Effects of stabilized Criegee Intermediates (sCI) on the sulfate formation: A sensitivity analysis during summertime in Beijing-Tianjin-Hebei (BTH), China

Lang Liu1,3,4, Naifang Bei5, Jiarui Wu1,3, Suixin Liu1,3, Jiamao Zhou1,3, Xia Li1,3, Qingchuan Yang1, Tian Feng1, Junji Cao1,3, Xueyi Tie1, Guohui Li1,3*

1Key Lab of Aerosol Chemistry and Physics, SKLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi’an, 710061, China
2School of Human Settlements and Civil Engineering, Xi’an Jiaotong University, Xi’an, Shaanxi, 710049, China
3CAS Center for Excellence in Quaternary Science and Global Change, Xi’an, 710061, China
4University of Chinese Academy of Sciences, Beijing, 100049, China

Correspondence to: Guohui Li (ligh@ieecas.cn)

Abstract: Sulfate aerosols exert profound impacts on climate, ecosystem, visibility, and public health, but the sulfate formation pathway remains elusive. In the present study, a source-oriented WRF-Chem model is applied to simulate a persistent air pollution episode from 04 to 15 July 2015 in Beijing-Tianjin-Hebei (BTH), China to study contributions of four pathways to the sulfate formation. When comparing simulations to measurements in BTH, the index of agreement (IOA) of meteorological parameters, air pollutants and aerosol species generally exceeds 0.6. On average in BTH, the heterogeneous reaction of SO2 involving aerosol water and the SO2 oxidation by OH constitutes the two most important sulfate sources, with a contribution of about 35–38% and 33–36% respectively. The primary emission accounts for around 22–24% of sulfate concentrations due to high SO2 emissions. The SO2 oxidation by stabilized Criegee Intermediates (sCI) also plays an appreciable role in the sulfate formation, with a contribution of around 9% when an upper limit of the reaction rate constant of sCI with SO2 ($k_{SCI+SO2} = 3.9 \times 10^{-11}$ cm$^3$ s$^{-1}$) and a lower limit of the reaction rate constant of sCI with H2O ($k_{SCI+H2O} = 1.97 \times 10^{-18}$ cm$^3$ s$^{-1}$) are used. Sensitivity studies reveal that there still exist large uncertainties in the sulfate contribution of the SO2 oxidation by sCI. The sulfate contribution of the reaction is decreased to less than 3% when $k_{SCI+SO2}$ is decreased to $6.0 \times 10^{-13}$ cm$^3$ s$^{-1}$. Furthermore, when $k_{SCI+H2O}$ is increased to $2.38 \times 10^{-15}$ cm$^3$ s$^{-1}$ based on the reported ratio of $k_{SCI+H2O}$ to $k_{SCI+SO2}$ ($6.1 \times 10^{-5}$), the sulfate contribution becomes insignificant, less than 2%. Further studies need to be conducted to better determine $k_{SCI+SO2}$ and $k_{SCI+H2O}$ to evaluate effects of the sCI chemistry on the sulfate formation.
1 Introduction

As a major component of fine particulate matters (PM$_{2.5}$) in the atmosphere, sulfate aerosols not only directly and indirectly influence regional and global climate, also impair ecosystem, visibility and potentially public health (e.g., Wang and Hao, 2012; Guo et al., 2014; Gao et al., 2016; Tao et al., 2017). Sulfate aerosols are primarily formed through homogeneous and heterogeneous oxidations of sulfur dioxide (SO$_2$) emitted from anthropogenic and natural sources (Seinfeld and Pandis, 2006). The sulfate formation pathway via the SO$_2$ oxidation includes aqueous reactions in cloud or fog droplets, heterogeneous reactions associated with aerosol water, and gas-phase reactions with hydroxyl radicals (OH) and stabilized Criegee Intermediates (sCI) (Seinfeld and Pandis, 2006; Wang et al., 2016; Li et al., 2017). Recent studies have revealed that the SO$_2$ oxidation by sCI could constitute an important sulfate source in the atmosphere (Welz et al., 2012; Mauldin et al., 2012; Boy et al., 2013; Pierce et al., 2013; Percival et al., 2013).

Carbonyl oxide intermediates formed in the ozonolysis reaction of alkenes, often known as sCI, are proposed to be important radicals in the atmosphere. In the gas phase, sCI can act as an additional atmospheric oxidant. Laboratory studies in the 1970s have shown that the SO$_2$ oxidation is enhanced in the presence of alkenes and ozone, providing the first evidence that sCI could react with SO$_2$ (Cox and Penkett, 1971). In the 2010s, Welz et al. (2012) have used photoionization mass spectrometry to make the first direct measurement of individual sCI isomers. They have found that the reaction rate of the simplest sCI, H$_2$COO, with SO$_2$ is faster than expected by up to three orders of magnitude, whereas the removal of sCI by water vapor is comparatively slow. The result has also indicated that the sCI chemistry potentially contributes substantially to the SO$_2$ oxidation, and exerts profound effects on the sulfate formation. Basing on the laboratory experiments and theoretical considerations, Mauldin et al. (2012) have reported the reaction rate of the sCI originated from the ozonolysis reaction of...
α-pinene and limonene with SO$_2$ under boundary layer atmospheric conditions. The new reaction rates are slower than those found in Welz et al. (2012), but still about one order of magnitude faster than previously used (Jenkin et al., 1997).

Further studies have been conducted to evaluate contributions of the SO$_2$ oxidation by sCI to the sulfate in the atmosphere, based on the results of Welz et al. (2012) and Mauldin et al. (2012). Boy et al. (2013) have examined effects of the increased reaction rate of sCI with SO$_2$ on the atmospheric sulfuric acid (H$_2$SO$_4$) concentration at two stations, showing that the reaction contributes as much as 33-46% of H$_2$SO$_4$ concentrations at the ground level. Using the results of Welz et al. (2012), Sarwar et al. (2013) have shown that the SO$_2$ oxidation by sCI does not substantially influence sulfate concentrations in the USA due to the competing reaction of sCI with water vapor. However, when using the high reaction rate constant of sCI with SO$_2$ ($\kappa_{sCI+SO_2}$) and the low reaction rate constant of sCI with H$_2$O ($\kappa_{sCI+H_2O}$) simultaneously, the SO$_2$ oxidation by sCI considerably enhances the sulfate formation (Sarwar et al., 2014). Li et al. (2013) have demonstrated that the SO$_2$ oxidation by sCI contributes about 18% of the sulfate concentration during summertime in the eastern USA, when using the $\kappa_{sCI+SO_2}$ reported by Welz et al. (2012). Pierce et al. (2013) have used the same $\kappa_{sCI+SO_2}$ in simulations of the GEOS-CHEM model, showing that the reaction increases the H$_2$SO$_4$ production globally by 4%, and the induced H$_2$SO$_4$ enhancement is almost entirely distributed over the forested continental regions with large fluxes of biogenic alkene emissions.

With rapid industrialization and urbanization, heavy air pollution with high levels of PM$_{2.5}$ and/or ozone (O$_3$) frequently occurs in Beijing-Tianjin-Hebei (BTH), and sulfate aerosols have become a main component of PM$_{2.5}$ (e.g., Zhang et al., 2012; Zhao et al., 2013; Sun et al., 2015; Li et al., 2017; Wu et al., 2017). Considering the high alkenes emissions and increasing trend of O$_3$ concentrations during summertime in BTH, it is imperative to assess
effects of the sCI chemistry on the sulfate formation. In the present study, a source-oriented
WRF-Chem model has been developed and applied to study the contribution of different
pathways to the sulfate formation in BTH during the summer of 2015. The model
configuration and methodology are described in Section 2. Results and discussions are
presented in Section 3. The conclusions and summaries are drawn in Section 4.

2 Model and methodology

2.1 WRF-CHEM model and configuration

A specific version of the WRF-Chem model (Grell et al., 2005) developed by Li et al.
(2010; 2011a; 2011b; 2012) at the Molina Center for Energy and the Environment is used in
the present study. Detailed model description can be found in previous studies (Li et al., 2018;
Wu et al., 2017; Feng et al., 2016; Xing et al., 2019). Briefly, the model includes a new
flexible gas-phase chemical module and the Community Multi-scale Air Quality (CMAQ)
aerosol module developed by the US EPA (Binkowski and Roselle, 2003). The wet
deposition uses the method in the CMAQ module and the dry deposition of chemical species
is parameterized following Wesely (1989). The photolysis rates are calculated using the Fast
Tropospheric Ultraviolet and Visible Radiation Model (FTUV; Li et al., 2005; Tie et al.,
2003), with the aerosol and cloud effects on the photochemistry (Li et al., 2011a). The
ISORROPIA Version 1.7 is applied to calculate the inorganic components (Nenes et al.,
1998). The secondary organic aerosol (SOA) is simulated using a non-traditional module,
including the volatility basis-set (VBS) modeling approach and SOA contributions from
glyoxal and methylglyoxal.

Traditionally, the brute force method (BFM) is generally used to quantify the formation
pathway of particulate matters and chemical compounds in modeling studies (Dunker et al.,
1996). The BFM method evaluates the importance of the certain formation pathway through
including and excluding the pathway in simulations, but it lacks consideration of interactions of the complicated physical and chemical processes in the atmosphere (Zhang and Ying, 2011). The source-oriented method introduces additional chemical species to represent formations from different pathways, providing direct and quantitative determination of contributions of different pathways (Ying and Krishnan, 2010). The coupled source-oriented method air quality models have been widely used to study source apportionment of particulate matters and chemical compounds. Detailed description about the method can be found in previous studies (Ying and Kleeman, 2006; Ying and Krishnan, 2010; Zhang and Ying, 2011). In the present study, four reactive tagged species are introduced to track the sulfate formation pathways.

A persistent air pollution episode with high levels of O$_3$ and PM$_{2.5}$ from 04 to 15 July 2015 in BTH is simulated in association with the observation of air pollutants and secondary aerosols. Detailed information about the episode can be found in Wu et al. (2017). Figure 1 shows the WRF-Chem model simulation domain and Table 1 presents the model configuration.

### 2.2 Simulations for the sulfate aerosols

Four sulfate formation pathways are considered in the WRF-Chem model, including (1) the heterogeneous reaction of SO$_2$ involving aerosol water (hereafter referred to as HR$_{SO_2}$), (2) the SO$_2$ oxidation by OH (hereafter referred to as OH$_{SO_2}$), (3) the primary emission, and (4) the SO$_2$ oxidation by sCI (hereafter referred to as sCI$_{SO_2}$). The sulfate formed in the four pathways is tagged and traced in the model to study their contributions to the sulfate formation. It is worth noting that the WRF-Chem model cannot well resolve clouds formed in the planetary boundary layer (PBL), so the aqueous SO$_2$ oxidation in cloud or fog droplets is not considered in the study, which might cause the sulfate underestimation. The HR$_{SO_2}$ is parameterized as a first-order irreversible uptake of SO$_2$ by aerosol water, with a reactive
uptake coefficient of $0.5 \times 10^{-4}$, assuming that alkalinity is sufficient to maintain the high iron-catalyzed reaction rate in BTH (Li et al., 2017).

Effects of the sCI chemistry on the sulfate formation depend on $\kappa_{\text{sCI}+\text{SO}_2}$ and $\kappa_{\text{sCI}+\text{H}_2\text{O}}$, as well as the sCI precursor concentration. In the study, sCI are assumed to yield from the ozonolysis reaction of five alkenes based on the SAPRC99 mechanism, including ethene (ETHE), terminal olefin (OLE1), internal olefin (OLE2), isoprene (ISOP), and monoterpenes (TERP). Detailed information about the sCI chemistry associated with the sulfate formation can be found in Table 2.

CH$_2$OO (sCI$_1$) is used to represent sCI produced from the ozonolysis reaction of ETHE and OLE1 and the sCI yield of the two reactions are described in Sarwar et al. (2013). CH$_3$CHOO (sCI$_2$) is formed from the ozonolysis reaction of OLE2, and proposed to have two isomers: syn-CH$_3$CHOO and ant-CH$_3$CHOO (Anglada et al., 2011). The reported reaction rate constants of syn-CH$_3$CHOO and ant-CH$_3$CHOO with H$_2$O are $3.23 \times 10^{-18}$ and $3.23 \times 10^{-13}$ cm$^3$ s$^{-1}$, respectively. We use syn-CH$_3$CHOO (sCI$_2$) to represent the sCI from the ozonolysis reaction of OLE2 to minimize the removal of sCI by water vapor and maximize sulfate production following Ying et al. (2014). sCI$_3$ is used to represent sCI from the ozonolysis reaction of isoprene and monoterpenes, and the detailed chemistry of sCI$_3$ is described in Sarwar et al. (2013, 2014).

In the base case (hereafter referred to as B-case) simulation used to compare with observations in BTH, we use a single $\kappa_{\text{sCI}+\text{SO}_2}$ reported by Welz et al. (2012) for reactions of SO$_2$ with sCI$_{1,2,3}$. For removal of sCI$_{1,2,3}$ by water vapor, we employ the $\kappa_{\text{sCI}+\text{H}_2\text{O}}$ suggested by Ying et al. (2014). While not important, the reaction of sCI$_{1,2,3}$ with NO$_2$ is also implemented in the model, and the rate constant is taken from Welz et al. (2012).

2.3 Observations
Simulations are compared to available meteorological and air pollutants observations to validate the model performance. The meteorological parameters including surface temperature (TSFC), relative humidity (RH), wind speed and direction with a 3-hour interval are obtained from the website http://www.meteomanz.com. The hourly measurements of PM$_{2.5}$, O$_3$, SO$_2$, and NO$_2$ used in this study are downloaded from the website http://www.aqistudy.cn. The submicron sulfate, nitrate, ammonium, and organic particulate matters are observed by the Aerodyne Aerosol Chemical Speciation Monitor (ACSM) at the National Center for Nanoscience and Technology (NCNST), Chinese Academy of Sciences, Beijing (116.39°E, 39.99°N). Detailed description about the methods to obtain the primary organic aerosol (POA) and secondary organic aerosol (SOA) mass concentration from the results of ACSM are given in Wu et al. (2017). Figure 1 shows the locations of the ambient air quality monitoring sites and the NCNST observation site.

2.4 Statistical methods for model evaluation

In this study, the mean bias (MB), root mean square error (RMSE) and the index of agreement (IOA) are used to evaluate the model performance:

\[
MB = \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i) \quad (1)
\]

\[
RMSE = \left[ \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i)^2 \right]^{1/2} \quad (2)
\]

\[
IOA = 1 - \frac{\sum_{i=1}^{N} (P_i - O_i)^2}{\sum_{i=1}^{N} (|P_i - \bar{O}| + |O_i - \bar{O}|)^2} \quad (3)
\]

Where $P_i$ and $O_i$ are the simulated and observed variables, respectively. $N$ is the total number of the simulations for comparisons, and $\bar{O}$ donates the average of the observation.

The IOA ranges from 0 to 1, with 1 showing a perfect agreement of the simulation with the observation.

3 Results and discussions
3.1 Model evaluation

3.1.1 Meteorological parameters simulations in Beijing

Considering the key role of meteorological conditions in air pollution simulations (Bei et al., 2012, 2017), Figure 2 shows the temporal profiles of observed and simulated TSFC, RH, wind speed and wind direction from 04 to 15 July 2015 at the weather station in Beijing (Figure 1). The WRF-Chem model generally well replicates the temporal variation of the TSFC during the whole episode compared to observations, with the MB and IOA of 0.7°C and 0.95, respectively. The model considerably overestimates TSFC on July 4 and in the evening of July 13 and 14. The model also performs reasonably well in simulating the RH against observations, with the MB and IOA of -5.3% and 0.84, respectively. The observed high RH exceeding 75% during nighttime is generally well captured, except on July 4 and 14 when the TSFC is overestimated. In addition, the model also reasonably well tracks the temporal variations of the wind speed and direction compared to observations, with an IOA of around 0.60. In general, the reasonable simulations of meteorological fields provide a reliable basis for modeling the O₃ and PM₂.₅ pollution episode in the present study.

3.1.2 Air pollutant simulations in BTH

Figure 3 shows the diurnal profiles of measured and simulated PM₂.₅, O₃, NO₂, SO₂, and CO mass concentrations averaged over all ambient monitoring stations in BTH during the episode. Apparently, the WRF-Chem model exhibits good performance in simulating the temporal variations of PM₂.₅ and O₃ mass concentrations against observations in BTH, with the IOAs of around 0.90. However, the model fails to capture the observed high PM₂.₅ concentration on July 11 and 12, and frequently overestimates O₃ concentration in the evening, with a MB of 1.2 µg m⁻³. The simulated temporal variation of NO₂ mass concentrations is also generally consistent with observations in BTH, but the model frequently overestimates NO₂ concentrations against observations during nighttime, which
might be caused by the low simulated planetary boundary layer (PBL) height or the $O_3$ overestimation. Simulations of the $SO_2$ mass concentration are not as good as those of other pollutants in BTH during the episode, with an IOA of 0.45. During summertime, $SO_2$ is principally emitted by the point source, including the power plants and agglomerated industrial zones, so the uncertainties of simulated wind fields substantially affect the $SO_2$ simulations. Additionally, the model overestimation of $SO_2$ concentrations is also considerable during nighttime, which is perhaps due to the simulated low PBL height. It is worth noting that $NH_3$ plays an important role in the sulfate formation (Wang et al., 2016; Cheng et al., 2016), so it is imperative to validate $NH_3$ simulations using measurements. However, due to lack of routine measurements of $NH_3$ in BTH, the validation of the $NH_3$ simulation is not provided in the study.

Figure 4 presents the distributions of simulated and observed near-surface mass concentrations of $PM_{2.5}$, $O_3$, $NO_2$ and $SO_2$ along with the simulated wind fields averaged from 04 to 15 July 2015. Generally, the simulated wind in BTH is weak during the episode and the easterly wind prevails, which is favorable for the accumulation of air pollutants, particularly along the Taihang and Yanshan Mountains due to the blocking effect. The model generally well reproduces the spatial distribution of $PM_{2.5}$ concentrations against observations, with the $PM_{2.5}$ concentration exceeding 35 $\mu$g m$^{-3}$ in the plain area of BTH (Figure 4a). The average simulated peak $O_3$ concentrations are more than 200 $\mu$g m$^{-3}$ during the episode in the plain area of BTH, consistent with the measurement and showing the severe $O_3$ pollution (Figure 4b). High levels of $O_3$ indicate a strong atmospheric oxidation capacity (AOC), facilitating the photochemical reactions over BTH (Figure 4b). The simulated high $NO_2$ and $SO_2$ concentrations are generally concentrated in cities and their surrounding areas, in agreement with the measurement (Figures 4c and 4d). However, the model considerably overestimates the $NO_2$ concentrations against the measurement in Beijing,
Shijiazhuang and Handan city. In addition, the SO$_2$ concentrations in BTH are much lower than those during wintertime (Li et al., 2018; Xing et al., 2019), generally less than 30 µg m$^{-3}$.

Reduced SO$_2$ concentrations in BTH during summertime are caused by the efficient removal of gas-phase oxidations due to the high AOC, the reduction of residential coal combustion, and the increased PBL height.

3.1.3 Aerosol species simulations in Beijing

Figure 5 presents the temporal variations of simulated and observed submicron nitrate, ammonium, SOA and POA mass concentrations at NCNST site in Beijing from 04 to 15 July 2015. The WRF-Chem model reasonably reproduces the diurnal variation of the nitrate concentration compared to observations, with the MB and IOA of -0.7 µg m$^{-3}$ and 0.81, respectively (Figure 5a). Nitrate formation is sensitive to the air temperature, and its variation is generally negatively correlated with that of the temperature. When the temperature is lowest in the early morning, the nitrate concentration reaches its peaks; when the temperature is up to 30°C in the afternoon, the nitrate concentration is generally less than 1 µg m$^{-3}$. The simulated ammonium profile is generally in agreement with observations, with an IOA of 0.71, but the model biases are still large. The model underestimation of the ammonium concentration is considerable on July 11 and 12, and the overestimation is also noticeable on July 6 and 7. The model reasonably reproduces the temporal variation of the SOA and POA concentrations compared to the measurement at the NCNST site, with the IOA of around 0.60. The observed SOA concentration exhibits rather large fluctuations from 11 to 15 July 2015, which are not well tracked by the model. The model fails to capture the observed large fluctuations of POA concentrations. The POA concentration in Beijing is primarily contributed by direct emissions from vehicles, cooking, coal combustion, biomass burning, and trans-boundary transport from outside of Beijing (Wu et al., 2017; Wu et al., 2018), and
the uncertainties in various anthropogenic sources and simulated meteorological fields substantially affect the POA simulations (Bei at al., 2017; Bei et al., 2016).

In summary, the WRF-CHEM model performs reasonably well in simulating meteorological fields, air pollutants and aerosol species, providing the underlying basis for further evaluation of the sulfate formation pathway.

3.2 Contributions of four pathways to sulfate formation in Beijing and BTH

Figure 6a provides the diurnal profile of simulated and observed submicron sulfate concentrations at NCNST site in Beijing from 04 to 15 July 2015. The model reasonably well tracks temporal variations of the observed sulfate concentration, with the MB and IOA of -0.9 µg m⁻³ and 0.71, respectively. During 11 to 12 July 2015, the model noticeably underestimates the high sulfate concentrations against the measurement. As mentioned in Section 2, the aqueous oxidation of SO₂ in cloud or fog droplets is not considered in the simulation, which might constitute one of the most possible reasons for the underestimation.

Figures 6b-e present the contributions of the four pathways to the sulfate formation during the episode at NCNST site in Beijing. On average, the HR_SO₂ plays the most important role in the sulfate formation, with a contribution of about 32.1% (Figure 6b). Li et al. (2017) have also shown that the HR_SO₂ is the dominant sulfate source, contributing around 58.4% to sulfate concentrations in Beijing during wintertime due to the very humid conditions and inefficient sulfate formation from gas-phase SO₂ oxidation due to the low AOC. In this study, the average simulated RH is not high in Beijing, less than 50% during the episode, and high O₃ concentrations enhance the AOC to facilitate the gas-phase SO₂ oxidation, causing the decreased sulfate contribution of the HR_SO₂. It is worth noting that the HR_SO₂ relies on the assumption that alkalinity is sufficient to maintain the high iron-catalyzed reaction rate (Li et al., 2017). Figure 7 presents the temporal variation of the average simulated aqueous pH in Beijing during the episode. The simulated pH generally...
fluctuates between 5 and 7, with an average of 6.2, warranting the efficient iron-catalyzed reaction involving aerosol water. High O$_3$ concentrations substantially increase the sulfate formation efficiency through the SO$_2$ oxidation by OH and sCl. The OH-SO$_2$ plays considerable roles in the sulfate formation, with the contribution of 30.8\% (Figure 6c). It is worth noting that the primary emission pathway contributes 24.0\% of the sulfate concentration at NCNST site.

The sCl-SO$_2$ accounts for about 13.1\% of sulfate concentrations at NCNST site, less than the contribution of the other three pathways. Effects of the sCl-SO$_2$ on the sulfate formation depend on the $\kappa_{sCl+SO_2}$. The reported $\kappa_{sCl+SO_2}$ from previous studies spans orders of magnitude (Welz et al., 2012; Maudlin et al., 2012; Jenkin et al., 1997). In the present study, an upper limit of the $\kappa_{sCl+SO_2}$ (3.9×10$^{-11}$ cm$^3$ s$^{-1}$) is used in the B-case, which is reported by Welz et al. (2012). Furthermore, the reaction of sCl with H$_2$O is the main loss pathway for sCl in the atmosphere, and the $\kappa_{sCl+H_2O}$ used in this study represents a lower limit (1.97×10$^{-18}$ cm$^3$ s$^{-1}$) (Ying et al., 2014). Therefore, the contribution of the sCl-SO$_2$ to the sulfate formation might be overestimated in the present study.

Figure 8 presents the spatial distribution of contributions of the four pathways to the sulfate formation averaged during the episode. The contribution of the HR-SO$_2$ to the sulfate formation is substantial in BTH, particularly in the plain area with the sulfate contribution exceeding 4.0 μg m$^{-3}$ and being up to 7.0 μg m$^{-3}$ (Figure 8a). Under the condition of high O$_3$ concentrations, the OH-SO$_2$ oxidation also becomes an important sulfate source, with a sulfate contribution of more than 3.0 μg m$^{-3}$ in the plain area of BTH, which is comparable to the heterogeneous pathway (Figure 8b). Similar to the spatial distribution of SO$_2$ concentrations, the sulfate contribution of the primary emission is mainly concentrated in cities and their downwind areas (Figure 4c). In the plain area of BTH, the sulfate contribution of the primary emission is more than 2.0 μg m$^{-3}$ on average, and exceeds 7 μg m$^{-3}$ in
highly-industrialized cities, such as Shijiazhuang, Tangshan and Xingtai. The sulfate contribution of the sCI SO₂ is not as important as the other three sources, more than 0.8 µg m⁻³ in the plain area of BTH, and the most striking in Beijing, with a contribution exceeding 1.2 µg m⁻³.

### 3.3 Sensitivity studies

Considering the large variation of the reported \( k_{sCl+SO_2} \) and the importance of water vapor in the sCl removal, sensitivity studies are further conducted to evaluate the sulfate contribution of the sCl SO₂ in BTH when the different \( k_{sCl+SO_2} \) and \( k_{sCl+H_2O} \) are used in simulations. In the B-case simulation, an upper limit of the \( k_{sCl+SO_2} \) and a lower limit of \( k_{sCl+H_2O} \) are used. The simulated average sulfate concentration is 10.8 µg m⁻³ in BTH, constituting a major component of PM₂.₅. The HR SO₂ and OH SO₂ constitute the two most important sulfate sources, with the sulfate contribution of 35% and 33%, respectively. The primary emission makes up about 23% of the sulfate in BTH, caused by high SO₂ emissions.

The sulfate contribution of the sCl SO₂ is about 1.0 µg m⁻³ or 9.1%, less than that in Beijing with the higher O₃ concentration. Pierce et al. (2013) have used the same \( k_{sCl+SO_2} \) in GEOS-CHEM model as the B-case in the study, revealing that the H₂SO₄ concentration is increased by 4% due to the sCl SO₂ on global average. The H₂SO₄ enhancement is 10-25% over forested regions in the Northern Hemisphere (up to 100% in July), but is generally negligible elsewhere. The sulfate contribution of the sCl SO₂ in BTH is close to those over forested regions in Pierce et al. (2013), which is primarily caused by the increasing trend of O₃ and the high precursors emissions of sCl, such as ethene, isoprene and monoterpenes during summertime in the region. Additionally, Boy et al. (2013) have employed the \( k_{sCl+SO_2} \) reported by Mauldin et al. (2012) and Welz et al. (2012) to verify the sulfate contribution of the sCl SO₂ in European, showing a H₂SO₄ contribution of as much as 33-46% at the ground level. These different sulfate contributions of the sCl SO₂ are mainly caused by
the variation of the reaction constant of sCl with SO$_2$, NO$_2$, and H$_2$O and the sCl precursors concentration, as well as the atmospheric conditions in simulations (Taatjes, 2017).

Although the sCl_SO$_2$ is not an important sulfate source, its contribution might be overestimated. The $\kappa_{sCl+SO_2}$ used in the B-case is only measured for the smallest sCl, H$_2$COO, but the larger sCl (such as those produced from typical larger alkenes in the atmosphere) might have a lower reaction rate with SO$_2$ and produce stable low volatilities species such as sulfur-bearing secondary ozonides (Spracklen et al., 2011; Vereecken et al., 2012). Additionally, Welz et al. (2012) have measured $\kappa_{sCl+SO_2}$ at low pressure (4 Torr), making it unclear if those rates are appropriate for atmospheric conditions.

In the S1-case, the reported $\kappa_{sCl+SO_2}$ ($6.0 \times 10^{-13}$ cm$^3$ s$^{-1}$) by Mauldin et al. (2012) is used, which is deduced from ozonolysis of $\alpha$-pinene under boundary-layer atmospheric conditions, and the $\kappa_{sCl+H_2O}$ and $\kappa_{sCl+NO_2}$ are the same as those in the B-case. The sulfate contribution of the sCl_SO$_2$ becomes insignificant, around 0.3 µg m$^{-3}$ or less than 3% of the total simulated sulfate concentration on average during the episode in BTH (Figure 9).

Compared to the B-case, the sulfate contribution of the sCl_SO$_2$ is decreased by more than 70% in the S1-case. The substantial reduction reveals that further studies are needed to precisely determine the $\kappa_{sCl+SO_2}$.

One of the largest uncertainties concerning the lifetime of sCl is related to the $\kappa_{sCl+H_2O}$, but few studies have been conducted to directly measure the $\kappa_{sCl+H_2O}$. The reported $\kappa_{sCl+H_2O}$ varies widely, ranging from $2 \times 10^{-19}$ to $1 \times 10^{-15}$ cm$^3$ s$^{-1}$ (Hatakeyama and Akimoto 1994), and several studies show that the $\kappa_{sCl+H_2O}$ needs to be adjusted when the $\kappa_{sCl+SO_2}$ is adjusted (Li et al., 2013; Calvert et al., 1978; Suto et al., 1985). In order to evaluate the effect of water vapor on the sCl_SO$_2$, in the S2-case, the $\kappa_{sCl+H_2O}$ is increased to $2.4 \times 10^{-15}$ cm$^3$ s$^{-1}$ based on the reported ratio of $\kappa_{sCl+H_2O}$ to $\kappa_{sCl+SO_2}$ ($6.1 \times 10^{-5}$) (Calvert et al., 1978), and the
\( \kappa_{\text{sCl}+\text{SO}_2} \) and \( \kappa_{\text{sCl}+\text{NO}_2} \) are the same as those in the B-case. The average sulfate contribution of the \( \text{sCl}_2\text{SO}_2 \) in BTH is decreased to 0.2 \( \mu \text{g m}^{-3} \) or less than 2\% of the total simulated sulfate concentration due to the competition of water vapor with \( \text{SO}_2 \) for sCl (Figure 9). Additionally, if a low \( \kappa_{\text{sCl}+\text{SO}_2} \) is used in the S2-case, the effect of water vapor on the sCl removal becomes more substantial.

4 Summaries and Conclusion

In the present study, a persistent air pollution episode with high \( \text{O}_3 \) and \( \text{PM}_{2.5} \) concentrations from 04 to 15 July 2015 in BTH is simulated using a source-oriented WRF-Chem model to study the contributions of four pathways to the sulfate formation. The four sulfate formation pathways include the heterogeneous reaction of \( \text{SO}_2 \) involving aerosol water (HR\_\text{SO}_2), the \text{SO}_2 oxidation by OH (OH\_\text{SO}_2), the primary emission, and the \text{SO}_2 oxidation by sCl (sCl\_\text{SO}_2).

The WRF-Chem model reasonably reproduces the temporal variations of the meteorological parameters compared to observations at the weather station in Beijing. The model performs reasonably well in simulating the temporal profiles and spatial distributions of air pollutant mass concentrations against observations at monitoring sites in BTH. In addition, the simulated diurnal variations of submicron nitrate, ammonium, POA, SOA, and sulfate mass concentrations are generally in good agreements with the measurements at NCNST site in Beijing.

On average in BTH during the simulation episode, the HR\_\text{SO}_2 plays the most important role in the sulfate formation, with a sulfate contribution of about 35\%. Under conditions with the high \( \text{O}_3 \) concentration during summertime, the OH\_\text{SO}_2 also constitutes a major sulfate source comparable to the HR\_\text{SO}_2, accounting for about 33\% of the total simulated sulfate concentration in BTH. Due to high \( \text{SO}_2 \) emissions, the primary emission
contributes about 23% of the sulfate concentration in BTH, mainly concentrated in cities and
their downwind regions.

When an upper limit of the $\kappa_{\text{Cl}+\text{SO}_2}$ ($3.9 \times 10^{-11}$ cm$^3$ s$^{-1}$) and a lower limit of $\kappa_{\text{Cl}+\text{H}_2\text{O}}$
($1.97 \times 10^{-18}$ cm$^3$ s$^{-1}$) are used, the $\text{Cl}_2\text{SO}_2$ plays an appreciable role in the sulfate formation,
with a contribution of around 9%. However, there still exist large uncertainties in
contributions of the $\text{Cl}_2\text{SO}_2$ to the sulfate formation. Sensitivity studies reveal that the
sulfate contribution of the $\text{Cl}_2\text{SO}_2$ is substantially decreased to less than 3%, when the
$\kappa_{\text{Cl}+\text{SO}_2}$ is decreased to $6.0 \times 10^{-13}$ cm$^3$ s$^{-1}$ but the lower limit of $\kappa_{\text{Cl}+\text{H}_2\text{O}}$ remains.
Furthermore, when the $\kappa_{\text{Cl}+\text{H}_2\text{O}}$ is increased to $2.38 \times 10^{-15}$ cm$^3$ s$^{-1}$ based on the reported
ratio of $\kappa_{\text{Cl}+\text{H}_2\text{O}}$ to $\kappa_{\text{Cl}+\text{SO}_2}$ ($6.1 \times 10^{-5}$ cm$^3$ s$^{-1}$) but the upper limit of the $\kappa_{\text{Cl}+\text{SO}_2}$ remains,
the sulfate contribution of the reaction becomes insignificant, less than 2%. Future studies
still need to be conducted to measure the $\kappa_{\text{Cl}+\text{SO}_2}$ and $\kappa_{\text{Cl}+\text{H}_2\text{O}}$ under the atmospheric
condition to better evaluate effects of the $\text{Cl}$ chemistry on the sulfate formation.

Author contribution. Guohui Li, as the contact author, provided the ideas and financial
support, verified the conclusions, and revised the paper. Lang Liu conducted a research,
designed the experiments, carried the methodology out, performed the simulation, processed
the data, prepared the data visualization, and prepared the manuscript with contributions from
all authors. Naifang Bei, Jiarui Wu and Xia Li provided the treatment of meteorological data,
analyzed the study data, validated the model performance, and reviewed the manuscript.
Suixin Liu, Qingchuan Yang, Tian Feng, and Jiamao Zhou provided the observation data
used in the study, synthesized the observation, and reviewed the paper. Xuexi Tie and Junji
Cao provided critical reviews pre-publication stage.
Acknowledgements. This work is financially supported by the National Key R&D Plan (Quantitative Relationship and Regulation Principle between Regional Oxidation Capacity of Atmospheric and Air Quality (2017YFC0210000)) and National Research Program for Key Issues in Air Pollution Control (DQGG0105).
References


Table 1 WRF-CHEM model configurations.

<table>
<thead>
<tr>
<th>Regions</th>
<th>Beijing-Tianjin-Hebei (BTH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation period</td>
<td>July 4 to 15, 2015</td>
</tr>
<tr>
<td>Domain size</td>
<td>300 × 300</td>
</tr>
<tr>
<td>Domain center</td>
<td>38.0°N, 116.0°E</td>
</tr>
<tr>
<td>Horizontal resolution</td>
<td>6km × 6km</td>
</tr>
<tr>
<td>Vertical resolution</td>
<td>35 vertical levels with a stretched vertical grid with spacing ranging from 30m near the surface, to 500m at 2.5km and 1km above 14km</td>
</tr>
<tr>
<td>Microphysics scheme</td>
<td>WSM 6-class graupel scheme (Hong and Lim, 2006)</td>
</tr>
<tr>
<td>Boundary layer scheme</td>
<td>MYJ TKE scheme (Janjić, 2002)</td>
</tr>
<tr>
<td>Surface layer scheme</td>
<td>MYJ surface scheme (Janjić, 2002)</td>
</tr>
<tr>
<td>Land-surface scheme</td>
<td>Unified Noah land-surface model (Chen and Dudhia, 2001)</td>
</tr>
<tr>
<td>Long-wave radiation scheme</td>
<td>Goddard longwave scheme (Chou and Suarez, 2001)</td>
</tr>
<tr>
<td>Short-wave radiation scheme</td>
<td>Goddard shortwave scheme (Chou and Suarez, 1999)</td>
</tr>
<tr>
<td>Meteorological boundary and initial conditions</td>
<td>ERA-Interim 0.125°×0.125° reanalysis data (<a href="http://apps.ecmwf.int/datasets">http://apps.ecmwf.int/datasets</a>)</td>
</tr>
<tr>
<td>Chemical initial and boundary conditions</td>
<td>MOZART 6-hour output (Horowitz et al., 2003) (<a href="https://www.acom.ucar.edu/wrf-chem/mozart.shtml">https://www.acom.ucar.edu/wrf-chem/mozart.shtml</a>)</td>
</tr>
<tr>
<td>Anthropogenic emission inventory</td>
<td>SAPRC-99 chemical mechanism emissions (Zhang et al., 2009)</td>
</tr>
<tr>
<td>Biogenic emission inventory</td>
<td>MEGAN model developed by Guenther et al. (2006)</td>
</tr>
<tr>
<td>Four-dimension data assimilation</td>
<td>NCEP ADP Global Air Observational Weather Data (<a href="https://rda.ucar.edu/datasets">https://rda.ucar.edu/datasets</a>)</td>
</tr>
<tr>
<td>Model spin-up time</td>
<td>24 hours</td>
</tr>
</tbody>
</table>
Table 2 Reactions and rate constants related to the sCI chemistry

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant (cm$^3$ s$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ETHE + O$_3$ → ... + 0.37sCI$_1$</td>
<td>9.14×10$^{-15}$</td>
<td>Sarwar et al. (2013)</td>
</tr>
<tr>
<td>OLE1 + O$_3$ → ... + 0.319sCI$_1$</td>
<td>2.62×10$^{-15}$</td>
<td>Sarwar et al. (2013)</td>
</tr>
<tr>
<td>OLE2 + O$_3$ → ... + 0.319sCI$_2$</td>
<td>5.02×10$^{-16}$</td>
<td>Sarwar et al. (2013)</td>
</tr>
<tr>
<td>ISOP + O$_3$ → ... + 0.22sCI$_3$</td>
<td>7.88×10$^{-15}$</td>
<td>Sarwar et al. (2013)</td>
</tr>
<tr>
<td>TERP + O$_3$ → ... + 0.21sCI$_3$</td>
<td>1.08×10$^{-15}$</td>
<td>Sarwar et al. (2013)</td>
</tr>
<tr>
<td>sCl$_{1,2,3}$ + SO$_2$ → SULF</td>
<td>3.9×10$^{-11}$</td>
<td>Welz et al. (2012)</td>
</tr>
<tr>
<td>sCl$_{1,2,3}$ + NO$_2$ → NO$_3$</td>
<td>7.0×10$^{-12}$</td>
<td>Welz et al. (2012)</td>
</tr>
<tr>
<td>sCl$_{1,2,3}$ + H$_2$O →</td>
<td>1.97×10$^{-18}$</td>
<td>Ying et al. (2014)</td>
</tr>
</tbody>
</table>

Note: SULF represents sulfuric acid.
Figure Captions

Figure 1 WRF-Chem simulation domain with topography height. The red filled circles show the locations of the cities with ambient air quality monitoring sites, and the size of the circles represents the number of sites in each city. The white and black filled rectangle denotes the weather station and NCNST observation site in Beijing.

Figure 2 Temporal variations of the simulated (blue line) and observed (black dots) near-surface (a) temperature, (b) relative humidity, (c) wind speed, and (d) wind direction at the weather station in Beijing from 04 to 15 July 2015.

Figure 3 Comparison of observed (black dots) and simulated (blue line) diurnal profiles of near surface hourly (a) PM$_{2.5}$, (b) O$_3$, (c) NO$_2$, and (d) SO$_2$ averaged over all ambient monitoring stations in BTH from 04 to 15 July 2015.

Figure 4 Spatial distributions of average (a) PM$_{2.5}$, (b) peak O$_3$, (c) NO$_2$, and (d) SO$_2$ mass concentrations from 04 to 15 July 2015. Colored dots, colored contour, and black arrows are observations and simulations of air pollutants, and simulated surface winds, respectively.

Figure 5 Comparison of observed (black dots) and simulated (blue line) diurnal profiles of hourly submicron (a) nitrate, (b) ammonium, (c) SOA, and (d) POA mass concentrations at NCNST site in Beijing from 04 to 15 July 2015.

Figure 6 (a) Comparison of observed (black dots) and simulated (blue line) diurnal profiles of hourly submicron sulfate mass concentration, and temporal variation of simulated sulfate contribution of the (b) HR_SO$_2$, (c) OH_SO$_2$, (d) primary emission, and (e) sCI_SO$_2$ to the sulfate concentration at NCNST site in Beijing from 04 to 15 July 2015.

Figure 7 Temporal variation of the average simulated pH in Beijing from 04 to 15 July 2015.

Figure 8 Spatial distributions of average sulfate contributions of the (a) HR_SO$_2$, (b) OH_SO$_2$, (c) primary emission, and (d) sCI_SO$_2$ in BTH from 04 to 15 July 2015.

Figure 9 Temporal variations of the simulated average sulfate concentration contributed by the sCI_SO$_2$ (Blue line: B-case; Red line: S1-case; Green line: S2-case) in BTH from 04 to 15 July 2015.
Figure 1 WRF-Chem simulation domain with topography height. The red filled circles show the locations of the cities with ambient air quality monitoring sites, and the size of the circles represents the number of sites in each city. The white and black filled rectangle denotes the weather station and NCNST observation site in Beijing.
Figure 2 Temporal variations of the simulated (blue line) and observed (black dots) near-surface (a) temperature, (b) relative humidity, (c) wind speed, and (d) wind direction at the weather station in Beijing from 04 to 15 July 2015.
Figure 3 Comparison of observed (black dots) and simulated (blue line) diurnal profiles of near surface hourly (a) PM$_{2.5}$, (b) O$_3$, (c) NO$_2$, and (d) SO$_2$ averaged over all ambient monitoring stations in BTH from 04 to 15 July 2015.
Figure 4 Spatial distributions of average (a) PM$_{2.5}$, (b) peak O$_3$, (c) NO$_2$, and (d) SO$_2$ mass concentrations from 04 to 15 July 2015. Colored dots, colored contour, and black arrows are observations and simulations of air pollutants, and simulated surface winds, respectively.
Figure 5 Comparison of observed (black dots) and simulated (blue line) diurnal profiles of hourly submicron (a) nitrate, (b) ammonium, (c) SOA, and (d) POA mass concentrations at NCNST site in Beijing from 04 to 15 July 2015.
Figure 6 (a) Comparison of observed (black dots) and simulated (blue line) diurnal profiles of hourly submicron sulfate mass concentration, and temporal variation of simulated sulfate contribution of the (b) HR\_SO\_2, (c) OH\_SO\_2, (d) primary emission, and (e) sCl\_SO\_2 to the sulfate concentration at NCNST site in Beijing from 04 to 15 July 2015.
Figure 7 Temporal variation of the average simulated pH in Beijing from 04 to 15 July 2015.
Figure 8 Spatial distributions of average sulfate contributions of the (a) HR$_2$SO$_4$, (b) OH$_2$SO$_4$, (c) primary emission, and (d) sCl$_2$SO$_4$ in BTH from 04 to 15 July 2015.
Figure 9 Temporal variations of the simulated average sulfate concentration contributed by the \( \text{sCl}_\text{SO}_2 \) (Blue line: B-case; Red line: S1-case; Green line: S2-case) in BTH from 04 to 15 July 2015.