



Ammonium nitrate promotes sulfate formation through uptake kinetic regime

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Abstract:

Although the anthropogenic emissions of SO₂ have decreased significantly in China, the decrease in SO₄²⁻ in PM_{2.5} is much smaller than that of SO₂. This implies an enhanced formation rate of SO₄²⁻ in the ambient air, and the mechanism is still under debate. This work investigated the formation mechanism of particulate sulfate based on statistical analysis of long-term observations in Shijiazhuang and Beijing supported with flow tube experiments. Our main finding was that the SOR was exponentially correlated with ambient RH in Shijiazhuang ($SOR=0.15+0.0032\times\exp(RH/16.2)$) and Beijing ($SOR=-0.045+0.12\times\exp(RH/37.8)$). In Shijiazhuang, the SOR is linearly correlated with the ratio of aerosol water content (AWC) in PM_{2.5} ($SOR=0.15+0.40\times AWC/PM_{2.5}$). Kinetics studies suggest that uptake of SO₂ instead of oxidation of S(IV) in particle-phase is the rate determining step for sulfate formation. NH₄NO₃ plays an important role in the AWC and the transition of particle phase, which is a crucial factor determining the uptake kinetics of SO₂ and the enhanced SOR during haze days. Our results show that NH₃ significantly promoted the uptake of SO₂, subsequently, the SOR, while NO₂ had little influence on SO₂ uptake and SOR in the presence of NH₃.



1. Introduction

40 Atmospheric particulate matter (PM) is a world-wide concern due to its adverse effect
on human health, such as association with respiratory and cardiovascular diseases, lung
cancer and premature death (WHO, 2013;Lelieveld et al., 2015). The Chinese
government has made great efforts to improve the air quality (Cheng et al., 2019). For
example, the annual PM_{2.5} concentration in Beijing decreased from 89.5 $\mu\text{g m}^{-3}$ in 2013
45 to 58 $\mu\text{g m}^{-3}$ in 2017 due to the stringent reduction of local and regional emissions
(Cheng et al., 2019;Ji et al., 2019). However, the PM_{2.5} concentrations in most regions
of China (Cheng et al., 2019;Chen et al., 2019c;Huang et al., 2019;Tian et al., 2019) are
still significantly higher than the PM_{2.5} standard recommended by World Health
Organization (WHO) (WHO, 2006). Haze events also occur with high frequency,
50 especially, in autumn and winter.

Secondary aerosol, including sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+)
(SNA) and secondary organic aerosol (SOA) usually contributes to ~70 % of PM_{2.5}
mass concentration in different regions (Huang et al., 2014;An et al., 2019). SNA often
accounts for more than a half of PM_{2.5} mass in severe pollution events (Zheng et al.,
55 2015;Wang et al., 2016). Even SO_4^{2-} exceeds more than 20 % of PM_{2.5} mass (Guo et al.,
2014;Wang et al., 2016;Xie et al., 2015;He et al., 2018). Interestingly, the anthropogenic
emissions of SO_2 in 2017 reduced by ~90 % when compared with 2000 in Beijing
(Cheng et al., 2019;Lang et al., 2017). However, the decrease rate of particulate SO_4^{2-}
concentration (Lang et al., 2017;Li et al., 2017) is much smaller than SO_2 (Lang et al.,
60 2017;Zhang et al., 2020). This implies an enhanced oxidation rate of SO_2 in the



atmosphere (Lang et al., 2017). However, the mechanisms and kinetics of particulate SO_4^{2-} formation in the real atmosphere are still open questions in many regions of China although they have been extensively discussed (Ervens, 2015;Warneck, 2018).

Particulate SO_4^{2-} can be formed through homogeneous oxidation of SO_2 by hydroxyl radicals (OH) and Stabilized Criegee Intermediates (SCIs) (Seinfeld and Pandis, 2006;Liu et al., 2019a). Modeling studies greatly underestimated ($\sim 54.2\%$) SO_4^{2-} concentration in severe pollution events in Beijing if only considering gas-phase oxidation of SO_2 , while the normalized mean bias (NMB) decreased significantly after heterogeneous oxidation of SO_2 being considered (Zheng et al., 2015). Several heterogeneous and/or multiphase oxidation pathways, such as oxidation of SO_2 or sulfite by NO_2 (He et al., 2014), H_2O_2 (Huang et al., 2015;Maaß et al., 1999;Liu et al., 2020a), HONO (Wang et al., 2020a) and O_3 (Maahs, 1983) or photochemical oxidation of SO_2 (Yu et al., 2017;Xie et al., 2015) on dust surfaces, catalytic oxidation of SO_2 by transition metal ions (TMI) (Warneck, 2018;Martin and Good, 1991;Wang et al., 2021) and oxidation of SO_2 by NO_2 (Clifton et al., 1988;Wang et al., 2016;Cheng et al., 2016;Wu et al., 2019) in aqueous phase and heterogeneous oxidation of SO_2 on black carbon (Zhao et al., 2017;Zhang et al., 2020;Yao et al., 2020), have been proposed based on field measurements, laboratory and modeling studies. However, it is still controversial about the relative contribution of these pathways to SO_4^{2-} production. For example, the contribution of heterogeneous oxidation to SO_4^{2-} production had been evaluated to be $(48\pm 5)\%$ based on oxygen isotopic measurements (He et al., 2018), while it was 31% even in the nighttime calculated by an observe based modeling (OBM)



simulation (Xue et al., 2016). Oxidation by OH could explain 33-36 % of SO_4^{2-} production in BTH (Liu et al., 2019a), while it was negligible based on isotopic measurements (He et al., 2018) and OBM simulation (Xue et al., 2016). As for the 85 oxidation of S(IV) species, which includes SO_2 , HSO_3^- and SO_3^{2-} , in aqueous phase, oxidation by H_2O_2 (Liu et al., 2020b; Liu et al., 2020a), NO_2 (Wang et al., 2020a; Wang et al., 2016; Cheng et al., 2016), O_3 (Fang et al., 2019), or TMI (Mn^{2+}) (Wang et al., 2021) was proposed as the most important pathway by different researchers. It should 90 be noted that some reaction mechanisms mentioned above were proposed based on case studies in short-term observations. Thus, long-term observations at different environments are required to verify whether these mechanisms are statistically important. In addition, the previous studies mainly focused on oxidation process of SO_2 in particle phase, while it is unclear what the control factors are from gas-phase SO_2 to 95 particle-phase sulfate. In particular, it has been found that the mass fraction of NO_3^- and NH_4^+ is increasing gradually (Lang et al., 2017; Li et al., 2018). It is still poorly understood about the feedback between aerosol physics and aerosol chemistry.

In this work, one-year field observations have been performed in Shijiazhuang and Beijing, synchronously. The formation mechanism of particulate sulfate has been 100 statistically discussed. The conversion ratio of SO_2 to sulfate is statistically and linearly correlated to the aerosol water content (AWC), which is mainly modulated by particulate ammonium nitrate. The reaction kinetics and other factors affecting sulfate production have also been discussed.

2. Material and methods



105 **2.1 Field measurements.** Field measurements were performed at Shijiazhuang
University (SJZ, Lat. 38.0281° and Lon. 114.6070°) and the west campus of Beijing
University of Chemical Technology (BUCT, Lat. 39.9428° and Lon. 119.2966°) from
March 15, 2018 to April 15, 2019. The SJZ station is on a rooftop of the main teaching
building (5 floors, ~23 m above the surface), which is around 250 m from the Zhujiang
110 road of Shijiazhuang. The BUCT station is on a rooftop of the main building (5 floors,
~18 m above the surface), which is around 550 m from the 3rd ring road of Beijing. The
distance between the two stations, which are the representative cities of BJH, is 260 km
(Figure S1). Both stations are surrounded by traffic and residential emissions, thus, are
typical urban observation sites. The details about the observation stations have been
115 described in our previous work (Liu et al., 2020e; Liu et al., 2020d; Liu et al., 2020c).

Ambient air was drawn from the roof of the corresponding building. At the SJZ
station, the mass concentration of PM_{2.5} was measured by a beta attenuation mass
monitor (BAM-1020, Met One Instruments, USA) with a smart heater (Model BX-830,
Met One Instruments Inc., USA) to control the RH of the incoming air to 35% and a
120 PM_{2.5} inlet (URG) to cut off the particles with diameter larger than 2.5 μm. Particle
phase Fe and Mn were measured using a heavy metal analyzer (EHM-X100, Skyray
Instrument). Water-soluble ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, SO₄²⁻, Cl⁻ and NO₃⁻) in
PM_{2.5} and gas pollutants (HCl, HONO, HNO₃, SO₂ and NH₃) were measured using an
analyzer for Monitoring Aerosols and Gases (MARGA, ADI 2080, Applikon Analytical
125 B.V., Netherlands) with 1 hour of time resolution. At the BUCT station, the mass
concentration of PM_{2.5} was the mean concentration obtained from four surrounding



monitoring stations (including Wanliu, Gucheng, Wanshouxigong and Guanyuan) of
China Environmental Monitoring Centre (<http://www.cnemc.cn>). The chemical
composition of PM_{2.5} was measured using a Time-of-Flight Aerosol Chemical
130 Speciation Monitor (ToF-ACSM, Aerodyne) after the ambient air went through a PM_{2.5}
inlet (URG) and a Nafion dryer (MD-700-24, Perma Pure). The configuration and the
operation protocol of ToF-ACSM have been described well in previous work (Fröhlich
et al., 2013). IE calibration for ACSM was performed using 300 nm dry NH₄NO₃ every
month. Ambient air was drawn from the roof using a Teflon sampling tube (BMET-S,
135 Beijing Saak-Mar Environmental Instrument Ltd.) with the residence time <10 s for
gas-phase pollutant measurements. Trace gases including NO_x, SO₂, CO and O₃ were
measured with the corresponding analyzer (Thermo Scientific, 42i, 43i, 48i and 49i) at
both the SJZ and BUCT stations. Meteorological parameters including temperature,
pressure, relative humidity (RH), wind speed and direction were measured using
140 weather stations (WXT 520 at HAS/SJZ station and AWS 310 at AHL/BUCT station,
Vaisala).

2.2 Uptake kinetics of SO₂ on dust internally mixed with NH₄NO₃. To understand
the influence on RH on uptake kinetics of SO₂, the γ_{SO_2} on dust internally mixed with
NH₄NO₃ was measured using a coated-wall flow tube reactor. The configuration of the
145 reactor and data process protocol have been described in detail previously (Han et al.,
2013; Liu et al., 2015). The γ , presenting the mass transfer kinetic of gas phase SO₂ to
particle phase, is defined by the net loss rate of SO₂ per collision onto the surface
(Ravishankara, 1997; Usher et al., 2003), namely,



$$\gamma_{obs} = \frac{-\frac{dc}{dt}}{\omega} = \frac{2k_{obs}r_{tube}}{\langle c \rangle} \quad (1)$$

150 where $-dc/dt$ is the net loss rate of SO_2 when the surface is exposed to SO_2 (molecules s^{-1}); ω is the collision frequency (s^{-1}); k_{obs} , r_{tube} and $\langle c \rangle$ are the first-order rate constant of SO_2 , the flow tube radius and the average molecular velocity of SO_2 , respectively. A correction for gas phase diffusion limitations was considered for γ_{obs} calculations using the Cooney–Kim–Davis (CKD) method (Cooney et al., 1974; Murphy and Fahey, 1987).
155 The BET uptake coefficients ($\gamma_{\text{SO}_2, \text{BET}}$) was obtained from the mass dependence of γ_{obs} as follows (Han et al., 2013; Liu et al., 2015):

$$\gamma_{\text{SO}_2, \text{BET}} = [\text{slope}] \frac{A_g}{S_{\text{BET}}} \quad (2)$$

where [slope] is the slope of the plot of γ_{obs} versus the sample mass in the linear regime (mg^{-1}); A_g is the inner surface area of the sample tube (cm^2); and S_{BET} is the specific
160 surface area of the particle sample ($\text{cm}^2 \text{mg}^{-1}$).

Similar to a previous work (Zhang et al., 2019), dust internally mixed with NH_4NO_3 was used in the kinetics study because it was difficult to deposit enough real ambient particles onto the inner surface of the sample holder. Although the composition of the model particles is much simpler than that of ambient particles, it is still
165 meaningful because we mainly focused on the influence of RH or aerosol water content (AWC) on uptake kinetics of SO_2 . The mixture (mass ratio = 2:1) of A1 Ultrafine test dust (Powder Technology Inc.) and NH_4NO_3 (AR, Sinopharm Chemical Reagent Co. Ltd, China) were suspended in the mixture of ethanol and water (v:v=1:3). The inner surface of the Pyrex quartz tube (sample holder) was uniformly coated by the above
170 mixture and dried overnight in an oven at 393 K. The sample mass was calculated



according to the weighted mass of the dry tube before and after coating. To avoid the wall loss of SO₂ on the sample holder, all the inner surface of the sample holder was covered with particles. The wall loss of SO₂ on the remained surface (the inner surface of the outside tube and the outside surface of the sample holder) was subtracted in a steady-state at the corresponding RH before the uptake experiment as done in our previous work (Liu et al., 2015). The mean concentrations of SO₂, NO₂ and NH₃ were 8.3±5.2 (0.4-49.1), 31.5±13.2 (2.5-85.1) and 41.0±18.4 (0.3-126.4) ppb, respectively, in polluted events (with the PM_{2.5} concentration higher than 75 µg m⁻³ and the RH less than 90%) in Shijiazhuang. The initial concentrations of SO₂, NO₂ and NH₃ in the reactor were 190 ± 2.5, 100 ± 2.5 and 50 ± 2.5 ppb, respectively. The initial concentrations of NO₂ and NH₃ were close to their ambient concentrations, while a high initial SO₂ concentration was used here to obtain a good signal to noise ratio for γ_{SO_2} measurements. In this work, we aimed to understanding the influence of AWC on the uptake kinetics of SO₂. Therefore, we fixed the initial concentrations of pollutants and the temperature at 300 K. SO₂ and NO₂ were measured using the corresponding analyzer (Thermo 43i and 42i) and NH₃ was measured by an ammonia analyzer (EAA-22, LGR, USA). The specific surface area of the mixture of A1 dust and NH₄NO₃ was 0.813 m²·g⁻¹, measured by a nitrogen Brunauer-Emmett-Teller (BET) physisorption analyzer (Quantachrome Autosorb-1-C). RH from 0 to 80 % was adjusted by varying the ratio of dry to wet zero air (water bubbler) and measured by a RH sensor (HMP110, Humicap). Control experiments demonstrate that adsorption of SO₂ on the quartz tube is negligible.



2.3 Calculations of AWC, aerosol pH and production rates of sulfate in aerosol

liquid water. The AWC and aerosol pH in Shijiazhuang were calculated using the

195 ISORROPIA II model using the measured concentrations of SO_4^{2-} , NH_4^+ , NH_3 , NO_3^- ,
 HNO_3 , Cl^- , HCl , Na^+ , Ca^{2+} , K^+ and Mg^{2+} , RH and temperature as input. The particles
were assumed in metastable phase using a forward method (Song and Osada, 2020; Shi
et al., 2019). The dataset with RH lower than 35 % were excluded (Pye et al., 2020) due
to large uncertainties of aerosol pH (Ding et al., 2019; Guo et al., 2016; Pye et al., 2020).

200 pH was then calculated according to:

$$\text{pH} = -\log_{10} \frac{1000\gamma_{\text{H}^+}c_{\text{H}^+}}{\text{AWC}} \quad (1)$$

where γ_{H^+} is the activity coefficient of H^+ . The AWC of model particles for laboratory
studies was also calculated with the known composition, while the aerosol pH in Beijing
were not calculated because the concentrations of Na^+ , Ca^{2+} , K^+ and Mg^{2+} were
205 unavailable.

Similar to previous studies (Liu et al., 2020a; Cheng et al., 2016), four oxidation
pathways of S(IV) in aqueous-phase were accounted for, i.e., oxidation by O_3 , H_2O_2 ,
 NO_2 and TMI (Fe^{3+} and Mn^{2+}), according to following equations:

$$-\left(\frac{d[\text{S(IV)}]}{dt}\right)_{\text{O}_3} = (k_0[\text{SO}_{2,aq}] + k_1[\text{HSO}_3^-] + k_2[\text{SO}_3^{2-}])[\text{O}_{3,aq}] \quad (3)$$

210 $-\left(\frac{d[\text{S(IV)}]}{dt}\right)_{\text{H}_2\text{O}_2} = \frac{k_3[\text{H}^+][\text{HSO}_3^-][\text{H}_2\text{O}_{2,aq}]}{1+K[\text{H}^+]} \quad (4)$

$$-\left(\frac{d[\text{S(IV)}]}{dt}\right)_{\text{TMI}} = k_4[\text{H}^+]^\alpha[\text{Mn}^{2+}][\text{Fe}^{3+}][\text{S(IV)}] \quad (5)$$

$$-\left(\frac{d[\text{S(IV)}]}{dt}\right)_{\text{NO}_2} = k_5[\text{NO}_{2,aq}][\text{S(IV)}] \quad (6)$$

where $k_0 = 2.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $k_1 = 3.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $k_2 = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_3 = 7.45 \times 10^7 \text{ M}^{-1}$
 s^{-1} , $K = 13 \text{ M}^{-1}$, $k_4 = 3.72 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, and $\alpha = -0.74$ (for $\text{pH} \leq 4.2$) or $k_4 = 2.51 \times 10^{13} \text{ M}^{-1}$



215 s^{-1} , and $\alpha = 0.67$ (for $\text{pH} > 4.2$) and $k_5 = (1.24 - 1.67) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (for $5.3 \leq \text{pH} \leq 8.7$; the
linear interpolated values were used for pH between 5.3 and 8.7) at 298K (Clifton et al.,
1988; Liu et al., 2020a). $[\text{O}_3, \text{aq}]$, $[\text{H}_2\text{O}_2, \text{aq}]$ and $[\text{NO}_2, \text{aq}]$ were calculated according
to the Henry's constants, which are 1.1×10^{-2} , 1.0×10^5 and $1.0 \times 10^{-2} \text{ M atm}^{-1}$ at 298 K
for O_3 , H_2O_2 and NO_2 , respectively. H_2O_2 concentrations were unavailable during our
220 observations. It was fitted based on temperature like a previous work (Fang et al., 2019)
and varied from 0.05 to 3.7 ppbv, with a mean value of 0.62 ± 0.52 ppbv. The
concentrations of Fe^{3+} and Mn^{2+} were calculated according to the measured total Fe and
Mn concentrations assuming 18% of total Fe and 30 % of total Mn were soluble (Wang
et al., 2014; Cui et al., 2008) and the precipitation equilibriums of $\text{Fe}(\text{OH})_3$ and
225 $\text{Mn}(\text{OH})_2$ depending on pH . The concentrations of Fe and Mn before December 2018
were estimated according to their mean ratios to $\text{PM}_{2.5}$ mass concentration (Wang et al.,
2014) because the instrument was unavailable.

3. Results and discussion

230 **3.1 Variation of sulfate in $\text{PM}_{2.5}$.** Figure 1A shows the hourly mean mass concentration
of $\text{PM}_{2.5}$ measured at SJZ and BUCT stations from March 15, 2018 to April 15, 2019.
The mass concentration of $\text{PM}_{2.5}$ in Shijiazhuang generally coincided well with that in
Beijing. This highlights the regional characteristic of air pollution in BJH. However,
Shijiazhuang usually showed significantly higher $\text{PM}_{2.5}$ concentration than that in
Beijing. The hourly mean $\text{PM}_{2.5}$ concentration varied in the range of 0 - $650 \mu\text{g m}^{-3}$ with
235 an annual mean concentration of $86.4 \pm 77.8 \mu\text{g m}^{-3}$. The corresponding values in
Beijing were 1.5 - 556 and $55.0 \pm 51 \mu\text{g m}^{-3}$. Particularly, the wintertime mass



concentration of PM_{2.5} in Shijiazhuang was as around 2.4 times as that in Beijing. This is well consistent with previous results that Shijiazhuang is suffering from more serious air pollution (Chen et al., 2019b) because of its larger population of heavy industries and more intensive emissions than Beijing (Chen et al., 2019a).

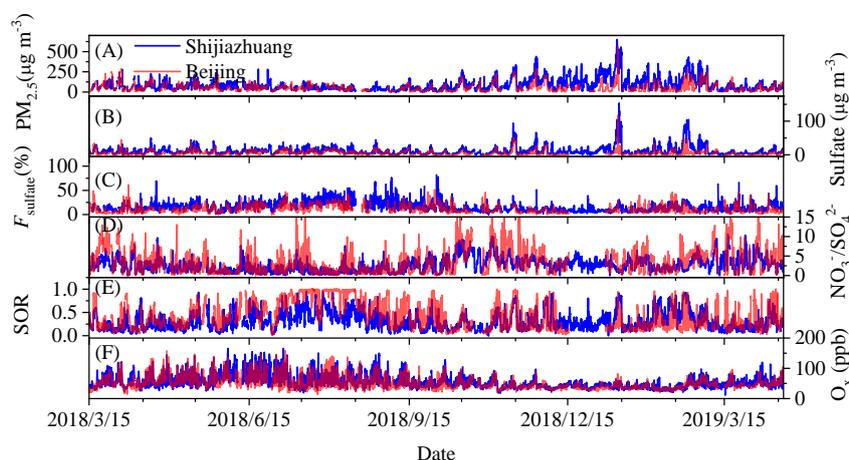


Fig. 1. The hourly mean (A) mass concentration of PM_{2.5}, (B) sulfate concentration, (C) sulfate fraction in PM_{2.5}, (D) molar ratio of nitrate to sulfate, (E) sulfur oxidation ratio (SOR) and (F) O_x (=NO₂+O₃) concentration in Shijiazhuang and Beijing from March 15, 2018 to April 15, 2019.

Like the mass concentration of PM_{2.5}, both the mass concentration (Fig. 1B) and the fraction of sulfate in PM_{2.5} (Fig. 1C) in Shijiazhuang were usually higher than those in Beijing. The annual mean sulfate concentrations in Shijiazhuang and Beijing were 11.7 ± 12.7 and $5.4 \pm 6.9 \mu\text{g m}^{-3}$, which annually contributed $15.3 \pm 8.7\%$ and $10.7 \pm 7.3\%$ to the PM_{2.5} mass concentrations, respectively. However, the molar ratio of NO₃⁻ to SO₄²⁻ (3.37 ± 3.05) corresponding to the mass ratio (2.17 ± 1.97) in Beijing was significantly higher than that in Shijiazhuang (2.69 ± 1.80 , corresponding to mass ratio



of 1.77 ± 1.72) at 0.05 level. This is consistent with the emission inventories of air pollutants, in which Shijiazhuang had larger SO_2 emissions than Beijing, and vice versa
255 for NO_x emissions (Yang et al., 2019; Liu et al., 2017a; Chen et al., 2019a). A decrease of sulfate concentration ($5.4 \pm 6.9 \mu\text{g m}^{-3}$) in Beijing was significant even when compared with that in $\text{PM}_{1.0}$ ($8.1 \pm 8.3 \mu\text{g m}^{-3}$) measured from July 2011 to June 2012 (Sun et al., 2015), while the mass ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ (2.17 ± 1.97) in Beijing showed an obvious increase compared with those in 2011-2012 (1.3-1.8) (Sun et al., 2015) and
260 2008 (0.8-1.5) (Zhang et al., 2013). This can be ascribed to the effective reduction of SO_2 emissions and the increased traffic emissions in Beijing.

The ground surface concentrations of pollutants are prone to be affected by variation of mixing layer height (MLH) (Zhong et al., 2018; Tang et al., 2016). Sulfur oxidation ratio (SOR), which is defined as the molar ratio of sulfate to total sulfur^{41,42},
265
$$\text{SOR} = \frac{n_{\text{SO}_4^{2-}}}{n_{\text{SO}_4^{2-}} + n_{\text{SO}_2}} \quad (7)$$
 was calculated and should be less affected by the MLH variation. As shown in Figure 1E, the SOR in Beijing was overall higher than that in Shijiazhuang. Thus, the annual mean SOR in Beijing (0.42 ± 0.29) was comparable with that reported in literatures (Fang et al., 2019), while it was significantly higher than that in Shijiazhuang
270 (0.31 ± 0.19) at 0.05 level. This implies the oxidation capacity in Beijing might be stronger than that in Shijiazhuang or the air mass might be more aged in Beijing than that in Shijiazhuang. However, the O_x ($\text{O}_x = \text{NO}_2 + \text{O}_3$) concentration in Shijiazhuang was usually higher than that in Beijing (Fig. 1F). The annual mean O_x concentration in Shijiazhuang was 55.2 ± 22.3 ppb, which was significantly higher than that in Beijing



275 (50.7 ± 21.5 ppb) at 0.05 level. This means that a higher SOR should be observed in Shijiazhuang than Beijing if gas phase oxidation mainly contributed to sulfate formation. These results suggest that heterogeneous and/or multi-phase reactions play important roles in particulate sulfate formation (Zheng et al., 2015; Martin and Good, 1991; Wu et al., 2019).

280 Figure 2A-C shows the mass concentration of PM_{2.5} colored according to the mass concentration of sulfate, the fraction of sulfate in the soluble PM and the SOR in Shijiazhuang. In most severe pollution events, high PM_{2.5} mass concentration well kept pace with the high sulfate concentration, the fraction of sulfate and the SOR (colored in grey color). For example, the mean PM_{2.5} concentration was 411.7 ± 98.1 μg m⁻³
285 during the pollution event occurred from 8:00 on January 12, 2019 to 0:00 on January 15, 2019. The corresponding sulfate concentration, fraction of sulfate in soluble PM and SOR were 80.6 ± 24.0 μg m⁻³, 39.4 ± 3.6 % and 0.79 ± 0.09, respectively. Other pollution episodes, which were highlighted in grey color in Fig. 2, showed the similar trend. The variations of the sulfate concentration, the fraction of sulfate in non-
290 refractory PM_{2.5} and the SOR with PM_{2.5} mass concentration in Beijing were similar to Shijiazhuang and shown in Fig. S2. These results confirm that the conversion rate of SO₂ to sulfate is promoted in pollution days when compared with that in clean days.

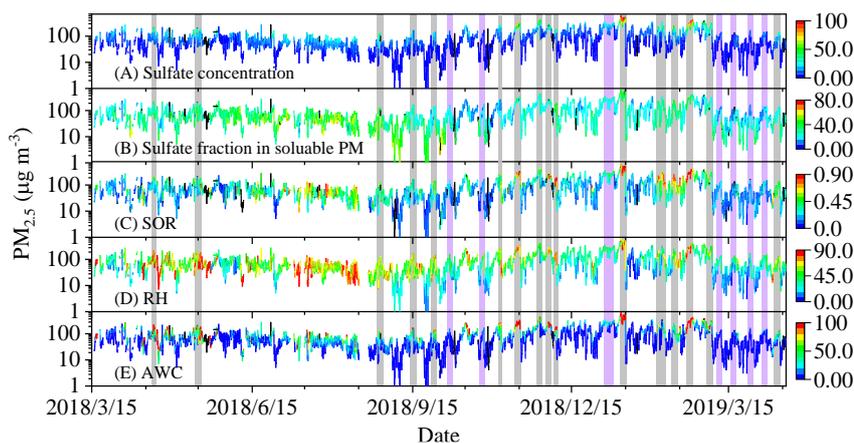


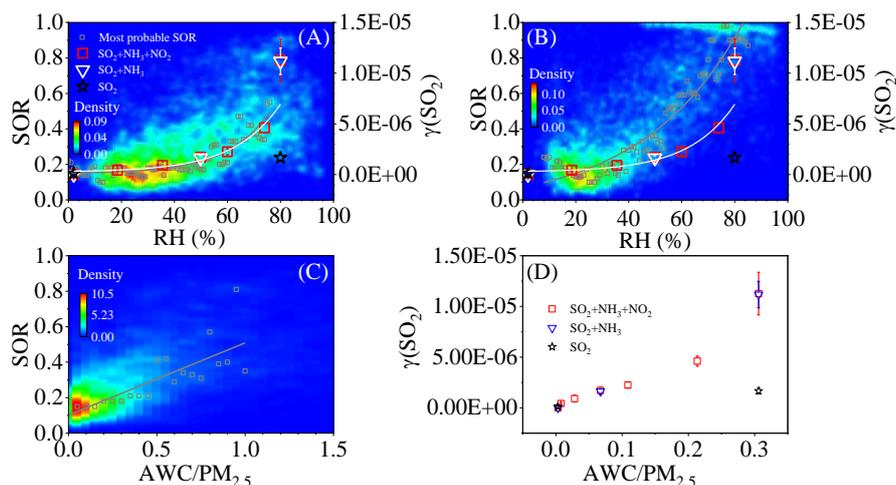
Fig. 2. Mass concentration of $PM_{2.5}$ colored according to (A) sulfate concentration, (B) sulfate fraction in soluble PM, (C) SOR, (D) RH and (E) AWC in Shijiazhuang. The shade areas in grey indicate the pollution events with high concentration of sulfate at high RH, while the purple ones the mean pollution events with low sulfate fraction at high RH.

3.2 Role of aerosol water content in sulfate formation. Previous studies have found that severe pollution events are frequently accompanied with high RH (Zhang et al., 2018; Tang et al., 2016; Wu et al., 2018; Liu et al., 2019b; Clifton et al., 1988; Maahs, 1983; Martin and Good, 1991). As shown in Fig. 2D, the high concentration of sulfate positively correlated with high RH in most cases, which were shaded in grey columns. However, some pollution events (shaded in purple columns) also occurred under high RH but the sulfate concentration or sulfate fraction in soluble PM was not so high. This means that high RH is a necessary but not a sufficient condition for sulfate conversion in severe haze pollution events. Thus, it is difficult to fully understand the general regularity behind the dataset or overemphasize the importance of a specific process in



the atmosphere based on case studies. This might be the reason why contrary
310 conclusions about the formation path of sulfate were drawn by different researchers.
We statistically analyzed the relationship between the SOR and the RH. All the hourly
mean data of the SOR and RH have been binned into 100×100 boxes. Then, the density
of data points, which statistically indicates the occurrence of the events at given values
of RH and SOR, was calculated using a bivariate kernel density estimator (Wand and
315 Jones, 1993).

Figure 3A and B show the 2D Kernel density graphs between the SOR and the RH
in Shijiazhuang and Beijing. The color bar shows the density of data points. Although
the SOR varied obviously at a certain RH, the most probable distribution of SOR could
be exponentially fitted as a function of RH in Shijiazhuang (Fig. 3A), that's,
320 $SOR=0.15+0.0032\times\exp(RH/16.2)$ ($R=0.79$). This is consistent with the dependence of
SOR on RH based on previous studies (Tian et al., 2019;Wu et al., 2019). It should be
noted that both SOR and RH showed obvious diurnal variation (Fig. S3). Their diurnal
variations were somewhat similar, but a four-hours of time lag was observed between
their minimum values. This means that the diurnal variations of SOR and RH might
325 also contribute to the strong dependency of SOR on RH (Fig. 3A and B). However, the
exponential dependency of SOR on RH was still observable in the night or in the day
(Fig. S4A and B). It did so in winter or summer (Fig. S4C and D). This means that
aqueous reactions is important for sulfate formation even if the influence of diurnal and
seasonal variations are ruled out (Wang et al., 2016;Cheng et al., 2016).



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Fig. 3. Relationship between SOR and $\gamma_{\text{SO}_2,\text{BET}}$ on dust internally mixed with NH_4NO_3 (2:1) and RH in (A) Shijiazhuang and (B) Beijing, and the correlation of (C) SOR in Shijiazhuang and (D) $\gamma_{\text{SO}_2,\text{BET}}$ with $\text{AWC}/\text{PM}_{2.5}$. The initial concentrations of SO_2 , NO_2 and/or NH_3 in the flow tube reactor were 190 ± 2.5 , 100 ± 2.5 and/or 50 ± 2.5 ppb, respectively. The grey lines are the fitting curves for the most probable SOR and the white lines are the fitting curves for the $\gamma_{\text{SO}_2,\text{BET}}$.

In Fig. 3A, 72.5 % of the data points of Shijiazhuang (6509 over 8980 effective points, which shown in small grey dots) were in the domain with the RH range of 10 % - 70 % and the SOR range of 0.05 – 0.42, while 10.1 % of data points were in the region with the RH greater than 70 % and the SOR greater than 0.42. The first region corresponded to a lower mean $\text{PM}_{2.5}$ concentration, sulfate concentration and SOR ($76.1 \pm 62.78 \mu\text{g m}^{-3}$, of $8.1 \pm 6.3 \mu\text{g m}^{-3}$, and 0.21 ± 0.09 , respectively) compared with the second one ($115.7 \pm 96.7 \mu\text{g m}^{-3}$, $22.4 \pm 20.4 \mu\text{g m}^{-3}$ and 0.62 ± 0.14 , respectively). As shown in Fig. 3B, the SOR also exponentially increased as a function of RH in Beijing. 74.6 % of 8169 data points were in the first region. The mean $\text{PM}_{2.5}$ concentration,

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sulfate concentration and SOR were $48.2 \pm 44.8 \mu\text{g m}^{-3}$, $2.9 \pm 3.0 \mu\text{g m}^{-3}$ and 0.21 ± 0.10 in the low RH region, while they were $69.9 \pm 50.9 \mu\text{g m}^{-3}$, $9.4 \pm 8.5 \mu\text{g m}^{-3}$ and 0.83 ± 0.15 in the high RH region. The most probable distribution of SOR in Beijing could also be exponentially fitted as a function of RH (SOR=
350 $0.045+0.12 \times \exp(\text{RH}/37.8)$, $R=0.92$). However, the SOR was more sensitive to RH in Beijing than that in Shijiazhuang. This might be explained by the increased importance of sulfate formation via gas phase reactions in Beijing (Fang et al., 2019;Hollaway et al., 2019) because the $\text{PM}_{2.5}$ mass concentrations in Beijing were significantly lower than that in Shijiazhuang (Fig. 1).

355 Formation of particle phase sulfate through heterogeneous or multiple phase oxidations includes the uptake of SO_2 and the following oxidation in particle phase. Thus, it is meaningful to identify the rate determining step (RDS) for understanding the evolution of the SOR. As shown in Fig. 3, the initial $\gamma_{\text{SO}_2, \text{BET}}$ increased exponentially from 0 to $(1.13 \pm 0.21) \times 10^{-5}$ when the RH increases from 2 % to 80 % in the presence
360 of 50 ± 2.5 ppb NH_3 with or without 100 ± 2.5 ppb NO_2 . The dependence of $\gamma_{\text{SO}_2, \text{BET}}$ on RH was $\gamma_{\text{SO}_2, \text{BET}} = 2.44\text{E-}7 + 6.69\text{E-}8 \times \exp(\text{RH}/17.4)$ with a correlation coefficient of 0.96. A transition region of the $\gamma_{\text{SO}_2, \text{BET}}$ verse the RH was observable when the RH ranged from 60 % to 80 %. When the RH was higher than 70%, the $\gamma_{\text{SO}_2, \text{BET}}$ increased quickly as a function of the RH. The similar dependency on RH for the $\gamma_{\text{SO}_2, \text{BET}}$ and the
365 SOR suggests that the uptake kinetic of SO_2 might determine sulfate formation.

In a previous work (Zhang et al., 2019), it has been found that all the uptake of SO_2 on dust or nitrate coated dust can be transformed into sulfate over the time scale of



uptake experiment using the similar coated-wall flow tube reactor. Another study also observed the quick formation of sulfate on the surface of aqueous microdroplets without the addition of other oxidants, which was explained by the direct interfacial electron transfer from SO₂ to O₂ on the aqueous microdroplets (Hung et al., 2018). This means that oxidation of S(IV) might not be a RDS of sulfate formation. The oxidation processes can be ascribed to catalytic oxidation by O₂ in the presence of transition metal, oxidation by O₂ and nitric acid promoted by protons in the presence of nitrate (Zhang et al., 2019), and the oxidation by other dissolved oxidants in liquid phase (Chen et al., 2019d; Cheng et al., 2016; Wang et al., 2016). To further validate this assumption, the formation rates of SO₄²⁻ ($d[\text{SO}_4^{2-}]/dt$) in aerosol liquid phase were calculated according to the method used in previous work (Liu et al., 2020a; Cheng et al., 2016). If oxidation of S(IV) is the rate determining step, the formation rate should show a similar dependence on RH like the SOR.

As shown in Fig. S5, the relative contributions of different oxidation paths of S(IV) varied obviously case by case. In summer and autumn, oxidation by H₂O₂ was the most important path followed by TMI. In winter, however, either NO₂, O₃ or H₂O₂ could contribute to the major oxidation path. Figure 4A and B show the dependence of the formation rate of sulfate on RH in the range of 35%-100% in Shijiazhuang. The dataset for RH below 35 % were omitted due to the large uncertainty in aerosol pH calculations (Ding et al., 2019; Guo et al., 2016; Pye et al., 2020). The relative contributions of different oxidation paths of S(IV) also varied obviously as a function of RH. NO₂ and O₃ played important role in aqueous S(IV) oxidation when RH was from 35 % to 45%,



390 while TMI became the dominator when RH ranged from 45% to 70%. Above 70% RH,
the contribution of H₂O₂ was dominant, which is consistent with several recent studies
(Liu et al., 2020a;Liu et al., 2020b). However, the total formation rate of sulfate in
aerosol liquid phase slightly decreased as RH increasing. A weak downward trend of
the $d[\text{SO}_4^{2-}]/dt$ with RH was also observable in the 2D Kernel density graphs as shown
395 in Fig. 4B. This is opposite to the dependencies of the SOR and the γ_{SO_2} on RH as
discussed above, which means the RDS for sulfate formation should be the uptake of
SO₂ instead of oxidation of S(IV) in aqueous phase.

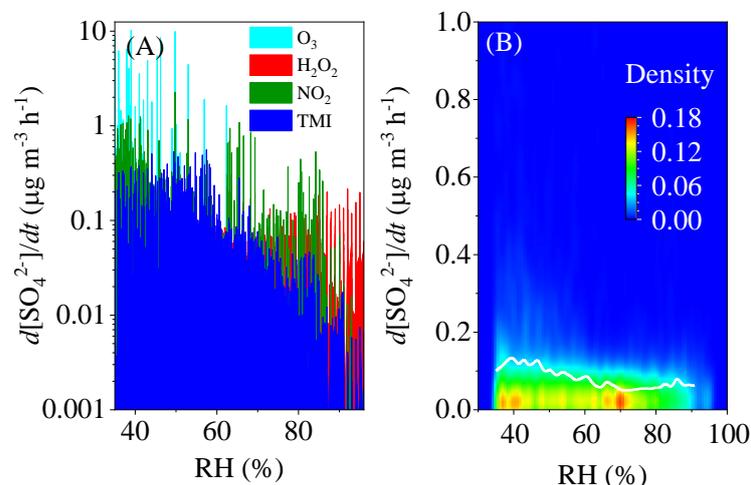


Fig. 4. Dependence of sulfate formation rates on RH in Shijiazhuang. The white line is
400 the probability weighted $d[\text{SO}_4^{2-}]/dt$.

Phase state is a crucial factor determining the mass transfer of pollutants from gas
phase to particle phase (Davis et al., 2015;Marshall et al., 2018;Shiraiwa et al., 2011;Liu
et al., 2014), while the AWC or RH greatly affects the phase state of aerosol particles
(Duan et al., 2019;Liu et al., 2019b;Shiraiwa et al., 2017). For example, ambient
405 particles were found to change from semi-solid to liquid state when the RH was above



~60 % (Liu et al., 2019b;Liu et al., 2017b) corresponding to the AWC higher than ~15
 $\mu\text{g m}^{-3}$ (Liu et al., 2017b) under the typical urban environment in Beijing based on
rebound fractions measurements. It was also confirmed that haze particles displayed a
solid-aqueous equilibrium state when the RH was around 60-80% using an individual
410 particle hygroscopicity system (Sun et al., 2018). As shown in Fig. S6, the most
probable distribution of the AWC exponentially increased with the RH ($\text{AWC} = -5.76$
 $+ 5.15 \times \exp(\text{RH}/36.1)$, $R=0.98$) in Shijiazhuang. An obvious transition region of the RH
between 60 % and 80 % was also observed. These results indicate that the liquid phase
aerosol should appear when the RH is higher than ~60 % (Liu et al., 2019b;Liu et al.,
415 2017b), subsequently, promote the conversion of SO_2 to sulfate. The SOR increased as
a power function of AWC ($\text{SOR} = 0.072 + 0.043 \times \text{AWC}^{0.53}$, $R=0.78$), while it was
linearly correlated with the ratio of $\text{AWC}/\text{PM}_{2.5}$ ($\text{SOR} = 0.15 + 0.40 \times \text{AWC}/\text{PM}_{2.5}$,
 $R=0.78$) as shown in Fig. 3C. Similarly, the AWC of dust internally mixed with
 NH_4NO_3 was also calculated using the ISORROPIA II model. The $\gamma_{\text{SO}_2,\text{BET}}$ also showed
420 a similar trend as a function of $\text{AWC}/\text{PM}_{2.5}$ ($\gamma_{\text{SO}_2,\text{BET}} = 3.08\text{E-}5 \times \text{AWC}/\text{PM}_{2.5}$, $R=0.95$)
(Fig. 3D) although the ranges of $\text{AWC}/\text{PM}_{2.5}$ were different due to the difference in
aerosol composition. This means that the fraction of aerosol liquid water governs both
the conversion of SO_2 to sulfate and uptake kinetics of SO_2 .

It should be noted that although the SOR showed a similar RH dependence as the
425 SO_2 , a deviation was observed in both Shijiazhuang and Beijing (Fig. 3). The γ_{SO_2} was
measured at a fixed temperature and initial SO_2 concentration. In the atmosphere, both
of them varied obviously. This might lead to the observed deviation. On the other hand,



the coexisted components such as organic aerosol and black carbon in atmospheric particles should have complicated influence on the hygroscopicity and the phase-
430 change of particles. The difference between the model particles and the real ambient aerosol particles might also partially lead to the deviations of the RH dependence between the SOR and the $\gamma_{\text{SO}_2, \text{BET}}$. In addition, it also implies that besides the reaction in aerosol liquid phase, other reaction paths such as oxidation of SO_2 by gas phase oxidants should also play an important role in sulfate formation (Duan et al., 2019).

435 **3.3 Influence of particle composition on AWC and sulfate formation.** Besides RH, particle composition is another important factor to affect the AWC. According to the ions balance (Fig. S7A), ammonia was adequate to neutralize the anions in $\text{PM}_{2.5}$, which is consistent with the results in the literature (Wang et al., 2020b). In addition, (81.5±15.9) % (with the median of 87.1%) of ionic anions (nitrate, chloride, and sulfate)
440 were neutralized by ammonium (Fig. S7B). This means NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$ and NH_4Cl should be the dominant form of nitrate, sulfate, and chloride in $\text{PM}_{2.5}$. We further reconstructed the molecular composition from the ions based on the principles of aerosol neutralization and molecular thermodynamics (Kortelainen et al., 2017). The molecular concentrations were estimated according to the molar ratio of NH_4^+ -to- SO_4^{2-}
445 ($R_{\text{NH}_4^+/\text{SO}_4^{2-}}$) according to the following rules: i) if $0 < R_{\text{NH}_4^+/\text{SO}_4^{2-}} < 1$, NH_4^+ existed as the chemical forms of H_2SO_4 and NH_4HSO_4 . ii) $1 < R_{\text{NH}_4^+/\text{SO}_4^{2-}} < 2$, NH_4^+ existed as $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 . iii) if $R_{\text{NH}_4^+/\text{SO}_4^{2-}} > 2$, then the fraction NH_4^+ corresponding to twice the amount of SO_4^{2-} existed as $(\text{NH}_4)_2\text{SO}_4$ and the remaining fraction of NH_4^+ was associated with NO_3^- and Cl^- . iv) the rest of NO_3^- , which was not neutralized by



450 NH_4^+ was from NaNO_3 . Figure 5A and B show the variation of the molecular composition with RH in Shijiazhuang. Obviously, NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ were the major molecular components. Both of them showed upward trend as the RH increased. In particular, the fraction of NH_4NO_3 increased gradually from $\sim 10\%$ to $\sim 50\%$ when the RH increased from $\sim 30\%$ to 90% . Correspondingly, the fraction of $(\text{NH}_4)_2\text{SO}_4$
455 decreased as the RH increased.

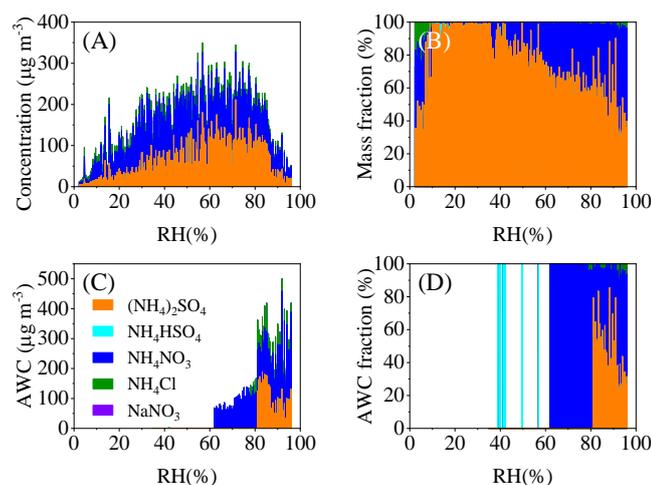


Fig. 5. Variations of (A) and (B) molecular composition of water-soluble ions, and (C) and (D) the corresponding contributions to AWC with RH in Shijiazhuang.

It should be noted that the deliquescence RH (DRH) of NH_4NO_3 (61.8 %) (Onasch
460 et al., 1999) is lower than those of NH_4Cl (78%) (Hu et al., 2011) and $(\text{NH}_4)_2\text{SO}_4$ (80 %) (Lightstone et al., 2000). This means ammonium nitrate should be the major contributor to the AWC compared with sulfate and chloride when both the concentrations and hygroscopicity were taken into consideration. We further calculated the AWC attributed to the individual molecular component. The deliquescence curve of each salt was
465 calculated at 298.5 K using the E-AIM model (Clegg et al., 1998). Then, the AWC was



calculated with the mass of the salt and the mass-based growth factor at the corresponding RH. As shown in Fig. 5C, NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ were the major contributors to the AWC. Especially, NH_4NO_3 dominated the AWC when the RH ranged from 60% to 80%, in which the SOR and the γ_{SO_2} were very sensitive to RH. These results suggest that NH_4NO_3 should be the most important mediator to AWC, subsequently, the uptake of SO_2 in the transition regime of RH in Fig. 3A. In previous work, it has been found that SO_2 oxidation can be promoted by particulate nitrate through the accumulation of proton (Zhang et al., 2019) and the formation of NO^+NO_3^- (Kong et al., 2014). Our results further showed the importance of NH_4NO_3 in the AWC, which possibly determines the phase state of particles, subsequently, the uptake kinetics of SO_2 and the SOR as discussed above. To further confirm the role of NH_4NO_3 in the uptake of SO_2 , uptake experiment of SO_2 on pure dust has been carried out at 2% and 80% RH, respectively. The corresponding $\gamma_{\text{SO}_2,\text{BET}}$ was $1.10 \pm 1.05 \times 10^{-7}$ and $1.66 \pm 0.28 \times 10^{-7}$ on pure dust sample in the presence of NH_3 and NO_2 . However, as discussed above, it was 0 and $1.12 \pm 0.15 \times 10^{-5}$ on dust internally mixed with 33 % NH_4NO_3 . This directly confirmed the role of NH_4NO_3 in SO_2 uptake via aerosol liquid water.

Figure S8 shows the dependencies of the $\text{AWC}/\text{PM}_{2.5}$ and SOR on the fraction of the individual molecular component. Both the $\text{AWC}/\text{PM}_{2.5}$ and SOR statistically increased as the fraction of NH_4NO_3 increased (Fig. S8A and D). A weak increase followed by a decrease was observed for the $\text{AWC}/\text{PM}_{2.5}$ as the fraction of $(\text{NH}_4)_2\text{SO}_4$ increased, while a negative correlation between the $\text{AWC}/\text{PM}_{2.5}$ and the fraction of



NH₄Cl was observed. It did so for the SOR and the fraction of NH₄Cl. These phenomena were overall consistent with the sequence of their hygroscopicity. In addition, chloride
490 is a primary pollutant mainly from coal combustion and biomass burning (Bi et al., 2019). Besides chloride, other primary particles from combustion such as soot, which were not accounted for in this work, might also decrease the uptake capability of water, subsequently, be unfavorable for SO₂ uptake.

To assess the relative importance of sulfate and nitrate (the major SNA component)
495 to AWC, the sensitivity of their fraction to AWC in Shijiazhuang was tested using the ISOPRRIA II model and shown in Fig. S9. The base case means the AWC was calculated using the measured concentration of the ions. Then, we reduced the fraction of NH₄NO₃ or (NH₄)₂SO₄ from 0 to 80 % individually compared with the base case. Figure S9A shows the time series of the calculated AWC after reducing 50 % of
500 NH₄NO₃ or (NH₄)₂SO₄. Reduction of either NH₄NO₃ or (NH₄)₂SO₄ resulted into obvious decrease of AWC during pollution events. In most cases, the reduction amplitude of AWC was larger when reducing 50 % of NH₄NO₃ than (NH₄)₂SO₄. Figure S9B shows the mean ratio of AWC at a certain reduction fraction of NH₄NO₃ or (NH₄)₂SO₄ to that under the base case. When NH₄NO₃ was reduced from 0 % to 80 %,
505 the AWC linearly reduced from 0 % to 61.1±0.1 % with a slope of 0.48%. It varied from 0 % to 66.0±0.2 % for (NH₄)₂SO₄ (with a slope of 0.41%). This means that the AWC is more sensitive to the fraction of NH₄NO₃ than (NH₄)₂SO₄ in Shijiazhuang. This also implies the importance of NH₄NO₃ in the observed high AWC in haze days. On the other hand, reducing 10 % of NH₄NO₃ can lead to a reduction of 5.2±1.0% AWC during



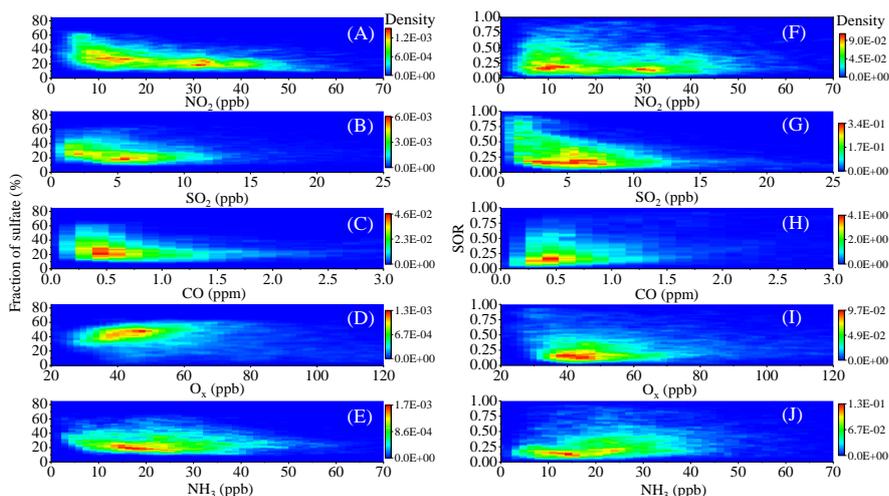
510 haze days. Subsequently, we can roughly estimate that the SOR might be reduced by
~4 % through a linear interpolation according to the equation of the SOR and the
AWC/PM_{2.5} ($SOR = 0.15 + 0.40 \times AWC/PM_{2.5}$) fitted in Fig. 3C. This means reduction
of NO_x and NH₃ should lead to additional reduction of particulate sulfate.

3.4 Influence of other factors on sulfate formation. Several studies have proposed
515 out that NO₂ can promote the oxidation of SO₂ on particle surfaces and in aqueous
phase. For example, laboratory studies have found that ppm level of NO₂ can promote
sulfate formation on the surface of dust through NO⁺NO₃⁻ which is disproportionated
from N₂O₄ intermediate (He et al., 2014; Liu et al., 2012; Ma et al., 2008), or ppm level
of NO₂ can promote the oxidation of SO₂ in the deliquesced oxalic acid (Wang et al.,
520 2016). This is supported by the evidence that high fraction of sulfate in PM_{2.5} is
positively correlated with NO₂ concentration (Xie et al., 2015) and high PM_{2.5}
concentration is accompanied with high ratio of NO₂/SO₂ in several case studies (He et
al., 2014). The importance of the SO₂ oxidation by NO₂ in aqueous phase has also been
confirmed in modeling studies (Cheng et al., 2016; Xue et al., 2016). However, this
525 reaction path is still under debate because of the following reasons: 1) The
concentration of NO₂ in laboratory studies was about 2 orders of magnitude higher than
that in ambient air. This will affect the surface concentration of the intermediate (N₂O₄)
and the concentration of solved NO₂ in aqueous phase. 2) The dissolved NO₂
concentration is highly sensitive to pH. The pH value in aerosol was 5.6-6.2 estimated
530 in modeling study (Cheng et al., 2016). However, a recent work found that it varied
from 3.8 to 4.5 at RH > 30 % and showed a moderate acidity because of the



thermodynamic equilibrium between NH_4^+ and NH_3 (Ding et al., 2019). 3) The relative importance of each path depends on the concentration of the relevant pollutants including H_2O_2 and TMI (Liu et al., 2020a). Therefore, it is necessary to verify the importance of this process by long-term observation at different environments.

Figure 6 shows the 2D Kernel density graph of the sulfate fraction in soluble PM and the SOR in Shijiazhuang as a function of the concentration of different gas phase pollutants. It should be pointed out that the SOR or the γ_{SO_2} should be positively correlated to NO_2 concentration if it can promote the conversion of SO_2 to sulfate or the uptake of SO_2 . However, both sulfate fraction and SOR were negatively correlated with the concentration of NO_2 in a point view of statistics. A same trend was observed in Beijing (Fig. S10). This is similar to recent studies that observed the opposite correlation between SOR and NO_x concentration in Sichuan Basin (Tian et al., 2019) and in Beijing (Fang et al., 2019). This means that NO_2 concentration is statistically not a determining factor for sulfate formation in the atmosphere. This is well supported by the uptake kinetics of SO_2 measured using a flow tube reactor. As shown in Fig. 3A and B, when 50 ± 2.5 ppb of NH_3 presenting in the reactant gases, no difference was observable about the $\gamma_{\text{SO}_2, \text{BET}}$ between in the presence (red squares) and absence of 100 ± 2.5 ppb of NO_2 (white triangles). This is consistent with these previous studies that found NO_2 having no influence on SO_2 uptake when NH_3 was abundant in the atmosphere (Wu et al., 2019; Wang et al., 2021). In addition, it is consistent with the fact that H_2O_2 dominated the oxidation of S(IV) in aerosol liquid water when RH was higher than 60% (Fig. 4A).



555 Fig. 6. Dependence of the sulfate fraction in soluble PM and the SOR on gaseous pollutant concentration in Shijiazhuang.

Both the fraction of sulfate and the SOR in Shijiazhuang statistically decreased as a function of SO_2 and CO concentration, respectively (Fig. 6B, C, G and H). This might be explained by the high concentration of primary aerosol components when pollution events occurred with high concentration of primary gas phase pollutants. However, the fraction of sulfate increased as a function of O_3 (Fig. 6D). When the O_3 concentration was greater than 50 ppb, the SOR slightly increased with the O_3 concentration (Fig. 6I). A more obvious positive dependence of sulfate fraction on O_3 concentration was observed in Beijing (Fig. S6D). This means oxidation capacity also plays an important role in sulfate formation, especially in Beijing. This is consistent with the recent finding that O_3 plays an important role in SO_2 oxidation at different locations (Fang et al., 2019; Tian et al., 2019; Duan et al., 2019). As shown in Fig. 6J, the SOR positively correlated with the concentration of NH_3 in Shijiazhuang. This means that NH_3 can

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promote the conversion of SO₂ to sulfate. This is well in agreement with laboratory
570 studies that observed the promotion effect by NH₃ to the heterogeneous reaction of SO₂
on different mineral oxides (Yang et al., 2016). In addition, flow tube experiments were
also carried out by exposing the internal mixing sample (2:1 dust and NH₄NO₃) to 200
± 2.5 ppb SO₂ in the absence of NH₃ and NO₂ at 2 % and 80 % RH, respectively. As
shown in Figure 3A and B, the $\gamma_{\text{SO}_2, \text{BET}}$ was zero regardless of the reactants under dry
575 condition (2 % RH), while it increased to $(1.66 \pm 0.28) \times 10^{-6}$ at 80 % RH. However, it
was significantly smaller than the $\gamma_{\text{SO}_2, \text{BET}}$ $((1.13 \pm 0.21) \times 10^{-5})$ in the presence of 50
± 2.5 ppb NH₃ with or without 100 ± 2.5 ppb NO₂. These results further confirm that
NH₃ can promote the uptake of SO₂ at high RH, possible through enhancing the
solubility of SO₂ in water (Chen et al., 2019d; Cheng et al., 2016; Wang et al., 2016).

580 **4. Conclusions and atmospheric implications.**

Based on one-year of observations, we confirmed that high PM_{2.5} mass concentration
in pollution events usually coincided with the high sulfate concentration, the fraction
of sulfate and the SOR in both Beijing and Shijiazhuang. In Shijiazhuang, the SOR
exponentially increased as a function of RH in the point view of statistics, which was
585 similar to the RH dependence of the γ_{SO_2} on the model particles containing 33%
NH₄NO₃ in the presence of NH₃. The SOR and γ_{SO_2} linearly increased as a function of
the fraction of aerosol water content in PM_{2.5}. The enhanced uptake coefficient of SO₂
at high RH after the liquid phase aerosol appeared might explain the increased SOR
because uptake of SO₂ was the rate determining step for the conversion of SO₂ to
590 particulate sulfate. NH₄NO₃ played an important role in the AWC, the phase state of



aerosol particles, subsequently, the uptake kinetics of SO_2 in haze days under high RH conditions.

The contribution of nitrate to $\text{PM}_{2.5}$ is increasing in China (Li et al., 2018; Tian et al., 2019) due to the intensive emissions of NO_x from steel production and cement manufacturing (Wu et al., 2018; Qi et al., 2017) and the increasing NO_x emissions from traffic (Liu et al., 2007; Wang et al., 2011). The mean fraction of nitrate in $\text{PM}_{2.5}$ was 21.4±12.4 % in Shijiazhuang and 15.8±13.4 % in Beijing, respectively. They were close to the reported values in $\text{PM}_{1.0}$ during the summer of Beijing (24 %) (Li et al., 2018) and in $\text{PM}_{2.5}$ during the winter of Chengdu (23.3 %) and Chongqing (17.5 %) (Tian et al., 2019). It has been found that the fraction of nitrate and ammonium usually increases as a function of $\text{PM}_{2.5}$ mass concentration (Li et al., 2018). Therefore, NO_x should be an urgent air pollutant in the future in China even from the point view of its contribution to $\text{PM}_{2.5}$ mass.

As observed in this work, NH_4NO_3 has importance contribution to $\text{PM}_{2.5}$ mass concentration and the aerosol water content, subsequently, the phase state of particles in the RH range of 60-80%. Reduction of NO_x emissions should lead to decrease in NH_4NO_3 concentration, subsequently, the AWC during serve pollution events. This will lead to an additional reduction of SO_2 uptake and the formation of particulate sulfate through aqueous reactions. Based on our rough estimation, 4 % of sulfate might be reduced due to aqueous reaction in Shijiazhuang if the mass concentration of NH_4NO_3 was reduced by 10 %. More work is required to quantitatively assess the contribution of nitrate to sulfate formation from aqueous reactions in the future. It should be noted



that ozone pollution becomes more and more important in China (Chen et al.,
2019e; Ziemke et al., 2019). This requires to harmoniously reduce NO_x and volatile
615 organic compounds in the near future. It is also important to take actions on NH₃
emission control in the future as NH₃ can significantly promote the uptake of SO₂ in
liquid phase aerosol.

Data availability. The experimental data are available upon request to the
620 corresponding authors.

Supplement. The supplement related to this article is available online at:

Author contributions. YoL and XB designed the experiments. YoL and YuL wrote the
625 paper. ZF, FZ, YZ, XF, CY, BC, YW, WD, and JC carried out measurements at BUCT.
XB and TJ carried out measurements at SJZ. YG, YZ, and YoL carried out flow tube
experiments. PL, YM, and YoL performed sulfate formation calculations. YuL, FB, TP,
YM, HH, and MK revised the paper.

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

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