Inventory for China (MEIC). By employing the Weather Research and Forecasting Model with Chemistry (WRF-Chem), two simulations were executed to assess the atmospheric environmental change by using the original MEIC emission inventory and the MEIC inventory with the UEIPP. A synthetic analysis shows that (1) compared to the power emissions of MEIC, PM$_{2.5}$, PM$_{10}$, SO$_2$ and NO$_x$ were lower, and CO, black carbon (BC), organic carbon (OC) and NMVOCs were higher in the UEIPP, reflecting a large discrepancy in the power emissions over East China; (2) In accordance with the changes of UEIPP, the modeled concentrations were reduced for SO$_2$ and NO$_x$, and increased for most areas of primary OC, BC and CO, whose concentrations in atmosphere are highly dependent on emission changes.
Interestingly, when the UEIPP was used, the atmospheric oxidizing capacity significantly reinforced, reflecting by increased oxidizing agents, e.g. O$_3$ and OH, thus directly strengthened the chemical production from SO$_2$ and NO$_x$ to sulfate and nitrate, which offset the reduction of primary PM$_{2.5}$ emissions especially in the haze days. This study indicated the importance of updating air pollutant emission inventories in simulating the complex atmospheric environment changes with the implications on air quality and environmental changes.

**Keyword:** Emission inventory; haze pollution; air quality modeling; secondary aerosols; oxidizing agents

1 Introduction

East China is one of the regions with serious air pollution and frequent haze. In these highly polluted regions, air pollutant emissions play a determinant role in deteriorating air quality, and their variations can cause a large uncertainty in air pollution modeling and prediction. It is crucial for air pollution mitigation agency to comprehensively understand anthropogenic emissions and their impacts on atmospheric environment. Emission inventories are essential for atmospheric environment research, especially for modeling study and air quality policy making.

During past decades, emission inventories covering East China were established by several groups. These include the global-scale work, such as the Reanalysis of the Tropospheric chemical composition (RETRO) (Schultz, 2007; Zheng et al., 2009), the Hemispheric Transport of Air Pollution (HTAP) (Janssens-Maenhout et al., 2015), and the Emission Database for Global Atmospheric Research (EDGAR), and the national-scale studies including the Transport and Chemical Evolution over the Pacific mission (TRACE-P) (Olivier et al., 2005), the Intercontinental Chemical Transport Experiment-Phase B (INTEX-B) (Zhang et al., 2009), the Regional Emission inventory in Asia (REAS) (Ohara et al., 2007) and the Multi-resolution Emission Inventory for China (MEIC, http://www.meicmodel.org/). Owing to
less measurements, several of these studies were based on “top-down” algorithm, which rendered the
uncertainties in estimating of emission budget and subsequently decreased the accuracy in the modeling
study of atmospheric environment. For example, previous studies showed a difference of 30 % in CO
emission among various emission inventories over East Asia, leading to an up to 8 % simulated deviation
(Amnuylojaroen et al., 2014). Regional emission inventories were developed recently in China, for the
regions of Yangtze River Delta (Huang et al., 2011; Fu et al., 2013), North China Plain (Wang et al., 2010)
and Pearl River Delta (Zheng et al., 2009), as well as several provincial and urban areas (Zhao et al., 2015;
Jing et al., 2016; He et al., 2016), with more underlying data for activity levels, emission factors, energy
combustion and traffic database obtained.

Air pollution in East China is changing from coal-smoke to mix-source polluted type, particularly the
secondary aerosols surging in severe haze episodes (Huang et al., 2014a), with more complicated
chemical reactions involving particle formations, SO₂, NOₓ, O₃ and oxidizing radicals. As a single and the
largest coal-fired sector of emission framework in China, electric power generation is believed to be the
most important source of atmospheric pollutant emissions. The power plant emissions accounted for
31-59 % of national anthropogenic emissions of SO₂ and 21-44 % of NOₓ (Zhao et al., 2008; Wang et al.,
2012). An understanding of the power plant emissions in East China and subsequently a reliable
evaluation of their environmental changes and effects using air quality models largely depend on the
accuracy of pollutant emission inventory. The pollutant emissions from coal-fired power plants were
usually estimated by the widely adopted “bottom-up” approach (Hao et al., 2002; Zhang et al., 2007b;
Zhang et al., 2007a; Ohara et al., 2007; Zhao et al., 2008). However, due to limited access to specific
information about power plants, such as the mass of pollutant emitted per unit fuel consumption or per
unit industrial production, coal-fired boiler types or accurate location of power plants (Wang et al., 2012),
the inaccuracy in estimating individual power plant emissions is always a defect that rendering intrinsic
biases between observed and modeled air pollutant concentrations. Therefore, the validations of the power plant emissions and their impacts on atmospheric environment particularly in haze episodes are still a gap.

Jiangsu Province is one of the most developed areas in East China, providing living place for a population of 79.2 million with the highest gross domestic production (GDP) per capita in China (NBSC, 2013a; JSNBS, 2013). Severe air pollution episodes of haze and photochemical pollution repeatedly shrouded this region in recent years, attracting wide scientific and governmental attention (Fu et al., 2008; Wang et al., 2014; Qi et al., 2015). As elevated emission source, the power plants emit air pollutants with high inject height in the atmosphere, leading to more significant environmental effect through regional transport than the surface emissions (e.g. vehicle emission), reflecting a potential importance of accurately estimating the power plant emissions and their influences on air quality. Based on unit-based methodology, Zhao et al. (2008) developed an inventory of coal-consuming power plants for all the provinces in China, among which five provinces including Jiangsu take up the largest coal consumption, emitting over 1000 kilotons (kt) SO\(_2\) per year and NO\(_x\) emitted from Jiangsu province with about 626 kt and 781 kt in 2005 and 2010, respectively. Alternately, the NO\(_x\) emission from Jiangsu’s power plants was estimated about 748 kt in 2005 by Wang et al. (2012), reflecting the uncertainties in the estimation of NO\(_x\) emission from power plants. China is endeavoring to control air pollution that the recent measures including construction, transfer, and implementation of techniques (e.g. flue gas desulfurization (FGD), selective catalytic reduction (SCR)/selective non-catalytic reduction (SNCR), and dust collectors, etc.) to power plants need to be assessed for their effects on mitigating air pollution.

Zhang et al. (2015) established an emission inventory of coal-fired power plants (UEIPP) by collecting the online monitoring data from power plants in atmospheric verifiable accounting tables of
Jiangsu province for 2012. The volumes of flue-gas and pollutant concentrations were measured in-site for each unit, providing the more realistic data for calculating power plant emissions than that used in previous studies. In the current work, the UEIPP was integrated into MEIC to evaluate the impact of emission change on provincial atmospheric environment, which was a major objective of this study. We presented the details of model settings, observational data and emission inventories in Sect. 2 and the modeling evaluation in Sect. 3. The impact of emission change on atmospheric environment and the underlying mechanism were discussed in Sect. 4. The study was summarized in Sect. 5.

2 Data and method

2.1 Model description and configuration

In this study, the online coupled Weather Research and Forecasting Model with Chemistry (WRF-Chem) model was configured in three nesting domains with the horizontal resolution of 45 km covering most area of East Asia, the resolution of 15 km covering Eastern China and surrounding areas, and the resolution of 5 km covering Jiangsu province and surrounding areas (Fig. 1a). Vertically, there were 35 full eta levels from surface up to 100 hPa with 7 levels below 1 km. The National Center for Environmental Prediction Final Global Forecast System operational analysis data was utilized for providing the initial and lateral meteorological conditions to WRF-Chem. Grid nudging (Stauffer and Seaman, 1990) was employed for the outmost domain every 6 hours, treating temperature, horizontal wind, and water vapor, to guarantee the precision of large-scale meteorology during the simulations.

The selected physics configurations included Morrison double-moment microphysics scheme (Morrison et al., 2009), RRTMG (Rapid Radiative Transfer Model for GCMs (Global Climate Models)) long and short wave radiation scheme (Iacono et al., 2008), Grell 3D cumulus parameterization, Yonsei University planetary boundary layer scheme (Hong et al., 2006), and Noah land surface model. For
chemistry and aerosol mechanism, the CBM-Z (Carbon Bond Mechanism; Zaveri, 1999) coupling with the 8-bin sectional MOSAIC (Model for Simulating Aerosol Interactions and Chemistry) model with aqueous chemistry (Zaveri et al., 2008) was used. The MOSAIC, treating all the important aerosols, including nitrate, sulfate, ammonium, black carbon, and primary organic aerosols and other inorganic aerosols, is efficient without compromising accuracy and widely used in air quality and regional/global aerosol models (Zaveri et al., 2008). Since the MOSAIC is incapable of simulating secondary organic aerosols (SOAs), the simulated organic aerosols mentioned hereinafter all refers to primary organic aerosols. The crucial processes of radiation feedback, dry deposition, wet scavenging and cloud chemistry were turned on. Default initial and boundary chemistry profiles in the model were selected. Biogenic emissions were calculated online by the MEGAN model (Model of Emission of Gases and Aerosol from Nature) (Guenther et al., 2006).

December 1 – 31, 2013 were selected for simulation period, since severe haze pollution events occurred frequently in this month. To alleviate the effects of initial conditions, simulation of the first 46 hours as the spin-up was discarded.

2.2 Observational data

Meteorological fields simulated by WRF are crucial for the accuracy of air quality simulation. In this study, we selected three prefecture-level cities of Nanjing, Yancheng and Lianyungang, located in the south, middle and north parts of Jiangsu province, respectively, to evaluate the overall perspective of meteorological simulation. The observed meteorological data, consisting of 2-m temperature, 2-m relative humidity and 10-m wind speed was collected from the Jiangsu Provincial Meteorological Bureau and Meteorological Information Comprehensive Analysis and Process System (MICAPS) of China Meteorological Administration (CMA). Hourly surface concentrations of chemical constituents in 13
cities of Jiangsu, including \( \text{SO}_2 \), \( \text{NO}_2 \), \( \text{PM}_{2.5} \), CO and \( \text{O}_3 \), were obtained from Jiangsu Environmental Protection Bureau. Daily secondary inorganic aerosols (SIAs; sulfate, nitrate, ammonium) in \( \text{PM}_{2.5} \) were observed using MARGA (Online Analyzer of Monitoring of Aerosol and Gases) in Jiangsu Environmental Monitoring Center (Phoenix West Street, Nanjing). MARGA is a fully autonomous sampling and measurement system that continuously measures the gases (\( \text{HCl} \), \( \text{HNO}_3 \), \( \text{HNO}_2 \), \( \text{SO}_2 \), and \( \text{NH}_3 \)) and aerosol components (\( \text{Cl}^- \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{NH}_4^+ \), \( \text{K}^+ \), \( \text{Ca}^{2+} \), and \( \text{Mg}^{2+} \)) by ion chromatography with internal standard eliminates calibration.

### 2.3 Air pollutant emission inventory

#### 2.3.1 Two inventories for power plant emissions

This study utilized the MEIC inventory as the default anthropogenic emissions. This inventory included the emissions of sulfur dioxide (\( \text{SO}_2 \)), nitrogen oxides (\( \text{NO}_x \)), carbon monoxide (\( \text{CO} \)), \( \text{NH}_3 \), black carbon (BC), organic carbon (OC), non-methane volatile organic compounds (NMVOCs), \( \text{PM}_{2.5} \), and \( \text{PM}_{10} \) by five sectors of power, industry, transportation, residential, and agriculture.

The UEIPP in Jiangsu for the year of 2012, actually consisting of six online species (\( \text{SO}_2 \), \( \text{NO}_x \), \( \text{PM}_{2.5} \), \( \text{PM}_{10} \), BC and OC), was established by Zhang et al. (2015) using the online monitoring data, which include daily concentrations of three pollutants (\( \text{SO}_2 \), \( \text{NO}_x \) and total suspended particles (TSP)) and volume of flue gases at unit and daily level. Atmospheric verifiable accounting tables, comprising accurate locations, boiler type, coal consumption, and control policies for individual plant, were adopted to calculate the CO and NMVOCs emissions in UEIPP by Zhang et al., (2016).

The \( \text{SO}_2 \), \( \text{NOx} \) and TSP emissions were reckoned directly from online concentrations and volumes of flue gases as follows:
where $A_{i,j,k}$ is the daily emitted volume of flue gas, and $c_{i,j,k}$ is the daily concentration, with $i$, $j$, and $k$ representing the pollutant species, individual plant, and day, respectively. The emissions of PM$_{2.5}$, PM$_{10}$, BC and OC were then calculated using the online TSP emissions:

$$E_{i,j,k} = T_{i,j,k} \cdot P,$$

(2)

where $T_{i,j,k}$ stands for the online TSP emissions; $P_i$ represents the PM$_{2.5}$, PM$_{10}$, BC and OC mass ratios to TSP. The online monitoring system is currently incapable of providing the mass ratios at unit level and thus, it’s given as a unified value referring to the work of Zhang et al. (2006) for each the four species, which was 52.7% (PM$_{2.5}$), 80.4% (PM$_{10}$), 8.6% (BC), and 6.1% (OC), respectively.

The annual emissions of CO and NMVOCs were calculated using Eq. (3):

$$E_{i,j,k} = A_{i,j,k} \cdot EF_{i,j,k} \cdot (1 - \eta_{i,j,k}),$$

(3)

where $A_{i,j,k}$ is the activity level, $EF_{i,j,k}$ is the uncontrolled emission factor, and $\eta_{i,j,k}$ is the removal efficiency of air pollutant control device. In refer to previous studies (Wang et al., 2005; Streets et al., 2006; Bo et al., 2008; Huang et al., 2011), the $EF_{i,j,k}$ of CO and NMVOCs was set at 4.03 g kg$^{-1}$ and 0.12 g kg$^{-1}$ respectively, and $\eta_{i,j,k}$ was set to 0.

Following the method used by Li et al., (2014) and the mechanism-dependent mapping tables developed by Cater (2013), the NMVOCs in UEIPP were specified to individual constituent in Regional Acid Deposition Model chemical mechanism (RADM2, Stockwell et al., 1990). The primary distinction, between UEIPP and the power emission inventory estimated in previous China studies, lies in the different data used and subsequently the estimation algorithm as well as the temporal resolution. Previously, power emission inventory was mostly estimated using various data such as activity levels, boiler types, fuel
types, control policies and emission factors, and the activity levels were usually collected at annually or monthly level. In the UEIPP, the emissions of SO₂, NOₓ, PM₂.₅, PM₁₀, BC, and OC were calculated using the online pollutant concentrations and volume of flue gases at daily level. Rejection heights of the UEIPP and the original power emission in MEIC were set at about 100 m and 200 m above ground, corresponding to the second and third model levels for this WRF-Chem simulation.

2.3.2 Differences between two power emission inventories

The UEIPP, MEIC power emissions and their share of total emissions over Jiangsu Province in 2012 were presented in Table 1 for contrastive analysis. Appreciable differences between the two power emissions were revealed. Firstly, in the MEIC, the power emissions of SO₂, PM₂.₅, PM₁₀ and NOₓ are 367.8 kt, 72.2 kt, 103.7 kt, and 733.8 kt respectively, and reduce to 105.6 kt, 21.6 kt, 32.6 kt and 277.9 kt respectively in the UEIPP. The notable reductions of SO₂ and NOₓ may largely due to comprehensive implementation of FGD and SCR/SNCR in Jiangsu Province, which was not promptly captured in national inventory. Application rate and average SO₂ removal efficiency of FGD in coal-fired power plants were obviously higher than those in other sectors (Zhou et al., 2016), further confirmed by abrupt decrease of SO₂’s power emission in China since 2006 (Liu et al., 2015). In addition, differences existed in estimation of NOₓ removal efficiency of SCR/SNCR for Jiangsu’s power plants in 2012 among different studies, reflecting 37 % (average of SCR/SNCR) calculated by Zhou et al. (2016) while 70 % (SCR) and 25 % (SNCR) calculated by Tian et al. (2013). In addition, due to inconsistent penetration rates and removal efficiencies of dust collectors determined at national and provincial levels, there also remained discrepancies in estimation of PM₂.₅ and PM₁₀ emissions (Xia et al., 2016; Zhou et al., 2016). However, the bias could be avoided in the UEIPP (see Section 2.3.1 for detail). The UEIPP produced higher CO (582.0 kt), BC (3.6 kt), OC (2.5 kt) and NMVOCs (17.3 kt) emissions compared to MEIC. The
power plants in MEIC produce very low emissions of BC and OC, particularly for OC with 0.0 kt, resulting largely from the high uncertainties in the emission factor of these species (Zhao et al., 2015; Zhao et al., 2011; Zhou et al., 2016). Secondly, in the MEIC inventory, the power emissions of \( \text{SO}_2 \), \( \text{PM}_{2.5} \), \( \text{PM}_{10} \) and \( \text{NO}_x \) shared larger (28.8 %, 11.3 %, 11.6 % and 35.4 %, respectively) relatively to CO, BC, OC and NMVOCs (3.7 %, 0.2 %, 0.0 % and 0.4 %, respectively) of the total emissions (Table 1). When the UEIPP was introduced to MEIC by replacing the original power emission, the shares changed. The UEIPP contributed 10.4 %, 3.7 %, 4.0 %, 17.2 %, 6.2 %, 4.3 %, 1.7 % and 0.9 %, to the total emissions of \( \text{SO}_2 \), \( \text{PM}_{2.5} \), \( \text{PM}_{10} \), \( \text{NO}_x \), CO, BC, OC and NMVOCs, respectively. The ratios of \( \text{PM}_{2.5} \) (3.7 %) and \( \text{PM}_{10} \) (4.0 %) of the UEIPP were approximate to the ratios of 4 % for \( \text{PM}_{2.5} \) and 6 % for \( \text{PM}_{10} \) calculated in Zhou et al. (2016).

Figure 2 shows the spatial distributions of two emission inventories in 2012 over Jiangsu. The two inventories exhibited the similar spatial distribution patterns with large emissions in southland and low emissions in midland and northland. The power plants around Xuzhou, an industrial city, formed a high emission center over the northwestern Jiangsu. In most areas of Jiangsu Province, the UEIPP presented lower emissions of \( \text{SO}_2 \), \( \text{PM}_{2.5} \), \( \text{PM}_{10} \) and \( \text{NO}_x \) (Fig. 2a-d), and higher emissions of BC, OC and NMVOCs (Fig. 2f-h).

To assess the simulation performance of the UEIPP and characterize changes of atmospheric environment in Jiangsu under updated emission conditions, two simulations with the original MEIC emission inventory (hereinafter referred as MOD1 simulation) and the MEIC emission inventory with the power generation replaced by UEIPP (hereinafter referred as MOD2 simulation) were carried out. The chemical differences between MOD1 and MOD2 simulations were used to assess atmospheric environmental changes in the following sections.
3 Modeling evaluation

3.1 Meteorological evaluation

An evaluation of the meteorological simulations was carried out with temperature, relative humidity (RH) and wind speeds in Nanjing, Yancheng and Lianyungang in southern, central and northern Jiangsu Province. The evaluation parameters included mean bias (MB), correlation coefficient (R) and root mean square error (RMSE) (Table 2). The R and RMSE of temperature in the three cities ranged from 0.86 to 0.94 and 2.0 °C to 3.0 °C, showing a close agreement between the simulation and observations. MB values of temperature manifested a slight underestimate in Nanjing (-1.0 °C) and Lianyungang (-0.5 °C), and overestimate in Yancheng (1.1 °C). The R of RH was 0.79, 0.79 and 0.82, with the RMSE values of 14.6%, 14.4% and 18.2%, respectively in Nanjing, Yancheng and Lianyungang, which were comparable to previous studies (Gao et al., 2016; Liu et al., 2016). The MB of RH was positive in Nanjing and Lianyungang, but negative in Yancheng. Although a slight overestimate, the variations of wind speed were well captured by the model with the R varying from 0.51 to 0.77 and the RMSE ranging from 1.8 m s⁻¹ to 2.1 m s⁻¹, conforming to the “good” model performance criteria prediction proposed by Emery et al. (2001). Overall, the meteorological fields in Jiangsu province were well reproduced by WRF-Chem during the simulation period.

3.2 Chemical evaluation

The surface observations of PM₂.₅, CO, NO₂, O₃ and SO₂ at 13 urban sites in Jiangsu (Fig. 1b) were collected for evaluating the chemical simulation in MOD1 and MOD2. Three evaluation parameters of R, mean fractional bias (MFB) and mean fractional error (MFE) were presented in Table 3. MFB and MFE could normalize bias and error for simulated-observed pair ranging from -200% to 200%, and from 0% to 200% respectively, indicating their appropriateness to evaluate performance over a wide range of
concentrations (Boylan and Russell, 2006). Normalized mean bias (NMB) and normalized mean error (NME) by individual site and pollutant were additionally presented in Table S1 in the Supplement. As shown in Table 3, the values of MFB and MFE indicated hourly variations of PM$_{2.5}$, CO and NO$_2$ were reasonably captured in both MOD1 and MOD2 simulations, conforming to the “satisfactory” criteria proposed by Morris et al. (2005) that MFB is within ±60 % and MFE is below 75 %. Given high dependence on emissions, the deviations of CO and NO$_2$ seemed largely due to their emission uncertainties. The higher R and the negative MFB of O$_3$ indicated the hourly variations were well captured but undervalued systematically, especially at night (Fig. 9b; Fig. S1). The CBM-Z scheme and the outdated land-use data from United States Geological Survey (USGS) were prone to undervalue O$_3$ concentrations near surface, due to produce high NO-titration and dry deposition rates, respectively (Balzarini et al., 2015; Park et al., 2014). Similar underestimations were previously simulated in Eastern China (Gao et al., 2015; Liao et al., 2015; Wang et al., 2016). The mean NMB and NME of O$_3$ in MOD1 simulation, calculated at -53.97 % and 67.00 % respectively (Table S1), were comparable to previous China studies (Li et al., 2012; Tang et al., 2015; Wang et al., 2016; Zhou et al., 2016), and were ameliorated respectively to -45.83 % and 63.61 % in MOD2 simulation, indicating the WRF-Chem modeling deviations of O$_3$ were acceptable. SO$_2$ was generally captured in the two simulations in terms of MFB and MFE, but with an overestimation and lower R, which may not purely due to uncertainty in emissions. In addition, absence of pathways converting SO$_2$ to sulfate in current WRF-Chem model, such as aqueous phase oxidation of dissolved S$_{\text{IV}}$ (the sum of hydrated SO$_2$ (SO$_2$ \cdot H$_2$O), bisulfite (HSO$_3^-$), and sulfite (SO$_3^{2-}$)) by dissolved NO$_2$ under conditions of high ammonia (NH$_3$) and NO$_2$ concentrations (Huang et al., 2014b; Xue et al., 2016), was partially responsible for the simulation deviations of SO$_2$ and NO$_2$. The modeled SIAs at Nanjing site (Fig. 1b) were assessed in addition. As can be seen from Table 4 and Fig. S2a, the simulated sulfate concentrations were obviously underestimated, providing further
evidence for the speculation above. Similar underestimation of sulfate was also modeled in North China Plain by Gao et al. (2016a, 2016b). The observed nitrate and ammonium concentrations were comparatively well caught, particularly the NMBs of nitrate ranged within \( \pm 20 \% \) in the two simulations. Thus, in general, the two simulations were reasonable compared with the observation data.

The R, MFB and MFE in the MOD1 and MOD2 simulations were compared in Table 3 to give an overall assessment of simulation with the UEIPP. A better simulation performance would be reflected by higher R, smaller absolute value of MFB and smaller MFE, respectively tagged with up arrows in Table 3. In response to the introduction of UEIPP, chemical simulation showed a comprehensive improvement in MOD2. The underestimation of PM\(_{2.5}\), CO and O\(_3\), and overestimation of NO\(_2\) and SO\(_2\) were simultaneously diminished in terms of MFB, respectively by 0.07, 0.21, 10.78, 3.6 and 8.26 percentage points in MOD2, where the improvements of modeling NO\(_2\), O\(_3\) and SO\(_2\) were more remarkable by the changes of R and MFE (see the up arrows in Table 3). The reason, towards primary pollutants, was the concentrations of NO\(_2\), SO\(_2\) and CO were prone to be determined by emissions under similar meteorology and thus, the deviations of NO\(_2\) and SO\(_2\) in MOD2 were mitigated more obviously due to the larger emission changes in the UEIPP (aforementioned in Section 2.3.2). In respect of secondary formation, it is difficult to explicitly characterize the evolution of PM\(_{2.5}\) and O\(_3\) through perspective of emission changes, yet their simulations in MOD2 were improved as well. The improvement of PM\(_{2.5}\) was seemingly limited when using the UEIPP, making it hardly to affirm it’s attributed to the emission improvement rather than accidental error of WRF-Chem model. However, as can be seen from Table 4, the SIAs in PM\(_{2.5}\) at Nanjing site were ameliorated, especially the nitrate and ammonium with the NMBs changed from -19.47 \% to 16.38 \%, and from -55.12 \% to -53.47 \% respectively. A logical inference was that the UEIPP provided a more realistic power emission, at least around Nanjing.
The spatial patterns in MOD1 and MOD2 simulations as well as their differences (Fig. 3) provided the further evidences for the improvement in MOD2 simulation, which could be confirmed with the improvement in the difference between observation and simulation in MOD2 in Fig. 3. The overestimates of SO₂ in MOD1 were mainly occurred in south urban areas and the vicinity of Xuzhou (Fig. 3a), where the SO₂ overestimates were mostly improved in MOD2 (Fig. 3k, f). For NO₂ simulation, the overestimates lay in the majority cities throughout Jiangsu province with a few cities underestimated such as Suzhou (Fig. 3b), and were mitigated correspondingly in MOD2 as well (Fig. 3l, g). As a common feature of MOD1 simulation, CO, PM₂.₅ and O₃ were undervalued throughout the province (Fig. 3c-e), while in response to the usage of UEIPP, their concentrations in MOD2 were comprehensively improved (Fig. 3m-o, h-j).

As above mentioned, due to the introduction of UEIPP, the MOD2 improved the simulation of air pollutants, especially of O₃, SO₂, and NO₂ according to the statistic validations and the spatial simulation performance compared with observations, which could conclude that a more realistic power emission was provided from UEIPP.

4 Environment changes with two emission inventories

4.1 Influence of emission changes on air pollutant modeling

Aside from estimating more accurate emission inventories, another important and meaningful work in this study is to explore how the emission changes affect the atmospheric environment especially in severe pollution episodes for better understanding the complexity of atmospheric environment. To this end, we presented the differences of some other compositions simulated in MOD1 and MOD2 in Figure 4. Consistently with the emission changes (Fig. 2), the concentrations is reduced for SO₂ and NO₂ (Figs. 3k and 3l), and enhanced for OC and BC (Figs. 4c and 3d) in most areas. However, it’s not clear yet what
was responsible for the enhanced O$_3$ concentration in MOD2, and why the PM$_{2.5}$ concentration enhanced when the PM$_{2.5}$ primary emission largely reduced, which were urgently needed to address especially for the abnormal increase of PM$_{2.5}$, since more implemented restrictions on power plants are being executed in East China.

As a secondary air pollutant in the boundary layer, O$_3$ is highly subjected to its precursors, solar radiation and process of planet boundary layer (Ou Yang et al., 2012; Gao et al., 2005). The Yangtze River Delta was characterized of VOC-limited, especially in winter, indicating O$_3$ concentrations were depressed by NO$_x$ and sensitive to VOC (Liu et al., 2010; Wang et al., 2008; Tie et al., 2013). Therefore, either the increase of VOC or the reduction of NO$_x$ could enhance the surface O$_3$ level. Coincidentally, the lower NO$_x$ emissions and the stronger VOC emissions are found in the UEIPP (Fig. 2). In addition, a high anti-correlation exists between the spatial difference patterns of O$_3$ and NO$_2$ (Figs. 3l and 3o) as well as the diurnal difference patterns (Figs. 9a-b). Therefore, we could attribute the underestimated O$_3$ to the overestimation of NO$_2$ in the original MEIC, and the O$_3$ simulation was improved by the UEIPP, indicating the complexity of air quality control in this region.

Quite surprising to us, the surface PM$_{2.5}$ concentrations (Fig. 3n) didn’t follow the reducing emissions of primary PM$_{2.5}$, but increased over almost all the province. As PM$_{2.5}$ is highly dependent on three factors of primary emissions, physical processes and chemical reactions in the atmosphere, the latter two factors were more likely to dominate in the simulation of increasing PM$_{2.5}$ concentrations. It was deemed that the interesting phenomenon would be induced by some physical processes. Due to the absorbing effects of BC to solar radiation and the higher rejection height of power plants (the chimney height of new constructed coal-consuming power plants of larger than 300 MW is higher than 200 m according to Environmental Protection Agency (EPA) in China; the rejection height was set at two model
levels of 100 m and 200 m in this study), the enhancement of BC concentrations (Fig. 4f; Table 5) would result in an elevated warmer layer in the atmosphere, and thus suppressing vertical diffusion below it and accumulating more pollutants near surface. The changes of downward short wave flux at ground surface (SWDOWN) and 2 m air temperature as well as boundary layer height (BLH) could be also used to interpret the speculation. The SWDOWN reduced 0.65 W m$^{-2}$, 2 m air temperature decreased about 0.005 K, and BLH reduced 0.4 m averaged over the province in MOD2 simulation, which revealed the increased air stability for more air pollutant accumulation.

4.2 Reinforcing atmospheric oxidation capacity and enhancing secondary inorganic aerosols

As described in Sect 4.1, the declined emissions of primary PM$_{2.5}$ could not enhance the ambient PM$_{2.5}$ concentrations, implying the contribution of chemical production to the ambient PM$_{2.5}$ enhancement. We here studied the chemical production of SIAs, since the CBM-Z/MOSAIC used is incapable of simulating SOAs with missing pathways of SOAs formation in the WRF-Chem. Previous studies had revealed that SIAs played an important role in PM$_{2.5}$, particularly in the haze pollution over Eastern China (Huang et al., 2014a; Wang et al., 2014; Gao et al., 2016). Given the reduction of SO$_2$ and NO$_x$ emissions in the UEIPP, the simulated sulfate and nitrate should be lower from the oxidation of SO$_2$ and NO$_2$. However, as shown in Fig. 4, both sulfate and nitrate are increased in MOD2, with more significantly during haze episode (Dec.3-8; Fig. 5). In the atmosphere, sulfate is formed through oxidation of SO$_2$ by gas-phase reactions with OH (Stockwell and Calvert, 1983; Blitz et al., 2003) and stabilized Criegee intermediate (which is formed by O$_3$ and alkenes) (Mauldin III et al., 2012) as well as by heterogeneous reactions with H$_2$O$_2$, O$_3$, OH, organic peroxides, and various oxides of nitrogen in clouds (Seinfeld and Pandis, 2012). Nitrate is mostly formed from the gas-phase reactions of NO$_2$ with OH during daylight and heterogeneous reactions of nitrate radical (NO$_3$) at night. Therefore, the formations
of secondary sulfate and nitrate depend not only on their precursors, but also on oxidizing capacity of atmosphere.

In this section, the variations of O$_3$, a major oxidizing agent in atmosphere, were employed to evaluate the changes of atmospheric oxidizing capacity between MOD1 and MOD2. Figure 6 showed the ratios of surface HCHO/NO$_y$ in Jiangsu province averaged over the simulation. The ratio of HCHO/NO$_y$ concentrations increased from 0.039 in MOD1 to 0.047 in MOD2 when using the UEIPP with lower NO$_x$ and higher VOC emissions. The atmospheric environment in VOC-limited condition indicates that the MOD2 condition could level up O$_3$ concentration. Additionally, as a precursor of O$_3$, high CO concentrations in MOD2 would contribute to the build-up of O$_3$ as well. The OH radical concentrations were also increased (Fig. 4b) because of its high dependence on O$_3$, thus resulting in enhanced oxidizing capacity of the atmosphere in Jiangsu region.

To evaluate how the formation of secondary aerosols responded to the enhanced oxidizing capacity, we analyzed the BC-scaled concentrations for sulfate and nitrate. The purpose was to eliminate the influence of air pollutant dilution and mixing in atmospheric physical process. Since BC is quite inertial to chemical reactions, its variations could well reflect the atmospheric physical processes. Thus, the BC-scaled concentration will better represent the contribution of chemical reaction (Zheng et al., 2015). Figure 7 presents the daily averaged variation of BC-scaled concentrations for sulfate and nitrate, appending the differences of O$_3$ as an indicator for the change of atmospheric oxidizing capacity. As can be seen from Fig. 7, the enhancement of chemical production simulated in MOD2 was consistent well with the variations of O$_3$ difference between MOD2 and MOD1. During the haze episode of Dec. 3-8, 2013 the chemical production of sulfate and nitrate enhanced obviously, which exactly in accordance with the rapid build-up of O$_3$, which indicated the chemical production is intensified by strengthen of oxidizing
capacity during the episode.

The SOR (molar ratio of sulfate to sum of sulfate and SO$_2$) and NOR (molar ratio of nitrate to sum of nitrate and NO$_2$) were used as indicators of secondary transformation (Sun et al., 2006), since the BC-scaled concentrations just represent the intensity of chemical reaction effects with overlooking the precursors for individual compounds. The SOR and NOR would give insights to the chemical transformation of SO$_2$ and NO$_2$. As shown in Figure 8, aside from the haze period of Dec. 3-8, 2013, the chemical transformations from SO$_2$ and NO$_x$ to sulfate and nitrate were always strengthened in MOD2. That could be why the chemical production of sulfate and nitrate in MOD2 increased (Figs. 7a-b) even with less precursor concentrations. Additionally, in response to the enhanced atmospheric oxidizing agents, the secondary ammonium was also increased (Fig. 6) under the same NH$_3$ emission conditions in MOD1 and MOD2.

As shown in Table 5, the total concentration of sulfate, nitrate and ammonium increased by 1.32 ug m$^{-3}$ during the whole month and 4.77 ug m$^{-3}$ in the haze episode of Dec. 3-8, 2013, higher than the increment of PM$_{2.5}$ as well as the total increment of BC and OC, which could clearly reveal that enhancement of SIAs in response to the reinforced atmospheric oxidizing capacity contributed the majority to the increased PM$_{2.5}$ concentrations. This conclusion could be verified by an emission sensitivity study in the North China Plain performed by Wang et al., (2016), who found that the 30 % emission reduction of NO$_x$ led to a notable increase in PM$_{2.5}$ concentrations contributing to NH$_3$-rich and VOC-limited conditions in the winter there.

**5 Conclusions**

Power plant, as a major air pollution source in China, had been imposed restrictions by the government in response to the increasing air pollution, which led power plant emissions to large variations
during the past few years. Due to various underlying data and approaches, there remained uncertainties in estimating the power plant emission inventory. In the present study, the UEIPP in Jiangsu province for 2012 was introduced in the MEIC inventory as major point sources of emissions. The variation and complexity of atmospheric environment in response to the change of power plant emissions over Jiangsu were studied, by executing two WRF-Chem simulations using the original emissions of MEIC and the MEIC with its power emission inventory updated by the UEIPP.

The study revealed the uncertainty and complexity in estimating the power plant emissions due to various data and strategies, such as implementation of FGD, SCR/SNCR and dust collectors over recent years in East China. In the UEIPP, the emission amounts of SO$_2$, PM$_{2.5}$, PM$_{10}$, NO$_x$, CO, BC, OC and NMVOCs were 105.6 kt, 21.6 kt, 32.6 kt, 277.9 kt, 582.0 kt, 3.6 kt, 2.5 kt, and 17.3 kt, respectively, manifesting obvious difference with the MEIC emission inventory. The reduction of SO$_2$, NO$_2$, PM$_{2.5}$ and PM$_{10}$ in the UEIPP quantified the effects of FGD, SCR/SNCR and dust collectors, which partially omitted in national works.

The UEIPP drove the simulation performance superior to the original power emission of MEIC inventory in terms of the proximity between simulated and observed air pollutant concentrations, suggesting a more realistic power emission inventory was provided. The complexity of atmospheric environment and difficulty in policy making to protect air quality were revealed as well, through comparing the changes of various primary and secondary compositions in atmosphere. Atmospheric oxidizing capacity was reinforced in response to the enhancement of O$_3$ and OH, which was largely due to lower NO$_x$ and higher VOC emissions in the UEIPP and the VOC-dominated conditions. PM$_{2.5}$ increased almost all over the province even the primary emission reduced by 7.6%. This anomaly phenomenon was mainly attributed to the enhanced formation of SIAs, induced by the enhanced
atmospheric oxidizing capacity, revealing the complex mechanism of air pollution from fine particulate matter to atmospheric oxidants. Our study also revealed the reaction of physical processes in response to the chemical changes through investigating the changes in surface solar radiation, temperature and boundary layer height.

Given the complicated processes in environmental change, the restrictions of emissions should be comprehensively considered rather than one single factor. Furthermore, the effects of emission inventories on seasonal variation in air quality could be assessed based on long-term observation and simulation studies, and formation of SOAs would be also enhance due to the reinforced atmospheric oxidizing capacity and higher VOC emissions, which needs to be addressed in future studies.

6 Acknowledgements

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Zhou, Y., Zhao, Y., Mao, P., Zhang, Q., Zhang, J., Qiu, L., and Yang, Y.: Development of a high-resolution emission inventory and its evaluation through air quality modeling for Jiangsu Province, China, Atmospheric Chemistry and Physics Discussions, 1-50, 10.5194/acp-2016-567, 2016.
Table 1: The UEIPP, MEIC’s power emission inventory and their ratio in total emission inventory over Jiangsu Province in 2012.

<table>
<thead>
<tr>
<th></th>
<th>UEIPP</th>
<th></th>
<th>MEIC power emission</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Emission (kt year⁻¹)</td>
<td>Ratio in total (%)</td>
<td>Emission (kt year⁻¹)</td>
<td>Ratio in total (%)</td>
</tr>
<tr>
<td>SO₂</td>
<td>105.6</td>
<td>10.4</td>
<td>367.8</td>
<td>28.8</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>21.6</td>
<td>3.7</td>
<td>72.2</td>
<td>11.3</td>
</tr>
<tr>
<td>PM₁₀</td>
<td>32.6</td>
<td>4.0</td>
<td>103.7</td>
<td>11.6</td>
</tr>
<tr>
<td>NOₓ</td>
<td>277.9</td>
<td>17.2</td>
<td>733.8</td>
<td>35.4</td>
</tr>
<tr>
<td>CO</td>
<td>582.0</td>
<td>6.2</td>
<td>343.5</td>
<td>3.7</td>
</tr>
<tr>
<td>BC</td>
<td>3.6</td>
<td>4.3</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>OC</td>
<td>2.5</td>
<td>1.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>NMVOCs</td>
<td>17.3</td>
<td>0.9</td>
<td>7.2</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 2: Statistics between observed and simulated meteorology.

<table>
<thead>
<tr>
<th></th>
<th>Nanjing</th>
<th>Yancheng</th>
<th>Lianyungang</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs.</td>
<td>Mod.</td>
<td>MB</td>
<td>R</td>
</tr>
<tr>
<td>T (°C)</td>
<td>4.8</td>
<td>3.8</td>
<td>-1.0</td>
</tr>
<tr>
<td>RH (%)</td>
<td>63.0</td>
<td>63.6</td>
<td>0.6</td>
</tr>
<tr>
<td>WS (m s⁻¹)</td>
<td>2.0</td>
<td>3.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 3: Statistics variables between observed and simulated PM₂.₅, CO, NOₓ, O₃ and SO₂.

<table>
<thead>
<tr>
<th></th>
<th>MOD1</th>
<th>MOD2</th>
<th>MOD1</th>
<th>MOD2</th>
<th>MOD1</th>
<th>MOD2</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>0.568</td>
<td>0.571 †</td>
<td>-8.31</td>
<td>-8.24 †</td>
<td>45.40</td>
<td>45.65</td>
</tr>
<tr>
<td>MFB (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>0.516</td>
<td>0.515</td>
<td>-36.05</td>
<td>-35.84 †</td>
<td>52.05</td>
<td>52.10</td>
</tr>
<tr>
<td>CO</td>
<td>0.456</td>
<td>0.466 †</td>
<td>14.08</td>
<td>10.48 †</td>
<td>39.37</td>
<td>38.77 †</td>
</tr>
<tr>
<td>NOₓ</td>
<td>0.600</td>
<td>0.625 †</td>
<td>-121.46</td>
<td>-110.68 †</td>
<td>131.74</td>
<td>124.67 †</td>
</tr>
<tr>
<td>O₃</td>
<td>0.260</td>
<td>0.261 †</td>
<td>24.88</td>
<td>16.62 †</td>
<td>65.18</td>
<td>63.20 †</td>
</tr>
<tr>
<td>SO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Up arrows indicate the chemical simulation results in MOD2 are better than those in MOD1; R, MFB and MFE are calculated using the following equations (P and O are simulation and observation, respectively; N is the number of measurements, and M is the number of monitoring sites):

\[
R = \frac{1}{M} \sum_{i=1}^{M} \left[ \frac{1}{N} \sum_{j=1}^{N} (P_{ij} - \bar{P})(O_{ij} - \bar{O}) \right] \sqrt{\frac{1}{N} \sum_{j=1}^{N} (O_{ij} - \bar{O})^2} 
\]

\[
MFB = \frac{1}{N \cdot M} \sum_{i=1}^{N} \sum_{j=1}^{M} \left( \frac{P_{ij} - O_{ij}}{P_{ij} + O_{ij}} \right) \cdot 100\% ; \quad MFE = \frac{1}{N \cdot M} \sum_{i=1}^{N} \sum_{j=1}^{M} \left| \frac{P_{ij} - O_{ij}}{P_{ij} + O_{ij}} \right| \cdot 100\%
\]
Table 4 Performance statistics of SIAs in PM$_{2.5}$ at Nanjing site.

<table>
<thead>
<tr>
<th></th>
<th>MOD1</th>
<th>MOD2</th>
<th>MOD1</th>
<th>MOD2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate</td>
<td>-87.61</td>
<td>-87.29</td>
<td>87.61</td>
<td>87.29</td>
</tr>
<tr>
<td>Nitrate</td>
<td>-19.47</td>
<td>-16.38</td>
<td>29.06</td>
<td>28.61</td>
</tr>
<tr>
<td>Ammonium</td>
<td>-55.12</td>
<td>-53.47</td>
<td>55.12</td>
<td>53.47</td>
</tr>
</tbody>
</table>

* Up arrows indicate the same meaning as in Table 3. NMB and NME are calculated using the following equations:

\[
NMB = \frac{\sum_{i=1}^{N} (P_i - O_i)}{\sum_{i=1}^{N} O_i} \cdot 100\%; \quad NME = \frac{\sum_{i=1}^{N} |P_i - O_i|}{\sum_{i=1}^{N} O_i} \cdot 100\%.
\]

Table 5 Increased concentrations (ug m$^{-3}$) and percentages for the (1) PM$_{2.5}$, (2) total of BC and OC, and (3) total of sulfate, nitrate and ammonium, averaged over Jiangsu province in MOD2 simulation from that in MOD1 simulation.

<table>
<thead>
<tr>
<th></th>
<th>PM$_{2.5}$</th>
<th>BC+OC</th>
<th>Sulfate+Nitrate+Ammonium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hazy days (Dec.3-8)</td>
<td>3.38 (1.81 %)</td>
<td>1.04 (3.06 %)</td>
<td>4.77 (5.11 %)</td>
</tr>
<tr>
<td>The whole (Dec.1-31)</td>
<td>1.03 (0.83 %)</td>
<td>0.58 (2.38 %)</td>
<td>1.32 (3.96 %)</td>
</tr>
</tbody>
</table>
Figure 1 Model domains (a) and the locations of 13 cities in Jiangsu (b).

Cities:
1. Nanjing
2. Wuxi
3. Xuzhou
4. Changzhou
5. Suzhou
6. Nanjing
7. Lianyungang
8. Huai'an
9. Yancheng
10. Yangzhou
11. Zhenjiang
12. Taizhou
13. Suqian
Figure 2 Spatial distributions of power plant emissions of MEIC (shaded grids) and the UEIPP (shaded circles) in 2012 (unit: tons); the UEIPP has been mapped into 0.25°×0.25° grids, consistent with the spatial resolution of MEIC.
Figure 3 The spatial distributions of near-surface SO$_2$, NO$_2$, CO, PM$_{2.5}$ and O$_3$ mean concentrations from MOD1 (a-e), MOD2 (f-j) and their differences (MOD2-MOD1; k-o) in December 2013; the observed mean concentrations were indicated by shaded circles. Unit: ug m$^{-3}$.

Figure 4 Differences of chemical constituents in December 2013 (MOD2 - MOD1). Unit: “pptv” for OH; “ug m$^{-3}$” for the others.

Figure 5 Chemical species of PM$_{2.5}$ simulated in MOD1 (left) and MOD2 (right) in December 2013.
Figure 6 Ratios of HCHO/NO\textsubscript{y} simulated in MOD1 (blue) and MOD2 (red); the threshold ratio of VOC-limited and NO\textsubscript{x}-limited is 0.28.

Figure 7 Daily variations of sulfate/BC (a), nitrate/BC (b) and difference of O\textsubscript{3} ((c); MOD2 - MOD1) averaged over Jiangsu with the two red rectangular columns marking two haze episodes; the increase of sulfate/BC and nitrate/BC suggests enhanced chemical productions.
Figure 8 Daily variations of SOR (a) and NOR (b).

Figure 9 Diurnal variations of NO$_2$ (a) and O$_3$ (b) averaged over 13 cities in Jiangsu (Fig. 1b)