ELSEVIER

Parameterization of heterogeneous reaction of SO_2 to sulfate on dust with coexistence of NH_3 and NO_2 under different humidity conditions

Shuping Zhang[a,b,c], Jia Xing[b,*], Golam Sarwar[d], Yanli Ge[a,c], Hong He[a,c,e], Fengkui Duan[b], Yan Zhao[a,c], Kebin He[b], Lidan Zhu[b], Biwu Chu[a,c,e,**]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
[b] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing, 100084, China
[c] University of Chinese Academy of Sciences, Beijing, 100049, China
[d] National Exposure Research Laboratory, U.S. Environmental Protection Agency, 109 T.W. Alexander Drive, Research Triangle Park, NC, 27711, USA
[e] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021, China

GRAPHICAL ABSTRACT
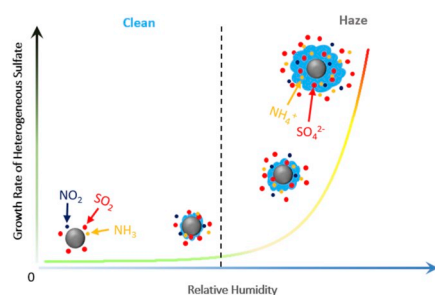
ARTICLE INFO

ABSTRACT

Sulfate plays an important role in atmospheric haze in China, which has received considerable attention in recent years. Various types of parameterization methods and heterogeneous oxidation rates of SO_2 have been used in previous studies. However, properly representing heterogeneous sulfate formation in air quality models remains a big challenge. In this study, we quantified the heterogeneous oxidation reaction using experimental results that approximate the haze conditions in China. Firstly, a series of experiments were conducted to investigate the heterogeneous uptake of SO_2 with different relative humidity (RH) levels and the presence of NH_3 and NO_2 on natural dust surfaces. Then the uptake coefficients for heterogeneous oxidation of SO_2 to sulfate at different RH under NH_3 and NO_2 coexistence were parameterized based on the experimental results and implemented in the Community Multiscale Air Quality modeling system (CMAQ). Simulation results suggested that this new parameterization improved model performance by 6.6% in the simulation of wintertime sulfate concentrations for Beijing. The simulated maximum growth rate of SO_4^{2-} during a heavy pollution period increased

---

* Corresponding author. State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China.

** Corresponding author. State Key Joint Laboratory of Environmental Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China.

E-mail addresses: xingjia@tsinghua.edu.cn (J. Xing), bwchu@rcees.ac.cn (B. Chu).

from $0.97\,\mu g\,m^{-3}\,h^{-1}$ to $10.11\,\mu g\,m^{-3}\,h^{-1}$. The heterogeneous oxidation of SO_2 in the presence of NH_3 contributed up to 23% of the sulfate concentration during heavy pollution periods.

1. Introduction

Sulfate (SO_4^{2-}) constitutes a significant fraction of atmospheric particulate matter, which has adverse impacts on human health and ecosystems (Harris et al., 2013). Due to its hygroscopicity, SO_4^{2-} can greatly influence the growth of aerosols, contribute to cloud condensation nuclei (CCN) and further influence rainfall, visibility and surface radiation. Therefore, accurately representing SO_4^{2-} in air quality models is of great significance. However, many current air quality models underestimate SO_4^{2-} and overestimate sulfur dioxide (SO_2) under heavy haze conditions (Chen et al., 2016; Wyat Appel et al., 2008). This phenomenon is partly due to the lack of chemical reactions oxidizing SO_2 (IV) to SO_4^{2-} (VI) in the models (Zheng et al., 2015b). At present, only the gas-phase and in-cloud aqueous phase SO_4^{2-} formation pathways are considered in the Community Multiscale Air Quality (CMAQ) model (v5.2) (www.epa.gov/cmaq) (Pye et al., 2018; Zheng et al., 2015a). However, according to a large number of laboratory and observational studies, the heterogeneous reactions of SO_2 on the surface of mineral dust, soot and some other inorganic particles could significantly contribute to SO_4^{2-} formation, which need to be considered in air quality models (He et al., 2014; Liu et al., 2012; Wang et al., 2016).

It is problematic that critical kinetic parameters of heterogeneous reactions proposed by previous studies do not comprehensively represent the heterogeneous reactions of SO_2 on particle surfaces for all atmospheric conditions and locations (Chen et al., 2016; Gankanda, 2016; Zheng et al., 2015a). First, previous studies were typically performed at low relative humidity (RH) conditions (Chapleski et al., 2016; Liu et al., 2012; Shang et al., 2010), while few studies have investigated the uptake kinetics of SO_2 on authentic mineral dust under varied RH conditions. More absorbed water at higher RH usually promotes the heterogeneous reaction of SO_2 (Huang et al., 2015); it has been reported that chemical composition therefore plays a critical role in the heterogeneous reaction of SO_2 (Cheng et al., 2016). Second, the relationship between the uptake coefficient and the RH in previous studies was assumed to be well-represented by a simple linear function or by power functions, which may not be representative of real atmospheric conditions in China. Third, to the best of our knowledge, there has been no systematic study on the uptake coefficient of SO_2 (γ_{SO_2}) on dust in the presence of ammonia (NH_3) in CMAQ simulation. Actually, NH_3 plays an important role in the heterogeneous oxidation of SO_2, according to laboratory experiments and field observation. The coexistence of NH_3 could introduce more surface Lewis basicity on particle

surfaces to adsorb SO_2 (Li et al., 2017; Normann et al., 2019; Yang et al., 2016), altering the rate-limiting step in the heterogeneous oxidation of SO_2, and resulting in an accelerated heterogeneous transformation of SO_2 to SO_4^{2-} (Jia et al., 2017; Pozzer et al., 2017). High emission of NH_3 and NO_2 in China and other developing countries (Wang et al., 2016) may result in significant synergistic effects in heterogeneous formation of sulfate and contribute to haze formation (Fu et al., 2017; He et al., 2014). Abundance of NH_3 (maximum concentration higher than 100 ppb) (Meng et al., 2018; Pan et al., 2012, 2018; Wen et al., 2015) and strong correlations between the peak levels of fine particles and large increases in NH_3 concentrations (Liu et al., 2015a; Ye et al., 2011) were usually observed in the heavy haze condition. Therefore, investigating the heterogeneous reaction of SO_2 at different RHs and the coexistence of NH_3 is important to improve the simulation of SO_4^{2-} in air quality models.

In this study, the γ_{SO_2} at different RHs and NH_3 levels were investigated by conducting a series of experiments at reaction conditions close to the real atmospheric environment (i.e., with coexisting NH_3, real dust, reasonable reactant concentrations and use of a flow tube for heterogeneous reaction measurements). Based on these experimental results, a new parameterization method was developed and implemented into CMAQ to represent the atmospheric heterogeneous reaction of SO_2 to SO_4^{2-} on particle surfaces. The role of heterogeneous SO_4^{2-} production during haze periods was examined using the CMAQ model with the new parameterization scheme for a heavily polluted area (i.e., Hebei-Tianjin-Beijing region in China) in January 2014.

2. Method

2.1. Experimental design

The parameter γ_{SO_2} depends on a number of factors including gas-phase concentrations, speciation and surface capacity, thus it is not a constant (Ammann et al., 2013). As summarized in Table 1, the measured γ_{SO_2} varies widely for different solid-phase media with different properties. For example, the γ_{SO_2} ($1–3 \times 10^{-3}$) measured on an amorphous carbon surface is considerably larger than that measured on other surfaces (Rogaski et al., 1997). On the surface of non-oxidic mineral oxides, such as Al_2O_3, TiO_2, CaO, MgO, sulfite is formed only at basic oxygen vacancies or hydroxyl sites, changing to SO_4^{2-} once sulfite is heated under aerobic conditions. In view of the large differences in mechanism and oxidation sites between different particles, authentic dust particles are required to study realistic heterogeneous reactions

Table 1
Summary of the values of γ_{SO_2} reported in literature.

Medium	γ_{SO_2}	RH	Reactive gas	Surface area calculation	Reference
Fe_2O_3	5.5×10^{-4}	water film		GEO	Judeikis et al. (1978)
Al_2O_3	4.0×10^{-4}	water film		GEO	Judeikis et al. (1978)
MgO	1×10^{-3}	water film		GEO	Judeikis et al. (1978)
Amorphous carbon	$1–3 \times 10^{-3}$	< 1	O_3	BET	Rogaski et al. (1997)
Water surface	0.11				Worsnop et al. (1989)
dust	$4.6 \pm 0.3 \times 10^{-6}$		NO_2	BET	Ullerstam et al. (2003)
dust	$1.3 \pm 0.3 \times 10^{-3}$		NO_2	GEO	Ullerstam et al. (2003)
$CaCO_3$	$1.3 \pm 0.13 \times 10^{-7}$	< 1	O_3	BET	Wu et al. (2011)
TiO_2	1.4×10^{-5}	40	O_3	BET	Shang et al. (2010)
TiO_2	2×10^{-6}	0		BET	Shang et al. (2010)
TiO_2、$CaCO_3$、MgO、Fe_2O_3 、Al_2O_3、China Loess、SiO_2	$7–50 \times 10^{-5}$		O_3	BET	Usher et al. (2002)
$CaCO_3$	0.1			BET	Santschi and Rossi (2003)
$CaCO_3$	$1.4 \pm 0.3 \times 10^{-7}$		O_3	BET	Li et al. (2006)
Saharan mineral dust	$6.6 \pm 0.8 \times 10^{-5}$		O_3		Adams et al. (2005)

(Ullerstam et al., 2003). Using different methods to calculate surface area also leads to discrepancies in the γ_{SO_2}. The γ_{SO_2} measured with the geometric surface area (GEO) can reach 10^{-4}, which is much higher than that calculated with Brunner−Emmett−Teller (BET) surface area (Judeikis et al., 1978). GEO was used for all calculations, which is consistent with our model. Different experimental designs to measure uptake coefficients, such as in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), Knudsen cell reactor, smog chamber and Coated Rod Flow Tube (CRFT), also yield quite different results (Usher et al., 2002). The uptake coefficient is estimated based on the gas consumption in Knudsen cell reactor and flow tube methods, while it is based on the SO_4^{2-} production in the DRIFTS method. Therefore, flow tube and Knudsen cell reactor results are more suitable for models calculated with SO_2 consumption. Differences in factors including solid phase composition, oxidation system, temperature, humidity, surface area calculation method, and experimental methods lead to several orders of magnitude difference in the values of γ_{SO_2} (Gankanda et al., 2016; Goodman et al., 2001; Li et al., 2006; Wu et al., 2011). It is important to wisely design these factors in the experimental study of atmospheric heterogeneous reactions.

In this study, we designed a series of experiments to examine the relationship between the heterogeneous uptake coefficient of SO_2 and RH, especially under the condition of NH_3 coexistence. Yang et al. (2018) reported that chemical compositions of mineral dust would lead to varying degrees of impacts of NH_3 on the heterogeneous oxidation of SO_2. The elements of Arizona Test Dust (ATD) and mineral dust particles from Mongolia are similar (Park et al., 2017). To better represent the real atmospheric mineral dust and also make the experimental results below their thresholds reproducible, we selected ATD to study heterogeneous reactions on the solid surface (Vlasenko et al., 2005), which represents a naturally occurring dust type and has also been used previously in studies addressing related issues (Bedjanian et al., 2013; Ma et al., 2008). The dust was internally mixed with preexisting deliquescent species such as nitrates (Gibson et al., 2007; Li and Shao, 2009; Wu and Okada, 1994) to consider the effect of soluble salts in real aerosol particles. The γ_{SO_2} on the dust surface was linearly related to the sample mass within a certain range ($0–100\,g\,m^{-2}$) (Ma et al., 2011). To ensure the single-layer coating effect, all our sample masses were controlled at about $2.4 \pm 0.8\,g\,m^{-2}$. The oxidizing gas was nitrogen dioxide (NO_2). A flow tube, one kind of commonly used method to obtain uptake coefficient, was chosen as the experimental device due to its stability (Ma et al., 2017; Ndour et al., 2008; Worsnop et al., 1989). This method has been verified in our previous work (Han et al., 2013; Liu et al., 2015b; Yang et al., 2016). The initial concentrations of SO_2, NO_2 and NH_3 were 5.11×10^{12} molecule cm^{-3} (190 ppb), 2.69×10^{12} molecule cm^{-3} (100 ppb), and 1.34×10^{12} molecule cm^{-3} (50 ppb), which are typical levels during heavy haze in China.

2.2. Model configuration

Meteorological fields were simulated with Weather Research and Forecasting model (WRF) version 3.8. The WRF model performance was examined by comparing against observations, and the results suggested acceptable performance, as the Mean Bias (MB)/Root Mean Square Error (RMSE) for temperature, wind speed and humidity were $0.31\,K/2.22\,K$, $0.15\,m\,s^{-1}/1.71\,ms^{-1}$, and $0.11\,g\,kg^{-1}/0.47\,g\,kg^{-1}$, respectively.

A unit-based emission inventory for industrial sectors in the Beijing, Tianjin and Hebei provinces (denoted as BTH) was used in this study, which resulted in better performance in simulating both $PM_{2.5}$ and gaseous pollutants than the proxy-based emission inventory. The Normalized Mean Bias (NMB) values for concentrations of SO_2, NO_2 and $PM_{2.5}$ were 81%, 21% and −7%, respectively (Zheng et al., 2018).

The CMAQ model (version 5.2) incorporates major processes that influence the transformation and transport of gases and aerosols, including advection, diffusion, aerosol dynamics, deposition, cloud

process, and chemical reaction (Byun and Schere, 2006). The modeling domain covered the BTH region and consisted of 204×150 horizontal grid-cells with a $4 \times 4\,km$ horizontal resolution. It had 14 vertical layers with a surface layer thickness of $36\,m$ above the ground. Boundary conditions were generated from $12\,km$ simulation over East China and $36\,km$ simulation over China (one-way nesting) (Zheng et al., 2018). To minimize the effect of initial conditions, a spin-up period of five days was used (Zheng et al., 2018). The simulations used the 2005 Carbon Bond chemical mechanism (CB05), which contains the gas-phase chemical reaction of SO_2 with hydroxyl radial (OH). The model also contains five in-cloud aqueous-phase reactions that treat the oxidation of S(IV) by hydrogen peroxide (H_2O_2), ozone (O_3), oxygen catalyzed by iron (Fe[III]) and manganese (Mn[II]), methylhydroperoxide (MHP), and peroxyacetic acid (PAA) (Binkowski, 2003; Pye et al., 2018; Sarwar et al., 2013). Thus, the CMAQ model can be used to evaluate the impacts of different oxidation pathways on atmospheric SO_4^{2-} concentrations (Binkowski, 2003; Pye et al., 2018; Sarwar et al., 2013). In this study, two scenarios (with/without SO_2 heterogeneous chemistry) were simulated, and the differences between the two simulations are attributed to the impact of the SO_2 oxidation heterogeneous pathway.

The SO_2 heterogeneous reaction can be assumed to be a pseudo-first-order reaction (Wang et al., 2012). The reaction rate coefficient is calculated as follows:

$$k_i = \left(\frac{d_p}{2D_i} + \frac{4}{v_i \gamma_i} \right)^{-1} S_p \tag{1}$$

where i represents the reactant for the heterogeneous reaction, d_p is the effective diameter of the particles (m), D_i is the gas-phase molecular diffusion coefficient for reactant i ($m^2\,s^{-1}$), v_i is the mean molecular speed of reactant i in the gas phase, γ_i is the uptake coefficient for reactant i (dimensionless), and S_p is the aerosol surface area per unit volume of air ($m^2 m^{-3}$). The parameters d_p, D_i, v_i, and S_p are calculated in CMAQ, and γ_i is a key parameter in determining the reaction rate and is obtained from the laboratory research measurement.

The observed SO_4^{2-} concentrations were collected on the roof of a three-story building on the campus of Tsinghua University in Beijing city (40.0°N, 116.3°E) from 1 to 31 Jan 2014. The hourly averaged concentrations of the main chemical species of fine particles ($PM_{2.5}$) were measured by a continuous dichotomous aerosol chemical speciation analyzer (Model ACSA-08; Kimoto Electric, Ltd., Japan) (Duan et al., 2016).

3. Results

3.1. Development of a new parameterization method of SO_2 uptake

The existing parameterization methods for SO_2 uptake vary greatly due to the lack of reliable experimental data under various environmental conditions. The first typical method (Method-1) is given by equation (2):

$$\gamma_g = \gamma_g' \times \left[1 + \frac{0.36}{0.029}(RH)^{3.7} \right] \tag{2}$$

where γ_g' (6.1×10^{-5}) is the uptake coefficient under dry conditions (Fu et al., 2016). This formula was established based on the regression of SO_4^{2-} ratio in total sulfur (i.e., the sum of SO_2 and SO_4^{2-}) against relative humidity from field observations (Sun et al., 2013). This empirical regression-based method suffers uncertainties from confounding factors such as aqueous pathways for SO_4^{2-} formation and other meteorological factors.

The second parameterization method (Method-2) uses a linear interpolation according to a certain range of RH (Chen et al., 2016; Zheng et al., 2015a), as follows:

$$\gamma_g = \begin{cases} \gamma_{low}, \; RH \in [0, 50\%] \\ \gamma_{low} + (\gamma_{high} - \gamma_{low})\frac{RH - 0.5}{RH_{max} - 0.5}, \;\; RH \in [50\%, RH_{max}] \\ \gamma_{high}, \; RH \in [RH_{max}, 100\%] \end{cases} \quad (3)$$

where, γ_{low} and γ_{high} are the minimum and maximum uptake coefficients determined based on experimental results and empirical estimations. It is assumed that the uptake coefficient is minimum at low humidity and maximum at high humidity scenarios. The uptake coefficients under other humidity condition are linearly interpolated based on the range of the maximum and minimum values. A previous study suggested that this method can improve the simulation accuracy of SO_4^{2-} concentrations (Chen et al., 2016). However, selection of the minimum and maximum uptake coefficient is challenging. It is difficult to find uptake coefficient at dry and high humidity under the same experimental condition from previous studies. Moreover, the change of γ_{SO_2} with RH might not be linear.

Clearly, the existing methods established parametric relationships between heterogeneous uptake coefficients and RH based on indirect observations. In addition, the role of ammonia has not been accounted for in both methods. It is desirable to develop a new parameterization scheme based on direct measurements under atmospheric conditions close to reality.

The measured γ_{SO_2} under different conditions in this study are shown in Table 2. The lowest γ_{SO_2} (about $1.48 \pm 1.14 \times 10^{-7}$) was found for dry dust particles (RH < 2%) under NH_3/NO_2-free conditions. The SO_2 uptake coefficient increased to $8.67 \pm 0.2 \times 10^{-7}$ under higher relative humidity level of 80%. With the coexistence of NO_2, the γ_{SO_2} will be also increased to $9.32 \pm 1.44 \times 10^{-6}$ even at low RH level (< 2%). The uptake coefficient further increased to $8.11 \pm 1.41 \times 10^{-5}$ when SO_2, NO_2, and NH_3 coexisted at a RH of 83%. NH_3 coexistence significantly increased the γ_{SO_2} by two orders of magnitude. This is mainly because the coexistence of NH_3 increases the pH, thereby facilitating the dissolution of SO_2. Previous study suggests that the heterogeneous oxidation of SO_2 can be divided into three stages (Shang et al., 2010). The first one is the formation of an alkaline surface. The second one is the adsorption of SO_2 on the alkaline surface to form sulfite, and the last one is sulfite oxidation to sulfuric acid. The formation of an alkaline surface (first stage) is the limiting step of this reaction. The NH_3 participation greatly enhances the formation of an alkaline surface, thus facilitating the heterogeneous oxidation of SO_2. Due to high solubility in water (1:700) and rapid dissolution rate of NH_3, γ_{SO_2} is very sensitive to the existence of NH_3. With the coexistence of NH_3, the positive correlation between the uptake coefficient and RH is more significant than under NH_3-free conditions. This result is supported by the study of (Benner et al., 1992), which found that the coexistence of NH_3 increased the SO_4^{2-} generation rate from 3% at dry conditions to 81% at 60% RH. When both NO_2 and NH_3 are present, γ_{SO_2} increases exponentially (not linearly as previous studies suggested) with the increase of RH (see Fig. 1). Such finding can explain the phenomenon that the cumulative growth rate of SO_4^{2-} under high humidity can reach tens of micrograms per cubic meter within few hours.

The exponential function of the relationship between γ_{SO_2} and RH is fitted in Fig. 1. The P-value of the variance analysis for the fitted curve is 1.8×10^{-4}, which is far less than 0.01. The adjusted R^2 can reach 0.99, indicating that this parametric result can explain 99% of the variance of all samples. We found that γ_{SO2} also increases exponentially with RH under extremely high NH_3 conditions (300 ppb). As an NH_3-rich region, the average winter level of NH_3 at BTH is only about 50 ppb (Fu et al., 2017). Therefore, this study only selected the γ_{SO2} at this level for parameterization in CMAQ.

According to the distribution of observed concentrations during haze in China, the threshold for the NH_3 coexistence condition is set as 15 ppb (Meng et al., 2018), and the threshold concentration for NO_2 coexistence is set as 30 ppb in this study. The times when NO_2 and NH_3

are below their thresholds are few (< 5%) (See Fig.S3). The γ_{SO_2} in this time is set to an average value of 1.36×10^{-7} according to the experimental γ_{SO2} without the coexistence of NO_2 and NH_3. This value is also consistent with previous studies (Li et al., 2006; Wu et al., 2011). The settings of uptake coefficients under other RHs when NO_2 and NH_3 are above their thresholds are shown in the following function.

$$\gamma_i = 2.22 \times 10^{-6} + 1.78 \times 10^{-8} e^{\frac{RH}{0.098}}, NO_2 > 30 ppb \; \& \; NH_3 > 15 ppb \quad (4)$$

The newly developed parameterization method (Method-3) is compared to the other two methods (i.e., Method-1 and Method-2) in Fig. 2. The uptake coefficient from the first method is the highest, about $10^{-5} \sim 10^{-4}$, followed by the parametric method (i.e., method-2) which is about 10^{-5}. The uptake coefficient from Method-3 is the lowest, around $10^{-6} \sim 10^{-5}$. However, Method-3 estimates the largest increase rate of γ_{SO_2} with RH compared to the other two methods, also exhibiting larger γ_{SO_2} under high RH conditions (> 70%) than that of Method-2.

3.2. Application of the updated parameterization method of SO_2 uptake

The new parameterization method for SO_2 heterogeneous reaction was applied in the simulation of SO_4^{2-} concentrations in Beijing during January 2014. The model using Method-1 and Method-2 exhibited excessively high SO_4^{2-} concentrations at the monthly average level (see Fig. 3). This is a result of the subjective selection of a high basic uptake coefficient (Gao and Chen, 2006; Usher et al., 2002). With the implementation of Method-3, the simulated monthly averaged SO_4^{2-} concentration (7.4 μg m^{-3}) was slightly underestimated (see Fig. 3). The underestimation in average concentration might be explained by other missing pathways or processes not considered in this study, such as aerosol radiative effects that could lead to a reduced Planetary Boundary Layer (PBL) height and enhance the pollution at the surface (Xing et al., 2015). However, the SO_4^{2-} concentrations during heavy pollution processes were well captured.

The increased SO_4^{2-} formation from the heterogeneous oxidation of S(IV) was investigated by comparing the simulated maximum SO_4^{2-} concentration with ("Method-3") and without ("BaseCase") the parameterization of SO_2 heterogeneous oxidation. During the simulation period, the observed SO_4^{2-} concentrations ranged from 0.8 to 95.8 μg m^{-3}. The simulated hourly SO_4^{2-} in Method-3 (ranging between 0.2 and 133.5 μg m^{-3}) could produce higher concentrations than the BaseCase (ranging between 0.6 and 16.4 μg m^{-3}). Compared to the BaseCase, the simulated peak value in Method-3 during two heavy pollution episodes in January (January 6 and 16) increased from 12.8 μg m^{-3} and 15.9 μg m^{-3} to 95.9 μg m^{-3} and 133.5 μg m^{-3}, respectively. Generally, the implementation of the heterogeneous chemistry of SO_2 improved the agreement with the observed SO_4^{2-}, with the MB reduced from 9.2 μg m^{-3} to 6.2 μg m^{-3} and the NMBs reduced from −58.6% to −38.3%. Meanwhile, SO_2 simulated in Method-3 decreased by 29.8 μg m^{-3} from the BaseCase, which is comparable with the

Table 2
The value of γ_{SO_2} in different atmospheres with different RH conditions measured in this study.

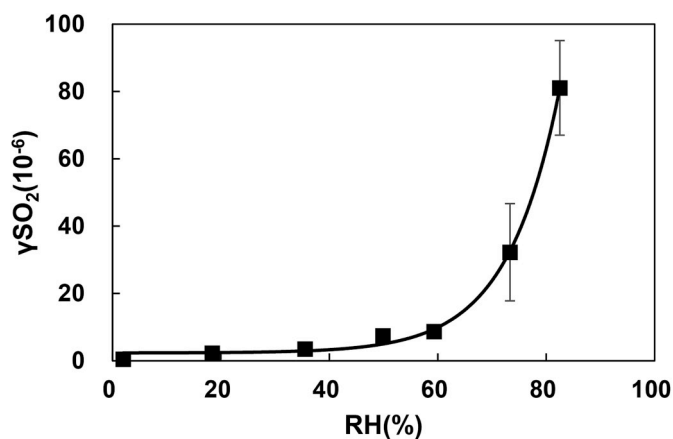| Atmospheres	RH	γ_{SO2}
SO_2	0.02	$1.48 \pm 1.14 \times 10^{-7}$
SO_2	0.80	$8.67 \pm 0.2 \times 10^{-7}$
SO_2 + NO_2	0.80	$9.32 \pm 1.44 \times 10^{-6}$
SO_2 + NO_2 + NH_3	0.02	$4.52 \pm 0.02 \times 10^{-7}$
SO_2 + NO_2 + NH_3	0.18	$2.28 \pm 0.43 \times 10^{-6}$
SO_2 + NO_2 + NH_3	0.36	$3.50 \pm 0.75 \times 10^{-6}$
SO_2 + NO_2 + NH_3	0.50	$7.41 \pm 1.59 \times 10^{-6}$
SO_2 + NO_2 + NH_3	0.59	$8.69 \pm 1.46 \times 10^{-6}$
SO_2 + NO_2 + NH_3	0.73	$3.22 \pm 1.44 \times 10^{-5}$
SO_2 + NO_2 + NH_3	0.83	$8.11 \pm 1.41 \times 10^{-5}$

Fig. 1. The relationship between γ_{SO_2} and relative humidity (RH) in the presence of NO_2 and NH_3.
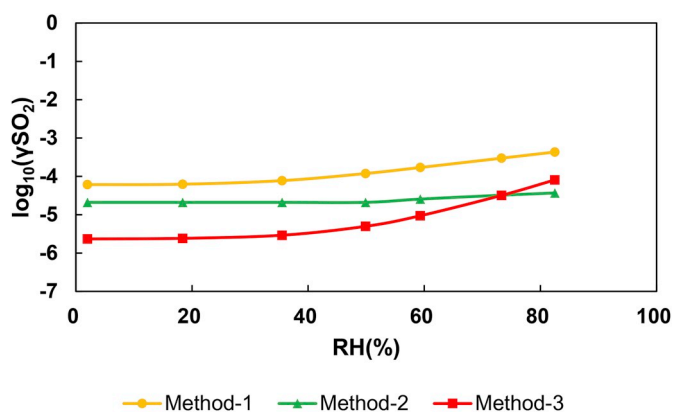

Fig. 2. Comparison of different parameterization methods in representing γ_{SO_2}.

observed SO_2 level of $31.7\,\mu g\,m^{-3}$. We further simulated SO_4^{2-} concentration in Beijing during a different observation period (December 2015) with this new parameterization method (see SI). The simulation of SO_4^{2-} concentration with Method-3 also showed the best performance, which further confirmed the proposed parameterization method was more reasonable compare to other methods.

As the formation of haze takes a certain amount of time, the cumulative rate of SO_4^{2-} in heavy haze periods is represented by the average 12-h growth of SO_4^{2-}.

$$SO_4^{2-}\ growth\ rate = \frac{1}{12}\sum_{i=h}^{12}\left(C_{so_4^{2-}(h+1)} - C_{so_4^{2-}(h)}\right) \quad (5)$$

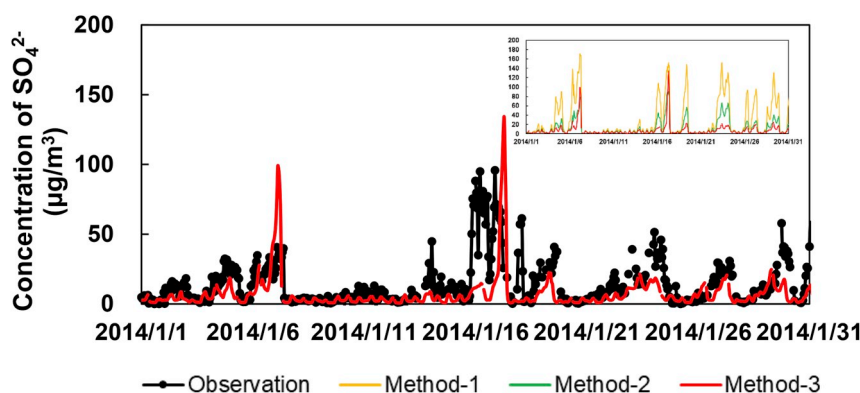Where $C_{so_4^{2-}(h)}$ and $C_{so_4^{2-}(h+1)}$ are SO_4^{2-} concentrations at hour h and h

+ 1. Since we found that Method-3 had the best performance in the simulation, it was deemed to also be the most accurate one among the three methods for studying the contribution of heterogeneous reactions (using the base case as reference for other processes contributing to sulfate formation) during heavy pollution. Then we compared the growth rate of SO_4^{2-} between BaseCase and Method-3. The maximum growth rate of SO_4^{2-} during the heavy pollution period increased from $0.97\,\mu g\,m^{-3}\,h^{-1}$ without the heterogeneous reaction to $10.1\,\mu g\,m^{-3}\,h^{-1}$ with the heterogeneous reaction (see Fig. 4). It is worth mentioning that when RH is above 85%, the growth rate of sulfate concentration can reach $22.1\,\mu g\,m^{-3}\,h^{-1}$. Almost every growth process can be simulated and improved. However, the heterogeneous uptake coefficient did not increase significantly in the RH range of 18.8%–40.2% during nighttime of January 15, when SO_4^{2-} increased from $5.6\,\mu g\,m^{-3}$ to $79.5\,\mu g\,m^{-3}$ in 2 h. Apparently, heterogeneous reaction is not the only factor that can promote the explosive growth of SO_4^{2-}, and other factors such as regional transport and aerosol-PBL interactions might also contribute to the fast increase of SO_4^{2-} concentrations.

Fig. 5 presents the spatial distribution of simulated SO_4^{2-} concentrations in the BTH region before and after the implementation of the SO_2 heterogeneous reaction. High SO_4^{2-} concentrations are found mainly in southern BTH, where abundant ammonia emissions are present (Wang et al., 2011). With the inclusion of SO_2 heterogeneous reactions, the simulated monthly averaged SO_4^{2-} concentrations in southern BTH and northern Shandong increased nearly $5\,\mu g\,m^{-3}$.

According to the national $PM_{2.5}$ standard, the $PM_{2.5}$ hourly data were classified into six levels, as shown in Table 3. The relative contribution of SO_2 heterogeneous reaction to total SO_4^{2-} formation was calculated for each level. The results show that SO_4^{2-} concentrations are higher under more severe $PM_{2.5}$ pollution conditions. The amount of SO_4^{2-} contributed by heterogeneous reaction (Method-3 minus BaseCase) also increases with higher pollution levels. Under excellent air quality conditions, the proportion of SO_4^{2-} contributed by heterogeneous reactions is only 1%, while the proportion of SO_4^{2-} contributed by heterogeneous reactions can reach 23% during severe pollution episodes.

4. Summary

In this study, a series of experiments was conducted to establish a new parameterization method for heterogeneous oxidation of SO_2 to SO_4^{2-} under the coexistence of NO_2 and NH_3. Results suggest that the SO_2 uptake coefficients rapidly rise with the increase of RH at an exponential growth rate, particularly when NH_3 is present. With the implementation of this newly developed parameterization in CMAQ, the simulated average SO_4^{2-} concentration in Beijing increased by 6.6%, which agreed better with observations. During a heavy haze period in January 2014, the maximum growth rate of SO_4^{2-} during the heavy pollution period increased from $0.97\,\mu g\,m^{-3}\,h^{-1}$ to $10.11\,\mu g\,m^{-3}\,h^{-1}$.

Fig. 3. Comparison of observed and simulated sulfate concentrations in Beijing (hourly data).
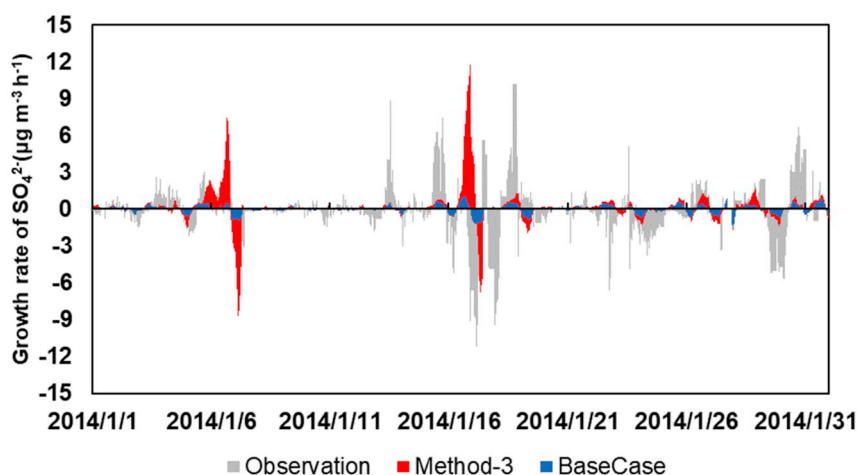
Fig. 4. Impacts on sulfate growth rate from the implementation of the parameterization of SO₂ heterogeneous oxidation.
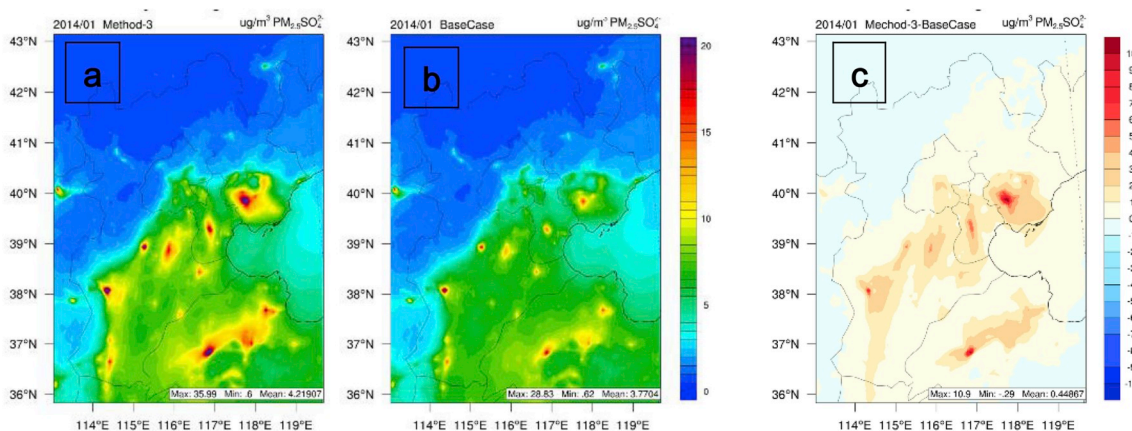

Fig. 5. Spatial distributions of monthly averaged sulfate concentrations in January 2014 simulated for (a) Method-3, (b) the BaseCase, and (c) the differences between the two simulations.

Table 3
The proportion of heterogeneous-produced sulfate at different PM$_{2.5}$ levels.

Pollution Type (μg m^{-3})	SO$_4^{2-}$ in BaseCase (μg m^{-3})	SO$_4^{2-}$ in Method-3 (μg m^{-3})	ΔSO$_4^{2-}$ (μg m^{-3})	ΔSO$_4^{2-}$ in total Sulfate (%)[a]
PM$_{2.5}$ < 35	1.96	1.99	0.03	1
35 ≤ PM$_{2.5}$ < 75	3.72	4.32	0.60	7
75 ≤ PM$_{2.5}$ < 115	5.26	8.75	3.49	12
115 ≤ PM$_{2.5}$ < 150	5.24	6.93	1.69	11
150 ≤ PM$_{2.5}$ < 250	6.85	14.21	7.36	23
PM$_{2.5}$ ≥ 250	9.17	15.49	6.31	23

[a] ΔSO$_4^{2-}$ in total SO$_4^{2-}$ is an average of all ΔSO$_4^{2-}$ divide SO$_4^{2-}$ in Method-3.

The heterogeneous oxidation of SO₂ can contribute up to 23% of the sulfate concentration, particularly during heavy pollution periods.

Disclaimer

The views expressed in this paper are those of the authors and do not necessarily represent the views or policies of the U.S. EPA.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2019.04.004.

References

Adams, J., Rodriguez, D., Cox, R., 2005. The uptake of SO₂ on Saharan dust: a flow tube study. Atmos. Chem. Phys. 5, 2679–2689.
Ammann, M., Cox, R.A., Crowley, J.N., Jenkin, M.E., Mellouki, A., Rossi, M.J., Troe, J., Wallington, T.J., 2013. Evaluated kinetic and photochemical data for atmospheric

chemistry: volume VI - heterogeneous reactions with liquid substrates. Atmos. Chem. Phys. 13, 8045–8228.

Bedjanian, Y., Romanias, M.N., El Zein, A., 2013. Interaction of OH radicals with Arizona test dust: uptake and products. J. Phys. Chem. A 117, 393–400.

Benner, W.H., Ogorevc, B., Novakov, T., 1992. Oxidation of SO_2 in thin water films containing NH_3. Atmospheric Environment. Part A. General Topics 26, 1713–1723.

Binkowski, F.S., 2003. Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component 1. Model description. J. Geophys. Res. 108.

Byun, D., Schere, K.L., 2006. Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system. Appl. Mech. Rev. 59, 51–77.

Chapleski, R.C., Zhang, Y., Troya, D., Morris, J.R., 2016. Heterogeneous chemistry and reaction dynamics of the atmospheric oxidants, O_3, NO_3, and OH, on organic surfaces. Chem. Soc. Rev. 45, 3731–3746.

Chen, D., Liu, Z., Fast, J., Ban, J., 2016. Simulations of sulfate–nitrate–ammonium (SNA) aerosols during the extreme haze events over northern China in October 2014. Atmos. Chem. Phys. 16, 10707–10724.

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., 2016. Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. Science Advances 2, e1601530.

Duan, F.K., He, K.B., Ma, Y.L., Ihozaki, T., Kawasaki, H., Arakawa, R., Kitayama, S., Tujimoto, S., Huang, C., Kimoto, T., Furutani, H., Toyoda, M., 2016. High molecular weight organic compounds (HMW-OCs) in severe winter haze: direct observation and insights on the formation mechanism. Environ. Pollut. 218, 289–296.

Fu, X., Wang, S., Chang, X., Cai, S., Xing, J., Hao, J., 2016. Modeling analysis of secondary inorganic aerosols over China: pollution characteristics, and meteorological and dust impacts. Sci. Rep. 6, 35992.

Fu, X., Wang, S., Xing, J., Zhang, X., Wang, T., Hao, J., 2017. Increasing ammonia concentrations reduce the effectiveness of particle pollution Control achieved via SO_2 and NO_X emissions reduction in East China. Environ. Sci. Technol. Lett. 4, 221–227.

Gankanda, A., 2016. Heterogeneous and Multiphase Chemistry of Trace Atmospheric Gases with Mineral Dust and Other Metal Containing Particles. The University of Iowa, pp. 152.

Gankanda, A., Coddens, E.M., Zhang, Y.P., Cwiertny, D.M., Grassian, V.H., 2016. Sulfate formation catalyzed by coal fly ash, mineral dust and iron(III) oxide: variable influence of temperature and light. Environmental Science-Processes & Impacts 18, 1484–1491.

Gao, Y., Chen, D., 2006. Heterogeneous reactions of sulfur dioxide on dust. Sci. China, Ser. B 49, 273–280.

Gibson, E.R., Gierlus, K.M., Hudson, P.K., Grassian, V.H., 2007. Generation of internally mixed insoluble and soluble aerosol particles to investigate the impact of atmospheric aging and heterogeneous processing on the CCN activity of mineral dust aerosol. Aerosol Sci. Technol. 41, 914–924.

Goodman, A.L., Bernard, E.T., Grassian, V.H., 2001. Spectroscopic study of nitric acid and water adsorption on oxide particles: enhanced nitric acid uptake kinetics in the presence of adsorbed water. J. Phys. Chem. A 105, 6443–6457.

Han, C., Liu, Y., He, H., 2013. Role of organic carbon in heterogeneous reaction of NO_2 with soot. Environ. Sci. Technol. 47, 3174–3181.

Harris, E., Sinha, B., van Pinxteren, D., Tilgner, A., Fomba, K.W., Schneider, J., Roth, A., Gnauk, T., Fahlbusch, B., Mertes, S., Lee, T., Collett, J., Foley, S., Borrmann, S., Hoppe, P., Herrmann, H., 2013. Enhanced role of transition metal ion catalysis during in-cloud oxidation of SO_2. Science 340, 727–730.

He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., Tang, G., Liu, C., Zhang, H., Hao, J., 2014. Mineral dust and NOx promote the conversion of SO_2 to sulfate in heavy pollution days. Sci. Rep. 4.

Huang, L., Zhao, Y., Li, H., Chen, Z., 2015. Kinetics of heterogeneous reaction of sulfur dioxide on authentic mineral dust: effects of relative humidity and hydrogen peroxide. Environ. Sci. Technol. 49, 10797–10805.

Jia, Y., Yin, L., Xu, Y., Chen, Y., Ding, X., 2017. Simulation of the absorption of SO_2 by ammonia in a spray scrubber. Chem. Eng. Process: Process Intensification 116, 60–67.

Judeikis, H.S., Stewart, T.B., Wren, A.G., 1978. Laboratory studies of heterogeneous reactions of SO_2. Atmos. Environ. 12, 1633–1641.

Li, G., Bei, N., Cao, J., Huang, R., Wu, J., Feng, T., Wang, Y., Liu, S., Zhang, Q., Tie, X., Molina, L.T., 2017. A possible pathway for rapid growth of sulfate during haze days in China. Atmos. Chem. Phys. 17, 3301–3316.

Li, L., Chen, Z.M., Zhang, Y.H., Zhu, T., Li, J.L., Ding, J., 2006. Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate. Atmos. Chem. Phys. 6, 2453–2464.

Li, W.J., Shao, L.Y., 2009. Observation of nitrate coatings on atmospheric mineral dust particles. Atmos. Chem. Phys. 9, 1863–1871.

Liu, C., Ma, Q., Liu, Y., Ma, J., He, H., 2012. Synergistic reaction between SO_2 and NO_2 on mineral oxides: a potential formation pathway of sulfate aerosol. Phys. Chem. Chem. Phys. 14, 1668–1676.

Liu, X., Sun, K., Qu, Y., Hu, M., Sun, Y., Zhang, F., Zhang, Y., 2015a. Secondary formation of sulfate and nitrate during a haze episode in megacity Beijing, China. Aerosol Air Quallity Research 15, 2246–2257.

Liu, Y., Han, C., Ma, J., Bao, X., He, H., 2015b. Influence of relative humidity on heterogeneous kinetics of NO_2 on kaolin and hematite. Phys. Chem. Chem. Phys. : Phys. Chem. Chem. Phys. 17, 19424–19431.

Ma, J., Liu, Y., Ma, Q., Liu, C., He, H., 2011. Atmospheric heterogeneous reactions and their environmental effects. Environ. Chem. 97–119.

Ma, Q.X., Liu, Y.C., He, H., 2008. Synergistic effect between NO_2 and SO_2 in their adsorption and reaction on gamma-alumina. J. Phys. Chem. A 112, 6630–6635.

Ma, Q.X., Wang, T., Liu, C., He, H., Wang, Z., Wang, W.H., Liang, Y.T., 2017. SO_2 initiates the efficient conversion of NO_2 to HONO on MgO surface. Environ. Sci. Technol. 51, 3767–3775.

Meng, Z., Xu, X., Lin, W., Ge, B., Xie, Y., Song, B., Jia, S., Zhang, R., Peng, W., Wang, Y., Cheng, H., Yang, W., Zhao, H., 2018. Role of ambient ammonia in particulate ammonium formation at a rural site in the North China Plain. Atmos. Chem. Phys. 18, 167–184.

Ndour, M., D'Anna, B., George, C., Ka, O., Balkanski, Y., Kleffmann, J., Stemmler, K., Ammann, M., 2008. Photoenhanced uptake of NO_2 on mineral dust: laboratory experiments and model simulations. Geophys. Res. Lett. 35.

Normann, F., Wismer, A.O., Muller, C.R., Leion, H., 2019. Oxidation of ammonia by iron, manganese and nickel oxides - implications on NOx formation in chemical-looping combustion. Fuel 240, 57–63.

Pan, Y., Tian, S., Zhao, Y., Zhang, L., Zhu, X., Gao, J., Huang, W., Zhou, Y., Song, Y., Zhang, Q., 2018. Identifying ammonia hotspots in China using a national observation network. Environ. Sci. Technol. 52, 3926–3934.

Pan, Y., Wang, Y., Tang, G., Wu, D., 2012. Wet and dry deposition of atmospheric nitrogen at ten sites in Northern China. Atmos. Chem. Phys. 12, 6515–6535.

Park, J., Jang, M., Yu, Z., 2017. Heterogeneous photo-oxidation of SO_2 in the presence of two different mineral dust particles: gobi and Arizona dust. Environ. Sci. Technol. 51, 9605–9613.

Pozzer, A., Tsimpidi, A.P., Karydis, V.A., de Meij, A., Lelieveld, J., 2017. Impact of agricultural emission reductions on fine-particulate matter and public health. Atmos. Chem. Phys. 17, 12813–12826.

Pye, H.O.T., Zuend, A., Fry, J.L., Isaacman-VanWertz, G., Capps, S.L., Appel, K.W., Foroutan, H., Xu, L., Ng, N.L., Goldstein, A.H., 2018. Coupling of organic and inorganic aerosol systems and the effect on gas–particle partitioning in the southeastern US. Atmos. Chem. Phys. 18, 357–370.

Rogaski, C.A., Golden, D.M., Williams, L.R., 1997. Reactive uptake and hydration experiments on amorphous carbon treated with NO_2, SO_2, O_3, HNO_3, and H_2SO_4. Geophys. Res. Lett. 24, 381–384.

Santschi, C., Rossi, M.J., 2003. Heterogeneous Reactions of HCl, HNO_3 and SO_2 on Calcium Carbonate Substrates. EGS-AGU-EUG Joint Assembly.

Sarwar, G., Fahey, K., Kwok, R., Gilliam, R.C., Roselle, S.J., Mathur, R., Xue, J., Yu, J., Carter, W.P.L., 2013. Potential impacts of two SO_2 oxidation pathways on regional sulfate concentrations: aqueous-phase oxidation by NO_2 and gas-phase oxidation by Stabilized Criegee Intermediates. Atmos. Environ. 68, 186–197.

Shang, J., Li, J., Zhu, T., 2010. Heterogeneous reaction of SO_2 on TiO_2 particles. Sci. China Chem. 53, 2637–2643.

Sun, Y., Wang, Z., Fu, P., Jiang, Q., Yang, T., Li, J., Ge, X., 2013. The impact of relative humidity on aerosol composition and evolution processes during wintertime in Beijing, China. Atmos. Environ. 77, 927–934.

Ullerstam, M., Johnson, M.S., Vogt, R., Ljungstrom, E., 2003. DRIFTS and Knudsen cell study of the heterogeneous reactivity of SO_2 and NO_2 on mineral dust. Atmos. Chem. Phys. 3, 2043–2051.

Usher, C.R., Al-Hosney, H., Carlos-Cuellar, S., Grassian, V.H., 2002. A laboratory study of the heterogeneous uptake and oxidation of sulfur dioxide on mineral dust particles. J. Geophys. Res.: Atmosphere 107 ACH 16-11-ACH 16-19.

Vlasenko, A., Sjögren, S., Weingartner, E., Gäggeler, H.W., Ammann, M., 2005. Generation of submicron Arizona test dust aerosol: chemical and hygroscopic properties. Aerosol Sci. Technol. 39, 452–460.

Wang, G., Zhang, R., Gomez, M.E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P.S., Duce, R.A., Kolb, C.E., Molina, M.J., 2016. Persistent sulfate formation from London Fog to Chinese haze. In: Proceedings of the National Academy of Sciences of the United States of America.

Wang, K., Zhang, Y., Nenes, A., Fountoukis, C., 2012. Implementation of dust emission and chemistry into the Community Multiscale Air Quality modeling system and initial application to an Asian dust storm episode. Atmos. Chem. Phys. 12, 10209–10237.

Wang, S.X., Xing, J., Jang, C.R., Zhu, Y., Fu, J.S., Hao, J.M., 2011. Impact assessment of ammonia emissions on inorganic aerosols in East China using response surface modeling technique. Environ. Sci. Technol. 45, 9293–9300.

Wen, L., Chen, J., Yang, L., Wang, X., Xu, C., Sui, X., Yao, L., Zhu, Y., Zhang, J., Zhu, T., 2015. Enhanced formation of fine particulate nitrate at a rural site on the North China Plain in summer: the important roles of ammonia and ozone. Atmos. Environ. 101, 294–302.

Worsnop, D.R., Zahniser, M.S., Kolb, C.E., Gardner, J.A., Watson, L.R., Van Doren, J.M., Jayne, J.T., Davidovits, P., 1989. The temperature dependence of mass accommodation of sulfur dioxide and hydrogen peroxide on aqueous surfaces. J. Phys. Chem. 93, 1159–1172.

Wu, L.Y., Tong, S.R., Wang, W.G., Ge, M.F., 2011. Effects of temperature on the heterogeneous oxidation of sulfur dioxide by ozone on calcium carbonate. Atmos. Chem. Phys. 11, 6593–6605.

Wu, P.M., Okada, K., 1994. Nature of coarse nitrate particles in the atmosphere - a single, particle approach. Atmos. Environ. 28, 2053–2060.

Wyat Appel, K., Bhave, P.V., Gilliland, A.B., Sarwar, G., Roselle, S.J., 2008. Evaluation of the community multiscale air quality (CMAQ) model version 4.5: sensitivities impacting model performance; Part II—particulate matter. Atmos. Environ. 42, 6057–6066.

Xing, J., Mathur, R., Pleim, J., Hogrefe, C., Gan, C.M., Wong, D.C., Wei, C., Wang, J.D., 2015. Air pollution and climate response to aerosol direct radiative effects: a modeling study of decadal trends across the northern hemisphere. J. Geophys. Res.-Atmos. 120, 16.

Yang, W., He, H., Ma, Q., Ma, J., Liu, Y., Liu, P., Mu, Y., 2016. Synergistic formation of sulfate and ammonium resulting from reaction between SO_2 and NH_3 on typical mineral dust. Phys. Chem. Chem. Phys. 18, 956–964.

Yang, W.W., Ma, Q.X., Liu, Y.C., Ma, J.Z., Chu, B.W., Wang, L., He, H., 2018. Role of NH_{UUU} in the heterogeneous formation of secondary inorganic aerosols on mineral oxides. J. Phys. Chem. A 122, 6311–6320.

Ye, X., Ma, Z., Zhang, J., Du, H., Chen, J., Chen, H., Yang, X., Gao, W., Geng, F., 2011. Important role of ammonia on haze formation in Shanghai. Environ. Res. Lett. 6, 024019.

Zheng, B., Zhang, Q., Zhang, Y., He, K.B., Wang, K., Zheng, G.J., Duan, F.K., Ma, Y.L., Kimoto, T., 2015a. Heterogeneous chemistry: a mechanism missing in current models to explain secondary inorganic aerosol formation during the January 2013 haze episode in North China. Atmos. Chem. Phys. 15, 2031–2049.

Zheng, G.J., Duan, F.K., Su, H., Ma, Y.L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Pöschl, U., Cheng, Y.F., He, K.B., 2015b. Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions. Atmos. Chem. Phys. 15, 2969–2983.

Zheng, H., Cai, S., Wang, S., Zhao, B., Chang, X., Hao, J., 2018. Development of a unit-based industrial emission inventory in the Beijing-Tianjin-Hebei region and resulting improvement in air quality modeling. Atmos. Chem. Phys. Discuss. 1–24.