Assessment of the impacts of cloud chemistry on surface SO_2 and sulfate levels in typical regions of China

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Abstract

A regional online chemical weather model WRF/ CUACE (China Meteorological Administration Unified Atmospheric Chemistry Environment) is used to assess the contributions of cloud chemistry to the SO_2 and sulfate levels in typical regions of China. By comparing with several time series of in-situ cloud chemical observations on Mountain Tai in Shandong Province of China, the CUACE cloud chemistry scheme is found to reasonably reproduce the observed cloud consumption of H_2O_2, O_3 and SO_2 and the production of sulfate, and consequently is used in the regional assessment for a heavy pollution episode and monthly average in December 2016. During the cloudy period in a heavy pollution episode, the sulfate production was increased by 60-95% and SO_2 was reduced by over 80%. The cloud chemistry mainly affects the middle and lower troposphere below 5 km as well as within the boundary

layer, and contributes significantly to the SO_2 reduction and sulfate production in east-central China. Among the four typical regions in China, the Sichuan Basin (SCB) is mostly affected by the cloud chemistry, with the average SO_2 abatement about 1.0-15.0 ppb and sulfate increase about 10.0-70.0 μg/m^3, followed by Yangtze River Delta (YRD) and southeast of North China Plain (NCP), where SO_2 abatement is about 1.0-3.0 ppb and sulfate increase is about 10.0-30.0 μg/m^3. However, the cloud chemistry contributions to the Pearl River Delta (PRD) and northwest of NCP are not significant due to lighter pollution and less water vapor than other two regions. This study provides a way to analyze the over-estimate phenomenon of SO_2 in many chemical transport models.

Keywords: SO_2, sulfate, cloud chemistry, WRF/CUACE

1 Introduction

Aerosols interact with radiation and clouds, directly or indirectly affecting the atmospheric radiation balance and precipitation, which in turn affects weather and climate (Twomey et al., 1984; Twomey, 1991; Charlson et al., 1992; Ramanathan et al., 2001; Pye et al., 2020) . Moreover, large amounts of aerosols dispersed in the atmosphere can reduce visibility and deteriorate air quality (Molina, 2002), which is harmful to human health and ecosystem (Xie et al., 2019; Sielski et al., 2021).

In addition to direct emissions, aerosols are mostly produced secondarily through the oxidation of precursor gases, and one of the important processes is the transformation in clouds. Global cloud coverage of about 21% to 95% provides an adequate environment for cloud chemistry processes (Kotarba, 2020; Ravishankara, 1997). As about 90% of the clouds formed in the atmosphere evaporate without deposition or forming the precipitation, large fractions of aerosols formed in them can then re-enter the atmosphere (Caffrey et al., 2001; Harris et al., 2013; Lelieveld et al., 1992). Globally, sulfate production from SO_2 oxidation accounts for about 80% of total sulfate, and more than half of it is produced in clouds (Hung et al., 2018; Faloona et al., 2010; Guo et al., 2012). Ge et al. (2021) found that cloud chemistry processes reduced the SO_2 concentrations by 0-50% in most of east-central China in all seasons. Li (2011) found that the average SO_4^{2-} concentration in cloud water accounted for 53.8% of the total aerosol concentration at a Mount site. Li et al. (2020) also found that cloud processes effectively

reduced atmospheric O_3 and SO_2 concentrations by an average of 19.7% and 71.2%, respectively, at Mount Tai.

Multiphase oxidation of SO_2 in aerosol particles in high humidity environment is one of the main causes of explosive growth of particulate matter in East Asia haze (Guo et al., 2014; Cheng et al., 2016; Song et al., 2019). From observations and laboratory works, four main pathways were found for this kind of oxidation of SO_2 , i.e. by H_2O_2, O_3, NO_2, and transition metal ions (TMIs) (IIbusuki and Takeuchi, 1987; Martin et al., 1991; Alexander et al., 2009; Harris et al., 2013; Cheng et al., 2016; Wang et al., 2016). Additional pathways of organic peroxides (ROOH) (Yao et al., 2019; Wang et al., 2019; Ye et al., 2018; Dovrou et al., 2019), photolysis products of nitrate (pNO_3^-) (Gen et al., 2019a; 2019b), and excited triplet states of photosensitizer molecules (T*) (Wang et al., 2020) have also been found recently to be important for multiphase oxidation of SO_2 during very heavy hazy days. Unfortunately there are still much uncertainties and gaps to put all of those pathways into model applications from observational and laboratory studies (Pye et al., 2020; Ravishankara, 1997; Liu et al., 2021). Several regional and global models have tried to include only two, O_3 and H_2O_2, in-cloud oxidant in cloud chemistry mechanisms (Park et al., 2003; Tie et al., 2005; Salzen et al., 2000; Chapman et al., 2009; Leighton and Ivanova, 2008; Ivanova and Leighton, 2008). A very few models can simulate the pathway of NO_2, TMIs of Fe or Mn ions (Ge et al., 2021; Binkowski and Roselle, 2003; Chang et al., 1987; Terrenoire et al., 2015; Meleux, et al., 2013).

There has been very serious air pollution in central-east China where four heavy pollution regions of North China Plain (NCP), Yangtze River Delta (YRD), Sichuan Basin (SCB) and Pearl River Delta (PRD) are located (Yao et al., 2021; Zhang et al., 2012). Although many global and regional models have contained sulfate formation mechanisms by cloud chemistry, few models have assessed its contribution, especially the lack of detailed assessment of regional cloud chemistry on sulfate and SO_2 in China.Regional chemical models have reported the over-estimate of SO_2 (Buchard et al., 2014; He et al., 2015; Wei et al., 2019; Sha et al., 2019; Georgiou et al., 2018). The inadequate inclusion or lack of cloud chemistry of SO_2 consumption simulations is one of the main causes (Ge et al., 2021). Therefore, it is very important and necessary to quantify the contribution of cloud chemistry in these typical regions in

central-east China and get a better understand of multi-dimensional pollution interactions, especially between the upper layer and the surface.

This study is intended to use an on-line coupled chemical weather platform of WRF/CUACE, to analyze and evaluate the SO_2 in-cloud oxidation process in the four polluted regions in China, with two objectives: (1) evaluating the cloud chemistry scheme in WRF/CUACE by the in-situ cloud chemistry observations at Mount Tai in summers of 2015 and 2018; and (2) quantifying the contributions of cloud chemistry to the SO_2 and sulfate changes in a typical winter pollution month of December 2016 with a very long lasting heavy pollution episode. It is aimed to establish a system to assess the relative contribution of cloud chemistry to SO_2 oxidation and sulfate productions vs. other clear-sky processes.

2 Model description and Methodology

2.1 Cloud chemistry in WRF/CUACE

WRF/CUACE is an on-line coupled chemical weather model under the WRF frame work with a comprehensive chemical module - CUACE, which is developed at CMA (China Meteorological Administration) with a sectional aerosol physics, gas chemistry, aerosol-cloud interactions and thermodynamic equilibrium (Zhou et al., 2012; Zhou et al., 2016; Gong et al., 2003; Gong and Zhang, 2008; Zhang et al., 2021), with seven types of aerosols, i.e. black carbon, organic carbon, sulfate, nitrate, ammonium, soil dust, and sea salt, and more than 60 gaseous species. The aerosol size spectrum is divided into 12 bins with fixed boundaries of 0.005-0.01, 0.01-0.02, 0.02-0.04, 0.04-0.08, 0.08-0.16, 0.16-0.32, 0.32-0.64, 0.64-1.28, 1.28-2.56, 2.56-5.12, 5.12-10.24 and 10.24-20.48 μm. The system can simulate the concentrations of PM_{10}, $PM_{2.5}$ and O_3 as well as visibility. A complete heterogeneous chemistry module has been built in CUACE for nine gas-to-particle heterogeneous reactions including SO_2 to sulfate (Zhou et al., 2021, Zhang et al., 2021). The cloud chemistry mechanism in CUACE considers the pathways of multiphase oxidation of SO_2 by H_2O_2 and O_3 in both stratocumulus and convective clouds (Gong et al., 2003; Von Salzen et al., 2000). The transport and chemical effects of sulfur in convective clouds are calculated based on a convective cloud model by WRF. Within the cloudy part of a grid box, the first-order rate constant (in s^{-1}) of S(IV) oxidation is given by the

following expression:

$$F = \left| \frac{1}{C_{S(IV)}} \frac{\mathrm{d}C_{S(IV)}}{dt} \right| = F_1 C_{O_3} + F_2 C_{H_2O_2} \quad (1)$$

where $C_{S(IV)}$ is the total concentration of S(IV) (gas phase plus dissolved), C_{O_3} is the total concentration of O_3, and $C_{H_2O_2}$ is the total concentration of hydrogen peroxide.

The effective rate constants F_1 and F_2 are given by the following expressions:

$$F_1 = R_{O_3} f_1 \quad (2)$$

$$F_2 = R_{H_2O_2} f_2 \quad (3)$$

The reaction rate constants R_{O_3} and $R_{H_2O_2}$ refer to Maahs (1983) and Martin et al. (1984):

$$R_{O_3} = \left\{4.4\times10^{11}\exp(-4131/T) + 2.61\times10^{3}\exp(-966/T)\left[H^+\right]^{-1}\right\}(Ms)^{-1} \quad (4)$$

$$R_{H_2O_2} = 8\times10^{4}\exp\left[-3650(1/T - 1/298)\right]\left\{0.1 + \left[H^+\right]\right\}^{-1}(Ms)^{-1} \quad (5)$$

In Equations (2) and (3), the factors f_1 and f_2 represent the partitioning of the substance between the aqueous and gas phases and are determined by the Henry's law coefficients.

$$f_1 = \gamma f_{SO_2} f_{O_3} K_S \overline{K}_{HO} \quad (6)$$

$$f_2 = \gamma f_{SO_2} f_{H_2O_2} \overline{K}_{HS} \overline{K}_{HP} \quad (7)$$

where γ is the dimensionless volume fraction of liquid water in the cloud. The parameters f_{SO_2}, f_{O_3} and $f_{H_2O_2}$ are the proportions of individual substances in the gas phase, which are calculated from the

dimensionless Henry's law constant and γ.

$$f_{SO_2} = \left(1 + \gamma \overline{K}_{HS} K_S\right)^{-1} \quad (8)$$

$$f_{O_3} = \left(1 + \gamma \overline{K}_{HO}\right)^{-1} \quad (9)$$

$$f_{H_2O_2} = \left(1 + \gamma \overline{K}_{HP}\right)^{-1} \quad (10)$$

with

$$K_S = \overline{K}_{HS}\left(1 + \frac{K_{1S}}{[H^+]} + \frac{K_{1S}K_{2S}}{[H^+]^2}\right) \quad (11)$$

The Henry's law constants used in (6) to (8) are listed in Table 1.

In order to consider the dependence of the oxidation rates on the pH, the H^+ concentration is calculated from ions balance.

$$[H^+] + [NH_4^+] = [OH^-] + 2[SO_4^{2-}] + 2[SO_3^{2-}] + [HSO_3^-] + [NO_3^-] + [HCO_3^-] \quad (12)$$

From Eqs. (1) ~ (12), CUACE can simulate the oxidation rates of SO_2 by H_2O_2 and O_3 mainly in the liquid and gaseous environment in both stratocumulus and convective clouds in three-dimensional way.

2.2 Assessment criteria

Three variables, RTCLD, DT, and RT, are defined to assess the impact of the cloud chemistry on SO_2 and sulfate. RTCLD refers to the concentration change ratio of substance i before and after the cloud chemical processes in a model run.

$$RTCLD(i) = 1 - \frac{BECLD(i)}{AFCLD(i)} \quad (13)$$

where BECLD and AFCLD denote the concentrations of component i before and after the cloud chemical processes, respectively, and i denotes the chemical component of SO_2, O_3, H_2O_2, and sulfate.

The DT indicates the difference in concentration of substance i with (CLD) and without (nCLD) cloud chemistry module activated.

$$DT(i) = CLD(i) - \mathrm{n}CLD(i) \quad (14)$$

and the RT represents the concentration ratio change of the substance i with and without cloud chemistry in separate model runs:

$$RT(i) = 1 - \frac{\mathrm{n}CLD(i)}{CLD(i)} \quad (15)$$

2.3 Methodology

2.3.1 Model Evaluation – Case 1

Mount Tai at an altitude of about 1545 m, located in central Shandong Province, is the highest point of the North China Plain. As the Riguan Peak of Mount Tai is far from pollution sources, and the water vapor conditions favors very much cloud formations in summer, it is an ideal observation site for cloud chemistry observation (Li et al., 2017; Li et al., 2020a; Li et al., 2020b). The observed concentrations of SO_2, O_3, H_2O_2 and sulfate in cloudy conditions from June 19 to July 30, 2015 and from June 20 to July 30, 2018 with time interval of 1 h are obtained to evaluate the cloud chemistry scheme in WRF/CUACE (Li et al., 2017; Li et al., 2020a; Li et al., 2020b).

WRF/CUACE is set up with two-domain nesting for the evaluation, with the Riguan Peak as the central point (Fig. 1a). The horizontal resolution of outer domain (O) is 9 km with 100×104, and of the

inner domain (I) is 3 km with 88×94 (Fig. 1a). There are 32 vertical layers with the top pressure of 100 hPa.

2.3.2 Simulations of Regional Characteristics – Case 2

In order to assess the regional contribution of cloud chemistry to SO_2 and sulfate in CUACE, December 2016 is selected with a widespread heavy pollution episode occurred in North and East China from Dec. 16 to 21, covering NCP, YRD and SCB with the highest hourly $PM_{2.5}$ concentration exceeding 1100 μg/m^3 (Yuan and Ma, 2017). The simulation region is set up as shown in Figure 1b with two-level domain nesting. The outer domain (O) covers Central and East Asia with a horizontal resolution of 54 km and a grid of 139×112. The inner domain (I) covers most of China on the eastern side of the Qinghai-Tibet Plateau with a horizontal resolution of 18 km and a grid of 157×166. The vertical layer number of the model is the same as that in the Case 1.

Since the cloud water is the reaction pool of cloud chemistry, whether the simulation of cloud water is reasonable or not is directly related to the effectiveness of cloud chemistry. Both the cloud water and rainwater from WRF are coupled to the cloud chemistry module and main physics configurations are listed in Table 2.

2.4 Meteorological, Pollution and Satellite Data

For both cases, the meteorological initial and boundary conditions for WRF/CUACE are from NCEP (National Centers for Environmental Prediction) FNL global reanalysis at a resolution of 1˚×1˚ with 6-h interval. The chemical lateral boundary conditions are from NOAA (National Oceanic and Atmospheric Administration) Meteorological Laboratory Regional Oxidant Model (NALROM) (Liu et al., 1996). The model is run in a restart way with a 5-day spin-up.

FY-2G cloud image data of CMA with an 1 h interval is used to evaluate the cloud in both cases. Routine observations in 3 h interval from 23 meteorological stations of CMA and hourly pollution observations from 132 stations of the China General Environmental Monitoring Station are used to evaluate the meteorological fields and pollutants for December 2016. Meteorological elements include 2

m temperature, 2 m relative humidity, and 10 m wind speed.

The MEIC (Multi-resolution Emission Inventory for China) inventory, at a resolution of 0.25˚, is used as the anthropogenic emissions with the species of sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), ammonia (NH_3), black carbon (BC), organic carbon (OC), non-methane volatile organic compounds (NMVOCs), $PM_{2.5}$ and PM_{10} by five sectors of power, industry, transportation, residential, and agriculture (Li et al., 2017; Zheng et al., 2018). The emission base year of 2015 and 2017 are used for Case-1, of 2016 for Case-2, respectively.

3 Results and Discussions

3.1 Evaluation of the cloud chemistry mechanism

In order to verify the cloud chemistry mechanism in WRF/CUACE, the simulation results are compared with the observations at Mount Tai. By analyzing the satellite cloud images in and around Mount Tai and matching with the available observed data, two time periods with clouds from June 19 to July 30, 2015 and June 20 to July 30, 2018 are selected for the comparisons, defined as "cloud process-1" (CP-1) and "cloud process-2" (CP-2), respectively. The simulated results for chemical species are illustrated in scatter plots (Fig. 2), which reveals that the simulated concentrations of SO_2, sulfate, O_3, and H_2O_2 are all within a factor of two of the observations when cloud chemistry occurs, indicating reasonable agreement between simulations and observations for both CP-1 and CP-2 cases. The sulfate underestimates are clear in both CP-1 and CP-2 cases, which was reported by other modeling results before as well (Tuccella et al., 2012; Huang et al., 2019; Ge et al., 2022).

The statistics of correlation coefficients (R), relative average deviation (RAD), and normalized mean deviation (NMB) between hourly simulated and observed SO_2, O_3, H_2O_2 and sulfate are shown in Table 3. Among them, the simulated and observed averages of SO_2 are very close in both CP-1 and CP-2, with the RAD about -3.4% and -6.1% and with the RAD for other species in the range of 8.7-55.0%. The R for the four species are 0.34, 0.33 and 0.78 and 0.32 for CP-1, and 0.47, 0.40, 0.06 and 0.54 for CP-2, respectively. Although the R, RAD, and NMB of H_2O_2 in CP-2 is only 0.06, 18.0%, and -19.6%,

the simulated mean value of H_2O_2 is closer to the observed mean value than that in CP-1 (RAD = 22.4%, NMB = -36.6%). For sulfate, the simulated correlations are good with R of 0.32 and 0.54 in CP-1 and CP-2, respectively, but the model underestimates sulfate concentrations with NMB of -71.0% and -59.4% in CP-1 and CP-2. This indicates that although the model is able to simulate the trend of sulfate concentrations, the simulated concentrations are lower than the observed values which may be due to the incompleteness of other cloud chemistry mechanisms or the bias of liquid water content in the cloud physics.

Another interesting point that is simulated correctly by the model is the increasing trend of H_2O_2 and the decreasing trend of SO_2 from CP-1 to CP-2 (Table 3), representing year of 2015 and 2018, respectively. It was found that the observed and simulated mean values of H_2O_2 are 26.5 and 16.8 μM in CP-1, to 46.9 and 32.4 μM in CP-2, respectively. For SO_2, the observed and simulated mean values are 2.2 and 2.3 μg/m^3 in CP-1, to 0.6 and 0.6 μg/m^3 in CP-2, respectively. The simulation results are consistent with the trends of other observational studies (Shen et al., 2012; Li et al., 2020b; Ren et al., 2009; Ye et al., 2021) The SO_2 trends may be attributed to the relevant national emission control measures, but the increasing trend of H_2O_2 and O_3, indicating an increasing oxidation ability of the atmosphere in the eastern part of China, needs further investigations.

To further evaluate the model performance, Figure 3 shows the satellite cloud maps, simulated column clouds, and simulated liquid water content at 8:00 LST on June 24, and 8:00 LST on June 25 in CP-1. At both times, the model's column clouds and liquid water distribution are consistent with the cloud distribution observed by the satellites. This indicates that the model's simulation of cloud distribution regions is realistic and the cloud chemistry initiation mechanism, cloud-water environment, is reasonably simulated.

Figure 4 shows the RTCLD of SO_2 and simulated liquid water contents at 2:00 and 8:00 LST on June 24, and 2:00 and 8:00 LST on June 25 in CP-1 at the Taishan's observation site. The results indicate that the RTCLD of SO_2 distribution simulated during these periods is consistent with the cloud liquid water, with a SO_2 RTCLD reduction of more than 80% within the cloud region of Mount Tai and most of Shandong province, which is consistent with the cloud chemistry observation studies by Li

(2020).

In summary, the cloud chemistry mechanism in WRF/CUACE is reasonable to reproduce the cloud chemistry for the gaseous pollutant SO_2, sulfate and the important oxidants of O_3 and H_2O_2 in a cloud environment. The simulations are within a factor of two of the observations, the bias is small, and the cloud chemistry occurs in agreement with the model cloud distribution. In addition, CUACE is also able to simulate the SO_2 decreasing trend and O_3 and H_2O_2 increasing trends with year.

3.2 Assessment of the impacts of cloud chemistry on regional SO_2 and sulfate

This session will further assess the contribution of cloud chemistry for the four main pollution regions of NCP, YRD, PRD, and SCB (Fig. 1) in China for the whole December of 2016 (as DEC thereafter) and a heavy pollution episode (as HPE thereafter) occurred during month (Dec. 16-22) as selected for Case 2.

3.2.1 Meteorological evaluation

As the driving force of air pollution and cloud chemistry, the simulated results of 2 m temperature (T2), 2 m relative humidity (RH2) and 10 m wind speed (WS10) in DEC and HPE are shows in Table 4. The correlations between simulated and observed values of all three meteorological elements are very close both in DEC and HPE for the four regions, indicating a good model performance. The temperature correlation is the best in DEC, followed by humidity and then wind speed, which is consistent with previous researches (Zhou et al., 2012; Wang et al., 2015; Gao et al., 2016). The RMSE of wind speeds all range from 1.03 to 1.50 m/s, falling within the criteria (less than 2 m/s) to define “good” model performance in stagnant weather proposed by Emery et al. (2001). The RSME of wind speed for HPE is smaller than that for DEC, which indicates that the model can well capture the static wind even though it is very small.

Figure 5 shows the satellite cloud image, simulated column cloud and simulated liquid water content for the maturation and dissipation stages (19-22 Dec.) of the HPE. The satellite image shows that the cloud coverage region is mainly in the southwest including SCB on the 19th, covering most of

eastern China including NCP, YRD, PRD and SCB on the 20th and the 21st, and then moving eastward outside of China on the 22nd (Fig. 4 a1-d1). The simulated clouds fit well with the satellite images (Fig. 4 a2-d2). Since the cloud chemistry occurs in the cloud area, the cloud chemistry mainly affects NCP, YRD and SCB regions as PRD has relatively much less cloud. The column liquid water distribution also moves from west to east as the episode developed (Fig. 5 a3-d3), but is located more southern part of eastern China than that of the clouds. In SCB and YRD, the liquid water content is more abundant, reaching over 100.0 g/m^2, than that in PRD, only up to 10.0 g/m^2. NCP has the least liquid water content of about 0.001-100.0 g/m^2 among the four regions, especially in Beijing, Tianjin and Hebei Province less than 10.0 g/m^2, mostly due to the dry environment and partly due to the overestimated temperature and underestimated humidity in Table 4.

The above analysis shows that the model basically reproduces the meteorological field in December and heavy pollution periods, which provides a reasonable meteorological background basis for the effective simulation of pollution as well as cloud chemistry.

3.2.2 Pollutants Evaluation

The simulated hourly $PM_{2.5}$, O_3 and SO_2 concentrations in four regions are compared with the observations (Table 5). The simulations are all within a factor of two of the observations (figure omitted), and the mean values of the three pollutants simulated in the four regions are very close to the observations, indicating that model captures well the variability of $PM_{2.5}$, O_3 and SO_2 concentrations for both DEC and HPE. Specifically, O_3 correlates well with observations in all four regions for the DEC, but less satisfactory during HPE for YRD and SCB regions. For $PM_{2.5}$, the correlation is high for HPE in PRD with R of 0.84, and with R of 0.39 for DEC. The correlation is high for DEC in NCP, with R of 0.62, and with R of 0.30 for HPE. The correlation is high for DEC and HPE in YRD, with R of 0.73 and 0.70. The difference in correlation between DEC and HPE is small in YRD and SCB. For SO_2, the model simulations are better for HPE in the three regions of NCP, YRD and SCB, than that for DEC. The R during the HPE and the DEC are 0.60 and 0.48 in NCP, 0.61 and 0.45 in YRD, and 0.49 and 0.19 in SCB, respectively. The correlations between observations and simulations for HPE and DEC in PRD are not significantly different, with R of 0.32 and 0.39, respectively. Therefore, the following part of this

paper will focus on assessing the effects of cloud chemical processes.

3.2.3 Assessment of regional contributions

The regional impacts of cloud chemical processes on surface SO_2 and sulfate are analyzed for DEC and for HPE. The pollution episode (HPE) is investigated with respect to the developing stage HPE-1 (Dec. 16-18), the maturity stage HPE-2 (Dec. 19-21) and to the dissipation stage HPE-3 (Dec. 22) for the four pollution regions of NCP, YRD, PRD and SCB.

The average impact of cloud chemistry on surface SO_2 and sulfate for DEC (Fig. 6, DT(SO_2) and DT (sulfate)) is assessed. It is found that SO_2 declination for DEC is concentrated mostly in the central-eastern part of China, by an average of 0.1-1.0 ppb in most regions by cloud chemistry. SO_2 concentrations are reduced by 0.5-3.0 ppb in most part of NCP, YRD, PRD and SCB regions. Among them, there is a relatively strong center by declining 3.0-10.0 ppb in SCB. Correspondingly, sulfate growth is mainly centering in SCB, with the increased maximum center up to 20.0-50.0 μg/m^3. Sulfate concentrations are increased by 10.0-20.0 μg/m^3 in most part of NCP, YRD and PRD, and increased 5-10.0 μg/m^3 in others.

The spatial distribution of cloud chemistry contribution to SO_2 and sulfate during HPE-2 is analyzed (Fig. 7, DT(SO_2) and DT(sulfate)) on the HPE-2. It is shown that the SO_2 concentration decreases most significantly in SCB, exceeding 1.0-3.0 ppb in most region, to 3.0-10.0 ppb in the central region. In YRD, PRD and NCP, the reduction reaches 1.0-3.0 ppb in most region while the smallest decrease is below 1.0 ppb in the northern part of NCP. Meanwhile, in terms of regional distribution, the regions of increasing sulfate and decreasing SO_2 concentrations are correlated, but not identical. Sulfate concentration increases by more than 10.0 μg/m^3 from the southern part of NCP to central China and from most of the eastern part of SCB to the YRD region. Sulfate concentration increases by more than 20.0 μg/m^3 in SCB and up to more than 50.0 μg/m^3 in the central region of SCB, by 20.0-30.0 μg/m^3 in the central region of YRD, and by 5.0-20.0 μg/m^3 in the whole PRD region. The sulfate concentration increases up to 10.0 μg/m^3 in the south of NCP and along the Yangtze River from the east of SCB to the west of YRD.

In summary, comparing the contribution of cloud chemistry in DEC with HPE-2, it is found that the cloud chemistry in heavy pollution weather for SO_2 depletion and sulfate increase is mainly concentrated in the central-eastern part of China, and the four major pollution regions are also more obvious. However, SO_2 consumption and sulfate increase are not consistent, which is not only influenced by the local SO_2 concentration, but also by the cloud amount. Therefore, for SCB, where there is less polluted and has much more clouds than that in NCP, the impact of cloud chemistry on sulfate and its precursor SO_2 is always the most significant, for both HPE and DEC.

Exploring details into the HPE, three moments, 21:00 and 17:00 on the 20th and 21st of the HPE-2, and 12:00 on the 22nd of the HPE-3, are used to specifically analyze the contribution of cloud chemistry. It is found that the cloud chemistry influence is mainly on SCB and YRD at 21:00 LST on Dec. 20. The sulfate concentration increases (DT(sulfate)) by about 20.0-100.0 μg/m^3 in most parts of SCB, and the highest is about 150.0-225.0 μg/m^3 in its southwest (Fig. 8a). The increase is about 10.0-40.0 μg/m^3 in most parts of YRD, and the highest increase can reach 40-100 μg/m^3 in the southeast near Hangzhou Bay. At 21st 17:00 LST, it is shown that the pollution episode has moved eastward and the cloud chemistry process has a stronger impact on NCP than at the previous time (Fig. 8b). The increase center is located in Shandong Province, with up to 100.0-225.0 μg/m^3, and with about 10.0-60.0 μg/m^3 in most of NCP. In PRD, the impact of the cloud chemistry is the least, with sulfate concentration increase of 10.0-40.0 μg/m^3. At 22nd 12 LST. Although the episode has gradually dissipated, the impact still exist, with sulfate increase about 10.0-40.0 μg/m^3 in most of these four regions (Fig. 8c).

Above all, the contribution of cloud chemistry to surface sulfate during this HPE is the highest in the SCB, followed by the NCP, YRD and PRD, with maximum concentration increases of 225.0 μg/m^3, 200.0 μg/m^3, and 100.0 μg/m^3, 40.0 μg/m^3, respectively, and an increase of 1.0-40.0 μg/m^3 in other areas of the four regions. Of particular note is the North China region, where the contribution of cloud chemistry is not significant on a monthly average but is very significant and exceeds that of the YRD region at certain moments during HPE. This also provides an explanation for the explosive increase in particulate matter concentrations during HPE in this region.

Further analysis of the simulation characteristics with and without cloud chemistry on all the

regions during the HPE-2 stage (Fig. 9) and the DEC (Fig. 10), is carried out. Compared with nCLD, R of SO_2 in CLD increases by 0.60, 0.14, and 0.10 in YRD, SCB, and NCP, respectively, and the overestimation in NCP and PRD has been corrected during HPE-2. R also increases by 0.10, 0.03 and 0.04 in YRD, SCB and NCP for the DEC, respectively. It is obvious that the model simulates SO_2 concentrations better at NCP during HPE-2 than for DEC with cloud chemistry.

For $PM_{2.5}$, the statistical results of the simulated mean, R and NMB in CLD and nCLD in the four polluted regions do not differ significantly between HPE-2 and DEC, but there is a significant improvement in the underestimate in NCP and SCB. Under cloud chemistry, the deviation in the NCP increases from -45.7% to -35.7% for DEC and from -52.6% to -48.2% for HPE-2. The deviation in SCB increases from -44.2% to -29.1% for DEC and from -46.5% to -32.9% for HPE-2. A significant reduction in the model's $PM_{2.5}$ concentration simulation bias after considering cloud chemistry, and an improvement in the underestimation at NCP and SCB has been achieved.

Moreover, the statistical results of all stations (SUM in Fig. 11) show that after considering cloud chemical simulation (CLD), the NMB of SO_2 decreased from 39.3% to 13.8% and the NMB of sulfate increased from -40.6% to -31.6% during the HPE-2 after the addition of cloud chemistry simulation, decreasing the simulation bias of both SO_2 and sulfate. This indicates that the addition of cloud chemistry to the model improves the model for SO_2 and sulfate simulations. The improvement of sulfate simulation in the presence of clouds also contributes to the improvement of the simulation accuracy of $PM_{2.5}$ mentioned above.

3.3 Site evaluation of cloud chemistry

Representative sites of Beijing, Nanjing, Guangzhou and Chengdu at NCP, YRD, PRD and SCB are selected to quantify the impact of cloud chemistry during the HPE. The net depletion ratio of SO_2 column concentration ($RT(SO_2)$) during cloud chemistry is shown in Figure 12. It is found that SO_2 column concentration reduction maintained mostly a high value of over 60%, even to 80% sometimes, in Chengdu during HPE-2. In Nanjing, the SO_2 level is reduced by about 20-50% from 17th to 19th and up to 80% from 20th to 21st when the episode matures there. The changes of SO_2 in these two cities are

consistent with the changes in cloud and liquid cloud water content distributions during the HPE-2 in Figure 3. The SO_2 reduction in Beijing and Guangzhou is consistently maintained at around 40% during the time from 17th to 21th. The lower oxidative transformation is related to the lower liquid water content in Beijing, while in Guangzhou it is attributed to the combination of low pollution levels and low cloud water content. Figure 3 shows that Chengdu maintained abundant water vapor conditions from 17th to 21st, and so does Nanjing from 20th to 21st. However, the ambient water vapor content is quite low in Guangzhou and Beijing throughout the process and the SO_2 oxidation is much lower than that of Chengdu and Nanjing. In conclusion, the cloud chemistry process can lead to SO_2 column concentration consumption share of more than 60% when cloud water content is abundant, which is also consistent with the observations of Mount Tai by Li (2020).

The impact of cloud chemistry (RT) on surface SO_2 and sulfate in four sites is also shown in Figure 13. The overall trend shows that the peak and valley regions of surface SO_2 consumption and sulfate increase are coincident. The cloud chemical processes of the surface SO_2 oxidation vary greatly between cities in different regions (Fig. 13a). In HPE-2, the percentage of surface SO_2 consumption can reach more than 90% in Chengdu and Nanjing, while it is below 30% in Beijing and Guangzhou, and does not reach 40% until the 22nd. Although the percentage of surface SO_2 consumption varies greatly, the increase in the percentage of sulfate does not vary so much between cities. In HPE-2, the increase in surface sulfate in the four cities ranges from 60-95% (Fig. 13b), and the sulfate increase rate interval contains the results summarized by Turnock et al. (2019).

Figure 14 is the variation of vertical profiles of sulfate increase by the cloud chemistry at the four times at 12:00 LST on 20 for HPE-2, at 04:00 LST on 21 for HPE-2, at 04:00 and 12:00 LST on 22 for HPE-3 in Beijing, Nanjing, Chengdu and Guangzhou. It shows that the sulfate produced by the cloud chemistry during this pollution process is concentrated mostly below 5 km in the troposphere, especially under 2 km. Again, less sulfate has been produced in Beijing in vertical than that of others by the cloud chemistry.

4. Summary and conclusions

The cloud chemistry mechanism in WRF/CUACE has been assessed by using the in-situ cloud chemistry observations of SO_2, O_3, and H_2O_2 from Mount Tai in June-July 2015 and 2018. The results show that the mechanism well captures the cloud processes for the oxidation of SO_2, reducing SO_2 by more than 80% during the cloudy phase, which is in good agreement with the observations.

The cloud chemistry contributions to the changes of SO_2 and sulfate concentrations in NCP, YRD, PRD and SCB regions are assessed by WRF/CUACE. During heavy pollution (HPE-2), the four regions are significantly affected by cloud chemistry, with SCB being the most obvious. The surface SO_2 reduction in SCB is up to 1.0-3.0 ppb and reaches 3.0-10.0 ppb in the high value areas, and surface sulfate concentration is increased by 10.0-30.0 $\mu g/m^3$ on average, with a maximum of more than 70.0 $\mu g/m^3$. Most areas in NCP, YRD and PRD have an average SO_2 reduction of 0.5-3.0 ppb and sulfate increase of 5.0-30.0 $\mu g/m^3$. Meanwhile, the Beijing area of NCP has the least impact among the four typical cities of four regions. Although the monthly average impact of cloud chemistry is much weaker in the NCP due to less water vapor in December, the contribution of the southern part of NCP during heavy pollution time is still significant and cannot be ignored. In PRD, the contribution of cloud chemistry is weaker than other regions due to lighter pollution, although there are lots of clouds with abounded liquid water there. In addition, the cloud chemistry increases surface sulfate concentration by 60-95% and reduces surface SO_2 concentration by more than 80% in Beijing, Nanjing, Chengdu and Guangzhou in December during HPE-2, similar to that of previous studies (Turnock et al., 2019; Faloona et al., 2009). Above all, the average contribution of cloud chemistry during HPE-2 is significantly greater than that for DEC. Vertically, the cloud chemistry influence is mainly in the middle and lower troposphere below 2 km for four representative cities in HPE-2. Generally, the cloud chemistry can improve the model performance by reducing the overestimates of SO_2 and underestimates of sulfate.

This paper focuses on the cloud chemical mechanism evaluation, and assessed the contribution of cloud chemistry to SO_2 and sulfate changes. In the future, more mechanisms should be added to improve the cloud chemistry mechanism in CUACE to more accurately simulate SO_2 and sulfate and other

aerosol components such as nitrate, ammonium, carbonate, and organic aerosols.

Code/data availability

All source code and data can be accessed by contacting the corresponding authors Sunling Gong (gongsl@cma.gov.cn).

Authors contribution

CZ and SG put forward the ideas and formulated overarching research goals. JL carried them out and wrote the manuscript with suggestions from all authors. LZ and JZ participated in the scientific interpretation and discussion. JC was assisted with data acquisition and processing. All authors contributed to the discussion and improvement of the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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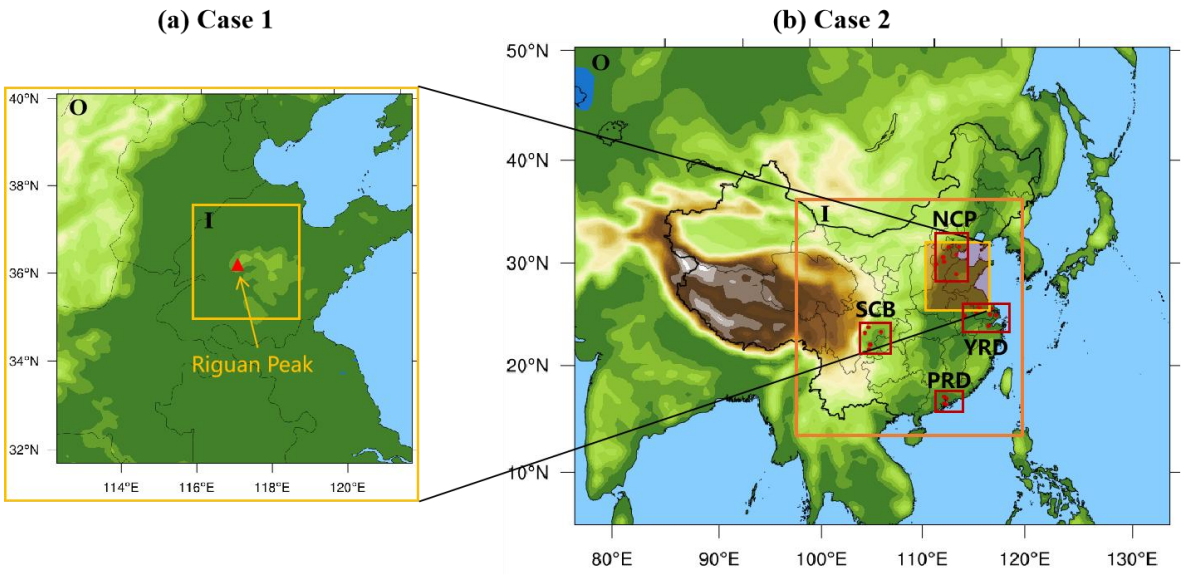

Figure 1. Model nesting domains and target regions: (a) domain for the Case 1. The red triangle is the Mount Tai site, (b) nesting domains for regional assessment for Case 2. Red dots are where the surface observations of air pollutants are. The target four regions are NCP for the North China Plain, YRD for the Yangtze River Delta, PRD for the Pearl River Delta and SCB for the Sichuan Basin.

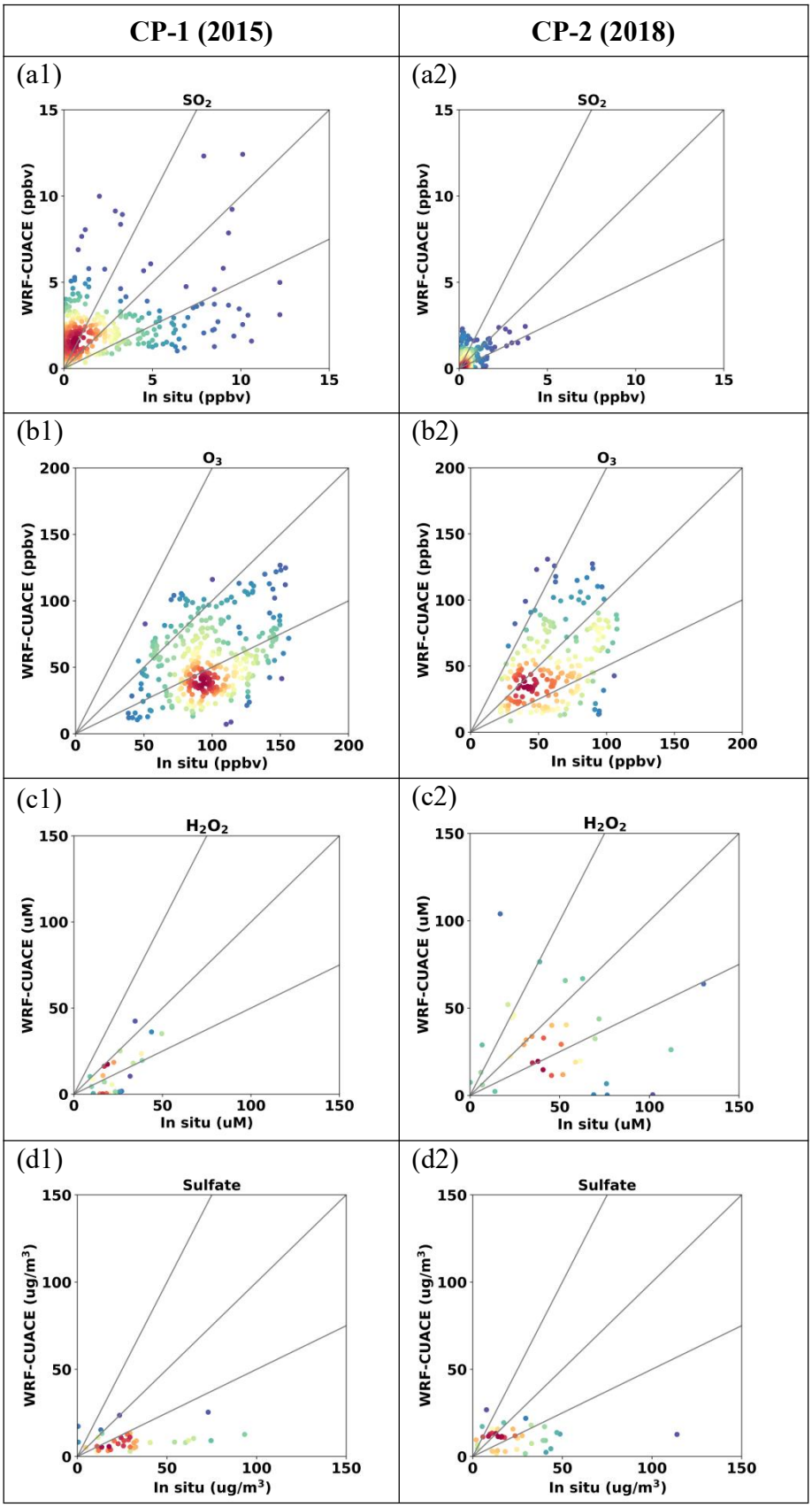

Figure 2. Scatter plots of hourly SO_2 (a1, a2), O_3 (b1, b2), H_2O_2 (c1, c2) and sulfate (d1, d2) concentrations between WRF/CUACE and in situ observations at Mount Tai in CP-1 and CP-2. Units: SO_2 and O_3 (ppbv), H_2O_2 (μM), and Sulfate (μg/m^3).

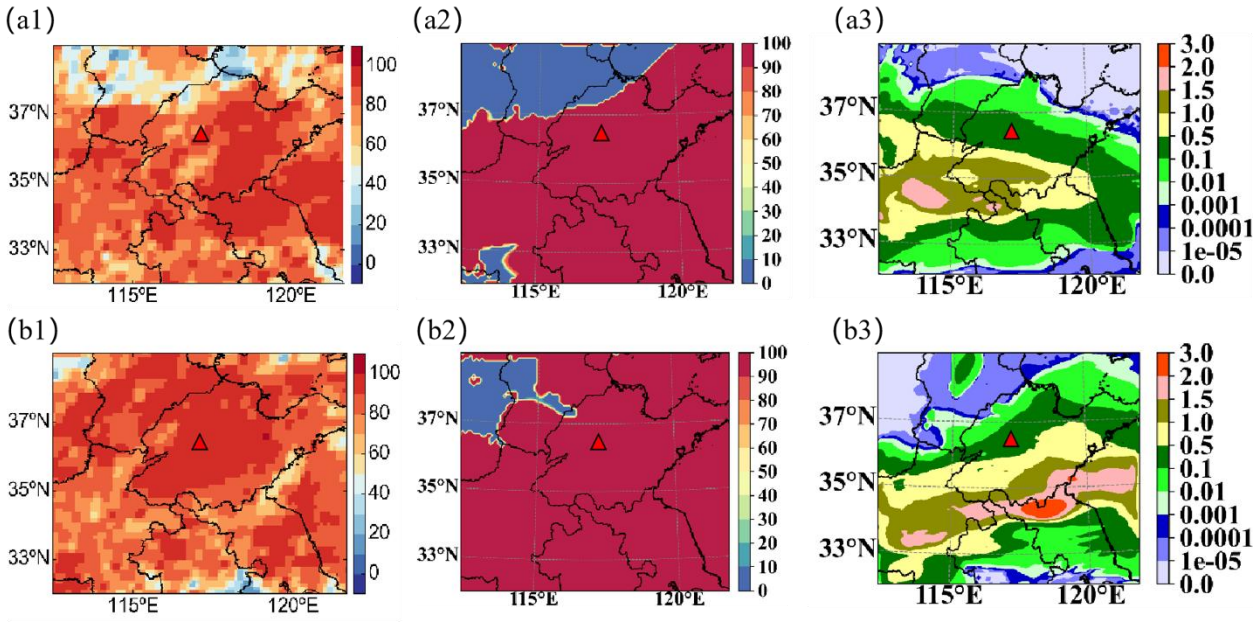

Figure 3.: The cloud image of FY2G, (a1, b1, Units: %), the cloud fraction by WRF/CUACE.(a2, b2, Units: %) and the column liquid water content by WRF/CUACE (a3, b3, Units: kg/m^2). (a) is for 8:00 LST on 24 June, (b) is for 8:00 LST on 25 June.

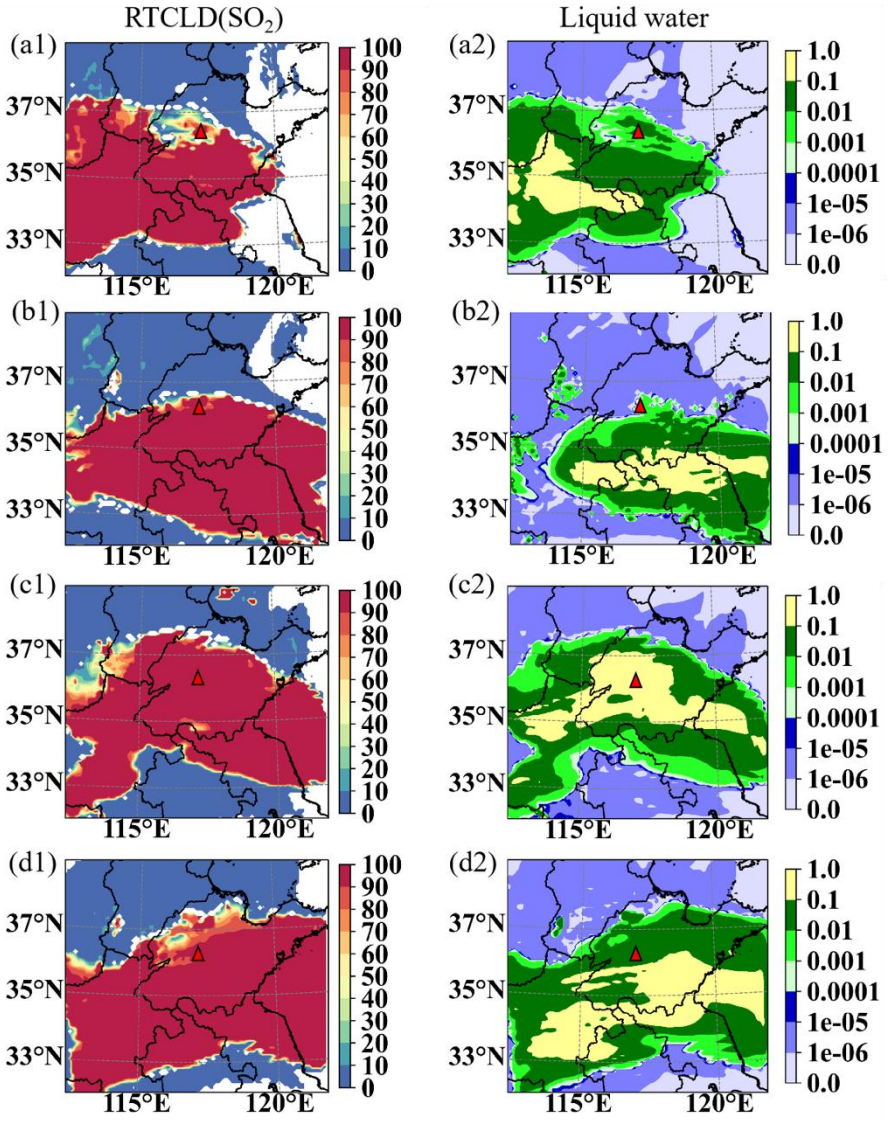

Figure 4. Distributions of SO_2 oxidation rate (a1, b1, c1 and d1, Units: %) and the liquid water content (a2, b2, c2 and d2, Units: g/kg) by WRF/CUACE, where (a) is for 2:00 LST on 24 June, (b) is for 8:00 LST on 24 June, (c) is for 2:00 LST on 25 June and (d) is for 8:00 LST on 25 June.

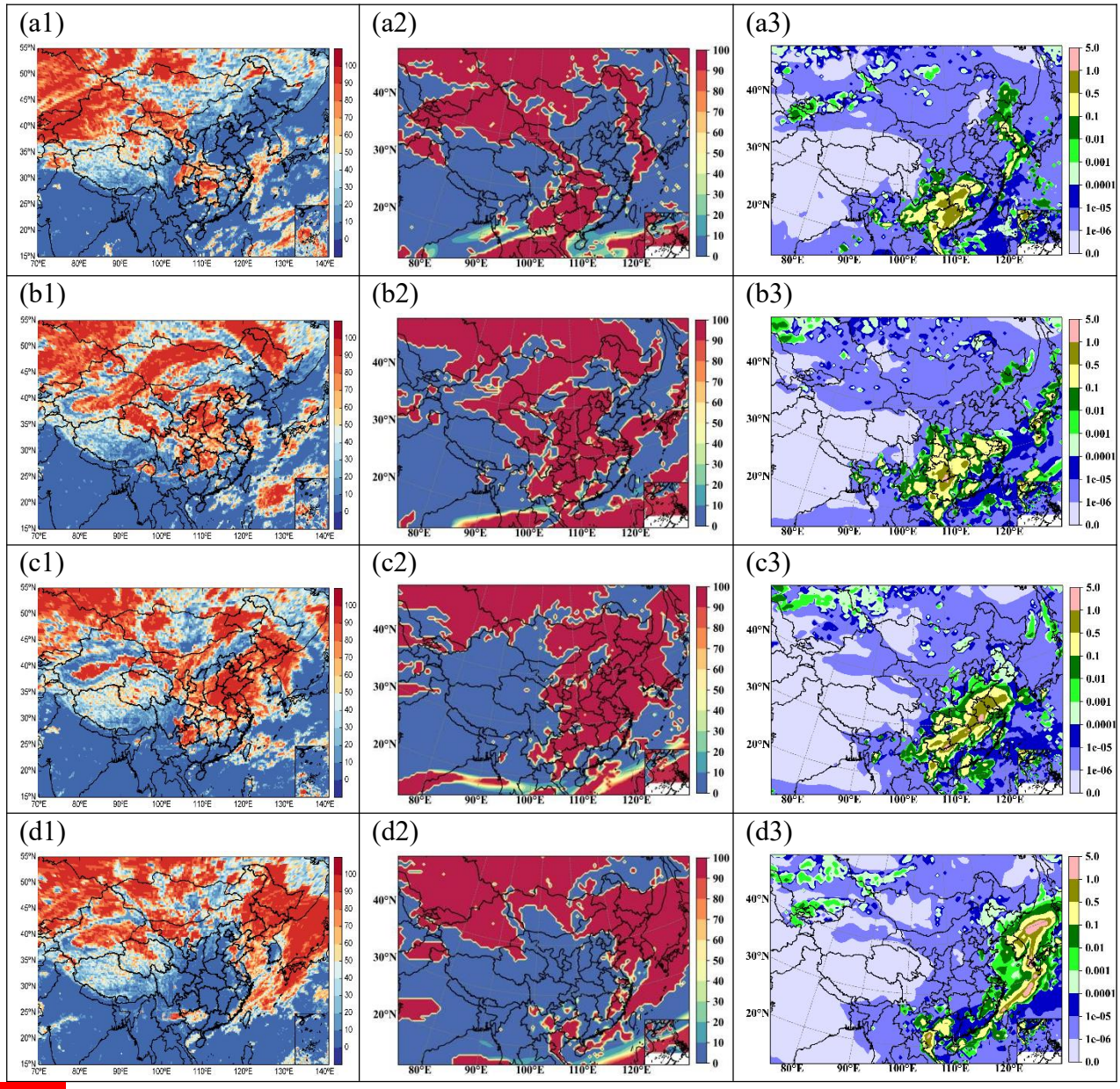

Figure 5. The cloud image of FY-2G (a1, b1, c1, d1, Units: %), the column cloud of WRF/CUACE (a2, b2, c2, d2, Units: %) and the column liquid water content of WRF/CUACE (a3, b3, c3, d3, Units: kg/m^2). (a) is for 8:00 LST on 19 Dec., (b) is for 8:00 LST on 20 Dec., (c) is for 8:00 LST on 21 Dec., and (d) is for 8:00 LST on 22 Dec.

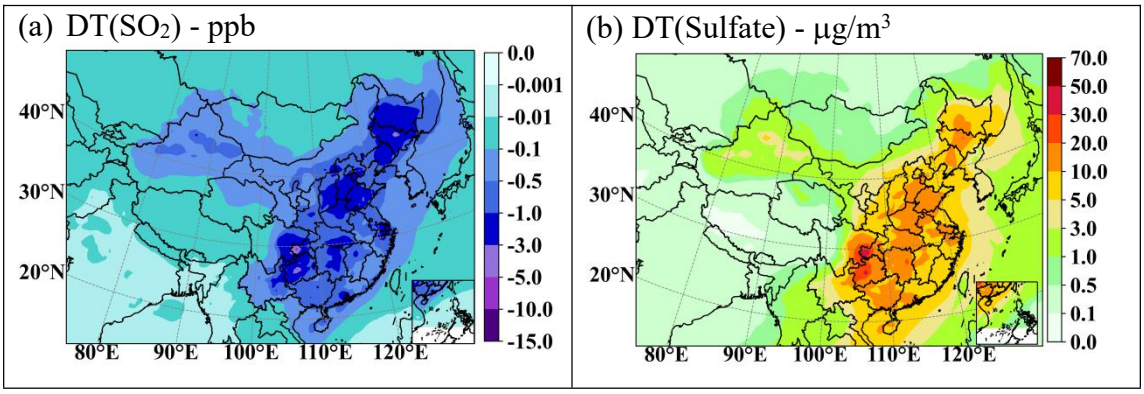

Figure 6. The mean SO_2 concentration decreased (a) and sulfate concentration increased (b) by cloud chemistry for DEC.

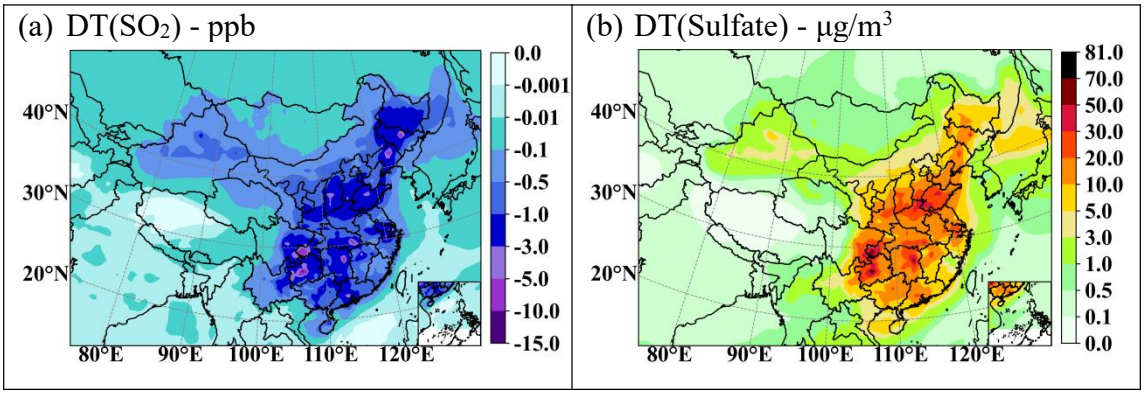

Figure 7. The mean SO_2 concentration decreased (a) and sulfate concentration increased (b) by cloud chemistry for HPE-2.

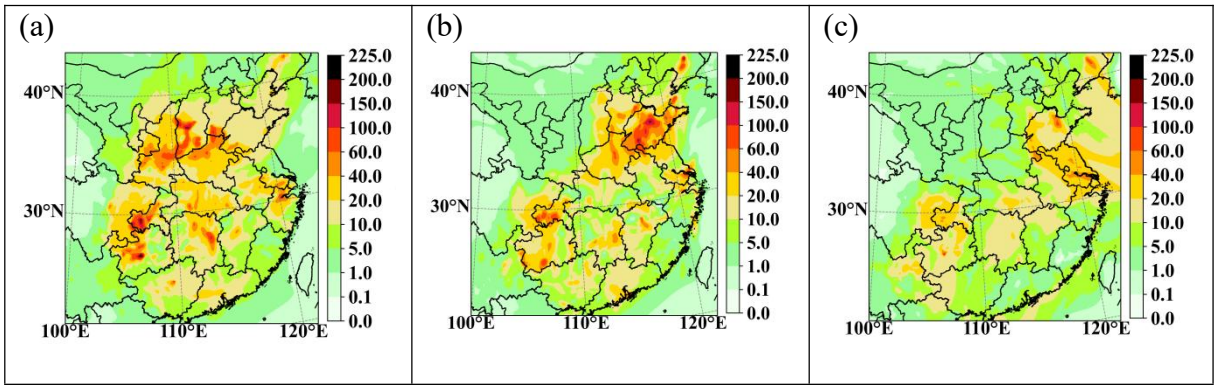

Figure 8. The differences in surface sulfate concentrations between with and without cloud chemistry at 21:00 on 20 Dec. (a), at 17:00 on 21 Dec. (b), and at 12:00 on 22 Dec. (c) (Units: μg/m^3).

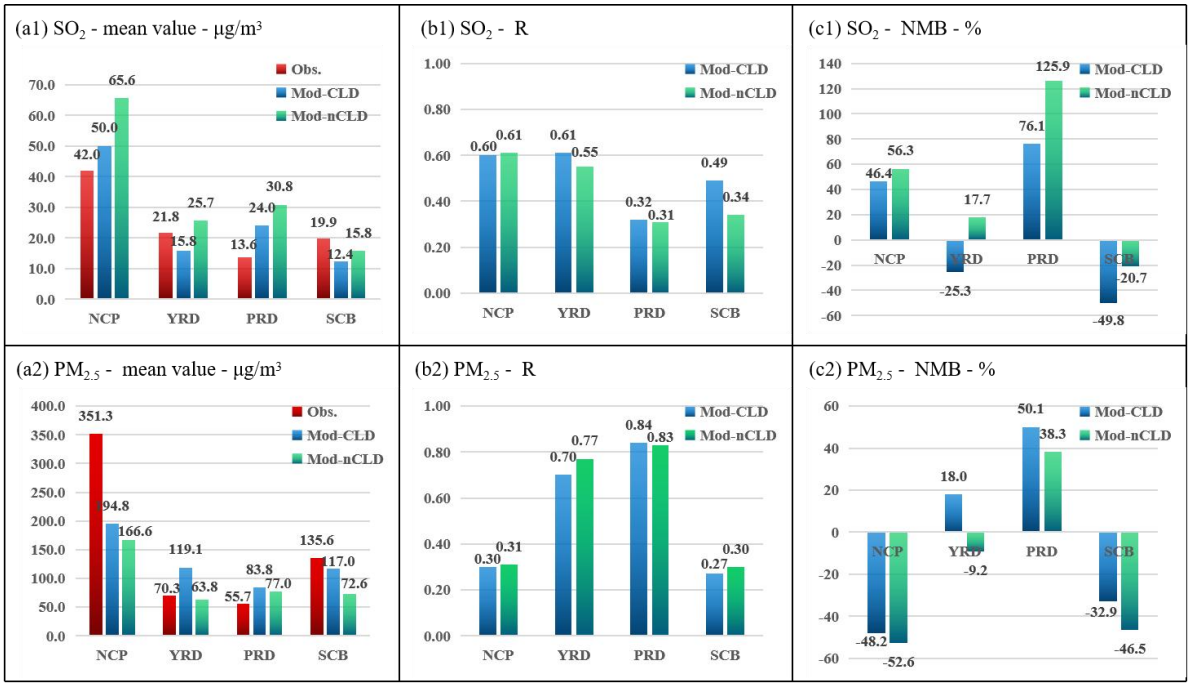

Figure 9. Statistical metrics for hourly SO_2 and $PM_{2.5}$ for four regions for HPE-2 with (Mod-CLD) and without (Mod-nCLD) cloud chemistry. The mean value (a1, Units: μg/m^3), R (b1) and NMB (c1, Units: %) of SO_2 as well as the mean value (a2, Units: μg/m^3) , R (b2) and NMB (c2, Units: %) of $PM_{2.5}$. Obs. denotes the observations.

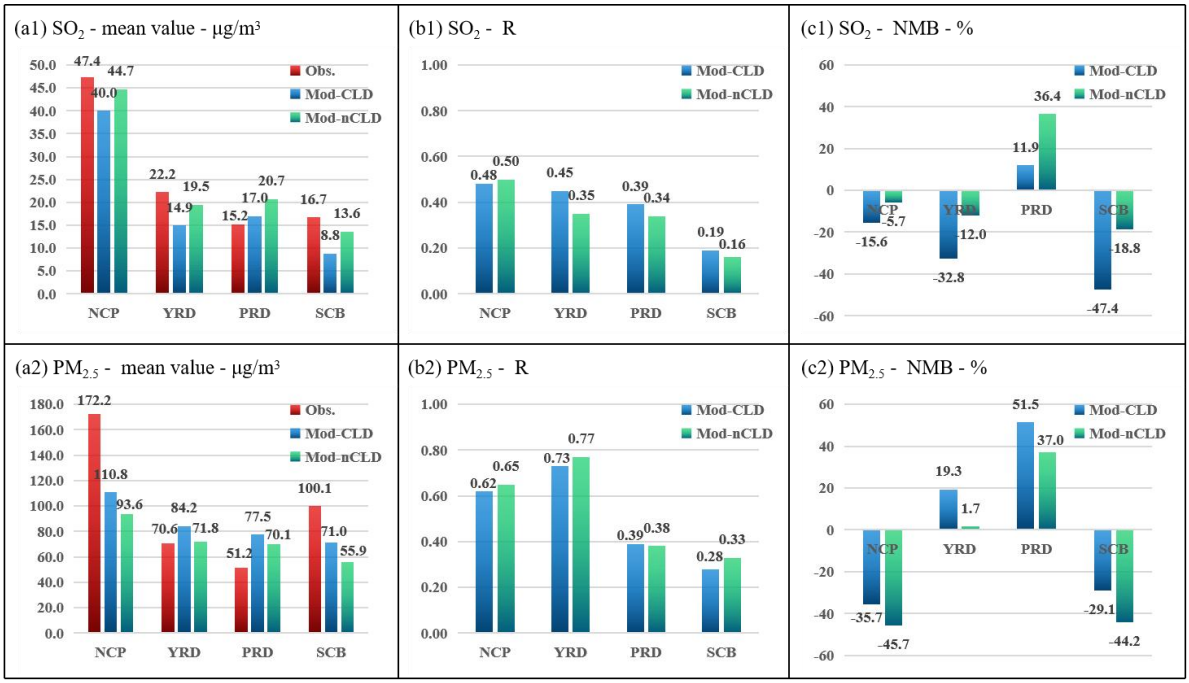

Figure 10. Statistical metrics for hourly SO_2 and $PM_{2.5}$ for four regions for DEC with (Mod-CLD) and without (Mod-nCLD) cloud chemistry. The mean value (a1, Units: μg/m^3) , R (b1) and NMB (c1, Units: %) of SO_2 as well as the mean value (a2, Units: μg/m^3) , R (b2) and NMB (c2, Units: %) of $PM_{2.5}$. Obs. denotes the observations.

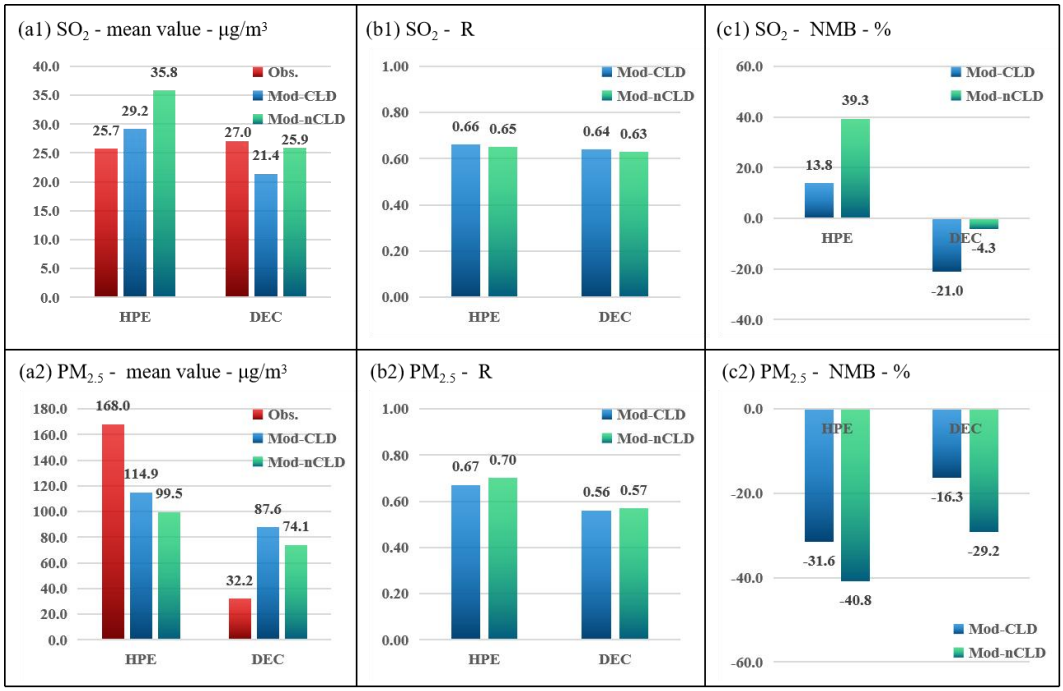

Figure 11. Statistical metrics for hourly SO_2 and $PM_{2.5}$ in all selected sites for HPE-2 and DEC with (Mod-CLD) and without (Mod-nCLD) cloud chemistry. The mean value (a1, Units: μg/m^3) , R (b1) and NMB (c1, Units: %) of SO_2 as well as the mean value (a2, Units: μg/m^3) , R (b2) and NMB (c2, Units: %) of $PM_{2.5}$. Obs. denotes the observations.

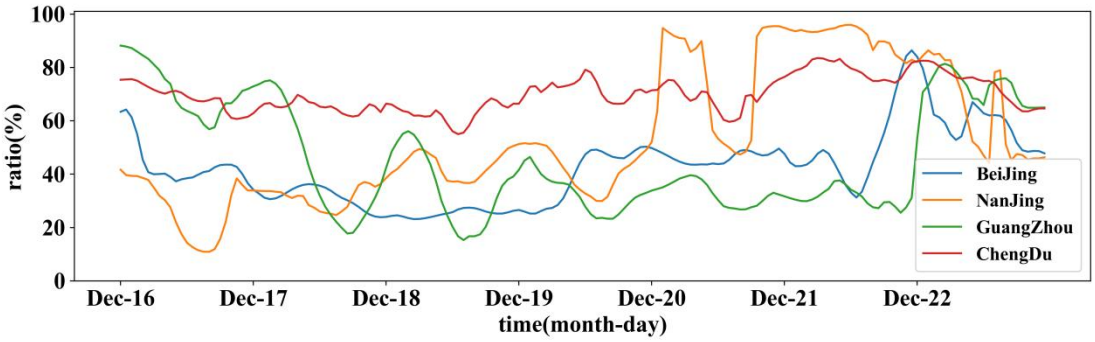

Figure 12. The rates of SO_2 column concentration reduced by cloud chemistry in Beijing (blue), Nanjing (yellow), Guangzhou (green) and Chengdu (red).

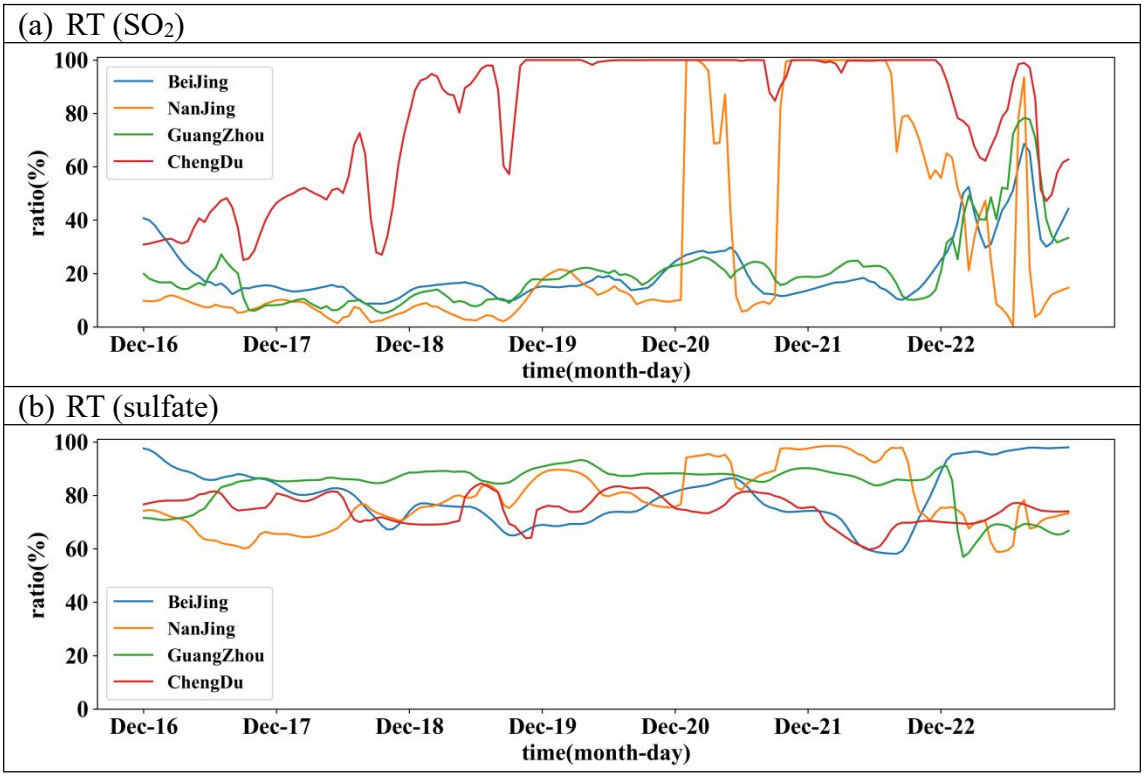

Figure 13. The rates of surface SO_2 reduced (a) and the surface sulfate increased (b) influenced by cloud chemistry in Beijing (blue), Nanjing (yellow), Guangzhou (green) and Chengdu (red).

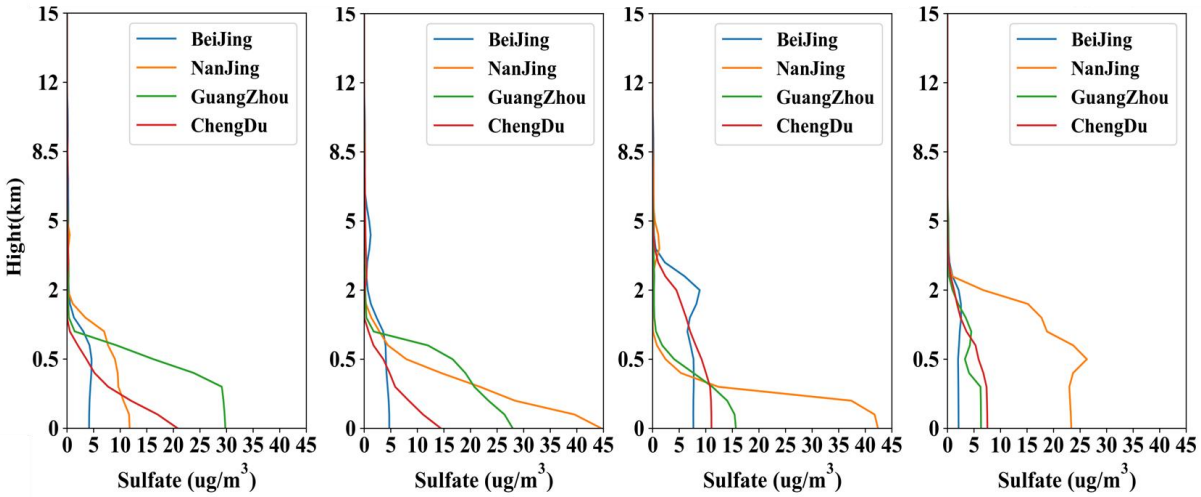

Figure 14. Vertical profiles of sulfate concentration difference (DT) at 12:00 on 20 Dec., at 21:00 on 20 Dec., at 17:00 on 21 Dec., and at 12:00 on 22 Dec. in Beijing (blue), Nanjing (yellow), Guangzhou (green) and Chengdu (red).

Table 1. Equilibrium Constants for the Parameterization of the Cloud Chemistry in CUACE.

Equilibrium Relation	Constant Expression	Equilibrium Constant		
		K(298)	a	Unit
$SO_2(g)+H_2O(aq)\leftrightarrow SO_2(aq)$	$K_{HS}=\frac{[SO_2(aq)]}{[SO_2(g)]}$	1.23	3120	$\frac{M}{\text{atm}}$
$SO_2(aq)\leftrightarrow H^+ + HSO_3^-$	$K_{1S}=\frac{[H^+][HSO_3^-]}{[SO_2(aq)]}$	1.7×10^{-2}	2090	M
$HSO_3^- \leftrightarrow H^+ + SO_3^{2-}$	$K_{2S}=\frac{[H^+][SO_3^{2-}]}{[HSO_3^-]}$	6.0×10^{-8}	1120	M
$O_3(g)+H_2O(aq)\leftrightarrow O_3(aq)$	$K_{HO}=\frac{[O_3(aq)]}{[O_3(g)]}$	1.15×10^{-2}	2560	$\frac{M}{\text{atm}}$
$H_2O_2(g)+H_2O(aq)\leftrightarrow H_2O_2(aq)$	$K_{HP}=\frac{[H_2O_2(aq)]}{[H_2O_2(g)]}$	9.7×10^{4}	6600	$\frac{M}{\text{atm}}$

Table 2. physics parameterization schemes in WRF.

Physical management	Parameterization	References
microphysics scheme	Lin	Lin et al. (1983)
shortwave radiation	Goddard	Chou and Suarez (1994)
longwave radiation	RRTM	Mlawer et al. (1997)
land surface scheme	Noah	Chen and Dudhia (2001)
boundary layer scheme	MYJ	Janjić (1994)
cumulus scheme	Grell-3D	Grell (1993)

Table 3. Statistics for SO_2, O_3, H_2O_2 and sulfate in cloud chemistry at Mount Tai site.

		Obs.	Mod	R	RAD(%)	NMB(%)
CP-1	SO_2	2.2	2.3	0.34	-3.4	7.1
	O_3	97.8	55.3	0.33	27.8	-43.5
	H_2O_2	26.5	16.8	0.78	22.4	-36.6
	Sulfate	31.7	9.2	0.32	55.0	-71.0
CP-2	SO_2	0.6	0.6	0.47	-6.1	12.9
	O_3	60.7	51.0	0.40	8.7	-16.0
	H_2O_2	46.9	32.4	0.06	18.4	-29.6
	Sulfate	28.1	11.4	0.54	42.2	-59.4

Note: unit of SO_2 and O_3 (ppbv), H_2O_2 (μM), and Sulfate ($\mu g/m^3$)

Table 4. Statistical metrics for meteorology in four regions for HPE and DEC

		Obs.		Mod		R		NMB(%)		RMSE	
		HPE	DEC	HPE	DEC	HPE	DEC	HPE	DEC	HPE	DEC
NCP	T2	1.0	1.1	2.8	2.1	0.70	0.84	187.3	84.9	3.3	2.5
	RH2	78.8	68.3	52.3	48.8	0.54	0.64	-33.7	-28.6	32.3	25.9
	WS10	1.5	1.7	1.7	2.2	0.49	0.54	14.1	27.5	1.2	1.3
YRD	T2	9.2	8.0	9.5	8.4	0.94	0.96	2.9	5.1	1.4	1.3
	RH2	79.2	75.6	73.8	73.0	0.86	0.85	-6.8	-3.5	10.7	9.3
	WS10	2.2	2.3	2.8	3.0	0.74	0.76	28.7	31.9	1.2	1.3
PRD	T2	18.3	17.3	19.0	17.9	0.93	0.92	3.6	3.8	1.9	1.9
	RH2	72.2	70.4	64.3	65.4	0.76	0.68	-10.9	-7.2	14.0	13.9
	WS10	1.8	2.4	2.0	3.2	0.67	0.72	13.6	37.1	1.0	1.5
SCB	T2	10.2	9.7	10.5	10.0	0.74	0.75	2.8	3.1	1.8	2.2
	RH2	81.6	79.9	74.1	71.3	0.66	0.60	-9.2	-10.8	12.7	15.5
	WS10	1.1	1.3	1.6	1.9	0.49	0.36	49.2	50.5	1.0	1.3

Note: unit of T2 (℃), RH2(%) and WS10 (m/s)

Table 5. Statistical metrics for hourly SO_2, O_3 and $PM_{2.5}$ in four regions for HPE and DEC

		Obs.(μg/m^3)		Mod(μg/m^3)		R		NMB(%)	
		HPE	DEC	HPE	DEC	HPE	DEC	HPE	DEC
NCP	SO_2	42.0	61.5	50.0	40.0	0.60	0.48	46.3	-15.6
	O_3	8.8	7.4	7.4	10.9	0.47	0.60	-15.3	-32.4
	$PM_{2.5}$	351.3	182.1	194.8	110.8	0.30	0.62	-48.2	-35.7
YRD	SO_2	21.8	16.3	15.8	14.9	0.61	0.45	-25.3	-32.8
	O_3	31.3	14.4	9.3	22.1	0.33	0.68	-54.0	-45.5
	$PM_{2.5}$	70.3	82.9	119.1	84.2	0.70	0.73	18.0	19.3
PRD	SO_2	13.6	24.0	24.0	17.0	0.32	0.39	76.1	11.9
	O_3	45.7	56.3	56.5	57.4	0.84	0.80	23.0	13.9
	$PM_{2.5}$	55.7	83.6	83.8	77.5	0.84	0.39	50.1	51.5
SCB	SO_2	20.0	10.0	12.4	8.8	0.49	0.19	-49.8	-47.4
	O_3	22.0	49.0	45.3	54.2	0.20	0.47	123.1	97.4
	$PM_{2.5}$	135.6	91.0	117.0	71.0	0.27	0.28	-32.9	-29.1