



Modeling atmospheric mineral aerosol chemistry to predict heterogeneous photooxidation of SO₂

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Received: 8 February 2017 – Discussion started: 9 March 2017

Revised: 16 July 2017 – Accepted: 17 July 2017 – Published: 25 August 2017

Abstract. The photocatalytic ability of airborne mineral dust particles is known to heterogeneously promote SO₂ oxidation, but prediction of this phenomenon is not fully taken into account by current models. In this study, the Atmospheric Mineral Aerosol Reaction (AMAR) model was developed to capture the influence of air-suspended mineral dust particles on sulfate formation in various environments. In the model, SO₂ oxidation proceeds in three phases including the gas phase, the inorganic-salted aqueous phase (non-dust phase), and the dust phase. Dust chemistry is described as the absorption–desorption kinetics of SO₂ and NO_x (partitioning between the gas phase and the multilayer coated dust). The reaction of absorbed SO₂ on dust particles occurs via two major paths: autooxidation of SO₂ in open air and photocatalytic mechanisms under UV light. The kinetic mechanism of autooxidation was first leveraged using controlled indoor chamber data in the presence of Arizona Test Dust (ATD) particles without UV light, and then extended to photochemistry. With UV light, SO₂ photooxidation was promoted by surface oxidants (OH radicals) that are generated via the photocatalysis of semiconducting metal oxides (electron–hole theory) of ATD particles. This photocatalytic rate constant was derived from the integration of the combinational product of the dust absorbance spectrum and wave-dependent actinic flux for the full range of wavelengths of the light source. The predicted concentrations of sulfate and nitrate using the AMAR model agreed well with outdoor chamber data that were produced under natural sunlight. For seven consecutive hours of photooxidation of SO₂ in an outdoor chamber, dust chemistry at the low NO_x level was attributed to 55 % of total sulfate (56 ppb SO₂, 290 µg m^{−3} ATD, and NO_x less than 5 ppb). At high NO_x (> 50 ppb of NO_x with low hydrocar-

bons), sulfate formation was also greatly promoted by dust chemistry, but it was suppressed by the competition between NO₂ and SO₂, which both consume the dust-surface oxidants (OH radicals or ozone).

1 Introduction

The surface of mineral dust particles is able to act as a sink for various atmospheric trace gases such as sulfur dioxide (SO₂), nitrogen oxides (NO_x, e.g., NO and NO₂), and ozone (O₃). Among trace gases, SO₂ has received much attention because heterogeneous oxidation of SO₂ produces non-volatile sulfuric acid, which is readily involved in the acidification of particles or the reaction with dust constituents such as alkaline metals (K⁺, Na⁺) or metal oxides (e.g., α-Al₂O₃ and Fe₂O₃). Such modification of the chemical composition of dust particles can influence the hygroscopic properties of mineral dust, which is essential to activate cloud condensation nucleation (Krueger et al., 2003; Zhang and Chan, 2002; Vlasenko et al., 2006; Liu et al., 2008; Tang et al., 2016).

Metal oxides (e.g., TiO₂ and Al₂O₃) have frequently been used in many laboratories to study the key role of mineral dust in the heterogeneous oxidation of SO₂ (Goodman et al., 2001; Usher et al., 2002; Zhang et al., 2006). However, these laboratory studies have been limited to a certain type of metal oxide and autooxidation of SO₂ without a light source. To date, only a few studies have attempted to study the photocatalytic characteristics of mineral dust in the oxidation of SO₂ and NO_x. For example, as noted by Park and Jang (2016), the reactive uptake coefficient (γ_{SO₂[−]}) of SO₂ in the presence of dry Arizona Test Dust (ATD) particles under UV light was

1 order of magnitude higher (1.16×10^{-6} using an indoor chamber with a light mix of UV-A and UV-B light) than that from autoxidation (1.15×10^{-7}) without a light source. Using an aerosol flow tube, Dupart et al. (2014) observed that the uptake rate of NO_2 by ATD dust particles was significantly enhanced (by 4 times) under UV-A irradiation compared to dark conditions. Field observations have also reported the promotion of SO_2 photooxidation in the presence of mineral dust. For instance, near Beijing, China (ground-based campaign in 2009), and in Lyon, France (remote-sensing campaign in 2010), Dupart et al. (2012) found that mineral dust was a source of OH radicals under UV radiation that promoted sulfate formation.

Semiconducting metal oxides (e.g., $\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$, and TiO_2) act as a photocatalyst in mineral dust particles that can yield electron (e_{cb}^-)–hole (h_{vb}^+) pairs, and that they are involved in the production of strong oxidizers, such as superoxide radical anions (O_2^-) and OH radicals (Linsebigler et al., 1995; Hoffmann et al., 1995; Thompson and Yates, 2006; Cwiertny et al., 2008; Chen et al., 2012; Dupart et al., 2014; Colmenares and Luque, 2014). These oxidizers enable rapid oxidation of adsorbed SO_2 and NO_x on the surface of mineral dust particles. For example, using transmission Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy, Nanayakkara et al. (2012) observed the oxidation of SO_2 by the photocatalytically generated OH radicals in the presence of titanium oxide particles. The heterogeneous formation of sulfate and nitrate can be highly variable and dependent on the chemical characteristics of dust aerosol (Gankanda et al., 2016). Authentic mineral dust particles differ from pure metal oxides in chemical composition. For example, Wagner et al. (2012) reported that the content of metal oxides in Saharan dust samples collected from Burkina Faso includes 14 % Al_2O_3 , 8.4 % Fe_2O_3 , and 1.2 % TiO_2 .

Most research on dust photochemistry has been limited to qualitative studies and lacks kinetic mechanisms that are linked to a predictive model. The typical wave-dependent photolysis of gas-phase trace gases has long been subject to atmospheric photochemistry. This photolysis rate is a first-order reaction and is calculated via the coupling actinic flux (the quantity of photons) with the characteristics (cross section area and quantum yield) of a light-absorbing molecule (McNaught and Wilkinson, 1997). In order to model dust photochemistry, the integration of wavelength-dependent actinic flux with the photocatalytic activity of mineral dust is needed.

In addition to sunlight intensity, humidity also influences heterogeneous dust chemistry. Humidity governs particle water content, which influences the gas–dust sorption process of trace gases (Navea et al., 2010) and the formation of dust-phase oxidants. Huang et al. (2015) found that the $\gamma_{\text{SO}_4^{2-}}$ of SO_2 autoxidation in ATD particles increased by 142 % because the relative humidity (RH) changed from 15 to 90 %. In the presence of UV light, the particle water content can

act as an acceptor for h_{vb}^+ and produce surface OH radicals, promoting heterogeneous photochemistry of SO_2 on mineral dust. In the presence of UV light, Shang et al. (2010) reported that sulfate production on the surface of TiO_2 increased by 5 times because of the increase in RH from 20 to 80 %. Park and Jang (2016) also reported the exponential increase in $\gamma_{\text{SO}_4^{2-}}$ as the RH increased from 20 to 80 % for both autoxidation and photooxidation of SO_2 in the presence of ATD particles. A few studies have attempted to simulate sulfate formation in the presence of mineral dust at regional scales using laboratory-generated kinetic parameters (Tang et al., 2004; Li and Han, 2010; Dong et al., 2016). However, $\gamma_{\text{SO}_4^{2-}}$ applied to the regional simulations originated from pure and dry metal oxides without UV light, and thus will differ from those of ambient dust exposed to natural sunlight. It is expected that the typical regional simulations during dust events might underestimate the formation of sulfate.

In this study, the Atmospheric Mineral Aerosol Reaction (AMAR) model was developed to predict atmospheric oxidation of trace gases such as SO_2 and NO_2 under ambient conditions. The kinetic mechanisms of dust-driven photochemistry, including autoxidation and photooxidation of SO_2 , were newly established in the model. The rate constant of dust photoactivation, which forms electron–hole pairs and sources dust-driven oxidants, was integrated into the model. The influence of meteorological variables, such as humidity, temperature, and sunlight, on SO_2 oxidation was investigated using the resulting AMAR model. The model also addresses the kinetic mechanism to simulate how atmospheric major pollutants such as NO_x and ozone are engaged in the oxidation of SO_2 in the presence of airborne dust particles. For environmental scenarios, the model was applied for polluted urban conditions (e.g., hydrocarbon ppbC / NO_x ppb < 5) and low- NO_x conditions (e.g., hydrocarbon ppbC / NO_x ppb < 5). The reaction rate constants for both autoxidation and photocatalytic reactions of SO_2 were obtained through the simulation of indoor chamber data, which were previously generated under various meteorological and environmental conditions (Park and Jang, 2016). The suitability of the resulting AMAR model was tested against sulfate formation in a large outdoor smog chamber at the University of Florida Atmospheric Photochemical Outdoor Reactor (UF-APHOR) under natural sunlight. The AMAR model of this study will vastly improve the accuracy of the prediction of sulfate and nitrate formation in regional and global scales where dust emission is influential.

2 Experimental

2.1 Chamber experiments

The indoor chamber data of this study were obtained from the recent laboratory study by Park and Jang (2016) to determine the kinetic rate constants that are needed to develop

the AMAR model. The indoor chamber operation has been reported previously (Park and Jang, 2016) (also see Sect. S1 in the Supplement). The indoor chamber data are listed in Table 1. The outdoor chamber experiments were performed in the UF-APHOR dual-chambers (52 m^3 for each chamber) to test the suitability of AMAR model to ambient condition. The light irradiation of the indoor-UV light and the sunlight is shown in Fig. S1. A detailed description of the operation of the outdoor chamber is also described in Sect. S1. The outdoor experimental conditions for SO_2 heterogeneous reaction in the presence of mineral dust particles are listed in Table 2.

2.2 Light absorption of ATD particles

The absorbance spectrum of ATD particles was measured to develop the reaction rate constants in the kinetic model. The detailed procedure for light absorption measurement of particle samples can be found in the previous study (Zhong and Jang, 2011). The particle size distribution of ATD is shown in Fig. S2. The suspended dust particles were sampled on a Teflon-coated glass fiber filter for 20 min. The masses difference of dust sample was measured using a microbalance (MX5, Mettler Toledo, Columbus, OH). The light absorbance of the dust filter sample (Abs_{ATD}) was measured using a Perkin-Elmer Lambda 35 UV–visible spectrophotometer equipped with a Labsphere RSA-PE-20 diffuse-reflectance accessory. The absorbance spectrum was normalized by particle mass and calculated to obtain the mass absorbance cross section (See Sect. S1). The resulting absorbance cross section and quantum yield of ATD dust are shown in Fig. S3.

3 AMAR model description

The overall schematic of the AMAR model is shown in Fig. 1. In the model, the total sulfate mass concentration ($[\text{SO}_4^{2-}]_{\text{T}}, \mu\text{g m}^{-3}$) is predicted from the reactions in three phases: the sulfate formed in the gas phase ($[\text{SO}_4^{2-}]_{\text{gas}}, \mu\text{g m}^{-3}$), the sulfate from the aqueous phase ($[\text{SO}_4^{2-}]_{\text{aq}}, \mu\text{g m}^{-3}$), and the sulfate from dust-driven chemistry ($[\text{SO}_4^{2-}]_{\text{dust}}, \mu\text{g m}^{-3}$). The key components of the model consist of the partitioning process and the kinetic mechanisms in three phases.

1. The gaseous inorganic species (e.g., SO_2 , NO_x and ozone) are partitioned onto both inorganic-salt (sulfuric acid and its salts) seeded aqueous particles and mineral dust particles. ATD particles are known to be coated with the multilayer of water due to their high affinity to water (Gustafsson et al., 2005) (Sect. 3.2.1). Therefore, we assume that gas–dust partitioning of tracers on multilayer water is processed in absorption mode.

2. SO_2 oxidation in the gas phase is simulated using mechanisms previously reported in the literature (Byun and Schere, 2006; Sarwar et al., 2013, 2014; Binkowski and Roselle, 2003) (Table S1 in the Supplement).
3. The partitioned SO_2 is heterogeneously oxidized in the inorganic-salt seeded aqueous phase based on the previously reported mechanisms (Liang and Jacobson, 1999).
4. The formation of sulfate ($[\text{SO}_4^{2-}]_{\text{dust}}$) in the dust phase is approached using two kinetic sub-modules: the production of sulfate ($[\text{SO}_4^{2-}]_{\text{auto}}, \mu\text{g m}^{-3}$) by autoxidation in open air and sulfate formation ($[\text{SO}_4^{2-}]_{\text{photo}}, \mu\text{g m}^{-3}$) by photocatalytic reactions. Overall, dust chemistry within the multilayer of water is treated in a similar manner to aqueous chemistry. However, aqueous chemistry is operated through the whole aerosol volume and dust chemistry is processed in the water layers on the surface of dust particles.

The simulation of chamber data using the model was performed using a kinetic solver (Morpho) (Jeffries, 1998). In these mechanisms, the symbols “g”, “aq”, and “d” denote the chemical species in the gas phase, inorganic-salt seeded aqueous phase, and dust phase, respectively. The unit of the concentration of chemical species is molecule per cubic centimeter of air. The rate constants associated with various reaction mechanisms in the AMAR model were determined by simulating pre-existing indoor chamber data obtained from controlled experimental conditions (Park and Jang, 2016). For example, the rate constant for SO_2 autoxidation ($k_{\text{auto}}, \text{s}^{-1}$) is semiempirically determined by fitting the predicted concentration of sulfate to the experimental data D1 in Table 1. The gas–dust partitioning constant (K_{d,SO_2} , Sect. 3.2.1) of SO_2 is dependent on temperature, aerosol water content, and acidity. K_{d,SO_2} values were semiempirically determined using data D1–D3 (three different RHs) and the literature parameters related to the effect of temperature and acidity on K_{d,SO_2} . The rate constant ($k_{\text{photo}}, \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the sulfate formation by photocatalytic reactions is semiempirically determined using data L1–L3 (three different RHs) in Table 1. In the presence of ozone, k_{auto} and k_{photo} are determined using datasets D4 and L4, respectively. In the following sections, the components of the AMAR model are described in detail.

3.1 SO_2 oxidation in gas phase and aerosol aqueous phase

3.1.1 Gas-phase oxidation

The oxidation of SO_2 in the gas phase has been extensively studied by numerous researchers (Baulch et al., 1984; Kerr, 1984; Atkinson and Liroyd, 1984; Calvert and Stockwell, 1984; Graedel, 1977; Atkinson et al., 1997). In this study,

Table 1. Experiment conditions and simulation results for SO₂ heterogeneous photooxidation on the surface of ATD particles at a variety of humidity conditions (RH), light sources, and initial concentrations of traces using indoor chamber data.

Exp. no. ^a	UV	RH ^b (%)	Temp. ^b (K)	Initial concentration				Duration ^e (min)	Exp. [SO ₄ ²⁻] _T ^f (μg m ⁻³)	Note ^g
				ATD dust ^c (μg m ⁻³)	SO ₂ ^d (ppb)	NO / NO ₂ ^d (ppb)	O ₃ ^d (ppb)			
D1	Off	21.0	295.9	295	267	n/a	n/a	150	0.61 ± 0.02	<i>K</i> _{d,SO₂} , <i>k</i> _{auto}
D2	Off	55.3	295.0	406	152	0.1/0.6	1.86	148	1.02 ± 0.01	
D3	Off	80.1	294.5	278	147	0.9/1.6	0.29	147	1.59 ± 0.02	
L1	On	20.4	297.0	123	87.8	0.3/1.7	0.30	120	1.66 ± 0.04	<i>k</i> _{OH,O₂} , <i>k</i> _{auto}
L2	On	55.2	299.3	120	82.3	0.2/1.9	1.79	120	2.54 ± 0.21	
L3	On	80.7	298.7	131	78.0	0.2/0.4	0.28	120	5.22 ± 0.19	
L4	On	21.0	296.9	130	78.1	0.1/1.35	64.8	120	4.48 ± 0.14	<i>k</i> _{OH,O₃} , <i>k</i> _{auto,O₃}
D4	Off	20.4	296.6	293	101.0	0.7/1.9	65.4	60	0.158 ± 0.01	

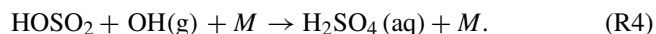
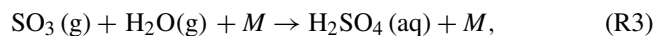
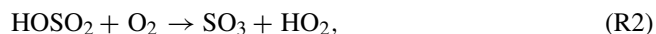
^a “D” denotes experiments under dark conditions. “L” denotes experiments with UV light. The dataset D1–D3 and L1–L4 were obtained from the recent laboratory data reported by Park and Jang (2016). Dataset D4 was newly added here to estimate the kinetic parameter of heterogeneous autoxidation of SO₂ in the presence of ozone. ^b The accuracy of RH is ±5 %. The accuracy of temperature is ±0.5 K. ^c The mass concentration of ATD particles were calculated combining SMPS data, OPC data, the density of dust particles (2.65 g cm⁻³), and the particle size distribution (< 3 μm). The errors associated with the dust particle mass concentration were ±6 %. ^d The errors associated with the observation of SO₂, NO, NO₂, and O₃ were ±0.9, ±12.5, ±6.9, and ±0.2 %, respectively. ^e The duration is the simulation time from the beginning of the experiment to the end of the experiment. ^f Sulfate concentrations were measured at the end of experiments using PILS-IC. The measurements were not corrected for the particle loss rate to the wall but corrected for the indigenous sulfate from dust particles. ^g The experiments are noted with the associated kinetic parameters that were empirically determined. n/a = not applicable

Table 2. Outdoor chamber experiment condition for SO₂ heterogeneously photooxidation on the ATD particles at variety initial concentration of SO₂, dust particle, and NO_x.

Exp. date	Purpose	RH ^a (%)	Temp. ^a (K)	Simulation time (EST)	Initial concentration ^b			
					ATD dust ^c (μg m ⁻³)	SO ₂ (ppb)	NO / NO ₂ (ppb)	O ₃ (ppb)
28 Mar 2015	SO ₂	18–67	277.1–301.9	11:10–16:30	n/a	60.1	0.1/0.9	6.3
28 Mar 2015	SO ₂ & dust	15–45	277.8–301.5	10:50–16:30	290.1	56.4	0.1/0.7	0.7
16 Jun 2015	Low dust	15–49	286.7–313.0	08:40–15:30	90.1	100.0	0.1/0.7	0.7
16 Jun 201	High dust	16–48	287.0–311.5	09:30–15:30	403.7	120.1	1.1/1.0	5
12 Nov 2015	Low SO ₂	24–71	287.8–312.9	08:40–17:30	239.2	119.0	0.5/2.0	3.0
12 Nov 2015	High SO ₂	14–42	287.3–311.06	09:00–17:30	229.0	271.6	0.2/2.1	2.6
14 Apr 2017	NO _x effect	33–95	287.8–314.3	06:30–17:30	496.2	88.1	88.9/13.5	3.0
25 Apr 2017–1	NO _x effect	18–89	283.8–313.6	06:00–16:00	414.0	15.0	112.0/13.2	2.2
25 Apr 2017–2	NO _x effect	26–94	284.1–312.7	06:00–16:00	478.7	17.5	35.9/3.6	1.9

^a The accuracy of RH is ±5 %. The accuracy of temperature is ±0.5 K. ^b The errors associated with the observation of SO₂, NO, NO₂, O₃, NH₄⁺, and the concentration of dust particle mass were ±0.9, ±12.5, ±6.9, ±0.2, ±5.0, and ±6 %, respectively. The detailed observations of the chemical species during the experiments were shown in Figs. S4 and S5 in the Supplement. ^c The mass concentrations of ATD particles were calculated combining SMPS data, OPC data, the density of dust particles (2.65 g cm⁻³), and the particle size distribution (< 3 μm). n/a = not applicable

the oxidation of SO₂ is described using comprehensive reaction mechanisms shown in Table S1. The mechanisms can also be simplified as follows:



3.1.2 Gas–aerosol partitioning

SO₂ is dissolved into hygroscopic sulfuric acid (H₂SO₄), which is formed in the gas phase, via a partitioning process and reacts with the aqueous-phase oxidants (e.g., H₂O₂

and O₃) to heterogeneously form H₂SO₄. The chemical species that were treated by the partitioning process include SO₂, NO_x, O₃, OH, HO₂, H₂O₂, HCOOH, CH₃OOH, HNO₃, CH₃O₂, HONO, CH₃COOH, and HCHO. In the model, the partitioning process is approached using the gas–particle partitioning coefficient *K*_{aq,SO₂} (m³ μg⁻¹) based on aerosol mass concentration. *K*_{aq,SO₂} is derived from Henry’s law constant of SO₂ (*K*_{H,SO₂} = 1.2 mol L⁻¹ atm⁻¹ at 298 K) (Chameides, 1984),

$$K_{\text{aq,SO}_2} = \frac{K_{\text{H,SO}_2} RT}{\rho_{\text{aq}}}, \quad (1)$$

where *R* is the ideal gas constant (J K⁻¹ mol⁻¹) and *ρ*_{aq} (g cm⁻³) is the density of the particle, which is calculated us-

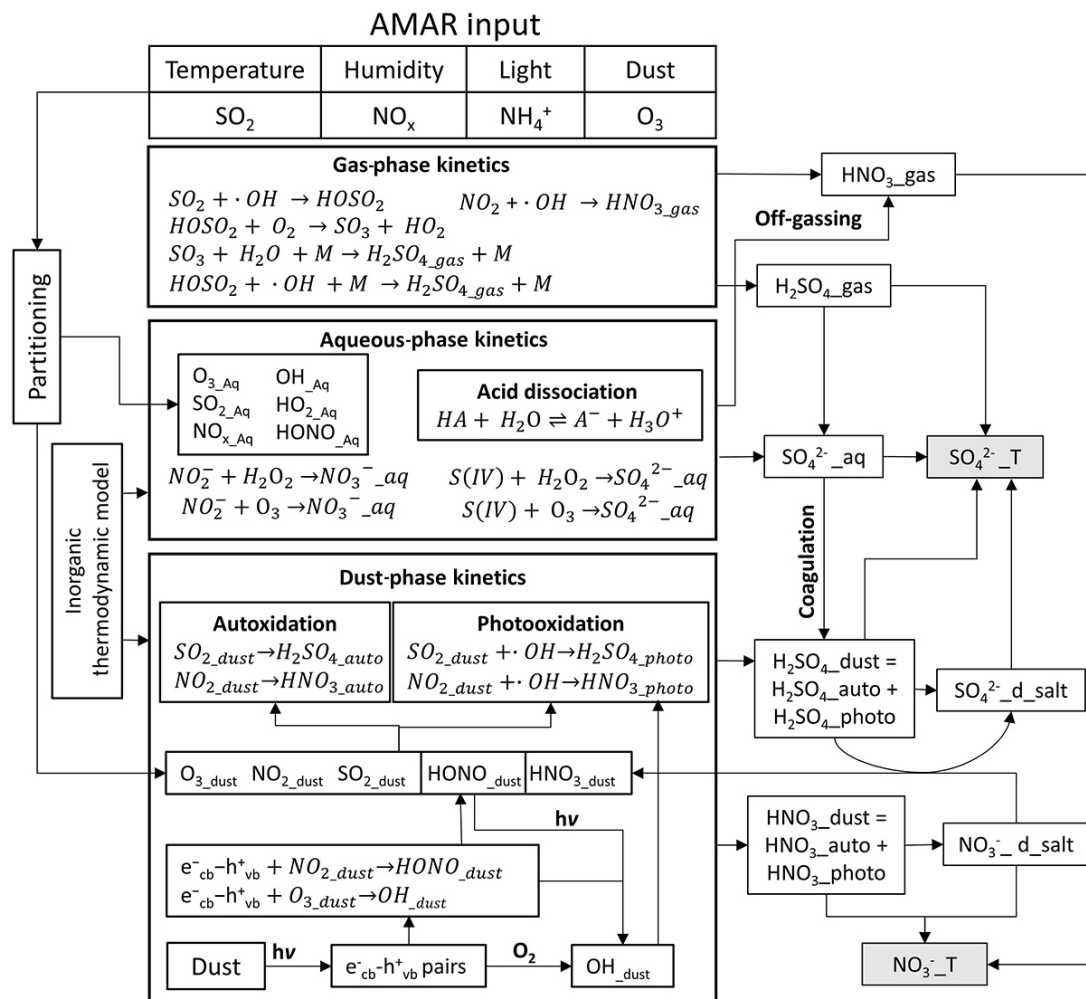
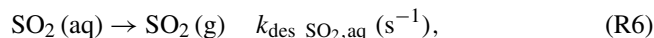
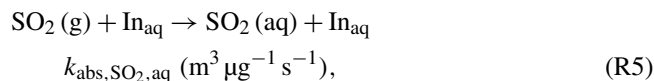


Figure 1. The overall schematic of the AMAR model to simulate heterogeneous SO₂ oxidation. For the description of chemical species, gas phase, aqueous phase, and dust phase are symbolized as “gas”, “aq”, and “dust”, respectively. SO₄²⁻_T, H₂SO_{4_gas}, SO₄²⁻_aq, and H₂SO_{4_dust} are the total sulfate formation and the formation of sulfate from gas phase, aqueous phase, and dust phase, respectively. SO₄²⁻_d_salt and NO₃⁻_d_salt are the neutralized sulfate and nitrate in the dust phase.

ing an inorganic thermodynamic model (E-AIM II) (Clegg et al., 1998; Wexler and Clegg, 2002; Clegg and Wexler, 2011) based on humidity and inorganic composition. The partitioning process of SO₂ on inorganic aerosol (In_{aq}, μg m⁻³) is expressed as



where $k_{\text{abs},\text{SO}_2,\text{aq}}$ (m³ μg⁻¹ s⁻¹) and $k_{\text{des},\text{SO}_2,\text{aq}}$ (s⁻¹) are the uptake rate constant and the desorption rate constant, respectively, and are calculated as follows:

$$k_{\text{abs},\text{SO}_2,\text{aq}} = f_{\text{abs},\text{aq}} \frac{\omega_{\text{SO}_2} f_{\text{aq},\text{S}_M}}{4}, \quad (2)$$

$$k_{\text{des},\text{SO}_2,\text{aq}} = \frac{k_{\text{abs},\text{SO}_2,\text{aq}}}{K_{\text{aq}}}, \quad (3)$$

where f_{aq,S_M} (5 × 10⁻⁴, m² μg⁻¹) is the coefficient to convert the aerosol mass concentration (μg m⁻³) to the surface area concentration (m² m⁻³) for particle size near 100 nm. $f_{\text{abs},\text{aq}}$ is the coefficient for uptake process and ω_{SO_2} is the mean molecular velocity (m s⁻¹) of SO₂ and can be calculated as follows:

$$\omega_{\text{SO}_2} = \sqrt{\frac{8RT}{\pi MW}}, \quad (4)$$

where MW is molecular weight (kg mol⁻¹). In our model, $f_{\text{abs},\text{aq}}$ was set at 2 × 10⁴ in Eq. (2) to have fast partition-

ing process. Table S2 summarizes the characteristic time that is estimated for diffusion, partitioning, and the reactions of major species with OH radicals in gas, aqueous, and dust phases. In general, the characteristic time (s) of a partitioning process (order of 10^{-7} s) is much faster than gas-phase oxidation (order of 10^6 s), aqueous-phase oxidation (order of 10^3 – 10^4 s), and dust-phase oxidation (order of 10^2 – 10^3 s at presence of $200 \mu\text{g m}^{-3}$ of dust particles). The mass concentration ($\mu\text{g m}^{-3}$) of inorganic seeded aqueous phase above the efflorescent relative humidity (ERH) is also dynamically calculated for the SO_4^{2-} – NH_4^+ – H_2O system. Colberg et al. (2003) semiempirically predicted ERH by fitting to the experimental data based on the ammonia-to-sulfate ratio in the SO_4^{2-} – NH_4^+ – H_2O system. AMAR model utilizes these parameterizations to predict ERH dynamically. Ammonia is inevitable in our chamber study and mainly acts as a carry-over from previous chamber experiments. Thus, H_2SO_4 is fully or partially neutralized by ammonia.

3.1.3 Aerosol aqueous-phase reaction

The AMAR model implements aqueous-phase chemistry that occurs in inorganic salted aqueous aerosol (SO_4^{2-} – NH_4^+ – H_2O system without dust) to form SO_4^{2-} (aq) and NO_3^- (aq). We employed the preexisting aqueous-phase kinetic reactions involving SO_2 (Liang and Jacobson, 1999) and NO_x chemistry (Liang and Jacobson, 1999; Hoyle et al., 2016). Thus, our simulation inherits all the possible uncertainties embedded in the original kinetic data.

The SO_2 dissolved in the aqueous phase is hydrolyzed into H_2SO_3 and dissociates to form ionic species (HSO_3^- and SO_3^{2-}). SO_4^{2-} (aq) is formed by reactions of the sulfur species in oxidation state IV (S(IV) (aq)) with OH (aq), H_2O_2 (aq), or O_3 (aq) (Table S1). The dissolved HONO can also dissociate to form NO_2^- (aq) and result to NO_3^- (aq). Each chemical species in S(IV) (aq) has a different reactivity for oxidation reactions. The distribution of chemical species is affected by aerosol acidity, which is controlled by humidity and inorganic composition. Hence, the formation of sulfate is very sensitive to aerosol acidity. For example, most of the S(IV) is consumed by H_2O_2 at $\text{pH} < 4$, whereas most of it is consumed by O_3 at $\text{pH} > 4$. Some strong inorganic acids, such as sulfuric acid, influence aerosol acidity. In AMAR, aerosol acidity ($[\text{H}^+]$) is estimated at each time step by E-AIM II (Clegg et al., 1998; Wexler and Clegg, 2002; Clegg and Wexler, 2011) corrected for the ammonia-rich condition (Li et al., 2015; Beardsley and Jang, 2016; Li and Jang, 2012) as a function of inorganic composition measured by a particle-into-liquid sampler coupled with ion chromatography (PILS-IC). When the ammonia-to-sulfate ratio is greater than 0.8, the prediction of $[\text{H}^+]$ is corrected based on the method described by Li and Jang (2012). At high NO_x levels, NO_2^- (aq) competes with S(IV) (aq) for the reaction with OH (aq), O_3 , or H_2O_2 (Table S1) (Ma et al., 2008). However, the HONO concentration becomes high at high NO_x lev-

els and enhances SO_2 oxidation in the inorganic-salt seeded aqueous phase due to the formation of OH radicals via photolysis of HONO.

3.2 Heterogeneous oxidation in the presence of mineral dust particles

The heterogeneous chemistry in the presence of dust particles has been newly established in the AMAR model. The dust-phase module consists of a partitioning process (Sect. 3.2.1) and heterogeneous chemistry for SO_2 and other trace gases (ozone, HONO, and NO_2) (Table 3) (Fig. 1). The heterogeneous chemistry of SO_2 is handled by autoxidation (Sect. 3.2.2) and photooxidation under UV light (Sect. 3.2.4). In dust-phase photochemistry, the central mechanism for SO_2 oxidation is operated by the surface oxidants (e.g., OH(d)), which is generated via the photoactivation process of semiconductive metal oxides in dust particles (Sect. 3.2.3).

3.2.1 Gas–dust particle partitioning

In an adsorptive mode, water molecules suppress partitioning of SO_2 because they compete for adsorptive sites with tracers (Cwiertny et al., 2008). However, the formation of the sulfate associated with ATD increased with increasing RH as shown in Table 1, suggesting that gas–dust partitioning is more likely operated by absorption on the multilayer coated dust with water molecules. ATD contains hygroscopic inorganic salts that form the thin water film on the surface of ATD particles when the salts are deliquescent (or above ERH). Some salts such as magnesium sulfate and calcium sulfate can be hydrated even at low humidity (Beardsley et al., 2013; Jang et al., 2010). Gustafsson et al. (2005) reported that ATD particles showed a substantially high affinity to water compared to pure CaCO_3 particles. In their study, the water content of ATD particles, which was measured using the thermogravimetric method, ranged from two monolayers to four monolayers based on the BET surface area between 20 and 80 % relative humidity. This water layer influences gas–dust partitioning of atmospheric tracers such as SO_2 and NO_2 . The gas–dust partitioning constant (K_{d,SO_2} , $\text{m}^3 \text{m}^{-2}$) of SO_2 is defined as

$$K_{\text{d},\text{SO}_2} = \frac{[\text{SO}_2]_{\text{d}}}{[\text{SO}_2]_{\text{g}} A_{\text{Dust}}} \quad (\text{m}^3 \text{m}^{-2}), \quad (5)$$

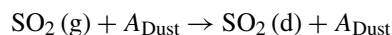
where A_{dust} ($\text{m}^2 \text{m}^{-3}$) is the geometric surface concentration of ATD dust particles and is calculated by multiplying the dust mass concentration ($\mu\text{g m}^{-3}$) by a geometric surface-mass ratio ($f_{\text{dust},\text{S}_M}$) of ATD particles (3.066×10^{-6} , $\text{m}^2 \mu\text{g}^{-1}$). The SO_2 absorption and desorption processes for the dust phase are expressed as

Table 3. Dust-phase heterogeneous reactions and their rate constants in the presence of ATD particles.

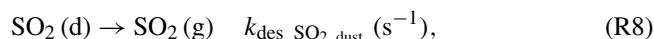
	Reaction ^a	Rate constant ^b	Coefficients of rate constants ^b		K_a^c	Reference ^d	Note ^e
			k_1	k_2			
Partitioning							
1	SO ₂ + Dust → SO ₂ (d) + Dust	k_{abs}	1×10^{-8}			AR05, HZ15	Reaction (R7)
2	SO ₂ (d) → SO ₂	k_{des}	1×10^9	3100	0.013	AR05, HZ15	Reaction (R8)
3	O ₃ + Dust → O ₃ (d) + Dust	k_{abs}	1×10^{-8}			MU03, US01	
4	O ₃ (d) → O ₃	k_{des}	3×10^{10}	2700	0	MU03, US01	
5	NO ₂ + Dust → NO ₂ (d) + Dust	k_{abs}	1×10^{-8}			CW84	
6	NO ₂ (d) → NO ₂	k_{des}	1×10^{10}	2500	0	CW84	
7	HNO ₃ + Dust → HNO ₃ (d) + Dust	k_{abs}	1×10^{-8}			SW81, Sc84	
8	HNO ₃ (d) → HNO ₃	k_{des}	1×10^{15}	8700	15.4	SW81, Sc84	
9	HONO + Dust → HONO (d) + Dust	k_{abs}	1×10^{-8}			BK96	
10	HONO(d) → HONO	k_{des}	1×10^{10}	4900	0	BK96	
11	N ₂ O ₅ + Dust → HNO ₃ (d) + Dust	k_{abs}	7.3×10^{-3}			WS09	
Dust phase							
1	Dust + $h\nu$ → Dust + e_{-h}	$k_{e_{-h}}^j$	$j[\text{ATD}]$			Sect. 3.2.3	Reaction (R10)
2	e_{-h} → energy	k_{recom}	1×10^{-2}			Sect. 3.2.3	Reaction (R11)
3	e_{-h} + O ₂ → OH(d)	k_{OH,O_2}	1×10^{-22}	2.3RH		Sect. 3.2.3	Reaction (R12)
4	SO ₂ (d) → SO ₄ ²⁻ (d)	k_{auto}	5×10^{-6}			Sect. 3.2.2	Reaction (R9)
5	SO ₂ (d) + OH(d) → SO ₄ ²⁻ (d)	k_{photo}	1×10^{-12}			Sect. 3.2.4	Reaction (R13)
6	SO ₂ (d) + O ₃ (d) → SO ₄ ²⁻ (d) + O ₂	$k_{\text{auto},\text{O}_3}$	2×10^{-11}			Sect. 3.3.1	Reaction (R14)
7	e_{-h} + O ₃ (d) → OH (d) + O ₂	k_{OH,O_3}	1×10^{-12}			Sect. 3.3.1	Reaction (R15)
8	NO ₂ (d) → NO ₃ ⁻ (d)	$k_{\text{auto},\text{NO}_2}$	6×10^{-5}			Sect. 3.3.2	Reaction (R18)
9	e_{-h} + NO ₂ (d) → HONO(d)	k_{e_{-h},NO_2}	6×10^{-12}			Sect. 3.3.2	Reaction (R16)
10	HONO (d) + $h\nu$ → OH (d) + NO	k_{HONO}^j	$j[\text{HONO}_{\text{to_OH}}]$			BK91, AB97	Reaction (R17)
11	NO ₂ (d) + OH(d) → NO ₃ ⁻ (d)	$k_{\text{photo},\text{NO}_2}$	1×10^{-10}			Sect. 3.3.2	Reaction (R19)

^a The unit of the chemical species (except dust) is molecule cm^{-3} for both partitioning process and dust-phase chemistry. The unit of the dust for model input is mass concentration ($\mu\text{g m}^{-3}$) and is multiplied by a factor of 2.45×10^{10} for simulation. ^b The unit of reaction rate constants is s^{-1} for the first-order reactions and $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ for the second-order reactions. k_{abs} is uptake rate constant. $k_{\text{abs}} = k_1 \omega f_{\text{dust}, \text{S}_M} / 4$, where $\omega = \sqrt{8RT/(\pi MW)}$ (m s^{-1}) and $f_{\text{dust}, \text{S}_M} = 3.066 \times 10^{-6}$ ($\text{m}^2 \mu\text{g}^{-1}$). R is the ideal gas constant and MW (g mol^{-1}) is the molecule weight of chemical species. k_{des} is desorption rate constant. $k_{\text{des}} = k_1 \exp\left(-\frac{k_2}{T}\right) / (F_{\text{water}}(1 + K_a/[H^+]))$, where F_{water} is calculated using Eq. (8). $[H^+]$ is dynamically calculated based on thermodynamic model (E-AIM II) (Clegg et al., 1998; Wexler and Clegg, 2002; Clegg and Wexler, 2011). The rate constants (k) for dust-phase reactions is $k = k_1 \exp(k_2)$. $k_{e_{-h}}^j$ and k_{HONO}^j are photocatalytic reaction rates. The cross sections and quantum yields of dust are estimated (see Sect. 2.2). ^c

Coefficient K_a is acid dissociation constant (see k_{des}). ^d The rate constant parameters, which are noted as “this study”, are determined using the simulation of indoor chamber data (Park and Jang, 2016) (see Sect. 3). AB97, Atkinson et al. (1997); AR05, Adams et al. (2005); BK91, Bongartz et al. (1991); BK96, Becker et al. (1996); CW84, Chameides (1984); HZ15, Huang et al. (2015); MU03, Michel et al. (2003); Sc84, Schwartz (1984); SW81, Schwartz and White (1981); US01, Underwood et al. (2001); WS09, Wagner et al. (2009). ^e The reactions are noted with the numbers associated with the reaction in the main text.



$$k_{\text{abs}, \text{SO}_2, \text{dust}} (\text{m}^3 \text{m}^{-2} \text{s}^{-1}), \quad (\text{R7})$$



where $k_{\text{abs}, \text{SO}_2, \text{dust}} (\text{m}^3 \text{m}^{-2} \text{s}^{-1})$ and $k_{\text{des}, \text{SO}_2, \text{dust}} (\text{s}^{-1})$ are the absorption rate constant and the desorption rate constant, respectively. At equilibrium, the absorption rate (R7) equals the desorption rate (R8). Thus, $K_{\text{d}, \text{SO}_2}$ can be expressed as

$$K_{\text{d}, \text{SO}_2} = \frac{k_{\text{abs}, \text{SO}_2, \text{dust}}}{k_{\text{des}, \text{SO}_2, \text{dust}}} (\text{m}^3 \text{m}^{-2}). \quad (6)$$

The $K_{\text{d}, \text{SO}_2}$ value at 20 % RH is set at $1.63 (\text{m}^3 \text{m}^{-2})$ based on the literature data (dust particles at 20 % RH) (Adams

et al., 2005; Huang et al., 2015). The characteristic time to reach to equilibrium is very short (Sect. 3.1.1). In kinetic mechanisms, $k_{\text{ads}, \text{SO}_2, \text{dust}}$ was set at $1.7 \times 10^3 \text{m}^3 \text{m}^{-2} \text{s}^{-1}$ for dry particles (20 % RH) using the same approach as Eq. (2). The resulting characteristic time for $k_{\text{ads}, \text{SO}_2, \text{dust}}$ is 10^{-6}s . The characteristic time of the reaction of SO_2 with an OH radical ($10^6 \text{molecules cm}^{-3}$) is about 10^6 – 10^7s in gas phase and 10^5 – 10^6s in both aqueous phase and dust phase.

To consider the effect of temperature on $K_{\text{d}, \text{SO}_2}$, the temperature dependency of $k_{\text{des}, \text{SO}_2, \text{dust}}$ (Eq. 6) is derived from the Henry's constant (Chameides, 1984). $K_{\text{d}, \text{SO}_2}$ (Eq. 5) is also influenced by aerosol water content (Zuend et al., 2011) as well as the dissociation of H_2SO_3 , which is operated by aerosol acidity ($[H^+]$) and an acid dissociation constant ($K_{\text{a}, \text{SO}_2}$) (Martell and Smith, 1976). Thus, $k_{\text{des}, \text{SO}_2, \text{dust}}$ is ex-

pressed as

$$k_{\text{des},\text{SO}_2,\text{dust}} = 1 \times 10^9 \exp\left(-\frac{3100}{T}\right) / \left(F_{\text{water}} \left(1 + \frac{K_{\text{aSO}_2}}{[\text{H}^+]}\right)\right) \quad (\text{s}^{-1}). \quad (7)$$

K_{aSO_2} is $0.013 \text{ (mol L}^{-1}\text{)}$ at 298 K (Martell and Smith, 1976). The influence of the dissociation of inorganic acid on K_{d,SO_2} is accounted for by the term $(1 + \frac{K_{\text{aSO}_2}}{[\text{H}^+]})$ in Eq. (7). The estimation of $[\text{H}^+]$ is treated in the same ways as aqueous chemistry (Sect. 3.1.3).

In order to estimate K_{d,SO_2} at different RH, F_{water} (coefficient of the mass fraction of water to dust particles) was introduced into the model. The hygroscopic property of mineral dust dynamically changes because dust can be substantially modified by direct reaction of some of its components (e.g., CaCO_3) with inorganic acids such as H_2SO_4 and HNO_3 . When dust forms $\text{Ca}(\text{NO}_3)_2$, dust becomes more hygroscopic. Nitrate salts deliquesce at very low RH (17 %) (Krueger et al., 2003, 2004). CaSO_4 is, however, relatively hydrophobic. Nitrate salts exist only when sulfate concentrations is very low. In the model, F_{water} is associated with the hygroscopic property of indigenous dust (first term in Eq. 8), the inorganic nitrates formed from the reaction of absorbed HNO_3 with dust (second term), and the inorganic sulfate ($\text{SO}_4^{2-}\text{--NH}_4^+\text{--H}_2\text{O}$ system, third term).

$$F_{\text{water}} = \exp(4.4\text{RH}) + 3.7 f_{\text{dust},\text{S}_M} \exp(4.4\text{RH}) \frac{[\text{NO}_3^-(\text{d_salt})]}{A_{\text{Dust}}} + \frac{f_{\text{dust},\text{S}_M} M_{\text{in,water}}}{A_{\text{Dust}}}, \quad (8)$$

where $M_{\text{in,water}}$ is the water concentration ($\mu\text{g m}^{-3}$) associated with inorganic sulfate and calculated using E-AIM II. Both $[\text{NO}_3^-(\text{d_salt})]$ and $M_{\text{in,water}}$ are normalized by the mass concentration of ATD particles ($[\text{Dust}]$, $\mu\text{g cm}^{-3}$). F_{water} is first determined using chamber simulation of SO_2 heterogeneous oxidation (first and third terms in Eq. 8) (D1–D3 in Table 1) under varied RH levels and extended to SO_2 oxidation in the presence of NO_x (Exp. 14 April 2017 in Table 2). Among temperature, RH, and aerosol acidity, the most influential variable is RH due to the variation in F_{water} (see sensitivity analysis in Sect. 5).

3.2.2 Autoxidation of SO_2 on dust surface

Typically, autoxidation of SO_2 is an oxidation process via the reaction of absorbed SO_2 (Reactions R7 and R8) with an oxygen molecule. In the model, $[\text{SO}_4^{2-}]_{\text{auto}}$ is defined as the sulfate resulted from any oxidation reactions (autoxidation in open air and oxidation with ozone) of SO_2 without UV light (Fig. 1). In autoxidation, the reaction of $\text{SO}_2(\text{d})$ with the oxygen molecules is treated as the first-order reaction (assuming the concentration of oxygen is constant as $2 \times 10^5 \text{ ppm}$).

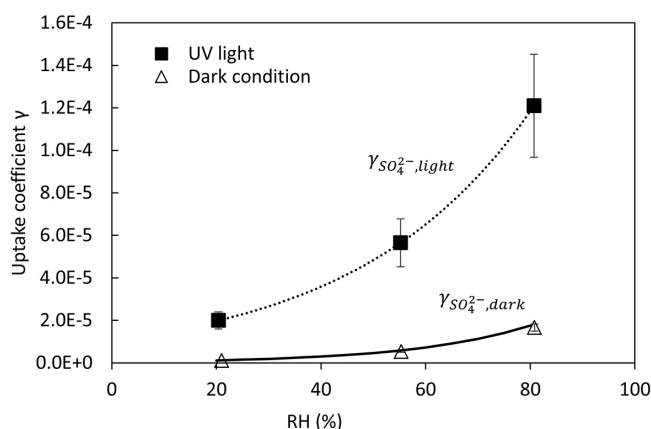
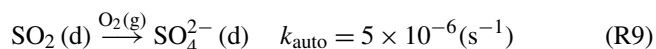


Figure 2. Uptake coefficient (γ) of SO_2 in the presence of the ATD particles under dark conditions and UV light conditions. The values of γ were obtained by kinetic model using indoor experimental data. The $\gamma_{\text{SO}_4^{2-},\text{light}}$ is correlated to concentration of OH radicals and RH (%). The $\gamma_{\text{SO}_4^{2-},\text{dark}}$ is a function of RH. The error bar of γ was derived from the model uncertainty.

Under dark conditions, the formation of sulfate is mainly sourced from autoxidation of SO_2 . For comparison with other studies, we estimate the reactive uptake coefficient ($\gamma_{\text{SO}_4^{2-},\text{auto}}$) of SO_2 onto ATD dust in the absence of ozone and NO_x (Fig. 2).

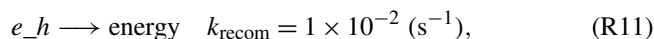
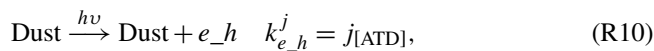
$$\gamma_{\text{SO}_4^{2-},\text{auto}} = \frac{4K_{\text{d},\text{SO}_2}k_{\text{auto}}}{\omega_{\text{SO}_2}}, \quad (9)$$

$\gamma_{\text{SO}_4^{2-},\text{auto}}$ is proportional to K_{d,SO_2} , and influenced by humidity (Eq. 7).

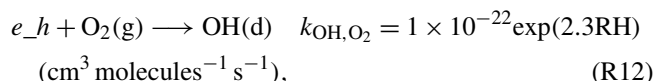
3.2.3 Photoactivation of dust particles and heterogeneous formation of OH radicals

The reactive uptake of SO_2 on particles is traditionally treated as a first-order process (Ullerstam et al., 2003; Li et al., 2007). Such an approach is appropriate for simple autoxidation mechanisms, but not for the complex heterogeneous photooxidation of SO_2 . In the AMAR model, the heterogeneous photooxidation of SO_2 is approached in three steps: (1) the formation of an e_{cb}^- – h_{vb}^+ pair via photoactivation of dust particles, (2) the formation of OH(d) via the reaction of an e_{cb}^- – h_{vb}^+ pair with a water or oxygen molecule, and (3) the reaction of absorbed SO_2 with the resulting OH(d) (second-order reactions) (Table S1).

The photoactivation of dust particles and the recombination reaction of an electron–hole pair (e_h) are added into the model.



where $k_{e_{-h}}^j$ is the photoactivation rate constant to form $e_{\text{cb}}^- - h_{\text{vb}}^+$ pairs and k_{recom} is the reaction rate constant of recombination (heat radiation) of an electron and a hole. The value of k_{recom} is set at a large number to prevent the accumulation of electron–hole pairs. The formation of OH(d) is expressed as



where k_{OH,O_2} is the reaction rate constant to form OH(d) and is first estimated using indoor chamber data (L1–L3 in Table 1) at RH 20, 55, and 80 % and then regressed against RH. The study by Thiebaud et al. (2010) reported the recombination of OH(d) near to TiO₂ surfaces. In our model, the mechanistic role of the catalytic formation of the electron–hole pairs (Reaction R10) and their recombination (Reaction R11) compensates the formation and the self-reaction of OH radicals.

In Reaction (R10), $k_{e_{-h}}^j$ is the operational rate constant for the photoactivation of dust particles and is dependent on the photolysis rate constant, $j_{[\text{ATD}]}$ (s^{−1}). Like the typical photolysis of a gaseous molecule, the photocatalytic production of $e_{\text{cb}}^- - h_{\text{vb}}^+$ pairs is linear to both the actinic flux ($I(\lambda)$, photons cm^{−2} nm^{−1} s^{−1}) originating from the light source and the photocatalytic property of dust particles. The value of $j_{[\text{ATD}]}$ is determined by $I(\lambda)$, the absorption cross section ($\sigma(\lambda)$, cm² μg^{−1}), and the quantum yield ($\phi(\lambda)$) of dust conducting matter at each wavelength range (λ , nm),

$$j_{[\text{ATD}]} = \int_{\lambda_1}^{\lambda_2} I(\lambda) \sigma(\lambda) \phi(\lambda) d\lambda. \quad (10)$$

In the model, $\sigma(\lambda)$ is the light absorption needed to activate dust-phase semiconducting metal oxides (excitation from a ground energy level to a conducting band), and $\phi(\lambda)$ is the probability of yielding the $e_{\text{cb}}^- - h_{\text{vb}}^+$ pair in the dust phase. Both $\sigma(\lambda)$ and $\phi(\lambda)$ cannot be directly measured because of complexity in the quantity of photoactive conducting matter in dust particles and the irradiation processes of the $e_{\text{cb}}^- - h_{\text{vb}}^+$ pair. In order to deal with $\sigma(\lambda) \times \phi(\lambda)$, we calculated the mass absorption cross section of dust particles (MAC_{ATD}, m² g^{−1}), which was determined using the absorption coefficient of ATD particles (b_{ATD} , m^{−1}) with the particle concentration (m_{ATD} , g m^{−3}):

$$\text{MAC}_{\text{ATD}} = \frac{b_{\text{ATD}}}{m_{\text{ATD}}}. \quad (11)$$

In Eq. (11), b_{ATD} can be calculated from the absorbance of dust filter sample (Abs_{ATD}, dimensionless) measured using a

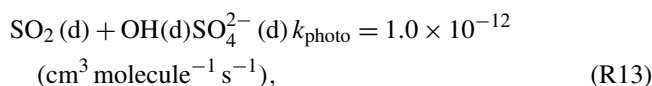
reflective UV–visible spectrometer (Fig. S3):

$$b_{\text{ATD}} = \frac{\text{Abs}_{\text{ATD}} A}{f V} \ln, \quad (12)$$

where $A = 7.85 \times 10^{-5}$ (m²) is the sampled area on the filter and V (m³) is the total air volume passing through the filter during sampling. In order to eliminate the absorbance caused by filter material scattering, a correction factor ($f = 1.4845$) is obtained from a previous study (Zhong and Jang, 2011) and coupled into Eq. (12). The preliminary study showed that the effect of aerosol scattering on the b_{abs} values of the aerosol collected on the filter was negligible. Further, Bond (2001) reported that particle light scattering does not significantly influence spectral absorption selectivity. The MAC_{ATD} of dust particles originates from photocatalytic conducting matter (e.g., TiO₂) as well as light-absorbing matter (e.g., gypsum and metal sulfate). Thus, the MAC_{ATD} spectrum is adjusted using the known TiO₂ absorption spectrum (Reyes-Coronado et al., 2008) and applied to $\sigma(\lambda) \times \phi(\lambda)$ (Fig. S3). The resulting $\sigma(\lambda) \times \phi(\lambda)$ spectrum is applied to Eq. (10) to calculate $j_{[\text{ATD}]}$ (Reaction R10).

3.2.4 Heterogeneous photooxidation of SO₂

SO₂ is oxidized by OH(d) on the surface of ATD particles as follows:



where k_{photo} is the reaction rate constant of SO₂ with OH(d) and is estimated from gas-phase Reaction (R1). Combining Eq. (4), (5), Reactions (R11) and (R15), the reactive uptake coefficient ($\gamma_{\text{SO}_4^{2-},\text{photo}}$) of SO₂ on ATD particles under UV light can be written as

$$\gamma_{\text{SO}_4^{2-},\text{photo}} = \frac{4K_{\text{d},\text{SO}_2} (k_{\text{photo}} [\text{OH(d)}] + k_{\text{auto}})}{\omega_{\text{SO}_2}}, \quad (13)$$

where $\gamma_{\text{SO}_4^{2-},\text{photo}}$ is the constant at a given concentration of OH(d) (for a given light source, dust concentration, and humidity) (Reactions R10 and R12). Figure 2 illustrates $\gamma_{\text{SO}_4^{2-},\text{photo}}$ values at three different RHs, which were obtained using indoor chamber data. $\gamma_{\text{SO}_4^{2-},\text{photo}}$ is significantly influenced by both UV light and humidity. For example, $\gamma_{\text{SO}_4^{2-},\text{photo}}$ is 1 order of magnitude higher than $\gamma_{\text{SO}_4^{2-},\text{auto}}$ at low NO_x levels (< 5 ppb), and $\gamma_{\text{SO}_4^{2-},\text{photo}}$ increased from 2.0×10^{-5} to 1.24×10^{-4} when the RH changed from 20 to 80 %.

3.3 Impact of ozone and NO_x on heterogeneous chemistry of SO₂

To date, most studies of the effect of NO_x on sulfate formation have been limited to the reaction under dark conditions.

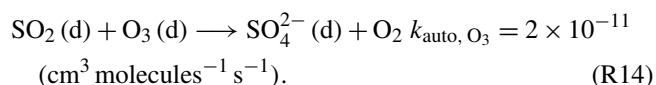
For example, previous laboratory studies using pure metal oxides reported the acceleration of the heterogeneous oxidation of SO₂ by NO_x under dark conditions (Ma et al., 2008; Liu et al., 2012). For the effect of ozone, the recent chamber study by Park and Jang (2016) showed significant enhancement of heterogeneous photooxidation of SO₂. In the AMAR model, the formation of sulfate is also modulated by the involvement of ozone and NO_x in both autoxidation and photochemistry on the surface of dust particles (Fig. 1).

3.3.1 Dust-phase ozone chemistry

The gas–dust partitioning coefficient of ozone is scaled using K_{d,SO_2} and the ratio of the Henry's law constant of SO₂ (K_{H,SO_2} , Eq. 1) to that of ozone ($K_{H,O_3} = 1.2 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at 298 K) (Chameides, 1984),

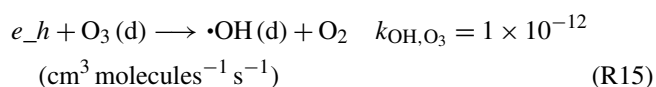
$$K_{d,O_3} = K_{d,SO_2} \frac{K_{H,O_3}}{K_{H,SO_2}} = 7.7 \times 10^{-7} F_{\text{water}} \exp\left(\frac{2700}{T}\right) \quad (\text{m}^3 \text{ m}^{-2}). \quad (14)$$

The partitioning process is also treated by the absorption–desorption kinetic mechanism as shown in Reactions (R7) and (R8) (Table 3: partitioning). Ozone can decay catalytically in the dust phase, forming an oxygen molecule and surface-bound atomic oxygen (Usher et al., 2003; Chang et al., 2005). The formed atomic oxygen reacts with SO₂(d) to form sulfate (Ullerstam et al., 2002; Usher et al., 2002):



In the presence of 300 μg m³ of ATD particles and 60 ppb of ozone, the concentration of O₃(d) is estimated as $2.4 \times 10^7 \text{ molecule cm}^{-3}$. Under this condition, the characteristic time of the autoxidation by ozone (Reaction R14) is $2 \times 10^3 \text{ s}$ and is much faster than the autoxidation by oxygen (Reaction R9, $2 \times 10^5 \text{ s}$). At nighttime, in the presence of ozone, the autoxidation of SO₂(d) yields a significant amount of sulfate.

Under UV light, ozone is also involved in the production of the surface oxidants (O₃[−], HO₃ radicals, and OH radicals) that further promote heterogeneous oxidation of SO₂. O₃(d) acts as an acceptor for $e_{\text{cb}}^- - h_{\text{vb}}^+$ and forms OH(d).



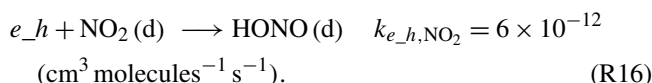
3.3.2 Dust-phase NO_x chemistry

The gas–dust partitioning coefficient of NO₂ (K_{d,NO_2}) is treated as the same approach with ozone, using K_{d,SO_2} and the ratio of K_{H,SO_2} (Eq. 1) to the Henry's law constant of NO₂ ($K_{H,NO_2} = 1.2 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$ at

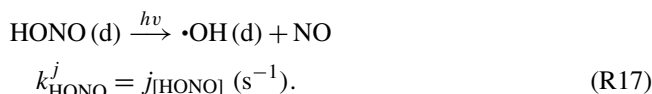
298 K) (Chameides, 1984).

$$K_{d,NO_2} = K_{d,SO_2} \frac{K_{H,NO_2}}{K_{H,SO_2}} = 1.5 \times 10^{-6} F_{\text{water}} \exp\left(\frac{2500}{T}\right) \quad (\text{m}^3 \text{ m}^{-2}) \quad (15)$$

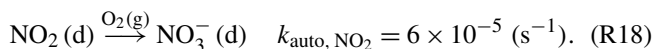
The absorbed NO₂ first reacts with e_{cb}^- (d) or $\bullet\text{O}_2^-$ (d) on the dust surface (Reaction R10) and forms HONO(d) (Ma et al., 2008; Liu et al., 2012; Saliba and Chamseddine, 2012; Saliba et al., 2014). In AMAR, the formation of HONO(d) is simplified into



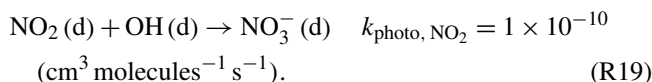
HONO(d) is further decomposed through photolysis and yields OH(d):



The photolysis rate constant of HONO(d) is treated with the one for gaseous HONO ($j_{[\text{HONO}]}$). Similar to autoxidation of SO₂ (Sect. 3.2.2), NO₂(d) autoxidizes to form nitrate:



NO₂ reacts with OH(d):



k_{auto,NO_2} and k_{photo,NO_2} was determined using the simulation of outdoor chamber data (Exp. 14 April 2017 in Table 2). The estimation of the gas–dust partitioning coefficients of HONO ($K_{d,HONO}$) (Becker et al., 1996) and HNO₃ (K_{d,HNO_3}) (Schwartz and White, 1981) was approached using the similar method for SO₂ (Table 3). N₂O₅ forms nitrate via a reactive uptake process as shown in Table 3 (partitioning Reaction 11).

4 Simulation of the AMAR model

At the beginning of the development of the AMAR model, the kinetic parameters to predict the formation of sulfate and nitrate in the presence of ATD particles were leveraged using an indoor chamber. In order to test the feasibility of the resulting AMAR model, the UF-APHOR data using natural sunlight were simulated (Table 2). The chamber dilution (measured by CCl₄) and the wall process of gaseous compounds (e.g., ozone, SO₂, HONO, NO₂) and particles were integrated with the kinetic mechanisms to simulate UF-APHOR data (Sect. S1). As shown in Fig. 1, the model inputs are the concentration of chemical species, the amount of dust, and the meteorological variables that are commonly found at regional scales. The dual chambers allow for two controlled experiments to be performed simultaneously under the same meteorological conditions.

4.1 Simulations for different dust loadings

Figure 3 shows that the predicted $[\text{SO}_4^{2-}]_{\text{T}}$ is in good agreement with experimental observations, which were performed under low- NO_x conditions ($\text{NO}_x < 5$ ppb) for two different dust loadings as well as two different SO_2 levels. The greater increase in $[\text{SO}_4^{2-}]_{\text{T}}$ appeared with the higher sunlight intensity (between 11:00 and 14:00). In Fig. 3a, the predicted $[\text{SO}_4^{2-}]_{\text{T}}$ increased by 63 % (at 3 PM) with $290 \mu\text{g m}^{-3}$ of ATD particles compared to the $[\text{SO}_4^{2-}]_{\text{T}}$ without dust particles. Figure 3b confirms that the larger dust particle loading yields more $[\text{SO}_4^{2-}]_{\text{T}}$. In Fig. 3c, $[\text{SO}_4^{2-}]_{\text{T}}$ was predicted with high and low initial concentrations of SO_2 for a given dust loading. The time profiles of the simulation of concentrations of NO_x , ozone, SO_2 , and dust are shown in Fig. S4.

Because of the large size of dust particles, the wall processes (e.g., settling and wall deposition) of dust particles is greater than that of the sulfate particles originated from $[\text{SO}_4^{2-}]_{\text{aq}}$ (no dust). Hence, the fraction of $[\text{SO}_4^{2-}]_{\text{dust}}$ to $[\text{SO}_4^{2-}]_{\text{T}}$ declines over the course of the chamber experiment. To estimate how the predicted $[\text{SO}_4^{2-}]_{\text{T}}$ is attributed to $[\text{SO}_4^{2-}]_{\text{aq}} + [\text{SO}_4^{2-}]_{\text{gas}}$ (non-dust sulfate) and $[\text{SO}_4^{2-}]_{\text{dust}}$ without wall processes, Fig. 3d, e, and f are reconstructed from Fig. 3a, b, and c, respectively. As shown in the inner pie chart of Fig. 3d, a significant fraction of $[\text{SO}_4^{2-}]_{\text{T}}$ is attributed to dust-phase chemistry ($[\text{SO}_4^{2-}]_{\text{auto}} + [\text{SO}_4^{2-}]_{\text{photo}}$: 0.58). In Fig. 3e, the fraction of final $[\text{SO}_4^{2-}]_{\text{photo}}$ to $[\text{SO}_4^{2-}]_{\text{T}}$ increases from 0.28 to 0.72 with the increase in dust loading from 90 to $403 \mu\text{g m}^{-3}$. The increased dust loading promotes both the absorption of SO_2 onto dust particles and the production of dust-phase oxidants and thus yields more sulfate production. With the increase in the initial concentration of SO_2 from 119 to 272 ppb in Fig. 3f, the fraction of $[\text{SO}_4^{2-}]_{\text{photo}}$ and $[\text{SO}_4^{2-}]_{\text{gas}} + [\text{SO}_4^{2-}]_{\text{aq}}$ are not much changed, while $[\text{SO}_4^{2-}]_{\text{T}}$ increases from 16.6 to $30.1 \mu\text{g m}^{-3}$. The elevation of the concentration of SO_2 produces more sulfate in all three phases (gas, aqueous, and dust phases). The sulfuric acid formed in the aqueous phase is hydrophilic and creates a positive feedback loop which aggravates the growth of aqueous aerosol. Overall, the variation in dust concentration is more influential on $[\text{SO}_4^{2-}]_{\text{photo}}$ than that of SO_2 .

4.2 Simulation of NO_x effect

Figure 4 shows that the model performs well in predicting $[\text{SO}_4^{2-}]_{\text{T}}$ in various levels of NO_x . Figure 4d is reconstructed from Fig. 4a, b, and c to illustrate how $[\text{SO}_4^{2-}]_{\text{T}}$ is attributed to the aqueous-phase reaction ($[\text{SO}_4^{2-}]_{\text{gas}} + [\text{SO}_4^{2-}]_{\text{aq}}$), dust-phase autooxidation ($[\text{SO}_4^{2-}]_{\text{auto}}$), and dust photochemistry ($[\text{SO}_4^{2-}]_{\text{photo}}$). Comparing Fig. 4b with c, $[\text{SO}_4^{2-}]_{\text{photo}}$ is suppressed at high NO_x levels because NO_2 competes for the consumption of dust-phase OH radicals with SO_2 . The reduction of $[\text{SO}_4^{2-}]_{\text{T}}$ in the afternoon is due to the particle loss

at the low concentrations of SO_2 . The simulated concentrations of NO_x , ozone, SO_2 , and dust are shown in Fig. S5.

The time profiles of the predicted $[\text{NO}_3^-]_{\text{T}}$ are also shown in Fig. 4a, b, and c. In the morning, NO_2 quickly oxidizes to accumulate nitric acid in the dust phase. The dust-phase nitric acid might rapidly react with alkaline carbonates (e.g., K, Na, Ca and Mg ions) in the dust phase and form nitrate salts (NO_3^- (d_salt) in Reaction S23 of dust-phase reactions in Table S1). As described in Sect. 3.2.1, these nitrate salts are very hygroscopic and further enhance gas–dust partitioning of gaseous species including HNO_3 , SO_2 , and HONO at high humidity (in the morning). With increasing sunlight intensity, the temperature increases but humidity decreases (20 %, Fig. S6) and thus increase the desorption of HNO_3 . In addition to meteorological conditions, the formation of low-volatility sulfuric acid can deplete nitrate via evaporation of volatile nitric acid (SO_4^{2-} (d_salt) in Reactions S24 and S25 of dust-phase reactions in Table S1) from the dust surface. The capacity of ATD particles to form nitrate salts (or sulfate salts) is limited by the amount of carbonates and metal oxides on the surface of dust particles. This capacity is estimated to be 0.6 ppb (the number concentration of reactive sites in air), which was determined by comparing the actual aerosol acidity, as measured by colorimetry integrated with a reflectance UV–visible spectrometer (C-RUV), to the aerosol acidity predicted by the inorganic thermodynamic model (E-AIM II) using the inorganic composition from PILS-IC (Li et al., 2015; Beardsley and Jang, 2016). As shown in Fig. 4, the effect of HNO_3 on the heterogeneous reaction is negligible during the daytime because sulfuric acid, a strong acid, depletes partitioning of HNO_3 (Eq. 15). At the end of the photooxidation, nitrate is slightly underestimated because some observed nitrate may be trapped under the layer of hydrophobic alkaline sulfate formed via aging of ATD particles (effloresced). The surface HONO(d), which formed via the photocatalytic process of NO_2 (Reaction R16), can influence the production of OH(d). However, the model analysis originated from the integrated reaction rate (IRR), an accumulated flux of chemical formation, suggests that the contribution of HONO(d) to OH(d) production is relatively small compared to the direct photocatalytic process caused by dust particles shown in Sect. 3.2.3.

5 Sensitivity and uncertainties

The sensitivity of sulfate prediction to major variables (e.g., temperature, humidity, sunlight profile, the concentration of SO_2 and NO_x , and dust loading) is illustrated in Fig. 5. To avoid the suppression of dust chemistry at high NO_x levels, the most sensitivity tests were performed at low levels of NO_x . The stacked chart normalized with $[\text{SO}_4^{2-}]_{\text{T}}$ in Fig. 5 shows how $[\text{SO}_4^{2-}]_{\text{T}}$ is attributed to $[\text{SO}_4^{2-}]_{\text{auto}}$, $[\text{SO}_4^{2-}]_{\text{photo}}$ and $[\text{SO}_4^{2-}]_{\text{aq}} + [\text{SO}_4^{2-}]_{\text{gas}}$ (non-dust chemistry).

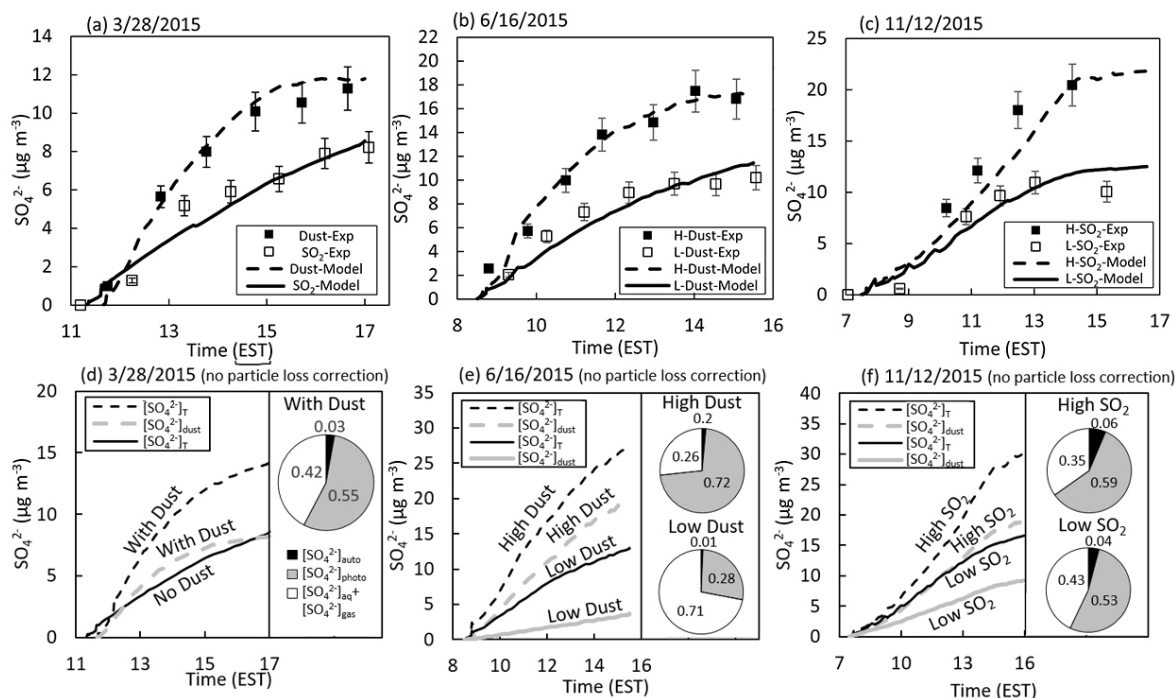


Figure 3. Time profiles of total sulfate concentration (SO_4^{2-} , $\mu\text{g m}^{-3}$) in the UF-APHOR. “Exp” denotes the experimentally observed sulfate ($[\text{SO}_4^{2-}]_{\text{T}}$) and “Model” denotes the model-predicted sulfate. “H” and “L” represent the high and the low initial concentrations of chemical species. The errors associated with the concentration of sulfate is $\pm 10\%$ originated from the PILS-IC measurement. (a) Sulfate formation with and without ATD particles (SO_2 60 ppb vs. SO_2 56 ppb and dust $290 \mu\text{g m}^{-3}$). (b) The high and low loadings of dust particles (dust $90 \mu\text{g m}^{-3}$ and SO_2 100 ppb vs. dust $404 \mu\text{g m}^{-3}$ and SO_2 120 ppb). (c) The high and the low concentrations of SO_2 (SO_2 119 ppb and dust $239 \mu\text{g m}^{-3}$ vs. SO_2 272 ppb and dust $230 \mu\text{g m}^{-3}$). For (a), (b), and (c), the simulations included the chamber dilution and the wall process of gaseous compounds and particles (Sect. S1). For (d), (e), and (f), the wall process for the particle loss was excluded to estimate the influence of ATD particles on sulfate formation without the chamber artifacts. In (d), (e), and (f), total sulfate was decoupled into the sulfate originated from dust chemistry ($[\text{SO}_4^{2-}]_{\text{dust}} = [\text{SO}_4^{2-}]_{\text{photo}} + [\text{SO}_4^{2-}]_{\text{auto}}$). The pie charts inserted into (d), (e), and (f) illustrate how total sulfate is attributed to major pathways at the end of the experiments.

Figure 5a illustrates that the reduction of $[\text{SO}_4^{2-}]_{\text{T}}$ at a higher temperature (273 vs. 298 K) is ascribed to the decrease in the partitioning process. Figure 5b shows that $[\text{SO}_4^{2-}]_{\text{T}}$ increases by a factor of 2.8 with RH increasing from 25 to 80 %. Humidity plays an important role in the modulation of both aerosol acidity and liquid water content, and ultimately influences the partitioning process (e.g., SO_2 partitioning on dust surface) and dust-phase chemistry (e.g., production of $\text{OH}(\text{d})$). In the stacked column chart of Fig. 5b, the contribution of $[\text{SO}_4^{2-}]_{\text{dust}}$ to $[\text{SO}_4^{2-}]_{\text{T}}$ increases from 0.73 to 0.86 with increasing RH, suggesting that dust chemistry is more sensitive to humidity than aqueous-phase chemistry. Figure 5c presents $[\text{SO}_4^{2-}]_{\text{T}}$ at two different sunlight intensities (winter on 12 November 2015 vs. summer on 25 April 2017) in Gainesville, Florida (latitude/longitude: $29.64185^\circ/-82.347883^\circ$). As shown in Fig. 5d, with SO_2 concentrations increasing from 20 to 100 ppb, $[\text{SO}_4^{2-}]_{\text{T}}$ increases by a factor of 4.4 in the given simulation condition. The effect of the concentration of SO_2 on $[\text{SO}_4^{2-}]_{\text{T}}$ has been discussed in Sect. 4.1 above. Figure 5e shows the

sensitivity of $[\text{SO}_4^{2-}]_{\text{T}}$ to the ATD loading (100, 200, and $400 \mu\text{g m}^{-3}$). With the increasing of dust loading, the contribution of $[\text{SO}_4^{2-}]_{\text{photo}}$ to $[\text{SO}_4^{2-}]_{\text{T}}$ also increases. Figure 5f illustrates how sulfate formation is suppressed by different NO_x levels (also see Sect. 3.3.2).

The inorganic thermodynamic model (E-AIM II) was employed to estimate $[\text{H}^+]$ and the liquid water content ($M_{\text{in,water}}$) for the $\text{SO}_4^{2-}\text{--NH}_4^+\text{--H}_2\text{O}$ system (excluding $\text{SO}_4^{2-}(\text{d}_{\text{salt}})$ in Reaction 13 of Table 3: dust phase) (Eq. 8) in both inorganic-salt seeded aqueous-phase and dust-phase chemistry. The uncertainty in $M_{\text{in,water}}$ and $[\text{H}^+]$ influences the partitioning tracers and consequently causes the uncertainty in $[\text{SO}_4^{2-}]_{\text{T}}$. The uncertainties in the prediction of $[\text{H}^+]$ using inorganic thermodynamic models are large because of the limited data (Clegg et al., 1998; Wexler and Clegg, 2002). In this study, $[\text{H}^+]$ is estimated by E-AIM II (Clegg et al., 1998; Wexler and Clegg, 2002; Clegg and Wexler, 2011) and corrected for the ammonia-rich condition (Li et al., 2015; Li and Jang, 2012). The reported uncertainty in $[\text{H}^+]$ associated with the C-RUV method is $\pm 18\%$. Figure S7 illustrates the

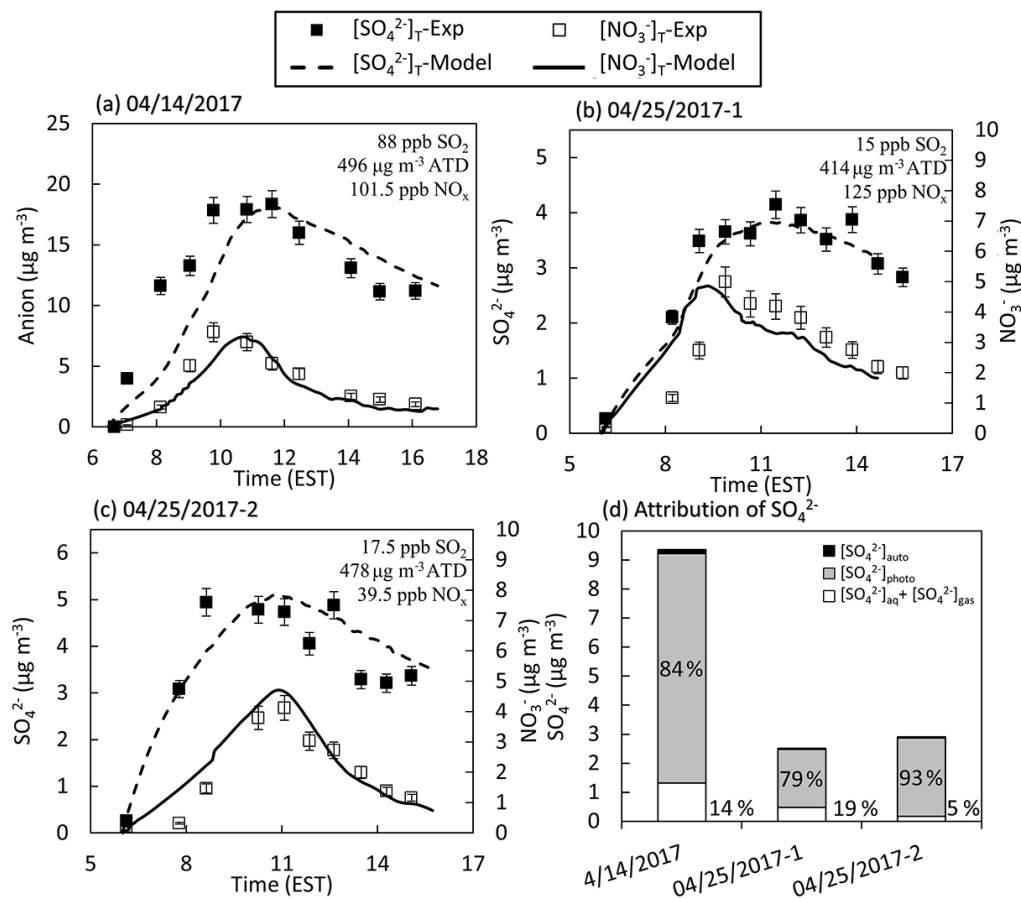


Figure 4. Time profiles of total sulfate concentration ($[\text{SO}_4^{2-}]_{\text{T}}$, $\mu\text{g m}^{-3}$) and nitrate concentration ($[\text{NO}_3^-]_{\text{T}}$, $\mu\text{g m}^{-3}$) in the dual-chamber experiments using UF-APHOR at different NO_x levels. The concentrations of sulfate and nitrate were measured using PILS-IC during the experiments. The error bars of the concentration of sulfate and nitrate is $\pm 10\%$ originated from the PILS-IC measurement. The detailed experimental conditions of (a), (b), and (c) are shown in Table 2. Panel (d) shows how total sulfate is attributed to aqueous-phase reaction (sulfate formation in gas phase + sulfate formation in inorganic salted inorganic aqueous phase) ($[\text{SO}_4^{2-}]_{\text{aq}} + [\text{SO}_4^{2-}]_{\text{gas}}$), dust-phase autoxidation ($[\text{SO}_4^{2-}]_{\text{auto}}$), and dust photochemistry ($[\text{SO}_4^{2-}]_{\text{photo}}$) at the end of the experiments. “Exp” denotes the experimental observation and “Model” denotes the simulation using the AMAR module. The chamber dilution and the wall process of gaseous compounds and particles were included in the simulation (Sect. S1).

uncertainties of the major model parameters ($[\text{H}^+]$, F_{water} , K_{d,SO_2} , k_{auto} and k_{OH,O_2}) and the prediction of $[\text{SO}_4^{2-}]_{\text{T}}$. The uncertainty in F_{water} ranges from -20 to 30% due to the uncertainty in the measurement of sulfate ($\pm 10\%$) and ammonia ions ($\pm 10\%$) using PILS-IC. The propagation error in Eqs. (6) and (7) is used to estimate the uncertainty in K_{d,SO_2} (-20 to 30%). The uncertainty in k_{auto} (-48 to 42%) and k_{OH,O_2} (-20 to 22%) are estimated by simulating $[\text{SO}_4^{2-}]_{\text{T}}$ within the uncertainty in K_{d,SO_2} and the measurement of sulfate ($\pm 10\%$). The uncertainty in $[\text{SO}_4^{2-}]_{\text{T}}$ was estimated to be $\pm 12\%$ at the end of the simulation. In this model, the Henry’s law constant that is applied to gas–dust partitioning of tracers (Sect. 3.2.1) may lead to some biases in the prediction of sulfate or nitrate.

6 Conclusion and atmospheric implication

The AMAR model of this study was developed to predict the oxidation of SO_2 and NO_x using comprehensive kinetic mechanisms in the gas phase, inorganic seeded aqueous phase, and dust phase. The thermodynamic parameters engaged in the partitioning process between gas, inorganic salted aqueous aerosol, and dust phases were obtained from known data in the literature (Table 3), and the kinetic parameters for dust chemistry were estimated using previously reported indoor chamber data (Park and Jang, 2016). Overall, the AMAR simulations were consistent with experimentally observed outdoor chamber data (Figs. 3 and 4) under ambient sunlight. As discussed in the sensitivity analysis (Sect. 5), both the $[\text{SO}_4^{2-}]_{\text{T}}$ and the relative distribution of mechanism-based sulfate formation are sensitive to all major variables

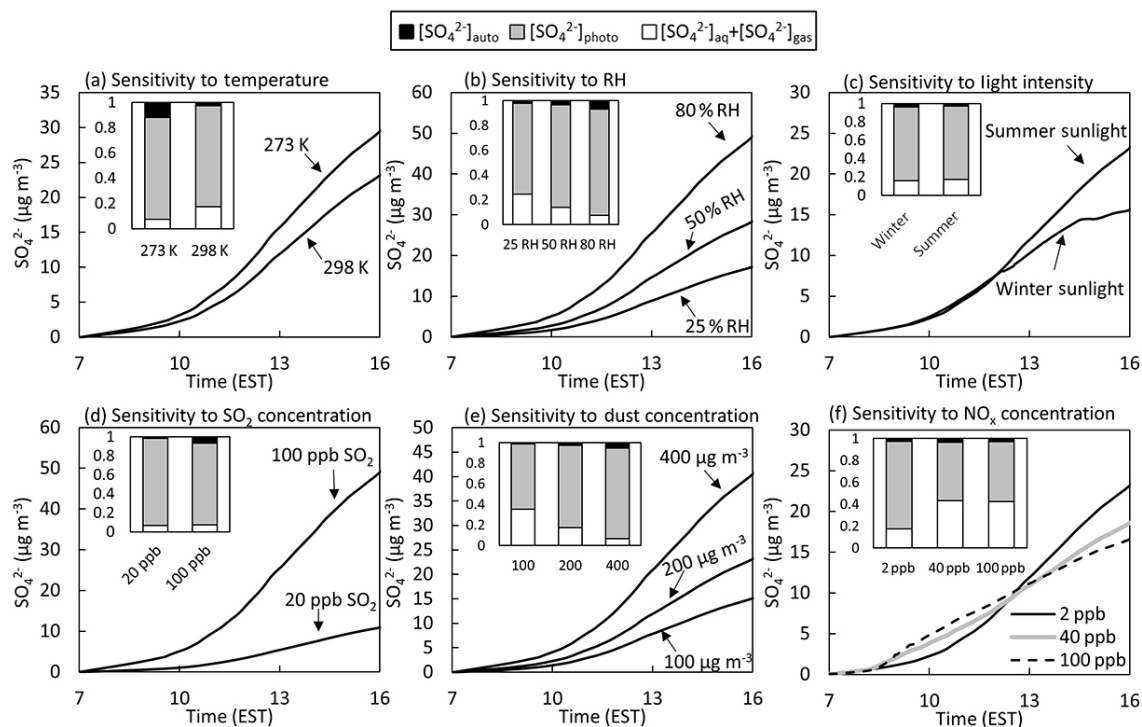


Figure 5. Sensitivity test of AMAR model to (a) temperature at 273 and 298 K; (b) RH at 25, 50, and 80 %; (c) sunlight profiles of summertime (25 April 2017) and wintertime (12 November 2015) at Gainesville, Florida (latitude/longitude: 29.64185°/−82.347883°); (d) the concentration of SO₂; (e) the concentration of dust particles; and (f) the NO_x concentration (initial NO:NO₂ = 1:1). The stacked column chart in each figure illustrates how total sulfate is attributed to major pathways at the end of each experiment. For the sensitivity test, the chamber simulation is conducted with 100 ppb of initial SO₂, 2 ppb of initial NO₂, 2 ppb of initial O₃, and 200 μg m^{−3} of ATD particles at *T* = 298 K and RH = 40 % under ambient sunlight on 25 April 2017. NO_x (rate of flux = 2.7 × 10⁶, s^{−1}) and isoprene (rate of flux = 2.7 × 10⁶, s^{−1}) were constantly added to simulate chamber dilution. The simulation was performed without considering the particle loss to the chamber wall.

(model inputs), including temperature, humidity, sunlight intensity, the quantity of dust loading, and concentrations of NO_x and SO₂.

In order to assess the importance of dust chemistry in ambient conditions, the prediction of sulfate formation in the presence of ATD dust needs to be extended to 24 h simulations under various environmental conditions. Figure S8 shows the output simulated for 24 h with 200 μg m^{−3} of ATD particle loading under urban (40 ppb NO_x; VOC/NO_x < 5; 20 ppb SO₂) and rural atmospheres (5 ppb NO_x; VOC/NO_x > 20; 2 ppb SO₂). At nighttime, when the temperature drops and humidity increases (70–90 %, Fig. S6), the contribution of [SO₄^{2−}]_{auto} to [SO₄^{2−}]_T becomes larger than the typical chamber simulation during the daytime. In a rural environment, [SO₄^{2−}]_{photo} is still the most influential on sulfate formation (0.76 fraction of [SO₄^{2−}]_T in Fig. S8a). For the simulation in a polluted area (Fig. S8b), the fraction of [SO₄^{2−}]_{photo} to [SO₄^{2−}]_T significantly decreases (0.61) because of the suppression induced by NO_x (Sect. 3.3.2), but the fraction of [SO₄^{2−}]_{auto} to [SO₄^{2−}]_T increases (0.28). With decreasing sunlight intensity

(after 5 PM), Fig. S8 shows the rapid increases in [SO₄^{2−}]_{auto} due to the reaction of dust-phase SO₂ with ozone, which is the result of daytime photooxidation (Sect. 3.3.1). Figure S8 suggests that the failure to predict sulfate formation without accurate dust chemistry ([SO₄^{2−}]_{auto} + [SO₄^{2−}]_{photo}) can lead to substantial underestimation of the quantity of total sulfate at regional or global scales. SO₂ autooxidation alone may partially improve the prediction of sulfate in the presence of mineral dust, but sulfate production can still be largely underestimated and incorrectly predicted in time series when heterogeneous photocatalytic reactions in kinetic mechanisms are not considered.

The ATD particles in this study have chemical and physical properties different from ambient mineral dust particles. In general, the uptake coefficient of SO₂ in authentic mineral dust particles (e.g., Gobi Desert dust and Saharan dust) is known to be higher than that of ATD particles (Crowley et al., 2010). Thus, the effect of ambient dust particles on heterogeneous photocatalytic oxidation would be much more important than that of the ATD particles of this study. To extend the AMAR model derived with ATD particle to ambient dust particles, the model parameters related to the rate constants and

physical characteristics (e.g., surface area and hygroscopic properties) of dust particles need to be modified using laboratory studies. Photocatalytic capacities of authentic mineral dust would be different from ATD due to the compositions and quantity of conductive metal oxides. Hence, the photoactivation rate constant ($k_{e,h}^j$ in Sect. 3.2.3) to form electron–hole pairs should also be revisited to apply the present model to different mineral dust systems. In addition to reactions of inorganic species (i.e., SO_2 and NO_x), that of organic species (e.g., HCOOH , HCHO , and CH_3CHO) on dust surface needs to be investigated in the future.

Data availability. The datasets generated during the current study are available from the corresponding author on reasonable request.

The Supplement related to this article is available online at <https://doi.org/10.5194/acp-17-10001-2017-supplement>.

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

Acknowledgements. This work was supported by grants from the National Institute of Metrological Science (NIMS-2016-3100), the Ministry of Science, ICT, and Future Planning at South Korea (2014M3C8A5032316) and the Fulbright Scholar Program (from USA to Mongolia).

Edited by: Barbara Ervens

Reviewed by: two anonymous referees

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