https://doi.org/10.5194/acp-2022-716
Preprint. Discussion started: 1 November 2022

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

Jian-yan Lu[1], Sunling Gong[1,5]*, Chun-hong Zhou[1]*, Jian Zhang[1], Jian-min Chen[2,3,4], Lei Zhang[1]

[1] State Key Laboratory of Severe Weather, Key Laboratory of Atmospheric Chemistry of CMA, Institute of Atmospheric Composition, Chinese Academy of Meteorological Sciences, Beijing 100081, China
[2] Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), Department of Environmental Science and Engineering, Fudan Tyndall Centre, Institute of Atmospheric Sciences, Fudan University, Shanghai, China
[3] Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Science, Xiamen, China
[4] Shanghai Institute of Eco-Chongming (SIEC), No.3663 Northern Zhongshan Road, Shanghai 200062, China
[5] National Observation and Research Station of Coastal Ecological Environments in Macao, Macao Environmental Research Institute, Macau University of Science and Technology, Macao SAR 999078, China

* Corresponding authors.
E-mail addresses: Sunling.Gong@cma.gov.cn (S Gong), zhouch@cma.gov.cn (C Zhou)

Abstract

A regional online chemical weather model WRF/ CUACE (China Meteorological Administration Unified Atmospheric Chemistry Environment) was used to assess the contributions of cloud chemistry to the SO_2 and sulfate levels in typical regions in 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 was found to well reproduce the cloud processing the consumptions of H_2O_2, O_3 and SO_2, and consequently was used in the regional assessment for a heavy pollution episode and monthly average in December 2016. During cloud availability in heavy pollution episode, the sulfate production increases 40-80% and SO_2 reduces over 80%. During the heavy pollution episode, it is found that the cloud chemistry mainly affects the middle and lower troposphere below 5 km as well as within the boundary layer, and contributes significantly to SO_2 reduction and sulfate increase in east-central China. Among the regions of North China Plain (NCP), Yangtze River Delta (YRD) and Sichuan Basin (SCB), the SCB is mostly affected by the cloud chemistry, with the average SO_2 abatement up to about 1-15 ppb and sulfate increase up to more than 50 μg m^{-3}, followed by YRD where the contribution of cloud chemistry is still significant, averaging up to 1-3 ppb for SO_2 abatement and 5-20 μg/m^3 for sulfate increase. The cloud chemistry contribution to PRD and NCP are not significant and weaker than other two regions due to lighter pollution and less water vapor, respectively. In addition, the average contribution of cloud chemistry during the pollution period was significantly greater than that for all December. This

https://doi.org/10.5194/acp-2022-716
Preprint. Discussion started: 1 November 2022


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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 (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 also 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 this sulfate is produced in clouds (Hung et al., 2018; Faloona et al., 2010; Guo et al., 2012). Ge et al. (2021) calculated the contribution of cloud chemistry to global SO_2 contribution, and found that cloud chemistry processes reduced SO_2 concentrations by 0 ~ 50% in most of east-central China in all seasons. In China, 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.

In addition to the observations, model simulations are an important way for cloud chemistry at different spatial-temporal scales. GEOS-Chem, CMAQ, WRF-Chem, CCAMx, ESM2, and other models have all been used to study the cloud chemical processes on SO_2 and sulfate (Tremblay and Leighton, 1986; Ge et al., 2021; Ervens, 2015; Shimadera et al., 2011) and the complex homogeneous, inhomogeneous and multiphase reactions in clouds due to the complex mixture of gaseous, liquid and solid phases (Pye et al., 2020; Ravishankara, 1997; Liu et al., 2021).

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 include sulfate formation mechanisms in cloud chemistry, few models have assessed its contribution, especially the lack of detailed assessment of regional cloud chemistry on sulfate and SO_2 in

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China and those pollution regions. Many regional chemical transport models have reported the results of SO_2 over-estimate problems (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 problems (Ge et al., 2021). Therefore, there is a very important need to accurately quantify the contribution of cloud chemistry in these regions and the central-east China when it comes to heavily polluted weather to get a better understand of multi-dimensional pollution distributions, especially in the upper layer besides the surface.

This study is intended to use an on-line coupled chemical weather platform of CMA: WRF/CUACE, to analyze and evaluate the SO_2 in-cloud oxidation process in the four regions, 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. It is aimed to establish a system to assess the relative contribution of cloud chemistry to SO_2 oxidation pathways and sulfate productions to other clear-sky processes.

2 Model description and Methodology

2.1 Cloud chemistry in WRF/CUACE

WRF/CUACE is an on-line coupled chemical transport model under the WRF frame work with a comprehensive chemical module – CUACE, which was developed at CMA 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). There are 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 was 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 PM_{10}, $PM_{2.5}$, O_3 and visibility. The cloud chemistry mechanism in CUACE is a scheme developed by Salzen et al. (Gong et al., 2003; Von Salzen et al., 2000), which considers the oxidation of SO_2 by H_2O_2 and O_3 in both stratocumulus and convective clouds. 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:

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

where $C_{S(IV)}$ is the total concentration of S(IV) (gas phase plus dissolved), C_{O3} is the total concentration of O_3, and C_{H2O2} is the

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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_{O3} and R_{H2O2} refer to Maahs (1983) and Martin et al. (1984):

$$R_{O3} = \{4.4 \times 10^{11}\exp(-4131/T) + 2.6 \times 10^3\, exp(-966/T)\,[H^+]^{-1}\}(Ms)^{-1} \quad (4)$$

$$R_{H2O2} = 8 \times 10^4\exp[-3650(1/T - 1/298)]\{0.1 + [H^+]\}^{-1}(Ms)^{-1} \quad (5)$$

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. They are calculated from the dimensionless Henry's law constant and γ.

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

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

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

with

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

The Herry'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.

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

Eqs. (1) ~ (12) can be used to calculate the oxidation rates of SO_2 by the oxidants H_2O_2 and O_3 in the liquid environment in the cloud in CUACE and the transformations of sulfate. In CUACE, the equilibrium constant K_{HS} has been corrected from 1.23 to $1.23*10^{-3}$ and added it into the cloud chemistry. At the same time, all the unit in those cloud chemical formula in Table 1 have been checked and unified in terms of the original references to make them reasonable.

2.2 Assessment criteria

To assess the effect of the cloud chemistry mechanism on SO_2 and sulfate, three variables, RTCLD, DT, and RT, are

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defined. The RTCLD is defined as the ratio of chemical species before and after the cloud chemistry mechanism.

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

where i denotes the chemical component of SO_2, O_3, H_2O_2, and sulfate, hereafter. The BECLD denotes the concentration of component i before cloud chemistry, and the AFCLD after the cloud chemistry.

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

$$DT(i) = CLD(i) - CCLD(i) \quad (14)$$

The RT represents the concentration ratio change of the substance i with and without cloud chemistry:

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

2.3 Methodology

2.3.1 Model Evaluation – Case 1

Mount Tai with an altitude of about 1500 m, located in central Shandong Province, is the high point of the North China Plain. As the Riguan Peak of Mount Tai is far from pollution sources, and the water vapor conditions in summer favors very much cloud formations, 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 and H_2O_2 in cloudy conditions from June 19 to July 30, 2015 and from June 20 to July 30, 2018 with time interval of 1 h were 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 with two-domain nested 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 was selected with a widespread heavy pollution episode occurred in North and East China from Dec. 16 to 21 and covering NCP, YRD and SCB with the highest hourly fine particulate matter ($PM_{2.5}$) concentration exceeding 1100 μg m^{-3} (Yuan and Ma, 2017). The simulation region is set up as shown in Figure1b also 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.

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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 and Satellite Data

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

FY-2G cloud image data of CMA with an 1 h interval was used to evaluate the cloud in both cases. Routine observations in 3 h interval from 31 meteorological stations of CMA and hourly pollution observations from 31 stations of the China General Environmental Monitoring Station were used to evaluate the meteorological fields and pollutants for December 2016. Meteorological elements include 2 m air temperature, 2 m relative humidity, and 10 m wind speed.

This study uses the MEIC inventory as the default anthropogenic emissions, with 0.25° spatial resolution, including the emissions 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 sets for years of 2015 and 2017 were 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 simulations were compared with the cloud chemistry observations at Mount Tai. By analyzing the distribution of satellite cloud images in and around Mount Tai and matching with the observed data, two time periods with clouds from June 19 to July 30, 2015 and June 20 to July 30, 2018 were selected for the comparative analysis, defined as "cloud process-1" (CP-1) and "cloud process-2" (CP-2), respectively. The statistics of correlation coefficients (R), relative average deviation (RAD), and normalized mean deviation (NMB) between hourly simulated and observed SO_2, O_3, and H_2O_2 are shown in Table 3. The results show that the RADs of SO_2, O_3 and H_2O_2 in CP-1 and CP-2 are in the range of 2% ~ 30%, and the simulated and observed averages are within the same magnitude and close to each other. Among them, the simulated and observed averages of SO_2 were very close in both CP-1 and

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CP-2, with RAD below 10 %. The R for the three species are 0.77, 0.49 and 0.72 for CP-1, and 0.49, 0.46 and 0.03 for CP-2, respectively. The analysis reveals that although the correlation of H_2O_2 in CP-2 is only 0.03, the RAD is -2 % and the NMB is 5.1 %. All the above results show that SO_2 and two important oxidants O_3 and H_2O_2 are reasonably simulated in both time periods.

It is also found that when cloud chemistry occurs, SO_2 concentration values range from 0-3 ppbv, mostly less than 1 ppbv, O_3 in the range of 25-125 ppbv, and H_2O_2 in the range of 0-100 uM (Fig. 2) in clouds. All three species are agreed within a factor two of observed concentrations. In addition, CP-2 shows increased concentrations of both oxidants of O_3 and H_2O_2, compared to CP-1. The SO_2 concentrations are small for both time periods. Shen et al. (2012) found mean SO_2 concentrations of 8.1 ppbv and 6.4 ppbv for the Mount Tai site in summer 2007 and 2008. Li et al. (2020) observed that the yearly mean summer SO_2 concentrations of 1.3 ± 1.1 ppbv, 0.3 ± 0.2 ppbv, and 0.4 ± 0.2 ppbv in 2014, 2015, and 2018, respectively. The average O_3 concentrations were 50.3 ± 10.9 ppbv, 73.1 ± 19.7 ppbv and 66.3 ± 18.3 ppbv, respectively. The mean H_2O_2 concentrations were 11.6 ± 13.1 μM, 22.8 ± 13.1 μM, and 45.1 ± 29.5 μM, respectively. Besides, H_2O_2 concentrations were 0.55 ± 0.67 ppbv in 2007 (Ren et al., 2009), 0.93 ± 1.01 ppbv in 2018 (Ye et al., 2021), 2.05 ± 1.20 ppbv in 2019 (Ye et al., 2021). The results of our simulations are consistent with the trends of other observational studies, which indicates an increase in the atmospheric oxidation and a decrease in the SO_2 concentration.

Figure 3 shows the satellite cloud maps, simulated column cloud and simulated liquid water content at 8:00 LST on June 24, and 8:00 LST on June 25 in CP-1. The results indicate that not only the simulated column cloud but also the cloud liquid water distribution simulated at the two times are consistent with the satellite observations.

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. The results indicate that the RTCLD of SO_2 distribution simulated at the four times are consistent with the cloud liquid water, so for the distribution of RTCLD of SO_2 with a 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 and the important oxidants of O_3 and H_2O_2. The model not only simulates the concentrations of the three species, but also the SO_2 decreasing trend and O_3 and H_2O_2 increasing trends with year.

3.2 Assessment of the cloud chemistry impacts 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,

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PRD, and SCB (Fig. 1) in China for the whole December of 2016 and a pollution episode occurred during this period (Dec. 16-21) as Case 2.

3.2.1 Meteorological evaluation

As the driving force of air pollution and cloud chemistry, the meteorological conditions simulated in the four major pollution regions (Table 4) were evaluated with observations. The correlations of all elements with observations were very close in both the whole December and the heavy pollution in four regions, indicating that the model performed well both in December and the heavy pollution episode. The temperature correlation is the best in December, 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 RMSEs of wind speeds all range from 1.03 to 1.50 m s^{-1}, falling within the criteria (less than 2 m s^{-1}) to define "good" model performance in stagnant weather proposed by Emery et al. (Emery et al., 2001). The RSME of wind speed during heavy pollution is smaller than that of December, which indicates that the model can well performance 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 of the episode. The satellite image shows that the cloud coverage region is mainly in the southwest including SCB on the 19th, almost covers most of eastern China including NCP, YRD, PRD and SCB on the 20th and the 21st, and then move 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 three regions of NCP, YRD and SCB of the four pollution regions as PRD has relatively much less cloud. The column liquid water distribution also moves from west to east as the episode develops (Fig.5 a3-d3), but is located more southern part of eastern China than that of the cloud. In SCB and YRD, there is more abundant in liquid water content, which can reach more than 500 g m^{-2}, while in PRD There is slightly less, up to 100 g m^{-2}, and in NCP there is the least liquid water content, 0.1 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 better 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 were also 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

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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 during both December 2016 and the heavy pollution episode. O_3 correlates well with observations in all four regions. $PM_{2.5}$ is better simulated in three regions, NCP, YRD and PRD, and worse in SCB. SO_2 performs better in YRD and PRD, and relatively worse in NCP and SCB. All the three pollutants are better simulated in YRD and PRD during the heavy pollution episode than those for December averages. The following section of this paper will focus on assessing the impact of cloud chemical processes.

3.2.3 Assessment of regional contributions

The regional impacts of cloud chemical processes on surface SO_2 and sulfate were analyzed for whole December and for a pollution episode of Dec. 16-21. The pollution episode was investigated with respect to the maturity stage (21:00 LST on Dec. 20 - 17:00 LST on Dec. 21) and to the dissipation stage (2:00 LST on Dec. 22) for the four pollution regions NCP, YRD, PRD, and SCB.

The average effect of cloud chemistry on surface SO_2 and sulfate in December (Fig. 6, DT(SO_2) and DT (sulfate)) was simulated. It is found that SO_2 declination in December is concentrated mostly in the central-eastern part of China, by an average of 0.1-0.5 ppb in most regions there. The SCB was maintained as a relatively stronger center by declining 1.0-5.0 ppb, far more than other areas. NCP has no obvious declination center, while YRD has a smaller scatter declination center. Correspondingly, sulfate growth is mainly centering in SCB and other areas along the Yangtze River, with the maximum center up to 10-30 μg/m^3 in most part of SCB and 3-10 μg/m^3 in the Yangtze River. In contrast, there are no obvious growth centers in NCP and PRD.

The spatial distribution of cloud chemistry contribution to SO_2 and sulfate during the whole mature stage of the heavy pollution was analyzed (Fig. 7, DT(SO_2) and DT(sulfate)) on the 19th to the 21st. It shows that SO2 decreased the most in the SCB, exceeding 1-3 ppb in most area, to 3-15 ppb in the central region, and also up to 1-3 ppb in most area of the YRD, while the NCP and PRD decreased the least, below 1 ppb in most area. The regional distribution of sulfate increase and SO2 consumption is roughly anticorrelated, but still with difference. Sulfate increases by more than 10 μg/m3 in the area of from southern of the NCP to central China and from most of the eastern part of the SCB to YRD. Sulfate increases more than 20 μg/m3 in the SCB with up to more than 50 μg/m3 in the center, while 5-20 μg/m3 in YRD and 3-5 μg/m3 in PRD without obvious growth center. In NCP, the southern part about 5-20μg/m3, but most part less than 3 μg/m3.

Comparing the contribution of cloud chemistry in the whole December with the pollution maturity stage of 19-21, it shows that cloud chemistry in heavy pollution weather for SO_2 depletion and sulfate increase is mainly concentrated in the

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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, which is less polluted and has much more clouds than NCP, the effect of cloud chemistry on sulfate and its precursor SO_2 is always the most significant in the SCB, both during heavy pollution and averaged over the whole December.

Exploring details into the pollution episode, it is found that the cloud chemistry influence was mainly on SCB and YRD at 21:00 LST on Dec. 20. The sulfate concentration increases (RT(sulfate)) by about 10-40 μg/m^3 in most parts of SCB, and the highest is about 150-225 μg/m^3 in its southwest (Fig. 8a). The increase is about 10-40 μg/m^3 in most parts of YRD, with 5-10 μg/m^3 in some parts of its northwest, and the highest increase can reach 100-150 μg/m^3. At 21st 17:00 LST, it shows that the pollution episode has moved eastward and the cloud chemistry process has a stronger impact on NCP, YRD, PRD than that of the previous time (Fig. 8b). The increase center is located in Shandong Province, with up to 100-150 μg/m^3, and with about 1-5 μg/m^3 in most of NCP. In PRD, it has been influenced the least by the cloud process with sulfate concentration increase of 5-40 μg/m^3 scattering partly only in some regions. At 22nd 12 LST, although the episode has gradually dissipated, it still had an impact on SCB and YRD with sulfate increase about 10-40 μg/m^3 in most of these areas (Fig. 8c).

Above all, the contribution of cloud chemistry to surface sulfate during this pollution process is the highest in the SCB, followed by the NCP and YRD, with maximum concentration increases of 225 μg m^{-3}, 150 μg m^{-3}, and 40 μg m^{-3}, respectively, and sulfate increases of 10-40 μg m^{-3} in most regions of these three areas.

Further analysis of the simulation characteristics of cloud chemistry on all the regions during the pollution maturity stage, i.e., the cloud process from Dec. 19 to 21, was investigated (Table 6). It can be seen that cloud chemistry reduces the overestimation of SO_2 simulation, and the NMB decreases from 28.4% to 12.2%. The simulation of $PM_{2.5}$ changes from an underestimation to a slight overestimation, with the NMB changing from -34.6% to 3.8%. The R at the time of cloud chemistry simulation is also improved compared to the simulation without cloud chemistry. In conclusion, cloud chemistry can effectively reduce the model's overestimation of SO_2 and underestimation of $PM_{2.5}$.

3.3 Site evaluation of cloud chemistry

Representative sites of Beijing, Nanjing, Guangzhou and Chengdu at NCP, YRD, PRD and SCB were selected to quantify the impact of cloud chemistry during the pollution episode. The net depletion ratio of SO_2 column concentration (RT(SO_2)) during cloud chemistry is shown in Figure 9. It is found that SO_2 column concentration reduction maintained mostly a high value of over 70%, even to 80% sometimes, in Chengdu from 17th to 21st. In Nanjing, the SO_2 level was reduced by about 10% during the time from 17th to 19th and up to 70% from 20th to 21st when the episode matures there. The changes of SO_2 in these

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two cities are consistent with the changes in cloud and liquid cloud water content distributions during the pollution period in Figure 3. The SO_2 reduction in Beijing and Guangzhou is below 20% for most time and is consistently maintained at around 10%. 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, so 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 70% when cloud water content is abundant, which is also consistent with the observations of Mount Tai by Li (2020).

The effect of cloud chemistry on surface SO_2 and sulfate in four sites are also shown in Figure 10. The overall trend shows that the peak and valley regions of surface SO_2 consumption and sulfate increase are coincident. The cloud chemical processes make the surface SO_2 oxidation vary greatly between cities in different regions (Fig. 10a). The percentage of surface SO_2 consumption can reach more than 90% from 16th to 21st in Chengdu and Nanjing, while in Beijing and Guangzhou it is below 10%, reaching 20% until 22nd. Although the percentage of surface SO_2 consumption varies greatly, the increase in the percentage of sulfate in different cities does not vary that much. The increase in surface sulfate (Fig. 10b) was between 60% and 80% in Chengdu on the 19th to 21st, between 80% and 100% in Nanjing on the 20th to 21st, between 50% and 80% in Guangzhou, and between 20% and 40% in Beijing. The increase ratios of sulfate by cloud chemistry in Chengdu and Nanjing, where the influence of cloud chemistry is more evident than that in other two cities, are consistent with the results of Turnock et al. (2019).

Figure 11 is the variation of vertical profiles of sulfate increase at the four sites at 12:00 and 21:00 LST on 20 Dec., 17:00 LST on the 21 Dec. and 12:00 LST on the 22 Dec.. It shows that the sulfate produced by cloud chemistry during this pollution process is concentrated mostly below 5 km in the troposphere. Again, more sulfate has been produced in Chengdu and Nanjing in vertical than that of Beijing and Guangzhou, especially under 2 km in the troposphere.

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 of heavy pollution, which is in good agreement with the observations.

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The assessment of cloud chemistry contributions to the changes of SO_2 and sulfate in NCP, YRD, PRD and SCB regions by WRF/CUACE revealed that except for PRD, all other three regions are significantly affected by the cloud chemistry, of which the SCB is the most obvious, with the strongest SO_2 abatement and sulfate increase, averaging up to 1-15 ppb for SO_2 abatement and more than 20 μg/m^3 with up to more than 50 μg/m^3 for sulfate increase in the central. Although the average effect of cloud chemistry is much weaker in the NCP with 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 many clouds with more water vapor there. In addition, surface sulfate increases by 40-80% in Beijing, Nanjing, Chengdu and Guangzhou in December during heavy pollution, similar to that of previous studies (Turnock et al., 2019). Above all, the average contribution of cloud chemistry during the pollution period was significantly greater than that for all December. Vertically, the analysis of the pollution process for the 2016 winter heavy pollution episode showed that the cloud chemistry influence was mainly in the middle and lower troposphere below 5 km for 4 representative cities. Generally, the cloud chemistry improved the model performance by reducing the SO_2 overestimates and enhancing the correlations with observations for both SO_2 and sulfate.

This paper has been focused 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 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.

Acknowledgements

The authors would like to thank the Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention of Fudan

https://doi.org/10.5194/acp-2022-716
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University for providing O_3, SO_2 and H_2O_2 datas at Mount Tai during cloudy periods.

Financial support

This research has been supported by the National Key Project of the Ministry of Science and Technology of China(2022YFC3700303); CMA Innovation Development Project (CXFZ2021J023).

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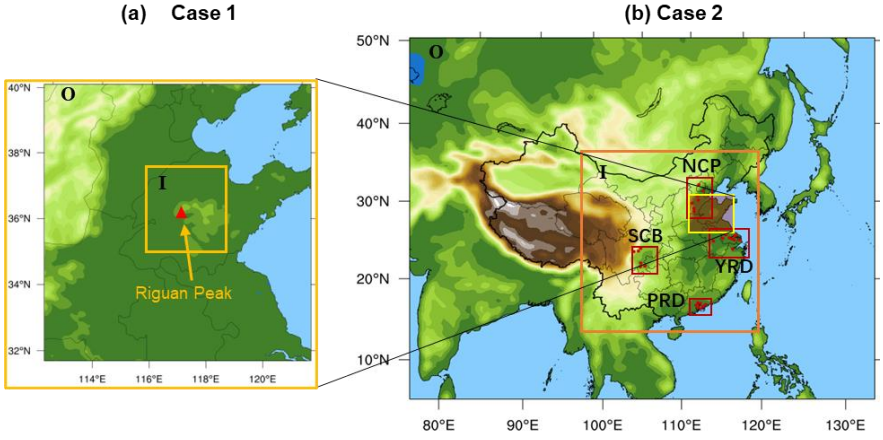

Figure 1. Model nesting domains and assessment regions: (a) finer grids for the Case 1, i.e., model evaluations. The red triangle is the Riguan Peak of the Mount Tai where the SO_2, O_3 and H_2O_2 were observed. and (b) larger grids for regional assessment for Case 2. The sites with the surface observations of air pollutants are illustrated with red dots. Four regional assessment regions, i.e., NCP, YRD, PRD and SCB are also outlined.

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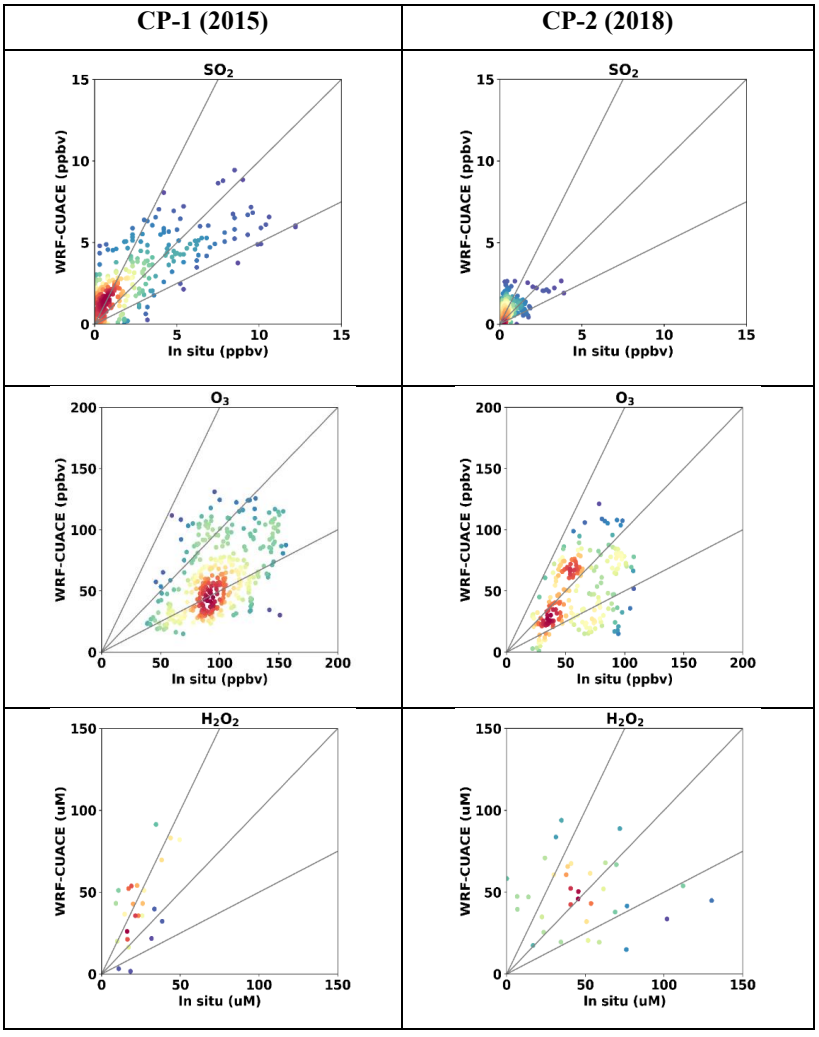

Figure 2. Scatter plots and correlation coefficients of hourly SO_2, O_3 and H_2O_2 concentrations between WRF/CUACE and in situ observations at Mount Tai.

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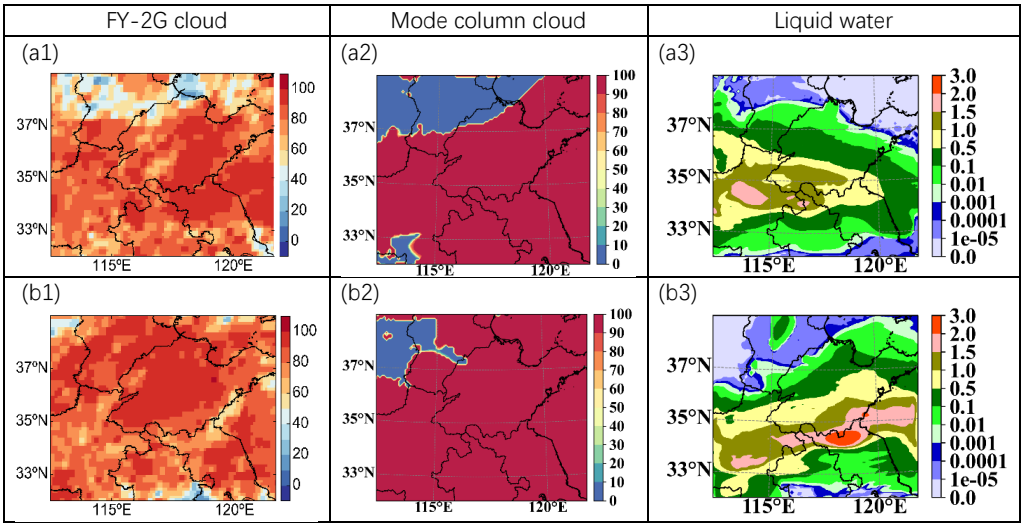

Figure 3. (a1, b1): the cloud image of FY2G, (a2, b2): the cloud fraction by WRF/CUACE. (a3, b3): the liquid water content by WRF/CUACE (Units: g m^{-2}). (a) is for 8:00 LST on 24 June, (b) is for 8:00 LST on 25 June.

https://doi.org/10.5194/acp-2022-716
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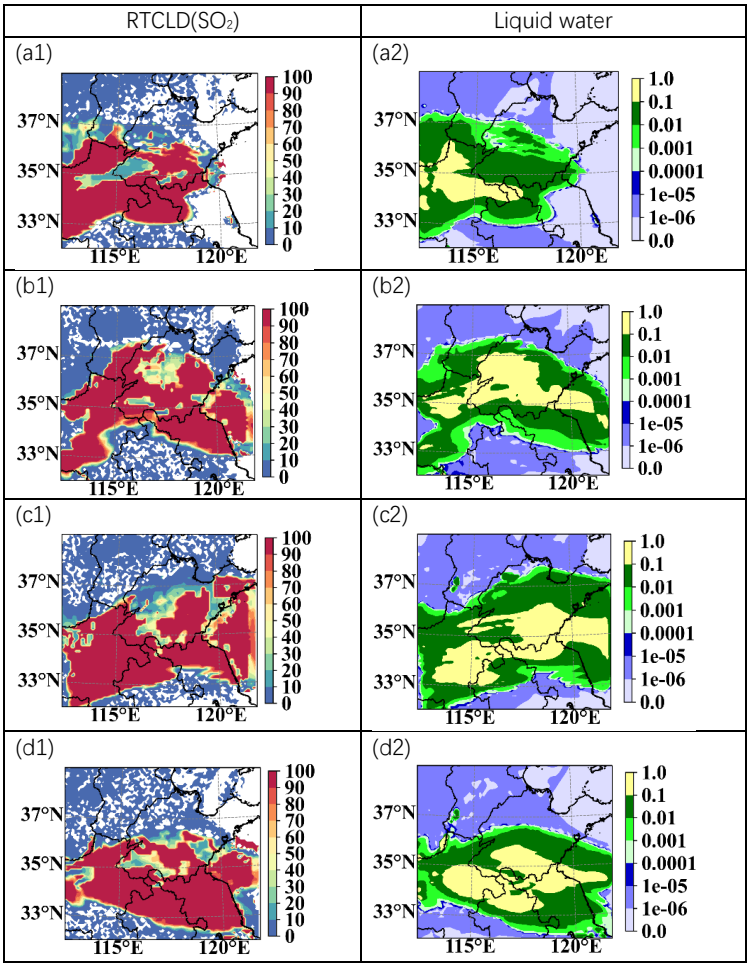

Figure 4. The percentage of SO_2 oxidized (a1, b1, c1 and d1) (%) and the liquid water content (a2, b2, c2 and d2) (g/kg) by WRF/CUACE, where (a) is for 2:00 LST on 24 June, (b) is for 8:00 LST on 24 June, (c) is for 2:00 LST on 25 June and (d) is for 8:00 LST on 25 June.

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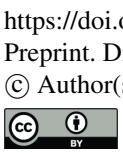

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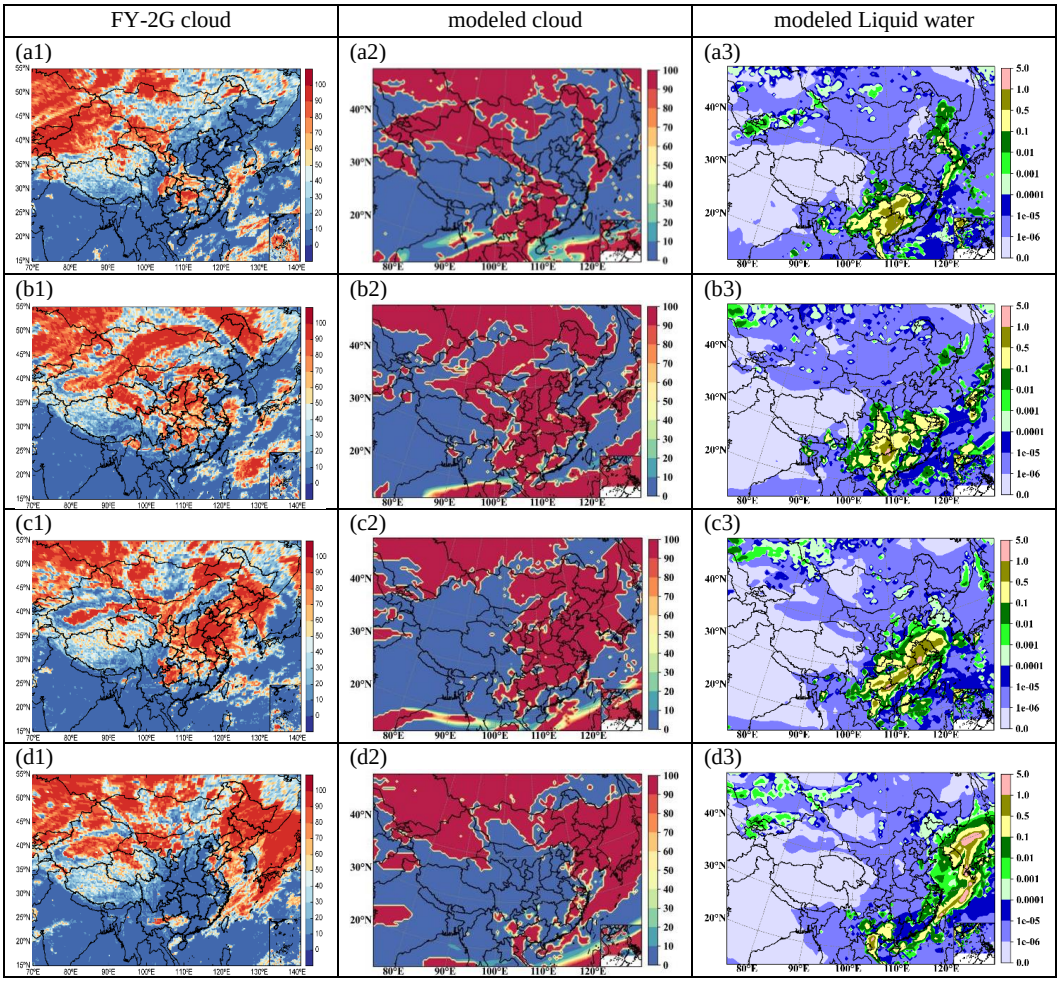

Figure 5. (a1, b1, c1, d1): the cloud image of FY-2G (%); (a2, b2, c2, d2): the column cloud of WRF/CUACE (%); (a3, b3, c3, d3): the liquid water content of WRF/CUACE (g/m²). (a) is for 8:00 LST on 19 Dec., (b) is for 8:00 LST on 20 Dec., (c) is for 8:00 LST on 21 Dec., and (d) is for 8:00 LST on 22 Dec.

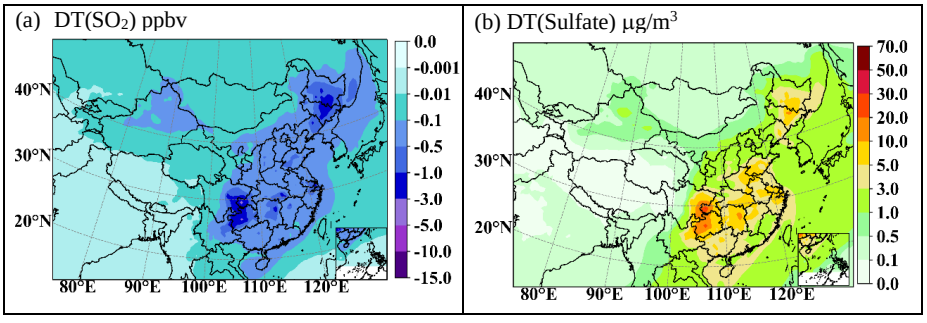

Figure 6. The mean SO_2 concentration decreased (a) and sulfate concentration increased (b) by cloud chemistry in Dec. 2016.

https://doi.org/10.5194/acp-2022-716
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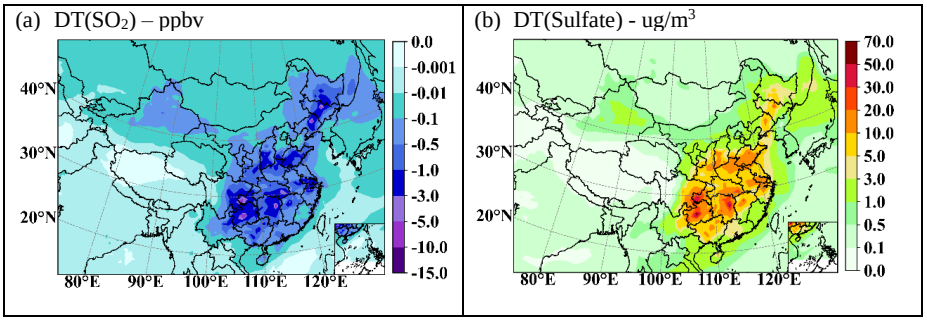

Figure 7. The mean SO_2 concentration decreased (a) and sulfate concentration increased(b) by cloud chemistry from 19-21 Dec., 2016.

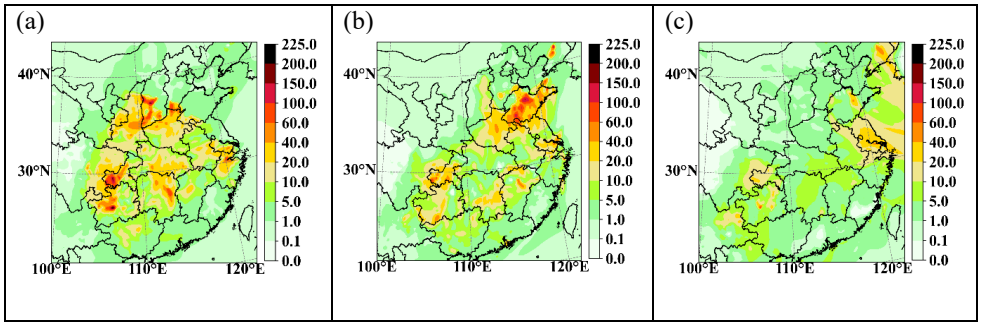

Figure 8. The differences in surface sulfate concentrations between with and without cloud chemistry at 21:00 on 20 Dec. (a), at 17:00 on 21 Dec. (b), and at 12:00 on 22 Dec. (c) (μ g/m³).

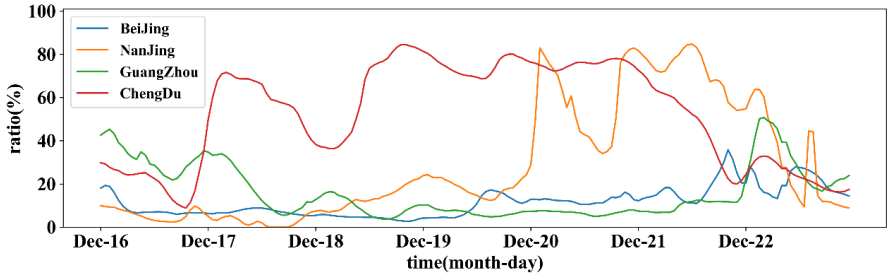

Figure 9. The percentage of SO_2 column concentration reduced due to oxidation in cloud chemistry.

https://doi.org/10.5194/acp-2022-716
Preprint. Discussion started: 1 November 2022

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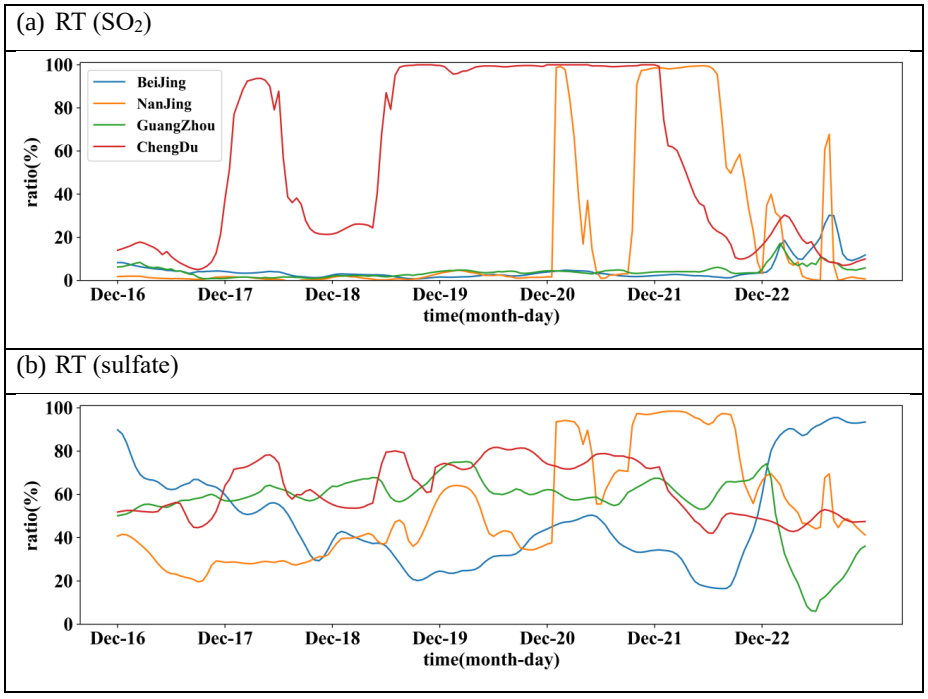

Figure 10. The percentage of surface SO_2 reduced (a) and the surface sulfate increased (b) influenced by cloud chemistry.

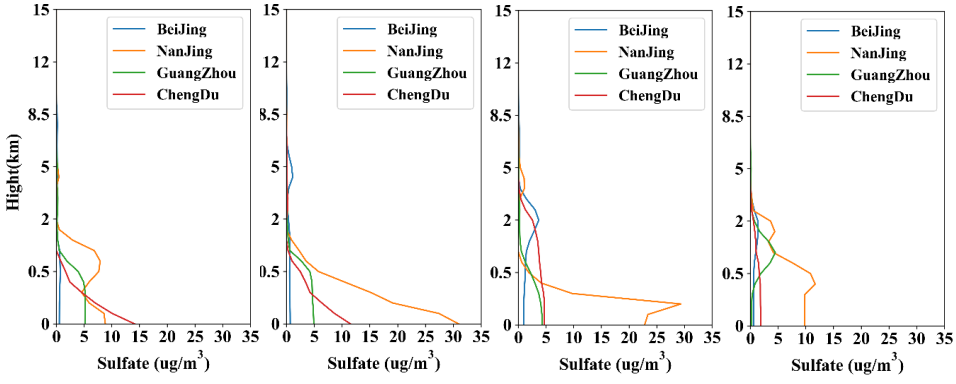

Figure 11. Vertical profile of sulfate concentration difference, i.e., DT (sulfate) at 12:00 on 20 Dec., at 21:00 on 20 Dec., at 17:00 on 21 Dec., and at 12:00 on 22 Dec.

https://doi.org/10.5194/acp-2022-716
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Table 1. Equilibrium Constants Used for the Parameterization of the Cloud Chemistry.

Equilibrium Relation	Constant Expression	Equilibrium Constant K(298)	a	Unit
$SO_2(g) + H_2O(aq) \leftrightarrow SO_2(aq)$	$K_{HS} = \frac{[SO_2(aq)]}{[SO_2(g)]}$	1.23×10^{-3}	3120	$\frac{M}{\text{atm}}$
$SO_2(\text{aq}) \leftrightarrow H^+ + HSO_3^-$	$K_{1S} = \frac{[H^+][HSO_3^-]}{[SO_2(aq)]}$	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 and H_2O_2 in cloud chemistry at Mount Tai site.

		Obs	Mod	R	RAD	NMB(%)
CP-1	SO_2(ppbv)	2.16	2.54	0.77	-0.08	17.4%
	O_3(ppbv)	97.79	61.70	0.49	0.23	-36.9%
	H_2O_2(uM)	26.52	49.11	0.72	-0.30	85.2%
CP-2	SO_2(ppbv)	0.56	0.81	0.49	-0.18	44.9%
	O_3(ppbv)	60.68	49.36	0.46	0.10	-18.7%
	H_2O_2(uM)	46.92	49.32	0.03	-0.02	5.1%

https://doi.org/10.5194/acp-2022-716
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Table 4. Statistical metrics for meteorology in NCP, YRD, PRD and SCB for Dec. 16-21 and the whole Dec. in 2016.

		Obs		Mod		R		NMB(%)		RMSE	
		16-21	Dec.	16-21	Dec.	16-21	Dec.	16-21	Dec.	16-21	Dec.
NCP	T2(℃)	0.99	1.11	2.83	2.05	0.70	0.84	187.31%	84.94%	3.30	2.51
	RH2(%)	78.83	68.31	52.30	48.75	0.54	0.64	-33.66%	-28.63%	32.24	25.89
	WS10(m/s)	1.47	1.69	1.67	2.16	0.49	0.54	14.05%	27.46%	1.15	1.26
YRD	T2(℃)	9.24	7.99	9.51	8.40	0.94	0.96	2.85%	5.08%	1.42	1.29
	RH2(%)	79.22	75.62	73.81	72.98	0.86	0.85	-6.83%	-3.49%	10.70	9.26
	WS10(m/s)	2.16	2.27	2.78	2.99	0.74	0.76	28.74%	31.93%	1.23	1.30
PRD	T2(℃)	18.31	17.27	18.98	17.93	0.93	0.92	3.64%	3.80%	1.85	1.92
	RH2(%)	72.19	70.43	64.31	65.35	0.76	0.68	-10.91%	-7.21%	13.97	13.92
	WS10(m/s)	1.78	2.36	2.02	3.24	0.67	0.72	13.57%	37.14%	0.97	1.49
SCB	T2(℃)	10.18	9.70	10.46	9.99	0.74	0.75	2.77%	3.08%	1.82	2.15
	RH2(%)	81.63	79.92	74.09	71.26	0.66	0.60	-9.23%	-10.84%	12.71	15.52
	WS10(m/s)	1.09	1.27	1.63	1.92	0.49	0.36	49.18%	50.48%	1.03	1.28

Table 5. Statistical metrics for hourly SO_2, O_3 and $PM_{2.5}$ in NCP, YRD, PRD and SCB for Dec. 16-21 and the whole Dec. in 2016.

		Obs		Mod		R		NMB(%)		RMSE	
		16-21	Dec.	16-21	Dec.	16-21	Dec.	16-21	Dec.	16-21	Dec.
NCP	SO2(ug/m3)	57.12	52.82	48.44	38.19	0.17	0.31	-15.2%	-27.7%	42.92	36.53
	O3(ug/m3)	11.15	15.46	9.35	11.16	0.35	0.55	-16.2%	-27.8%	13.05	14.60
	PM2.5(ug/m3)	319.30	186.66	296.41	196.24	0.40	0.59	-7.2%	5.1%	166.55	112.83
YRD	SO2(ug/m3)	22.37	19.55	22.48	19.82	0.55	0.42	0.5%	1.4%	13.09	12.81
	O3(ug/m3)	26.94	34.74	14.26	18.13	0.61	0.63	-47.1%	-47.8%	21.48	26.74
	PM2.5(ug/m3)	84.81	70.28	118.01	105.25	0.72	0.72	39.1%	49.8%	46.59	51.61
PRD	SO2(ug/m3)	15.19	15.18	28.45	19.51	0.46	0.35	87.3%	28.5%	21.36	13.30
	O3(ug/m3)	50.11	50.34	55.35	57.81	0.84	0.80	10.5%	14.8%	23.44	26.90
	PM2.5(ug/m3)	53.65	51.18	77.51	72.50	0.81	0.37	44.5%	41.7%	29.33	33.82
SCB	SO2(ug/m3)	22.03	20.31	16.55	12.49	0.32	0.24	-24.8%	-38.5%	14.58	14.72
	O3(ug/m3)	23.93	28.94	51.29	59.76	0.42	0.41	114.3%	106.5%	34.21	40.75
	PM2.5(ug/m3)	109.61	95.25	110.02	95.42	0.32	0.32	0.4%	0.2%	53.98	55.92

Table 6. Statistical metrics for hourly SO_2 and $PM_{2.5}$ for sites in NCP, YRD, PRD and SCB defined in Figure 1 for Dec. 19-21.

	Obs	Mod		R		NMB		RMSE	
		CLD	CCLD	CLD	CCLD	CLD	CCLD	CLD	CCLD
SO_2 (mg/m^3)	29.3	32.8	37.6	0.41	0.34	12%	28%	30.5	34.3
$PM_{2.5}$ (mg/m^3)	183.3	190.2	119.8	0.73	0.65	4%	-35%	121.1	150