Model Evaluation and Uncertainty Analysis of PM_{2.5} Components over Pearl River Delta Region Using Monte Carlo Simulations

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ABSTRACT

Sulfate, nitrate, ammonium, organic carbon (OC) and black carbon (BC) are the key components of PM_{2.5}, but predicting their concentrations remains a challenge because of high uncertainties in the modeling. Employing the Nested Air Quality Prediction Modeling System (NAQPMS) developed by the Institute of Atmospheric Physics, Chinese Academy of Sciences, this study investigated the uncertainties in Monte Carlo simulations of these aerosols in the Pearl River Delta (PRD) region during 2015. 50 ensemble simulations with a 15 km horizontal resolution were derived by perturbing the emission data for sulfate, nitrate, ammonium, OC and BC from an emission inventory, which is one of the largest sources of uncertainty. Then, surface observations of these species collected from 10 sites across the region for 1 year were used to evaluate the performance of the ensemble simulations. The high correlation coefficients (> 0.74) and low mean biases (< 2 µg m⁻³) between the mean values of the ensemble and the observation data suggested that the model fairly accurately reproduced spatial and temporal variations in the nitrate, ammonium, OC and BC. However, the predicted sulfate concentrations, which displayed a correlation coefficient of 0.26, were far less reliable, particularly owing to the significant underestimation during winter. Further analysis revealed that uncertainties in the emission data explained most of the discrepancies for the OC and BC, but the mean biases for the sulfate and ammonium, especially during winter, probably stemmed from uncertainties in the heterogeneous reaction modeling.

Keywords: PM_{2.5} components, PRD region, Monte Carlo simulations, Uncertainty analysis

1 INTRODUCTION

The PRD region is one of three major city clusters located in southern China, and frequently experiences serious levels of haze pollution (Zhang *et al.*, 2008; Fu *et al.*, 2019) with high concentrations of PM_{2.5} (particulate matter with aerodynamic diameter less than 2.5 µm), leading to the sharp decline of visibility and negative health effect (Zheng *et al.*, 2015; Liu *et al.*, 2016). Sulfate, nitrate, ammonium, organic carbon (OC) and black carbon (BC) are the key components

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found in $PM_{2.5}$. Among these components, the sum of sulfate, nitrate and ammonium is regarded as the secondary inorganic aerosol (SIA) (Wang *et al.*, 2019). The proportion of SIA often increases with the increase of the $PM_{2.5}$ concentrations, even can reach 50% during serious haze days (Zhang *et al.*, 2018), which indicates that SIA is a major cause of heavy pollution processes (Yue *et al.*, 2015). OC, as carbonaceous aerosols can change the global climate by impacting the surface tension of cloud droplets (Cao *et al.*, 2006), and BC plays an important role in radiative forcing due to its ability to absorb solar radiation (Hand *et al.*, 2013). Therefore, high-accuracy simulation of those components is very important for establishing effective control measures for air pollution, and it is also a key factor for climate modeling.

Air quality models are valuable tools to help scientists and policy makers to understand the process of air pollution better and to establish effective control measures for haze formation. However, many model evaluations have found that the prevailing air quality models still exhibit significant bias in the simulation of $PM_{2.5}$ components (Quan *et al.*, 2015; Zheng *et al.*, 2015; Li *et al.*, 2018). For example, Kim *et al.* (2006) did a 3-week simulation in East Asia and found that the simulated nitrate could exceed the actual concentrations by 2–8 times. Li *et al.* (2014) used the Community Multiscale Air Quality (CMAQ) model to simulate a heavy pollution process in the Yangtze River Delta and found that the model obviously underestimated sulfate. Zheng *et al.* (2015) found that CMAQ overestimated the OC and BC. The bias of $PM_{2.5}$ components will not only seriously affect the simulation of $PM_{2.5}$, but also bring great uncertainty to the studies of heavy pollution. Model biases in the $PM_{2.5}$ component may be caused by the uncertainty in the resolution of model grids (Mallet and Sportisse, 2006), meteorology simulations (Hou *et al.*, 2018; Ma *et al.*, 2020), emission (Renner and Wolke, 2010; Dong *et al.*, 2016), and the physical and chemical processes (Qiu *et al.*, 2019). For example, recent research shows that urban expansion and anthropogenic heat can change the weather conditions and air quality around the big cities of South China (Xie *et al.*, 2016; Zhu *et al.*, 2017), which are not considered in the current model and would bring uncertainty to simulations. In effort to improve the model performance and understand the atmospheric chemistry and physical process better, reasonably estimating the contribution of different potential sources of simulation biases of $PM_{2.5}$ components is necessary. The ensemble simulation based on Monte Carlo algorithm is one of the effective methods to identify modeling uncertainties. It can simultaneously analyze the uncertainty of hundreds of input and parameters of the model with relatively small computational cost and has been applied widely in the field of air quality. For example, Tang *et al.* (2010) used the ensemble simulation to evaluate the impact of emission on ozone simulation in Beijing and proposed a more reasonable direction for ozone management and control.

Although a large number of studies on $PM_{2.5}$ modeling have been carried out (Chen *et al.*, 2019; Zhai *et al.*, 2019), the research about evaluation and uncertainty investigation of $PM_{2.5}$ components modeling for long-term and multi-station observation over PRD region are still rare. Emission as one of the critical sources of uncertainty in the air quality model, assessing its uncertainty is of great significance to explain the simulation error of $PM_{2.5}$ components and also has important reference value for distinguishing the relative importance of emission error and other errors (such as meteorological error or chemical process error), which can deepen our understanding of the atmospheric chemical process to a certain extent. At the same time, considering that the Nested Air Quality Prediction Modeling System (NAQPMS) developed by the Institute of Atmospheric Physics, Chinese Academy of Sciences is the chemical transport model used by routine air quality forecast over PRD region, this paper used NAQPMS to construct a Monte Carlo-based ensemble simulation system, which took the emission uncertainty into account, to evaluate and investigate the simulating uncertainty of the key components (SO_4^{2-} , NO_3^- , NH_4^+ , OC and BC) over PRD region for long-term periods and multiple observation stations. The rest of the paper is organized as follows: The setting of the model and the construction of the ensemble system were introduced in “Methods.” Simulation performance and uncertainty analysis of $PM_{2.5}$ components were analyzed in “Results and Discussion.” Conclusions and recommendations for future research were provided in “Conclusions.”

2 METHODS

2.1 Model Description and Setup

2.1.1 Description of NAQPMS model

The air quality model adopted in this paper is the Nested Air Quality Prediction Modeling System developed by the Institute of Atmospheric Physics, Chinese Academy of Sciences (Wang *et al.*, 2006). The NAQPMS has been widely used in many scientific research and air quality forecasts (Wang *et al.*, 2001; Tang *et al.*, 2013). NAQPMS is a three-dimensional regional Eulerian chemical transport model that encompasses emissions, dry and wet deposition, diffusion, advection (convection), gas-phase reaction, aqueous-phase reaction, heterogeneous reaction and other major atmospheric physical and chemical processes. Dry deposition is simulated using the Wesely scheme (Walmsley and Wesely, 1996). Wet deposition and aqueous-phase chemistry module adopted the improved chemistry mechanism based on the Regional Acid Deposition Model (RADM) mechanism (Chang *et al.*, 1987). The gas-phase chemistry adopted the Carbon Bond Mechanism Z (CBM-Z) (Zaveri, 1999), including 134 gas chemical reactions. For the aerosol process, NAQPMS used the aerosol thermodynamic module ISORROPIA 1.7 to treat the gas-to-particle partitioning and thermodynamic equilibrium for sulfate, nitrate and ammonium (Nenes *et al.*, 1998). To consider the interaction between gas and aerosol, NAQPMS considered 14 chemical compounds and 28 heterogeneous reactions including sulfate, black carbon, dust and sea salt (Li *et al.*, 2012). Heterogeneous reactions are parameterized as a pseudo-first-order irreversible rate constant, which are calculated by Eq. (1) proposed by Jacob (2000):

$$K_i = \left(\frac{r}{D_i} + \frac{4}{v_i \gamma_i} \right) \times A \quad (1)$$

where i is the reactant for heterogeneous reactions, r is the mean radius of the particles, D_i is the gas-phase diffusion coefficient of reactant i , v_i is the mean molecular speed of the gas, γ_i is the uptake coefficient of reactant i , and A is the aerosol surface area per unit volume of air.

For different temperature, humidity and particle surface characteristics, the uptake coefficient may vary by several orders of magnitude. Therefore, for some specific particulate- and gas-phase pollutants, the influence of RH and temperature on the uptake coefficient is considered. Further detailed information on the uptake coefficient (γ) can be found in Li *et al.* (2012).

2.1.2 Setting of model

Fig. 1 demonstrates the model domain of the Weather Research and Forecasting model (WRF v3.6) in this study. The domain is defined in a Lambert conform projection, and Domain 2 includes 432×339 grid points with a 15 km horizontal resolution. Vertically, the model calculates pollutants' concentration among 20 layers with the height of the top layer being 20 km. The central longitude and latitude of the domain region are 34°N and 105°E , respectively, and we focus on the PRD region centered in Guangzhou.

We did a simulation period from 17 December 2014 to 31 December 2015. The first 15 days were used as the "spin-up" time of NAQPMS. The Weather Research and Forecasting model was employed to provide the hourly meteorological inputs to NAQPMS. In the daily meteorological simulation, WRF runs have been integrated over individual 36-hour period. Each run included a meteorological "spin-up" time that took place in the first 12 hours of meteorological input and the data of the remaining 24 hours were used for NAQPMS. The meteorological input is critical to the pollutant simulation since the meteorological parameter influences the transport process and aerosols formation. The meteorological simulation was evaluated with the daily observations from China Meteorological Administration. Fig. 2 shows a time series comparison of observed and simulated temperature, relative humidity and wind speed at Qingyuan site. This site also has been marked on Fig. 1 to show its position. In general, WRF can reproduce the temporal distribution characteristics of major meteorological factors during simulation period, which can provide reliable input data for NAQPMS. The initial and boundary conditions of WRF were

Fig. 1. Model domain (left) and the spatial distributions (right) of the monitoring stations used in the evaluation of aerosol component simulations over PRD region. The blue dot is the meteorological observation station. The full name of each station is shown in Table 2.

Fig. 2. Time series of simulated (red) and observed (black) daily averaged meteorological parameters at Qingyuan site in Guangdong Province during 2015.

provided by $1^\circ \times 1^\circ$ reanalysis data from the National Center for Atmospheric Research/National Centers for Environmental Prediction (NCAR/NCEP). The parameterized settings of WRF are as follows: The microphysics scheme used the WRF Single Moment 3 (WSM3) simple ice scheme, the boundary layer scheme selected the Yonsei University (YSU) scheme, the long-wave radiation chose the rapid radiative transfer model (RRTM) scheme, the short-wave radiation selected Dudhia scheme, and the land surface process used Noah land surface process scheme.

In this paper, anthropogenic emissions from Hemispheric Transport of Air Pollution (HTAP_v2.2) emissions inventory for the year 2010, including the Multi-resolution Emission Inventory for China (MEIC) that was developed by Tsinghua University and NH_3 emission inventory for China was updated by Peking University (Janssens-Maenhout *et al.*, 2015; Li *et al.*, 2017). HTAP_v2.2 also provided air and ship emissions with an annual resolution. Hourly biomass burning emissions were provided by the Global Fire Emissions Database (GFED v4; Randersom *et*

et al., 2017), and Model of Emissions of Gases and Aerosols (MEGAN v2.04) was employed for biogenic volatile organic compound (BVOC) emissions (Sindelarova *et al.*, 2014).

2.1.3 Ensemble simulations of PM_{2.5} components

Ensemble simulations with 50 ensemble members and a 15 km horizontal resolution were performed. The Monte Carlo method can simultaneously analyze the influence of multiple sources of uncertainty on the model and is frequently used to address the uncertainty issue.

The steps of Monte Carlo uncertainty analysis are as follows:

2.1.3.1 Estimation of uncertainty in emission inventory

Considering the emission inventory of Zhang *et al.* (2009) and the MEIC were developed by the same group of Tsinghua University that the uncertainty in emission inventory of Zhang *et al.* (2009) can roughly represent the uncertainty ranges in the MEIC (Li *et al.*, 2017). Therefore, the emission uncertainties in this paper were set according to estimation of uncertainty in emission inventory of Zhang *et al.* (2009), and the setting is shown in Table 1.

2.1.3.2 Random perturbations of the emissions

The ensemble samples of perturbed emissions can be regarded as a product of the initial emissions and the perturbation coefficient, as shown in Eq. (2), where X_j represents the j^{th} sample of perturbed emission, X represents the initial emissions, P_j is the j^{th} sample of perturbation coefficient, P of each species follows the Gaussian distribution with the mean of 1 and the standard deviation equal to the uncertainty in the initial emission of corresponding species. N is the size of the ensemble. The size of 50 can reduce spurious correlation in the case of using finite ensemble samples, which have been proved credible in previous studies (Hanna, 1998; Tang *et al.*, 2013). 50 smooth pseudo-random perturbation fields were generated based on the method of Evensen (1994), the algorithm used to obtain samples of perturbed emission was based on Fortran programming language and the statistical analysis was based on MATLAB programming language.

$$X_j = X \cdot P_j \quad j = 1, 2, \dots, N \quad (2)$$

2.1.3.3 Ensemble simulations of aerosol components

By taking 50 perturbed emissions as the input of NAQPMS to obtain 50 simulation results, a simulation set containing emission uncertainty was established to investigate the impact of emission uncertainty on the simulation of aerosol components.

2.1.3.4 Uncertainty analysis of aerosol component

The variation coefficient (CV) was employed to calculate the modeling uncertainty, which can quantify the impact of the uncertainties in emission inventory on the simulation of the PM_{2.5} components. The calculation formula is illustrated in Eq. (3), where σ is the standard deviation of ensemble simulation, $\bar{x}$ is the mean value of ensemble simulation. Then we display the spread of the simulated concentrations derived from the ensemble simulations by box plot. The spread represents the degree of the response of the PM_{2.5} components simulation to the emission perturbations. It can also be regarded as the “uncertainty” in simulations of PM_{2.5} components, which is caused by the assumed uncertainties of initial emissions. In addition, the comparison between ensemble simulation and observation can be used to analyze the contribution of emission uncertainty to the modeling errors of PM_{2.5} components.

$$CV = \frac{\sigma}{\bar{x}} \cdot 100\% \quad (3)$$

2.2 Observation Data

This study used the surface observations from 10 sites in PRD region for 1 year to evaluate the simulation of sulfate, nitrate, ammonium, OC and BC. The observation data was from the Secondary Composition Network in PRD region and provided by the Environmental Monitoring

Table 1. Uncertainty of initial emissions.

Species	SO ₂	NO _x	NH ₃	NMVOC	CO	PM ₁₀	PM _{2.5}	BC	OC
Uncertainty	±12%	±31%	±53%	±68%	±70%	±132%	±130%	±208%	±258%

Table 2. Information of monitoring stations.

City	Station	Long.	Lat.	Height	Type of station	Functional
Guangzhou	Modiesha (MDS)	113.33	23.11	50	Regional station	Residential area
Jiangmen	Huanguoshan (HGS)	112.93	22.73	–	Super station	Suburb
Guangzhou	Wanqinsha (WQS)	113.55	22.71	12	Regional station	School
Guangzhou	Tianhu (TH)	113.63	23.65	13	Regional station	Park
Zhaoqing	Chenzhong (CZ)	112.47	23.05	14	City station	Residential area
Dongguan	Nanchengyuanlin (NCYL)	113.75	23.03	36	City station	Park
Huizhou	Xijiao (XJ)	114.11	23.34	7	Regional station	Residential area
Jiangmen	Ruifen (RF)	112.76	22.06	15	Regional station	Residential area
Zhuhai	Jida (JD)	113.57	22.26	8	City station	Park
Shenzhen	Xili (XL)	113.97	22.60	–	Super station	School

Center in Guangdong Province. Samples were collected every 6 days, and each sampling period was 24 hours. The specific information of monitoring stations is described in Table 2 and the distribution of the monitoring stations is displayed in Fig. 1.

3 RESULTS AND DISCUSSION

3.1 Evaluation of Sulfate, Nitrate, Ammonium, BC and OC Simulations

In this section, we evaluated the model performance of PM_{2.5} components for 1 year and 10 observation sites by comparing the simulated ensemble mean and the observed concentrations of PM_{2.5} components.

Model performance has been evaluated by statistical metrics as follows: simulated mean, observed mean, mean bias (MB), correlation coefficient (R), root mean square error (RMSE), mean fractional error (MFE) and mean fractional bias (MFB). The complete definition of those statistical metrics are shown in the supplementary material.

3.1.1 Sulfate, Nitrate and Ammonium

Fig. 3 shows the spatial distributions of seasonal mean concentrations of sulfate, nitrate and ammonium. From the observations, the spatial distributions of sulfate, nitrate and ammonium presented a characteristic of “northwest–southeast” decreasing. The temporal distributions were characterized by high concentrations in winter and low concentrations in summer. The spatial and temporal distributions of nitrate and ammonium were strongly captured by the model, but the model failed to reproduce the high concentrations of sulfate in winter. Fig. 4 shows the time series of the modeled and observed monthly concentrations of sulfate, nitrate and ammonium among 10 sites over PRD region in 2015. For sulfate, the simulated annual mean concentration was 6.39 $\mu\text{g m}^{-3}$, which was 2.24 $\mu\text{g m}^{-3}$ lower than observations (8.63 $\mu\text{g m}^{-3}$), and RMSE was 4.01 $\mu\text{g m}^{-3}$. Compared to other aerosols, the RMSE and MB of sulfate were larger. Though MFB and MFE reached the “acceptable” range, the correlation was weak. From monthly variations, the sulfate was significantly underestimated in January to March, May, June, October to December, especially in January and February. Moreover, the model underestimated the annual mean sulfate concentrations at most sites. The above results suggested that the model significantly underestimated the sulfate concentrations over PRD region. For nitrate, the observed annual mean concentration was 3.38 $\mu\text{g m}^{-3}$, and the simulated annual mean concentration was 4.90 $\mu\text{g m}^{-3}$. The MB and RMSE were 1.52 $\mu\text{g m}^{-3}$ and 2.47 $\mu\text{g m}^{-3}$, respectively. Not only did the MFB and MFE have reached the “acceptable” range, but also the correlation was strong ($R = 0.85$). However, the model exhibited pronounced overestimation of nitrate in February, April,

Fig. 3. Simulated (shaded circles) and observed (solid circles) seasonal mean surface sulfate, nitrate and ammonium concentrations ($\mu\text{g m}^{-3}$) in PRD region in 2015. MAM = March, April, and May; JJA = June, July, and August; SON = September, October, and November; DJF = December, January, and February. The simulated results are from the simulation with $15\text{ km} \times 15\text{ km}$ horizontal resolution.

July to September and December. Overall, the model can simulate nitrate well, but there was a certain degree of overestimation. For ammonium, the simulation in general agreed well with the observation. The simulated ammonium had an RMSE of $1.45\text{ }\mu\text{g m}^{-3}$ and a correlation coefficient of 0.73. The MFB and MFE both reached the “excellent” range. For the monthly variations, the ammonium was underestimated by the model from January to March. Like sulfate, the simulation of ammonium at most sites also underestimated the observed annual concentrations.

3.1.2 OC and BC

Fig. 5 presents the spatial distribution of seasonal mean concentrations of OC and BC. The model can reproduce the main features of the spatial distribution of OC and BC. Both the simulations and observations showed that the concentrations of OC and BC were the highest in

Fig. 4. Time series (left) of modeled (red) and observed (blue) monthly mean concentrations in PRD in 2015 of (a) sulfate, (b) nitrate and (c) ammonium. Scatter plots (right) between observations (blue points) and simulations (green lines) at 10 stations over PRD region in 2015. Green line represents a range of 50 members of simulations. The simulated results are from the simulation with $15 \text{ km} \times 15 \text{ km}$ horizontal resolution.

winter, but BC had a more significant overestimation as a whole, especially in MDS and TH. Fig. 6 shows the time series of modeled and observed monthly concentration of OC and BC at 10 sites over the PRD in 2015. For OC, the simulated annual mean concentration was $8.20 \mu\text{g m}^{-3}$, which was close to the observation ($8.65 \mu\text{g m}^{-3}$) with a slightly positive bias of $0.45 \mu\text{g m}^{-3}$. For BC, the simulation was $3.00 \mu\text{g m}^{-3}$, which was higher than observation of $0.56 \mu\text{g m}^{-3}$. For monthly variations, the simulation of OC and BC showed month-to-month variations similar to the

Fig. 5. Simulated (shaded circles) and observed (solid circles) seasonal mean surface OC and BC concentrations ($\mu\text{g m}^{-3}$) in PRD region in 2015. MAM = March, April, and May; JJA = June, July, and August; SON = September, October, and November; DJF = December, January, and February. The simulated results are from the simulation with $15\text{ km} \times 15\text{ km}$ horizontal resolution.

observation. The correlation coefficients were around 0.8, the MB and RMSE of OC and BC were small. The MB was $-0.48\text{ }\mu\text{g m}^{-3}$ and $0.56\text{ }\mu\text{g m}^{-3}$, respectively. The RMSE was $2.10\text{ }\mu\text{g m}^{-3}$ and $0.82\text{ }\mu\text{g m}^{-3}$, respectively. The MFB and MFE were all in the “excellent” range, and the simulations of OC and BC at the 10 stations were also close to the observational results.

3.2 Uncertainty Analysis of Sulfate, Nitrate, Ammonium, BC and OC Simulations

Based on the above assessment, the model showed a good performance for OC and BC modeling, while it displayed lower skill for SIA modeling, especially for sulfate. Emission as an important input of the air quality model, its uncertainty is a key source of simulation errors. This section will evaluate the impact of emission uncertainty on the modeling of the $\text{PM}_{2.5}$ components in PRD region, and to explore other possible uncertainty sources and factors.

Fig. 6. Time series (left) of modeled (red) and observed (blue) monthly mean concentrations in PRD in 2015 of (a) OC and (b) BC. Scatter plots (right) between observations (blue points) and simulations (green lines) of (c) OC and (d) BC at 10 stations over PRD region in 2015. Green line represents a range of 50 members of simulations. The simulated results are from the simulation with 15 km $\times$ 15 km horizontal resolution.

3.2.1 Sulfate, Nitrate and Ammonium

Table 3 shows the uncertainties in the simulations of sulfate, nitrate, ammonium, organic carbon and black carbon induced by emission uncertainties, which was calculated by CV. According to Table 3, the modeling uncertainties of sulfate and ammonium in the annual simulation induced by emissions were 5% and 16%, respectively, suggesting that their modeling uncertainties were less sensitive to the emission uncertainties. However, as for nitrate, the emission uncertainty had a greater impact on the simulation results. The modeling uncertainty of nitrate can reach 40%, which was even higher than the uncertainty in the precursor emissions of NO_x (31%). This implies that there is a process of nonlinear growth of uncertainty in the model. It might be related to the simulation of the HO_x radical which influences the oxidation of NO_2 or to the heterogeneous reaction of NO_2 on the surface of BC, the uncertainty in the simulation of HO_x or the emission uncertainty of BC may have a nonlinear effect on the simulation of nitrate.

From the box plot in Fig. 7, there were no obvious monthly variations of the uncertainty in sulfate simulations. The uncertainty of each month was very small, and the range of the ensemble simulated concentrations cannot adequately cover the observed monthly mean concentrations. This result suggests that the emission uncertainty is not sufficient to explain the simulation errors of sulfate. The simulation errors are more likely induced by model uncertainties other than the emission uncertainty. Moreover, the evaluation of sulfate simulation suggested that sulfate concentrations were significantly underestimated by the model in winter. Because solar radiation

Table 3. Uncertainty of each PM_{2.5} component simulations caused by emission perturbation.

Species	Sulfate	Nitrate	Ammonium	OC	BC
Uncertainty	5%	40%	16%	74%	79%

Fig. 7. Box plot of simulated and observed monthly mean concentrations of (a) sulfate, (b) nitrate and (c) ammonium sampled from PRD region in 2015. The red asterisk (*) is the observed value, and the box plot represent the spread of 50 members. The red plus sign (+) was defined as values less than $Q1 - 1.5 \text{ IQR}$ or larger than $Q3 + 1.5 \text{ IQR}$, where $Q1$ is the 25th percentile, $Q3$ is the 75th percentile, and IQR is the value of $Q3 - Q1$.

decreased and photochemical reaction weakened in winter, the heterogeneous reaction was found to be a main pathway for SIA formation in China by previous studies. Wang *et al.* (2014) increased the proportion of sulfate in PM_{2.5} by 120% through introducing a parameterization of the heterogeneous uptake of SO₂ on deliquesced aerosols into the model. Li *et al.* (2018) also improved the sulfate modeling to a large extent by adding the heterogeneous reactions in Eq. (4) of Cheng *et al.* (2016) to the model.

In addition, the simulation error of sulfate may also be related to the simulation of dust (Tang *et al.*, 2020). On the one hand, dust can provide a reaction interface for heterogeneous reactions and allow gaseous pollutants to be adsorbed on its surface (Fu *et al.*, 2016). On the other hand, Fe³⁺ and Mn²⁺ in dust can catalyze the liquid oxidation of SO₂, which is also an important pathway

for the formation of sulfate (Shao *et al.*, 2019), but few models can take this into account. The sensitivity study of Qin *et al.* (2015) also suggested that high concentrations of Fe^{3+} and Mn^{2+} could increase sulfate concentrations in PRD region by 8–12%.

For nitrate, its uncertainty was large in winter and relatively small in summer and autumn. The spread of the simulated monthly concentrations covered part of the observed monthly mean concentrations, indicating that emission uncertainty can explain part of the simulation error of nitrate, while other errors may come from the model uncertainty. Many studies have shown that the overestimation of nitrate concentrations in most parts of China was related to the uncertainties in the photochemical process of nitrate and the conversion process of nitric acid to nitrate (Gao *et al.*, 2014). Moreover, the overestimation may also be due to the sampling artifact caused by the evaporative loss of semi-volatile ammonium nitrate (Slanina *et al.*, 2001; Pecorari *et al.*, 2014). This can result in the underestimation of the ambient concentrations of nitrate (Schaap *et al.*, 2004). The nitrate simulation is also affected by the simulation of sulfate under ammonia-rich conditions, and lower sulfate may lead to higher nitrate (Sartelet *et al.*, 2007; Qin *et al.*, 2015), which may be the reason why the model underestimated sulfate and also overestimated nitrate in winter.

The monthly variations of the uncertainty in ammonium simulations were similar to nitrate with a smaller magnitude. However, the spread of the monthly ammonium simulation did not cover the monthly mean of observation, especially during the winter when the simulation of ammonium was mainly underestimated. This indicated that emission uncertainty could not explain the simulation error of ammonium in winter. According to Qin *et al.* (2015), PRD is an ammonia-rich region, and the modeling errors of ammonium are mainly affected by the modeling errors of sulfate and nitrate. Furthermore, it is worth noting that the modeling uncertainties induced by emissions of SIA were very small during May and June, which was caused by the smaller magnitude of the concentrations in May and June.

3.2.2 OC and BC

Compared with SIA, the uncertainties in simulation of OC and BC induced by the emission uncertainties were larger, which were 74% and 79%, respectively. As can be seen from the box plot in Fig. 8, the uncertainties of OC and BC were the smallest in summer and larger in autumn and winter. The monthly mean observations of BC and OC were almost within the spread of the ensemble simulations, which implies that emission uncertainty would explain most of the simulation errors of OC and BC. The varied and complex sources for organic aerosols may be the reason why the simulation of OC has large uncertainties (Goldstein and Galbally, 2007). For BC, it has low reactivity in the atmosphere (Chen *et al.*, 2019) and the uncertainty in the initial

Fig. 8. Box plot of simulated and observed monthly mean concentrations of (a) OC and (b) BC sampled from PRD region in 2015. The red asterisk (*) is the observed value, and the box plot represent the spread of 50 members. The red plus sign (+) was defined as values less than $Q1 - 1.5 \text{ IQR}$ or larger than $Q3 + 1.5 \text{ IQR}$, where $Q1$ is the 25th percentile, $Q3$ is the 75th percentile, and IQR is the value of $Q3 - Q1$.

Table 4. The relative change rates of China's anthropogenic emission during 2010–2015.

Species	SO ₂	NO _x	NH ₃	NMVOC	CO	PM ₁₀	PM _{2.5}	BC	OC
Change	–39.2%	–10.5%	+0.2%	+10.0%	–17.6%	–24.5%	–22%	–11.7%	–21%

emissions has a direct impact on the simulated concentrations. Moreover, the error in the spatial distribution of combustion emission may also be one of several contributing factors for the overestimation of BC: The proportion of combustion in rural areas is greater, but the existing emission inventory is allocated based on GDP and population. It consequently leads to the overestimation of emissions in BC among urban areas (Zheng *et al.*, 2019). Furthermore, it is worth noting that the observed OC monthly mean values almost coincided with the simulated median values in March, April, August, September, and November, when the spread of OC ensemble concentrations was large. BC had the same situation but occurs in February, March and July to November. This indicates that the uncertainties in OC and BC emissions over PRD region might be overestimated by the emission inventory of Zhang *et al.* (2009). Therefore, although the uncertainty analysis results show that emission uncertainty can explain the simulation errors of OC and BC, there may be an overestimation of the assumed uncertainty in emission.

Through the uncertainty analysis with emission perturbations, we found that the emission uncertainty could not well explain the simulation error of SIA, but could explain most of the simulation error of OC and BC. It is worth noting that the 2010 emission inventory was used to simulate the 2015 concentration in our study. Table 4 shows the relative change rates of China's anthropogenic emission during 2010–2015. The emission of precursors such as SO₂ and NO_x has decreased in 2015 (Zheng *et al.*, 2018), but the simulation of sulfate and ammonium simulated with the 2010 emission inventory was still significantly underestimated, which further confirms that the model biases of sulfate and ammonium in winter are more likely caused by the chemical processes. Nevertheless, changes in emission over time do bring uncertainty to our results, which is also a limitation of our study. Besides, apart from the uncertainties in emissions and chemical process, the resolution of model grids and the uncertainties in meteorology simulations also play a crucial role in the simulation of sulfate, nitrate, ammonium, OC and BC. The meteorological verification shows that the bias of the meteorological simulation was small, but the uncertainties in the resolution of model grids and other factors also need to be evaluated for better investigating the uncertainties in the modeling of PM_{2.5} components.

4 CONCLUSIONS

This study evaluated and analyzed the uncertainties in sulfate, nitrate, ammonium, BC and OC modeling for the PRD region by comparing ensemble Monte Carlo simulation results to observation data from 10 stations for the entire year of 2015. Firstly, although the ensemble simulations performed well for OC and BC, the predictions for SIA were relatively poor, especially the significantly underestimated sulfate concentrations during winter. Secondly, uncertainties for BC and OC in the emission inventory (which was from 2010), despite being potentially overestimated, were identified as the main source of error in predicting these species. Last but not least, the discrepancies for the SIA concentrations were probably due to uncertainties in the heterogeneous chemistry modeling rather than the emission inventory, as the latter accounted for only a small portion of the simulation errors for SIA.

These results can be applied to improve the forecasting of PM_{2.5} and its components over the PRD region and China. Furthermore, they indicate that the uncertainties in a model can be effectively diagnosed by analyzing the uncertainties in its Monte Carlo simulations. Finally, a more comprehensive uncertainty analysis of SIA predictions can be conducted to investigate uncertainties in chemical process modeling.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.2020.02.0075>

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