A possible pathway for rapid growth of sulfate during haze days in China

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Abstract. Rapid industrialization and urbanization have caused frequent occurrence of haze in China during wintertime in recent years. The sulfate aerosol is one of the most important components of fine particles (PM₁₀) in the atmosphere, contributing significantly to the haze formation. However, the heterogeneous formation mechanism of sulfate remains poorly characterized. The relationships of the observed sulfate with PM₁₀, iron, and relative humidity in Xi’an, China have been employed to evaluate the mechanism and to develop a parameterization of the sulfate heterogeneous formation involving aerosol water for incorporation into atmospheric chemical transport models. Model simulations with the proposed parameterization can successfully reproduce the observed sulfate rapid growth and diurnal variations in Xi’an and Beijing, China. Reasonable representation of sulfate heterogeneous formation in chemical transport models considerably improves the PM₁₀ simulations, providing the underlying basis for better understanding the haze formation and supporting the design and implementation of emission control strategies.

1 Introduction

Sulfate is a main component of aerosols or fine particles (PM₁₀) in the atmosphere and plays a key role in global climate change. The direct and indirect radiative effects induced by sulfate aerosols have constituted one of the major uncertainties in current assessments of climate change (IPCC, 2013). In addition, deposition of sulfate aerosols exerts deleterious impacts on ecosystems through acidification of soils, lakes, and marshes (e.g., Schindler, 1988; Gerhardsson et al., 1994). Sulfate is also an important contributor to the haze formation and substantially reduces the atmospheric visibility during hazy days (e.g., He et al., 2014; Guo et al., 2014).

The main source of sulfate in the atmosphere is the oxidation of sulfur dioxide (SO₂), which is directly emitted from fossil fuel combustion, industrial processes, and volcanoes, or generated by oxidation of other sulfur-containing species, such as dimethyl sulfide (DMS). The conversion of SO₂ to sulfate involves various processes, including gas-phase oxidations by hydroxyl radicals (OH) and stabilized criegee intermediates (sCI) (Mauldin III et al., 2012), aqueous reactions in cloud or fog droplets, and heterogeneous reactions associated with aerosols (Seinfeld and Pandis, 2006).

Model studies have been performed to investigate the formation of sulfate aerosols on global or regional scales (Barrie et al., 2001). Previous global model results, considering the contribution of SO₂ gas-phase oxidation and aqueous reactions in cloud or fog droplets driven by ozone (O₃) and hydrogen peroxide (H₂O₂), have suggested that SO₂ mixing ratios are generally overestimated while sulfate concentrations tend to be underestimated, indicating that the two SO₂...
oxidation pathways still cannot close the gap between field observations and modeling studies (Kasibhatla et al., 1997; Laskin et al., 2003). Incorporation of aqueous SO$_2$ oxidation by oxygen catalyzed by transition metal ions in models has improved sulfate simulations compared to measurements (Jacob and Hoffmann, 1983; Jacob et al., 1984, 1989; Pandis et al., 1992; Alexander et al., 2009), and recent studies have further shown the enhanced role of transition metal ion catalysis during in-cloud oxidation of SO$_2$ (Harris et al., 2013). However, models still underestimate SO$_2$ oxidation in winter source regions due to lack of cloud or fog or a missing oxidation mechanism (Feichter et al., 1996; Kasibhatla et al., 1997; Barrie et al., 2001). Therefore, heterogeneous conversion of SO$_2$ to sulfate associated with aerosols provides a possible pathway for improving the sulfate simulations in chemical transport models (CTMs) (Kasibhatla et al., 1997; Zhang et al., 2015).

Many experimental studies have been conducted to investigate the heterogeneous reactions of SO$_2$ on various oxides and mineral dust, but the underlying sulfate formation mechanism is still not comprehensively understood. Generally, the complicated sulfate heterogeneous formation from SO$_2$ is parameterized as a first-order irreversible uptake by aerosols in CTMs, with a reactive uptake coefficient ranging from $10^{-4}$ to 0.1 and also heavily depending on relative humidity in the atmosphere (Wang et al., 2014). It is still imperative to develop a ubiquitous parameterization of the SO$_2$ heterogeneous reaction to reasonably represent sulfate formation in CTMs.

In recent years, China has frequently experienced severe and persistent haze pollution caused by elevated PM$_{2.5}$ concentrations, and field measurements have shown that sulfate aerosols are one of the most important species in PM$_{2.5}$ (He et al., 2014; Tian et al., 2016). Reasonable representation of sulfate aerosols provides an underlying basis for PM$_{2.5}$ simulations. Laboratory experiments, field measurements, and model simulations have significantly advanced our understanding of SO$_2$ heterogeneous reactions in the atmosphere, providing a good opportunity to develop a parameterization to more reasonably represent the sulfate formation in CTMs. In this study, a parameterization for sulfate formation from SO$_2$ heterogeneous reactions has been developed based on the daily filter measurements in Xi’an since 2003, and verified using the Weather Research and Forecast model with Chemistry (WRF-CHEM) in Xi’an and Beijing, China.

2 Model and methodology

2.1 WRF-CHEM model

In the present study, a specific version of the WRF-CHEM model (Grell et al., 2005) is utilized to assess the proposed heterogeneous sulfate parameterization, which is developed by Li et al. (2010, 2011a, b, 2012) at the Molina Center for Energy and the Environment. A new flexible gas-phase chemical module is incorporated into the model to consider different chemical mechanisms, and the CMAQ/Models3 aerosol module developed by US EPA is adopted for aerosol simulations. Surface dry depositions of chemical species are parameterized following Wesely (1989), and the wet deposition is calculated using the method in the CMAQ. The photolysis rates are calculated using the fast radiative transfer model (FTUV) in which the aerosol and cloud effects on photolysis are included (Li et al., 2005, 2011a).

The ISORROPIA Version 1.7 (Nenes et al., 1998) is used to predict inorganic aerosols in the WRF-CHEM model. A nontraditional SOA module is employed to calculate secondary organic aerosol (SOA) formation, including the volatility basis set (VBS) modeling method in which primary organic components are assumed to be semivolatile and photochemically reactive and are distributed in logarithmically spaced volatility bins. The SOA contributions from glyoxal and methylglyoxal are also considered to be first-order irreversible uptake by aerosol particles and cloud droplets in the model. Detailed information can be found in Li et al. (2011b).

Two persistent heavy haze pollution episodes are selected in the present study: (1) 16 to 27 December 2013 in the Guanzhong basin (GZB); and (2) 13 to 21 January 2014 in Beijing–Tianjin–Hebei (BTH) (Fig. 1). Detailed model configurations and aerosol species observation sites are given in Table 1. A very severe haze episode occurred in GZB during the period from 16 to 27 December 2013, with an average PM$_{2.5}$ concentration of 325.6 µg m$^{-3}$. The maximum of the average PM$_{2.5}$ concentration in GZB even exceeded 500 µg m$^{-3}$ during the episode. The average temperature and relative humidity in Xi’an were 3.7$^\circ$C and 72 % during the episode, respectively, and the average wind speed was around 3.7 m s$^{-1}$. The average PM$_{2.5}$ concentration from 13 to 21 January 2014 in BTH was 195.3 µg m$^{-3}$, with a maximum of 363.9 µg m$^{-3}$. The average temperature and relative humidity in Beijing during the episode was $–0.5^\circ$C and 42 %, respectively, and the average wind speed was about 7.4 m s$^{-1}$.

2.2 Statistical methods for comparisons

The mean bias (MB) and the index of agreement (IOA) are used to evaluate the performance of the WRF-CHEM model in simulating gas-phase species and aerosols against measurements. The IOA varies from 0 to 1, with 1 indicating perfect agreement of the prediction with the observation.

$$\text{MB} = \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i)$$

$$\text{IOA} = \frac{\sum_{i=1}^{N} \min(P_i, O_i) - \min_{P_i, O_i} \sum_{i=1}^{N} \max(P_i, O_i)}{\sum_{i=1}^{N} \max(P_i, O_i) - \min_{P_i, O_i} \sum_{i=1}^{N} \min(P_i, O_i)}$$
The observed high level of sulfate aerosols is hardly interpreted using SO$_2$ gas-phase oxidations by OH and sCl due to the low O$_3$ level in the winter. The insolation is weak during wintertime in northern China, and unfavorable for photochemical activities. The O$_3$ formation is slow and the observed O$_3$ concentrations are very low, particularly during haze episodes. The real-time hourly measurements of O$_3$ and PM$_{2.5}$ concentrations during the winters of 2013 and 2015 are analyzed as follows in GZB (5 cities, 39 sites, Fig. 1a), which have been released by China MEP since 2013. Values of the hourly PM$_{2.5}$ concentrations ([PM$_{2.5}$]) are first subdivided into 20 bins with the interval of 25 µg m$^{-3}$. O$_3$ concentrations ([O$_3$]) in the five cities as [PM$_{2.5}$] are assembled, and an average of [O$_3$] in each bin are calculated (Nakajima et al., 2001; Kawamoto et al., 2006). As shown in Fig. 3, when [PM$_{2.5}$] increase from 10 to 75 µg m$^{-3}$, [O$_3$] significantly decrease from around 41 to 23 µg m$^{-3}$, when [PM$_{2.5}$] exceed
[O$_3$] fluctuate between 18 and 21 µg m$^{-3}$. The average [O$_3$] in the five cities during the winters of 2013 and 2015 are 27 µg m$^{-3}$ (about 13.5 ppbv). Considering the determining role of O$_3$ in the formation of OH and sCl in the atmosphere, the very low level of [O$_3$] during wintertime significantly reduces the efficiency of the sulfate formation from SO$_2$ oxidation by OH and sCl.

Humid conditions have been observed to facilitate the sulfate formation in the atmosphere (e.g., Sun et al., 2013; Zheng et al., 2015). Figure 4 presents the scatter plot of the wintertime sulfate at IEECAS and the relative humidity (RH) at an adjacent meteorological station from 2003 to 2010. The observed sulfate displays a positive correlation with the RH with the correlation coefficient of 0.70, indicating that the aerosol water induced by the aerosol wet growth might play an important role in the sulfate formation. It is worthy to note that, since high RH often coincides with stagnation, the concentrations of a lot of pollutants also build up during high RH periods. There are two possible pathways for the sulfate formation: bulk aqueous-phase oxidation of SO$_2$ in aerosol water and heterogeneous reaction of SO$_2$ on aerosol surfaces involving aerosol water.

The heterogeneous reaction of SO$_2$ on dust surfaces has been investigated comprehensively, but the sulfate formation mechanism is still not completely understood. Possible mechanisms have been proposed, such as that mineral dust and NO$_2$ enhance the conversion of SO$_2$ to sulfate (He et al., 2014; Xie et al., 2015; Xue et al., 2016). Size-segregated particle samples in Beijing have shown that a considerable amount of sulfate is distributed in the coarse mode with particle diameters ranging from 2.1 to 9 µm, but sulfate peak concentrations still occur in the fine mode with particle diameters ranging from 0.43 to 1.1 µm (Tian et al., 2016). Oxidation of sulfite by NO$_2$ in aerosol water has also been proposed to contribute considerably to the sulfate production.
when NH$_3$ concentrations are sufficiently high (Pandis and Seinfeld, 1989; Xie et al., 2015).

Laboratory or field studies have suggested that O$_3$ or Fe$^{3+}$ can oxidize sulfite to sulfate. Considering the low [O$_3$] during wintertime (Fig. 3), the oxidation of sulfite by O$_3$ cannot constitute the main source of the wintertime sulfate. Mineral dust and coal combustion in China could provide sufficient iron. Measurements have indicated that mineral dust accounts for about 10% of PM$_{2.5}$ in Beijing (He et al., 2014). Observations at an urban site in Ji’nan, China have also shown enhanced iron concentrations during haze episodes, ranging from 0.7 to 5.5 µg m$^{-3}$, which are primarily emitted from steel smelting and coal combustion (Wang et al., 2012). Figure 5 shows the scatter plot of the wintertime PM$_{2.5}$ and iron at IEECAS site from 2003 to 2010. The iron mass concentration generally increases with [PM$_{2.5}$], varying from 0.7 to 5.5 µg m$^{-3}$, but does not correlate well with [PM$_{2.5}$] with the correlation coefficient of 0.34, showing considerable background iron contributions. We assume that 1% of iron in Xi’an is dissolved in aerosol water and 1% of dissolved iron is in the Fe$^{3+}$ oxidation state (Alexander et al., 2009). When the aerosol water concentration varies from 100 to 1000 µg m$^{-3}$, the Fe$^{3+}$ concentrations in Xi’an are between 0.18 and 180 µM, providing favorable conditions for the oxidation of adsorbed sulfite (Seinfeld and Pandis, 2006).

Here, we propose a SO$_2$ heterogeneous reaction parameterization in which the SO$_2$ oxidation in aerosol water by O$_3$ catalyzed by Fe$^{3+}$ is limited by mass transfer resistances in the gas-phase and the gas-particle interface.

$$\text{S(IV)} + \frac{1}{2} \text{O}_2 \rightarrow \text{Fe}^{3+} \rightarrow \text{S(VI)}$$

(3)

When the solution pH is between 5.0 and 7.0, the oxidation reaction is second order in dissolved iron and first order in S(IV) and can be expressed as follows (Seinfeld and Pandis, 2006):

$$\frac{d[S(\text{IV})]}{dt} = 1 \times 10^{-3} [S(\text{IV})] \hspace{1cm} 5.0 < \text{pH} < 6.0 \hspace{1cm} (4)$$

$$\frac{d[S(\text{IV})]}{dt} = 1 \times 10^{-4} [S(\text{IV})] \hspace{1cm} \text{pH} \sim 7.0, \hspace{1cm} (5)$$

where [S(IV)] is the sulfite (S(IV)) concentration. The measured SO$_2$ mass accommodation coefficient on aqueous surfaces is around 0.1 (Worsnop et al., 1989). Due to sufficient NH$_3$ and presence of mineral dust in the atmosphere in northern China, the calculated pH in aerosol water is between 5.0 and 7.0 (Cao et al., 2013). The SO$_2$ uptake coefficient on aerosol water surface is estimated to be about $10^{-4}$-$10^{-5}$ if the sulfite oxidation is catalyzed by Fe$^{3+}$. The sulfate heterogeneous formation from SO$_2$ is therefore parameterized as a first-order irreversible uptake by aerosols, with a reactive uptake coefficient of $0.5 \times 10^{-4}$, assuming that there is enough alkalinity to maintain the high iron-catalyzed reaction rate:

$$\frac{d[\text{SO}_2]}{dt} = - \left( \frac{1}{4} \gamma_{\text{SO}_2} v_{\text{SO}_2} A_w \right) [\text{SO}_2]. \hspace{1cm} (6)$$

where [SO$_2$] is the SO$_2$ concentration, $A_w$ is the aerosol water surface area, $\gamma_{\text{SO}_2}$ is the SO$_2$ reactive uptake coefficient, and $v_{\text{SO}_2}$ is the SO$_2$ thermal velocity. The aerosol hygroscopic growth is directly predicted by ISORROPIA (Version 1.7) in the model, and the aerosol water surface area is scaled from the calculated wet aerosol surface area using the third-moment of aerosol species. Considering that O$_3$ and NO$_2$ also play a considerable role in the sulfite oxidation when pH is high (Pandis and Seinfeld, 1989), future studies are needed to consider the O$_3$ and NO$_2$ contribution to the sulfate formation.

A box model is devised to interpret the rapid growth of sulfate observed at IEECAS site during winter 2013 in Xi’an.
In this model, the proposed heterogeneous reaction of SO₂ involving aerosol water (hereafter referred to as HR_SO₂) parameterization is included and ISORROPIA (Version 1.7) is used to simulate sulfate, nitrate, ammonium aerosols, and aerosol water. In addition, inorganic aerosols are represented by a two-moment modal approach with a lognormal size distribution. A severe haze episode occurred from 16 to 25 December 2013 in GZB, with the average observed [PM$_{2.5}$] exceeding 400 µg m$^{-3}$ during the period from 23 to 25 December 2013. The HR-ToF-AMS measured sulfate concentrations reaching about 250 µg m$^{-3}$ in the morning on 23 December and, in particular, the observed sulfate concentration increased from 132 µg m$^{-3}$ at 07:30 BJT to 240 µg m$^{-3}$ at 09:30 BJT. The box model is utilized to simulate the rapid sulfate growth from 07:30 to 09:30 BJT, constrained by the observed temperature, SO₂, nitrate, and ammonium (Table 2). There was no RH observation at the IEECAS site; the observed RH at adjacent meteorological stations ranged from 93 to 99 % during the time period. In addition, the atmosphere was calm and stable during the simulation period due to the control of a high pressure system over GZB, so the horizontal transport is not considered. VariousRHs from 93 to 99 % are used to calculate the sulfate growth in the box model. Figure 6 shows the calculated and observed sulfate concentrations from 07:30 to 09:30 on 23 December 2013. The RH significantly influences the sulfate formation and the sulfate concentrations increase nonlinearly with the RH. When the RH is 93 %, the sulfate concentration is increased by 22.7 µg m$^{-3}$ after 2 h integration, whereas the enhanced sulfate concentration reaches 216.6 µg m$^{-3}$ when the RH is 99 %. The simulated sulfate concentrations are best fit for the observation when the RH is 98 %. It is worth noting that, when RH is high (i.e., exceeding 95 % or so), there is always the possibility of the presence of fog. Studies have demonstrated that, for every observed sulfate peak in the 1980s in Los Angeles, there is fog present (Pandis and Seinfeld, 1989; Pandis et al., 1992). Hence, the box model simulations with RH ranging from 93 to 99 % strongly suggest that there was at least some patchy fog in the area, which would provide sufficient water for the rapid iron-catalyzed reaction. Further studies need to be performed to investigate the possible contributions of the patchy fog to the sulfate formation.

### 3.2 Sulfate simulations in GZB and BTH

The proposed HR_SO₂ parameterization is further incorporated into the WRF-CHEM model to simulate sulfate aerosols. Two simulations are performed for GZB and BTH respectively, including the base case (hereafter referred to as B-case) without the HR_SO₂ parameterization and the enhanced oxidation case (hereafter referred to as E-case) with the HR_SO₂ parameterization. In Figs. 7 and 8, we present the spatial distributions of calculated and observed near-surface [PM$_{2.5}$] at 00:00 BJT in the E-case on 6 selected days representing the haze development in GZB and BTH, along with the simulated wind fields. In general, the predicted PM$_{2.5}$ spatial patterns agree well with the observations at the ambient monitoring sites in GZB and BTH. The model reproduces the high [PM$_{2.5}$] in GZB well, although it tends to underestimate the observation in the west of GZB. Due to the specific topography, when the northeastern winds are prevalent in GZB, pollutants tend to accumulate, and simulated and observed [PM$_{2.5}$] can be up to 500 µg m$^{-3}$. When the northern winds are intensified on 26 December 2013, the pollutants start to be transported outside of GZB. In BTH,
simulated weak winds cause severe PM$_{2.5}$ pollution, with [PM$_{2.5}$] frequently exceeding 250 µg m$^{-3}$ in most areas of BTH, which is consistent with the observations over monitoring sites. Hence, in general, the model reproduces the haze formation in GZB and BTH reasonably well.

In the present study, ISORROPIA (Version 1.7) is employed to predict the thermodynamic equilibrium between the sulfate-nitrate-ammonium-water aerosols and their gas-phase precursors H$_2$SO$_4$-HNO$_3$-NH$_3$-water vapor. SO$_2$ and NO$_2$ are the precursors of H$_2$SO$_4$ and HNO$_3$, so it is imperative to evaluate the SO$_2$ and NO$_2$ simulations using the measurements to more reasonably calculate inorganic aerosol concentrations.

Figures 9 and 10 show the temporal profiles of observed and simulated near-surface [NO$_2$] and [SO$_2$] averaged over monitoring sites in GZB from 16 to 27 December 2013 and in BTH from 13 to 21 January 2014, respectively. The model performs well when simulating the [NO$_2$] temporal variations compared with observations in GZB and BTH, both of which have an IOA of 0.91 in the E-case. The difference in the simulated [NO$_2$] in the B-case and E-case is minor, and the average [NO$_2$] is increased by 0.69 % in GZB and decreased by 0.1 % in BTH in the E-case compared to the B-case, showing that the impact of the HRSO$_2$ parameterization on NO$_2$ simulations is not significant in GZB and BTH. Although the model replicates the temporal variations of [SO$_2$] compared to the measurements in GZB and NCP in the E-case with IOAs of around 0.80, the model biases still exist. The model generally underestimates [SO$_2$] in GZB and BTH, with MBs of $-3.4$ and $-0.8$ µg m$^{-3}$. One of the possible reasons for SO$_2$ simulation biases is that large amounts of SO$_2$ are emitted from point sources, such as power plants or agglomerated industrial zones, and the transport of SO$_2$ from point sources is more sensitive to the wind field simulation uncertainties (Bei et al., 2012, 2016). The HRSO$_2$ parameterization generally improves the SO$_2$ simulations by accelerating SO$_2$ conversions to sulfate, decreasing the MB from 11.0 µg m$^{-3}$ in the B-case to $-3.4$ µg m$^{-3}$ in the E-case in GZB and 5.0 µg m$^{-3}$ in the B-case to $-0.8$ µg m$^{-3}$ in the E-case in BTH. On average, inclusion of the HRSO$_2$ parameterization decreases the [SO$_2$] by 15.9 and 3.4 % in GZB and BTH, respectively. Overall, the model performs well when simulating the NO$_2$ and SO$_2$ temporal variations against the measurements in GZB and BTH in the E-case. Due to a lack of routine measurements of NH$_3$ in GZB and BTH, the evaluation of the model performance on NH$_3$ is not provided in the present study. It is imperative that future studies are performed to evaluate the model performance on NH$_3$, which plays an important role in the sulfate formation (Wang et al., 2016).
Figures 9 and 10 display the simulated and observed inorganic aerosol variations in Xi’an from 16 to 27 December 2013 and in Beijing from 13 to 21 January 2014, respectively. In Xi’an, the observed sulfate mass concentrations range from 50 to 250 µg m⁻³, constituting the second most important PM₂.₅ component during the episode. The HRSO₂ parameterization substantially improves the sulfate simulations in the E-case compared to those in the B-case against the measurements. In the B-case, the sulfate concentrations are remarkably underestimated, with a MB of −72.4 µg m⁻³ (Table 3). However, in the E-case, the WRF-CHEM model generally yields the observed sulfate variations during the 11-day episode, with a MB of −17.0 µg m⁻³ and an IOA of 0.89, and the average sulfate concentration is enhanced by 172% compared to the B-case. In Beijing, the model also reproduces the observed sulfate variations reasonably well during the 7-day episode in the E-case, with a MB of −0.8 µg m⁻³ and an IOA of 0.82 (Table 3), but cannot adequately predict the observed sulfate peaks. The average sulfate concentration is enhanced by 58.4% in the E-case compared to the B-case in Beijing. The improvement of sulfate simulations caused by the HRSO₂ parameterization in Beijing is not as obvious as that in Xi’an due to the very humid conditions in GZB during the simulation period, which facilitate the rapid conversion of SO₂ to sulfate and cause the SO₂ heterogeneous conversion to be the dominant sulfate source.

Considering the importance of RH in the SO₂ heterogeneous oxidation, Fig. 13 shows the simulated and observed RH diurnal profiles in Xi’an from 16 to 27 December 2013 and in Beijing from 13 to 21 January 2014. The model generally performs reasonably well when simulating the observed RH, with IOAs of 0.80 for Xi’an and 0.76 for Beijing. Overall, the model is subject to overestimating the RH, especially in Beijing, but captures the observed peaks of the RH in Bei-
Figure 11. Comparison of measured and simulated diurnal profiles of inorganic aerosols of (a) sulfate, (b) nitrate, and (c) ammonium in Xi’an from 16 to 27 December 2013. The black dots represent the observations, and the solid red and blue lines denote the simulations in the E-case and B-case, respectively.

Figure 12. Same as Fig. 11, but in Beijing from 13 to 21 January 2014.
Table 3. Statistical comparisons of simulated and measured sulfate, nitrate, and ammonium concentrations in Xi’an and Beijing.

<table>
<thead>
<tr>
<th>City</th>
<th>Species</th>
<th>E-case</th>
<th>B-case</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MB (µg m(^{-3}))</td>
<td>IOA</td>
</tr>
<tr>
<td>Xi’an</td>
<td>Sulfate</td>
<td>−17.0 0.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>−13.4 0.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ammonium</td>
<td>−5.1 0.92</td>
<td></td>
</tr>
<tr>
<td>Beijing</td>
<td>Sulfate</td>
<td>−0.8 0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitrate</td>
<td>−4.2 0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ammonium</td>
<td>−2.7 0.89</td>
<td></td>
</tr>
</tbody>
</table>

Figure 13. Comparison of measured (black dots) and simulated (blue lines, in the E-case) diurnal profiles of the relative humidity (a) in Xi’an from 16 to 27 December 2013 and (b) in Beijing from 13 to 21 January 2014.

jing and Xi’an well. The RH biases considerably affect the sulfate simulations. The underestimation of the high RH generally corresponds to the underestimation of the sulfate concentration, i.e., during nighttime on 15 and 16 January 2014 in Beijing, and in the morning from 23 to 25 December 2013 in Xi’an. It is worth noting that, during the two episodes, the SO\(_2\) oxidation by OH of the sulfate formation is not important. We have performed additional sensitivity simulations in which only the direct emissions of sulfate are considered. Comparisons of the sensitivity simulation with the B-case show that the SO\(_2\) oxidation by OH can explain about 5.1 and 11.7 % of the observed sulfate concentrations in Xi’an and Beijing on average, respectively.

Although the IOA for nitrate aerosols is 0.83, the nitrate underestimation is rather large from 17 to 21 December 2013 in Xi’an in the E-case. The nitrate simulations are improved in Beijing compared to those in Xi’an, with a MB of −4.2 µg m\(^{-3}\) and an IOA of 0.88 in the E-case. The nitrate simulations in the B-case are slightly better than those in the E-case, caused by the underestimation of sulfate aerosols in the B-case, which is favorable for more HNO\(_3\) to exist in the aerosol phase. The inclusion of the HRSO\(_2\) parameterization decreases the simulated nitrate concentration by 15.3 and 19.5 % in Xi’an and Beijing, respectively, on average. The model performs well when predicting the ammonium aerosols in Xi’an and Beijing, with IOAs of around 0.90 in the E-case. The ammonium simulations in the E-case are improved compared to those in the B-case against the measurement, showing that sulfate aerosols play an important role in ammonium aerosol formation. The average ammonium concentration is enhanced by 36.8 % in Xi’an and 7.2 % in Beijing by the inclusion of the HRSO\(_2\) parameterization. Considering the substantial influence of simulated meteorological fields uncertainties on the aerosol species comparison at a single site (Bei et al., 2012), the HRSO\(_2\) parameterization performs reasonably well when simulating the observed inorganic aerosol variations in Xi’an and Beijing in the E-case.

Recently, Wang et al. (2016) have also elucidated a specific mechanism for the sulfite–sulfate conversion, in which oxidation of sulfite by NO\(_2\) in aerosol water in case of high NH\(_3\) concentrations contributes considerably to sulfate production. They have also pointed out the critical role of sulfate formation in haze formation in China through further promoting the formation of SOA and nitrate due to enhanced hy-
Figure 14. Observed and simulated diurnal cycles of mass concentrations of NO$_2$ and SO$_2$ averaged over GZB and BTH and the sulfate, nitrate, and ammonium aerosols in Xi’an and Beijing during the simulated episodes.

groscopicity. Zhang et al. (1995) have reported that the high concentration of nitrate is attributed to an efficient heterogeneous conversion of NO$_x$ to HNO$_3$ due to the hydrolysis of N$_2$O$_5$ on sulfate aerosols. Zhao et al. (2006) have investigated the heterogeneous chemistry of methylglyoxal with liquid H$_2$SO$_4$, showing that the hydration and oligomerization reactions of methylglyoxal are enhanced by sulfate formation due to the high dependence of these reactions on particle hygroscopicity. Therefore, future studies need to be performed to incorporate the specific mechanism into CTMs to improve sulfate, nitrate, and SOA simulations.

Figure 14 presents the observed and simulated diurnal cycles of mass concentrations of NO$_2$ and SO$_2$ averaged over GZB and BTH and the sulfate, nitrate, and ammonium aerosols in Xi’an and Beijing during the simulated episodes. The WRF-CHEM model performs well when simulating the NO$_2$ diurnal cycles compared to measurements over GZB and BTH in the E-case. The model also reasonably reproduces the observed diurnal cycles of SO$_2$ over GZB, sulfate, nitrate, and ammonium aerosols in Xi’an in the E-case. In particular, the sulfate simulations are significantly improved in the E-case compared with the B-case against the measurements. However, the model does not predict the observed diurnal cycles of sulfate, nitrate, and ammonium aerosols in Beijing well, which shows the model biases when simulating the southern or eastern wind fronts.
As one of the most important components of PM$_{2.5}$, reasonable representation of sulfate heterogeneous formation in CTMs is imperative to PM$_{2.5}$ simulations and predictions. Figure 15 presents the temporal profiles of observed and simulated near-surface [PM$_{2.5}$] averaged over monitoring sites in GZB from 16 to 27 December 2013 and in BTH from 13 to 21 January 2014, respectively. Inclusion of the HRSO$_2$ parameterization in the E-case improves the ability of the model to reproduce the PM$_{2.5}$ measurements in GZB and BTH. In GZB, due to very humid conditions which facilitate the heterogeneous sulfate formation during the episode, the simulated PM$_{2.5}$ mass concentrations are increased by more than 40 µg m$^{-3}$ in the E-case compared to the B-case with an average increase of 12.3 %, and are more consistent with the measurements. The HRSO$_2$ parameterization also improves the PM$_{2.5}$ simulations in BTH, with an average increase of less than 3.0 %, reducing the underestimation from around $-13.3$ to $-5.1$ µg m$^{-3}$. The HRSO$_2$ parameterization considerably enhances the [PM$_{2.5}$] in GZB (Fig. 16a), with an average [PM$_{2.5}$] contribution of 10–50 µg m$^{-3}$ from 16 to 27 December 2013. The average [PM$_{2.5}$] contributions of the sulfate heterogeneous formation are around 2–30 µg m$^{-3}$ in GZB (Fig. 16b) from 13 to 21 January 2014, lower than those in GZB.

The sulfate aerosol significantly affects nitrate and ammonium formation in the atmosphere due to its stability and the deliberate thermodynamic equilibrium between inorganic aerosols and their precursors. The simulated hourly near-surface sulfate concentrations in the E-case during the whole episode are first subdivided into 20 bins with the interval of 5 µg m$^{-3}$. Inorganic aerosols and PM$_{2.5}$ concentrations in the B-case and E-case are assembled as the bin sulfate concentrations in the E-case following the grid cells respectively, and an average of inorganic aerosols and PM$_{2.5}$ concentrations in each bin are calculated. Figures 17 and 18 show the impacts of the HRSO$_2$ parameterization on the inorganic aerosols and PM$_{2.5}$ simulations in GZB and NCP, respectively. The heterogeneous sulfate formation determines the sulfate level when the sulfate concentration in the E-case is more than 25 µg m$^{-3}$, with the contribution exceeding 50 % in GZB. However, in BTH, the heterogeneous sulfate formation plays a more important role in the sulfate level only when the sulfate concentration in the E-case exceeds 45 µg m$^{-3}$. If the HRSO$_2$ parameterization is not considered, the model generally predicts more nitrate and less ammonium aerosol (Figs. 17b–c and 18b–c). In addition, the [PM$_{2.5}$] contributions of the heterogeneous sulfate formation exceed 5 and 10 % when the simulated sulfate concentrations in the E-case are more than 10 and 80 µg m$^{-3}$ in GZB, respectively (Fig. 17d). However, in BTH, the contributions exceed 5 % when the simulated sulfate concentrations in the E-case are higher than 50 µg m$^{-3}$ (Fig. 18d).
Figure 17. Average (a) sulfate, (b) nitrate, (c) ammonium, and (d) PM$_{2.5}$ mass concentrations in GZB during the simulation period as a function of the sulfate mass concentration in the E-case. The red and blue dots represent average mass concentrations in the E-case and B-case, respectively.

Figure 18. Same as Fig. 16, but in BTH from 13 to 21 January 2014.

4 Summary and conclusions

In the present study, a parameterization of sulfate heterogeneous formation involving aerosol water (HRSO$_2$) is developed based on daily filter measurements in Xi’an since 2003. A SO$_2$ heterogeneous reaction parameterization has been proposed, in which the SO$_2$ oxidation in aerosol water by O$_2$ catalyzed by Fe$^{3+}$ is limited by mass transfer resistances in the gas-phase and the gas-particle interface. The sulfate heterogeneous formation from SO$_2$ is parameterized as a first-order irreversible uptake by aerosol water surfaces, with a reactive uptake coefficient of $0.5 \times 10^{-4}$ assuming that there is enough alkalinity to maintain the high iron-catalyzed reaction rate. A box model with the HRSO$_2$ parameterization successfully reproduces the observed rapid sulfate formation at IEECAS site in Xi’an.

The HRSO$_2$ parameterization is implemented into the WRF-CHEM model to simulate sulfate aerosols. Two persistent heavy haze pollution episodes are simulated with and without the SO$_2$ heterogeneous reaction: (1) 16 to 27 December 2013 in GZB, and (2) 13 to 21 January 2014 in BTH. In general, the model performs reasonably well when simulating the PM$_{2.5}$ distributions and the NO$_2$ and SO$_2$ temporal variations compared with observations in GZB and NCP. The HRSO$_2$ parameterization improves the SO$_2$ simulations by accelerating SO$_2$ conversions to sulfate aerosols.

The HRSO$_2$ parameterization substantially improves the sulfate simulations compared to the measurements in Xi’an and Beijing, particularly under humid conditions. In Xi’an, the sulfate concentrations are substantially underestimated when the HRSO$_2$ parameterization is not considered in the
simulations. Inclusion of the HRSO$_2$ parameterization significantly enhances the sulfate formation, and the model generally produces the observed sulfate variations during the 11-day episode. In Beijing, improvement in sulfate simulations with HRSO$_2$ parameterization is not as obvious as in Xi’an because of the very humid conditions in GZB during the simulation period. The HRSO$_2$ parameterization also improves the ammonium simulations in Xi’an and Beijing compared to observations, as well as appreciably improving the PM$_{2.5}$ simulations against the measurements over monitoring sites in GZB and NCP.

In summary, a reasonable representation of sulfate heterogeneous formation not only improves the PM$_{2.5}$ simulations, but also helps to rationally verify the contribution of inorganic aerosols to PM$_{2.5}$, providing the underlying basis for better understanding the haze formation and supporting the design and implementation of emission control strategies.

Data availability. The real-time O$_3$ and PM$_{2.5}$ are accessible to the public on the website http://106.37.208.233:20035/ (China MEP, 2013a). One can also access the historic profile of observed ambient pollutants by visiting http://www.aqistudy.cn/ (China MEP, 2013b).

Competing interests. The authors declare that they have no conflict of interest.

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