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Atmospheric Chemistry and Physics Discussions

Particle acidity and sulfate production during severe haze events in China cannot be reliably inferred by assuming a mixture of inorganic salts

Gehui Wang[1,2,3], Fang Zhang[4,5], Jianfei Peng[5,6], Lian Duan[5,7], Yuemeng Ji[5,8], Wilmarie Marrero-Ortiz[5], Jiayuan Wang[2], Jianjun Li[2], Can Wu[2], Cong Cao[2], Yuan Wang[9], Jun Zheng[10], Jeremiah Secrest[5], Yixin Li[5], Yuying Wang[4,5], Hong Li[11], Na Li[5,12], and Renyi Zhang[5,6*]

[1] Key Laboratory of Geographic Information Science of the Ministry of Education, School of Geographic Sciences, East China Normal University, Shanghai 200241, China
[2] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, China Academy of Sciences, Xi'an 710061, China
[3] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Science, Xiamen, China
[4]Beijing Normal University, Beijing 100875, China
[5] Departments of Atmospheric Sciences and Chemistry, Texas A&M University, College Station, TX, 77843, USA
[6] State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China
[7] East China University of Science and Technology, Shanghai, China
[8] School of Environmental Science and Engineering, Institute of Environmental Health and Pollution, Control, Guangdong University of Technology, Guangzhou 510006, China
[9] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91125, USA
[10] Jiangsu Key Laboratory of Atmospheric Environment Monitoring and Pollution Control, Nanjing University of Information Science & Technology, Nanjing 210044, China
[11] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
[12] Key Laboratory of Songliao Aquatic Environment, Jilin Jianzhu University, Changchun, 130118, China

*Corresponding author:
Prof. Renyi Zhang, E-mail: renyi-zhang@tamu.edu

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Abstract: Atmospheric measurements showed rapid sulfate formation during severe haze episodes in China, with fine particulate matter (PM) consisting of a multi-component mixture that is dominated by organic species. Several recent studies using the thermodynamic model estimated the particle acidity and sulfate production rate, by treating the PM exclusively as a mixture of inorganic salts dominated by ammonium sulfate and neglecting the effects of organic compounds. Noticeably, the estimated pH and sulfate formation rate during pollution periods in China were highly conflicting among the previous studies. Here we show that a particle mixture of inorganic salts adopted by the previous studies does not represent a suitable model system and that the acidity and sulfate formation cannot be reliably inferred without accounting for the effects of multi-aerosol compositions during severe haze events in China. Our laboratory experiments show that SO_2 oxidation by NO_2 with NH_3 neutralization on fine aerosols is dependent on the particle hygroscopicity, phase-state, and acidity. Ammonium sulfate and oxalic acid seed particles exposed to vapors of SO_2, NO_2, and NH_3 at high relative humidity (RH) exhibit distinct size growth and sulfate formation. Aqueous ammonium sulfate particles exhibit little sulfate production because of high acidity, in contrast to aqueous oxalic acid particles with significant sulfate production because of low acidity. Our field measurements demonstrate significant contribution of water-soluble organic matter to fine PM in China and indicate that the use of oxalic acid in laboratory experiments is representative of ambient organic dominant aerosols. While the particle acidity cannot be accurately determined from field measurements or calculated using the thermodynamic model, our results reveal that the pH value of ambient organics-dominated aerosols is sufficiently high to promote efficient SO_2 oxidation by NO_2 with NH_3 neutralization under polluted conditions in China.

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1. Introduction

Atmospheric measurements have demonstrated rapid sulfate production during severe haze events in China (Guo et al., 2014; Wang et al., 2014; Zhang et al., 2015; Cheng et al., 2016; Wang et al., 2016). For example, Wang et al. (2016) showed that during pollution episodes in Xi'an of China the SO_4^{2-} mass concentration increased markedly from less than 10, 10-20, to greater than 20 μg m^{-3}, with the corresponding increases in the mean $PM_{2.5}$ mass concentrations from 43, 139, to 250 μg m^{-3} from clean, transition, to polluted periods, respectively. Among the $PM_{2.5}$ species in Xi'an, organic matter (OM), nitrate (NO_3^-), and SO_4^{2-} were most abundant, with the mass fractions of 55%, 14%, and 14%, respectively, during the polluted period. In addition, the work by Wang et al. (2016) demonstrated that the molar ratio of SO_4^{2-} to SO_2, which reflects sulfur partitioning between the particle and gas phases, exhibited an exponential increase with relative humidity (RH), with the values of less than 0.1 at RH < 20% to 1.1 at RH > 90% in Xi'an. Similar evolutions in SO_4^{2-} mass concentrations and the molar ratio of SO_4^{2-} to SO_2 were shown during the pollution development in Beijing (Sun et al., 2013; Wang et al., 2014; Wang et al., 2016). The rapid sulfate formation measured in China could not be explained by current atmospheric models and suggested missing sulfur oxidation mechanisms (Wang et al., 2014). Typically, high sulfate levels during haze events in China occurred concurrently with elevated RH, NO_x, and NH_3 (Wang et al., 2014; Zhang et al., 2015; Wang et al., 2016), implicating an aqueous sulfur oxidation pathway. On the basis of complementary field and experimental measurements, Wang et al. (2016) concluded that the aqueous oxidation of SO_2 by NO_2 is key to efficient sulfate formation, but is only feasible under two atmospheric conditions, i.e., on fine aerosols with high RH and NH_3 neutralization or under cloud conditions.

Several recent studies estimated the particle acidity and aqueous sulfate production during

severe haze events in China using the thermodynamic model (Cheng et al., 2016; Guo et al., 2017; Liu et al., 2017). For example, Cheng et al. (2016) estimated a pH range of 5.4 to 6.2 using a thermodynamic model (ISORROPIA-II) in Beijing. On the basis of their estimated pH and the previous experimental rates of SO_2 oxidation by NO_2 and the Henry's Law constants for sulfur dioxide (SO_2), bisulfite (HSO_3^-), and sulfite (SO_3^{2-}) from the literature (Lee and Schwartz, 1983; Clifton et al., 1988; Seinfeld and Pandis, 2006), the authors derived a sulfate production rate and concluded that reactive nitrogen chemistry in aerosol water explained the sulfate formation during polluted periods in Beijing. In contrast, other recent studies by Guo et al. (2017) and Liu et al. (2017) adopted the similar method as Cheng et al. (2016), but reported significantly different values of pH and the sulfate formation rates by the aqueous SO_2 oxidation by NO_2 in China. Those two later studies determined a pH range of 3.0-4.9 and suggested that fine particles were moderately acidic and the aqueous SO_2 oxidation by NO_2 was unimportant during severe wintertime haze periods in China.

In this article, we conducted laboratory measurements of the hygroscopicity for oxalic acid particles and particle growth of ammonium sulfate particles upon exposure to SO_2, NO_2, and NH_3 at high RH conditions, in order to evaluate the dominant factors regulating the aqueous oxidation of SO_2 by NO_2. In addition, field measurements of chemical compositions of water-soluble fraction for fine PM (including oxalic acid) in Beijing, Hebei Province, and Xi'an of China were performed during the winter haze episodes, showing significantly enriched water-soluble organic matter (WSOM). The implications for the multi-aerosol chemical compositions on the pH value and sulfate production during winter pollution periods in China are discussed.

2. Methods

2.1 Aqueous phase oxidation of SO_2 by NO_2 in an environmental chamber

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106 The experimental method using the environmental chamber has been discussed elsewhere
107 (Wang et al., 2016), and here we only provide a brief description. The aqueous SO_2 oxidation
108 experiments was conducted by exposing size-selected $(NH_4)_2SO_4$ seed particles to different
109 levels of SO_2, NO_2, and NH_3 at variable RH conditions in a 1 m^3 Teflon reaction chamber
110 covered with aluminum foil. A differential mobility analyzer (DMA) equipped with a
111 condensation particle counter (CPC) was used to measure the particle growth in diameter, in
112 order to determine sulfate formation on seeded particles (Wang et al., 2016).

113 **2.2 Measurement of hygroscopic growth factor of oxalic acid**

114 Hygroscopic growth factor (HGF) of oxalic acid was measured according to the method
115 previously discussed (Khalizov et al., 2009; Pagels et al., 2009). Briefly, a hygroscopicity
116 tandem differential mobility analyzer (HTDMA) coupled to a condensation particle counter
117 (CPC, TSI 3762) was used for the HGF measurement. Size-selected oxalic acid particles with the
118 dry diameter of 100 nm were exposed to increasing RH from 8% to 92% with a step range from
119 1%-10%. HGF is defined as the ratio of oxalic acid particle diameter (D_p) measured by the
120 second DMA at an elevated RH to the initial diameter (D_0 = 100 nm) of the particles selected by
121 the first DMA at the dry conditions of RH = 8% (Peng et al., 2016).

122 **2.3 Chemical composition of $PM_{2.5}$ in Beijing, Hebei Province, and Xi'an, China**

123 $PM_{2.5}$ samples were collected onto pre-baked (450^{o}C for 6 hr) quartz fiber filter by using a
124 high-volume air sampler with an airflow rate of 1.03 m^3 min^{-1}. The sample collection in Xi'an
125 was performed on the roof of a three-story building in the urban center with a 1-hour interval for
126 each sample during the winter of 2012 (Wang et al., 2016). The sample collection in Beijing was
127 conducted during the winter of 2016 on the roof of a four-story building on the campus of China
128 Research Academy of Environmental Sciences, which is located at the northern part of Beijing.

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The $PM_{2.5}$ samples in Hebei Province were collected during the winter of 2016 on the roof of a three-story building on the campus of the Institute of Hydrology and Environmental Geology, which is located in Zhengding County of Hebei Province. Both sample collections in Beijing and Hebei Province were performed on a day/night basis. After collection, all samples were sealed individually in an aluminum foil bag and stored in a freezer below -18^{o}C prior to analysis.

The detailed procedures for the analysis of inorganic ions and water-soluble organic matter (WSOM) in aerosols have been reported elsewhere (Wang et al., 2009; Wang et al., 2010; Wang et al., 2017). Briefly, one part of the filter sample (area about 5 cm^2) was divided into several pieces, extracted with Mili-Q pure water, and determined for WSOM and inorganic ions by using Shimadzu TOC-L CPH analyzer and Dionex-600 ion chromatography, respectively. Oxalic acid in $PM_{2.5}$ was analyzed according to Wang et al. (2002) and Cheng et al. (2015). One part of the filter sample was extracted with Milli-Q water, concentrated to dryness, and reacted with 14% BF3/butanol at 100^{o}C for 1 hr. After the reaction, the derivatized sample was extracted with hexane for three times and concentrated into 1 mL. Oxalic acid in the samples was identified by gas chromatography–mass spectrometry (GC–MS) and quantified by gas chromatography (Agilent GC7890A).

3. Results

3.1 Aqueous oxidation of SO_2 by NO_2 with NH_3 neutralization

We first evaluated the factors controlling the aqueous phase oxidation of SO_2 by NO_2 using the environmental chamber method. The evolution in the size of ammonium sulfate particles after exposure to SO_2, NO_2, and NH_3 at different RH and SO_2 levels is shown in Figure 1. In our experiments, monodisperse particles with the initial dry particle size ranging from 50 to 70 nm were selected for the exposure, and two different SO_2 concentrations (37.5 and 375 parts per

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152 billions or ppb) were used. RH was maintained at a level of 80-98%, above the deliquescence
153 point (79%) of ammonium sulfate (Qiu and Zhang, 2013) to ensure aqueous particles. As is
154 shown in Figure 1, the size of $(NH_4)_2SO_4$ particles remains nearly invariant (within the
155 experimental uncertainty) after exposure to SO_2, NO_2, and NH_3. A 10-fold increase in the SO_2
156 concentration has little effect on the growth of $(NH_4)_2SO_4$ particles. These results illustrate that
157 sulfate production is insignificant and SO_2 cannot be efficiently oxidized by NO_2 in the presence
158 of NH_3 on aqueous ammonium sulfate particles. The measurement of negligible growth for
159 $(NH_4)_2SO_4$ particles exposed to SO_2, NO_2, and NH_3 at high RH is in contrast to the previous
160 work by Wang et al. (2016), which showed large size growth and significant sulfate production
161 for oxalic acid particles with NH_3 neutralization and under high RH conditions.

162 To gain an insight into such a difference in the size growth between $(NH_4)_2SO_4$ and oxalic
163 acid particles, we measured the hygroscopic growth of oxalic acid particles. Figure 2 displays the
164 measured hygroscopic growth factor (HGF) of oxalic acid, showing an exponential increase with
165 an increase in RH. The measured HGF value is close to unity at RH < 40% and increases from
166 1.1 at RH = 60% to 1.5 at RH = 90%. Our measured HGF for oxalic acid is consistent with the
167 previous studies by Prenni et al. (2001) and Mikhailov et al. (2009). On the other hand, another
168 earlier experimental study showed little growth for oxalic acid particles under high RH
169 conditions (Peng et al., 2001). The measurements of HGF also provide information on the
170 particle phase-state. As evident from Figure 2, oxalic acid particles mainly exist in a non-
171 aqueous phase at RH < 40% but in the aqueous phase at RH > 60%.

172 Our present experiments of aqueous oxidation of SO_2 by NO_2 were performed at similar
173 conditions as those by Wang et al. (2016), i.e., with comparable concentrations for SO_2, NO_2,
174 and NH_3 and in the same phase-state (aqueous) for the particles. On the other hand, the particle

acidity is clearly distinct between the two studies. Our present experiment is characterized by a lower pH value, since ammonium sulfate is rather acidic. For example, the pH value of 0.1M $(NH_4)_2SO_4$ solution is 5.5. The overall aqueous reaction between SO_2 and NO_2 in the presence of NH_3 is suggested as the following (Wang et al., 2016),

$$2NH_3(g) + SO_2(g) + 2NO_2(g) + 2H_2O(aq) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq) + 2HONO(g) \quad (1)$$

Since the solubility of SO_2 and NO_2 decreases markedly with increasing particle acidity (Seinfeld and Pandis, 2006; Zhang et al., 2015), the heterogeneous reaction between SO_2 and NO_2 is prohibited on acidic $(NH_4)_2SO_4$ particles. On the other hand, under the experimental conditions by Wang et al. (2016), the heterogeneous reaction between oxalic acid and NH_3 occurred on aqueous particles in the presence of NH_3, yielding ammonium oxalate. The ammonium oxalate is less acidic than ammonium sulfate. The pH value of 0.1 M ammonium oxalate is 6.5, which is one unit higher than that of ammonium sulfate. As a result, SO_2 readily dissolves into aqueous ammonium oxalate particles and is oxidized by NO_2 into SO_4^{2-}, which is consequently neutralized by NH_3 to produce $(NH_4)_2SO_4$. The resulting aqueous ammonium oxalate/$(NH_4)_2SO_4$ particles exhibit a lower acidity than that of $(NH_4)_2SO_4$ particles, responsible for a significant growth in the dry particle size and sulfate formation for the previous experiments by Wang et al. (2016).

Hence, the experimental studies of our present work and that by Wang et al. (2016) reveal that sulfate production on fine particles is dependent on several factors, including the particle hygroscopicity, phase-state, acidity, and RH, in addition to the gaseous concentrations of SO_2, NO_2, and NH_3. These experimental results indicate that the acidity and sulfate formation are distinct for organic seed and ammonium sulfate seed particles. While oxidation of SO_2 by NO_2 on aqueous $(NH_4)_2SO_4$ particles does not represent a viable mechanism because of a higher

198 acidity, significant sulfate production occurs on oxalic acid particles because of a lower acidity.

199 **3.2 Field measurements of WSOM in China**

200 Atmospheric measurements have shown that the occurrence of severe haze episodes in
201 China is accompanied with high RH conditions and $PM_{2.5}$ particles consist of large amounts of
202 secondary organic and inorganic compounds. We present additional field measurements of the
203 chemical composition of $PM_{2.5}$ in Beijing, Hebei Province, and Xi'an of China. Figure 3 shows
204 that the wintertime $PM_{2.5}$ samples collected at the three locations. It is evident that WSOM is
205 considerably enriched and their concentrations are comparable to those of the total inorganic ions
206 (Figure 3a and b). For example, the mass concentration of WSOM ranges from 10 to 60 μg m^{-3}
207 in Beijing and Hebei Province during the winter of 2016 and from 10 to 180 μg m^{-3} in Xi'an
208 during the winter of 2012 (Figure 3c and d, respectively). In addition, the variation of WSOM
209 displays a temporal pattern similar to that of oxalic acid, with a linear correlation coefficient of
210 0.79, 0.88 and 0.72 in Beijing, Hebei Province, and Xi'an, respectively (Figure 3e and f). The
211 mass concentration of oxalic acid in fine PM during the haze episodes is about 500 ng m^{-3} in
212 Beijing and Hebei Province (Figure 3e) and more than 2000 ng m^{-3} in Xi'an (Figure 3f). Hence,
213 our field measurements indicate that oxalic acid represents one of the most abundant WSOM in
214 the aerosol-phase. Oxalic acid, a secondary product formed from the photochemical oxidation of
215 volatile organic compounds, has been also shown to exist with large abundance in China (Wang
216 et al., 2012; Cheng et al., 2013; Meng et al., 2014; Kawamura and Bikkina, 2016). In addition,
217 the previous field measurements also revealed that WSOM in China is not only enriched in
218 carboxylic acids (including oxalic acid) but also in other organic species, including carbonyls,
219 amines, and water-soluble nitrogen-containing organic compounds (Wang et al., 2010, 2013;
220 Zheng et al., 2015; Yao et al., 2016; Liu et al., 2017). The dominant organic acids and bases

indicate that haze particles in China are multi-component in nature and the estimations of the particle acidity (or pH) and the sulfate production rate need to take into account of the effects of organic species, in addition to inorganic ions.

4. Discussions

Several recent studies using the thermodynamic models (Wexler and Clegg, 2002; Fountoukis and Nenes, 2007) estimated the particle acidity and sulfate production during pollution episodes in China (Cheng et al., 2016; Guo et al., 2017; Liu et al., 2017). Those previous studies treated the PM exclusively as a mixture of inorganic salts dominated by ammonium sulfate and neglected the effects due to the presence of organic compounds. Apparently, the conclusions by those modeling studies hinge on the validity of several critical assumptions in their analyses, including the application of the thermodynamic model, the accuracy in determining the aerosol water content (AWC), and the applicability of the earlier experimental measurements for the aqueous oxidation of SO_2 by NO_2 to atmospheric conditions.

Estimation of the pH values using the thermodynamic models is typically of considerable uncertainty, because of several intricate difficulties. For example, the ISORRPIA-II model includes two modes, i.e., metastable (aerosols are assumed to be in the liquid-phase only and may reach supersaturation) and stable (aerosols are assumed in the liquid- and solid phases that are in equilibrium) (Guo et al., 2017). Since the thermodynamic model is established on the basis of the equilibrium principles, its application to non-equilibrium conditions needs to be rigorously assessed. Also, the phase (e.g., liquid, amorphorous, or crystalline) and mixing state of ambient aerosols are highly complex because of the presence of multi-component organic and inorganic species (Qiu and Zhang, 2013; Zhang et al., 2015), inevitably rendering high uncertainty in the thermodynamic calculations.

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Guo et al. (2017) suggested that the pH predictions using the metastable mode would be more reliable than that using the stable mode, on the basis of model evaluation from measured and predicted NO_3^- and NH_4^+ during the winter of 2012 in Xi'an. Figure 4 compares the concentrations of NH_3 (g) and aerosol species predicted by ISORROPIA-II with the field measurements under the metastable and stable modes in Xi'an during the winter of 2012. As evident in Figure 4a and b, NH_3 predicted is similar to the measured value with the metastable or stable mode. Furthermore, the predicted concentrations of NO_3^- and NH_4^+ using both the metastable and stable modes are nearly identical (Figure 4c-f). Guo et al. (2017) only compared the liquid NH_4^+ and NO_3^- predicted by the model with the field measured aerosols composed of both liquid and solid compounds, and their predicted concentrations were lower than those of the measurements (see Figure S1 in Guo et al, 2017). As a result, their statement that pH prediction with the metastable mode would be more reliable than that with the stable mode was unjustified. Noticeably, the pH values estimated by the ISORROPIA-II model under the two modes are significantly different, with the values of 4.57±0.40 under the metastable mode and 6.96 ±1.33 under the stable mode. Most recently, it was suggested that the large discrepancy in predicting pH is attributable to the differences in the model assumptions (Song et al., 2018).

In addition, the pH estimation by the thermodynamic model is highly dependent on the ratio of the concentration of hydrogen ions in the liquid-phase to AWC. Guo et al. (2017) and Liu et al. (2017) assumed negligible particle water associated with the organic aerosol mass. Such an assumption is clearly invalid since aerosols typically contain a large portion of WSOM in China (Fig. 3), including organic nitrogen species (Wang et al., 2010, 2013) and acids (Wang et al., 2006, 2009, 2010). Also, organic acids engage in particle-phase reactions with the basic species (i.e., NH_3 and amines), significantly enhancing the particle hygroscopicity and reducing the

acidity (Gomez-Hernandez et al., 2016). In addition, because of their strong basicity and high abundance, amines likely play a key role in reducing the particle-acidity in China (Wang et al., 2010a, b; Qiu et al., 2011; Qiu and Zhang, 2012; Dong et al., 2013; Zheng et al., 2015; Yao et al., 2016; Liu et al., 2017). Consequently, the acidity for organics-dominated aerosols is considerably different from that of ammonium sulfate aerosols, as demonstrated in our experimental results. While effort has been made to account for the effects of organic species on the aerosol properties (Clegg et al., 2013), the available thermodynamic models are still inadequate in representing complex multi-component aerosols. An inconsistency of the ammonium–sulfate ratios using the thermodynamic models was identified in the eastern US, also suggesting a possible role for organic species (Silvern et al., 2017).

Furthermore, the chemical mechanism leading to the aqueous conversion of SO_2 to sulfate by NO_2 is not well understood. The previous modeling studies adopted the aqueous reaction rate constants previously measured (Lee and Schwartz, 1983; Clifton et al., 1988), while the applicability of the earlier experimental studies to atmospheric conditions is uncertain. For example, Lee and Schwartz (1983) examined the oxidation of S(IV) by NO_2 in the liquid phase by flowing gaseous NO_2 through a $NaHSO_3$ solution at a constant pH by regulating NaOH and determined the rate constant of 1.4×10^5 M^{-1} s^{-1} at pH = 5 and with a lower limit of 2×10^6 M^{-1} s^{-1} at pH = 5.8 and 6.4 from measuring the electrical conductivity of the solution. Clifton et al. (1988) measured the rate constant for the reaction of NO_2 with S(IV) over the pH range of 5.3-13, by producing NO_2 from irradiation of $NaNO_2$ and N_2O solutions and mixing with Na_2SO_3 solutions, and obtained the second-order rate constant of 1.24×10^7 and 2.95×10^7 M^{-1} s^{-1} from the decay of NO_2 monitored by absorption spectroscopy. The results of the measured rate constants between the two earlier experimental measurements differed by 1-2 orders of

magnitude (Lee and Schwartz, 1983; Clifton et al., 1988). Also, both kinetic experiments employed bulk solutions and did not account for the gaseous uptake process (Lee and Schwartz, 1983; Clifton et al., 1988).

Wang et al. (2016) obtained the SO_2 uptake coefficient for sulfate production from combined field measurements and laboratory experiments, and their laboratory experiments using aqueous oxalic acid particles reproduced the rapid sulfate production measured under polluted ambient conditions. The results of the SO_2 uptake coefficients determined by Wang et al. (2016) are consistent with the modeling studies in quantification of the sulfate formation using atmospheric models in China (e.g., Wang et al., 2014). On the other hand, Liu et al. (2017) invoked the experimental work by Hung et al. (2015) as a plausible cause for rapid SO_2 oxidation by O_2 in the absence of photochemistry, but without noting the high acidity as a necessary condition in that experimental work (i.e., pH $\leqslant$ 3). Most recently, Li et al. (2018) suggested an indirect mechanism of SO_2 oxidation by NO_2 via HONO/NO_2^- produced in fast-hydrolytic disproportionation of NO_2 on the surface of $NaHSO_3$ aqueous microjets. In addition, another recent theoretical work by Zhang et al. (2018) indicated that under weakly acidic and neutral conditions (pH $\leq$ 7) the oxidation of $HOSO_2^-$ by dissolved NO_2 is a self-sustaining process, where the produced *cis*-HONO, HSO_4^- and H_2SO_4 promote the tautomerization from HSO_3^- to $HOSO_2^-$ as the catalysts.

5. Conclusions

In this paper we have presented experimental measurements of the growth of ammonium sulfate seed particles exposed to vapors of SO_2, NO_2, and NH_3 at variable RH, the HGF of oxalic acid particles, and field measurements of WSOM for $PM_{2.5}$ during the severe haze events in Beijing, Hebei Province, and Xi'an of China. Our experimental results reveal that sulfate

313 production on fine particles is dependent on the particle hygroscopicity, phase-state, and acidity,
314 as well as RH. The acidity and sulfate formation for ammonium sulfate seed particles are distinct
315 from those of oxalic acid seed particles. Aqueous ammonium sulfate particles show negligible
316 growth because of low pH, in contrast to aqueous oxalic acid particles with significant dry-size
317 increase and sulfate formation because of high pH. In addition, our atmospheric measurements
318 show significant concentrations of WSOM (including oxalic acid) in fine PM, indicating multi-
319 component haze particles in China. Our results reveal that a particle mixture of inorganic salts
320 adopted by the previous studies using the thermodynamic model does not represent a suitable
321 model system and that the particle acidity and aqueous sulfate formation rate cannot be reliably
322 inferred without accounting for the effects of multi-chemical compositions during severe haze
323 events in China. Our combined experimental and field measurements corroborate the earlier
324 finding that sulfate production via the particle-phase reaction involving SO_2 and NO_2 with NH_3
325 neutralization occurs efficiently on organics-dominated aerosols (Wang et al., 2016) but are in
326 contradiction to the most recent studies using the thermodynamic model (Guo et al., 2017; Liu et
327 al., 2017).

328 In conclusion, while the particle acidity or pH cannot be accurately determined from
329 atmospheric field measurements or calculated using the thermodynamic models, our combined
330 experimental and field results provide the compelling evidence that the pH value of ambient
331 organics-dominated particles is sufficiently high to promote SO_2 oxidation by NO_2 with NH_3
332 neutralization under polluted conditions in China.

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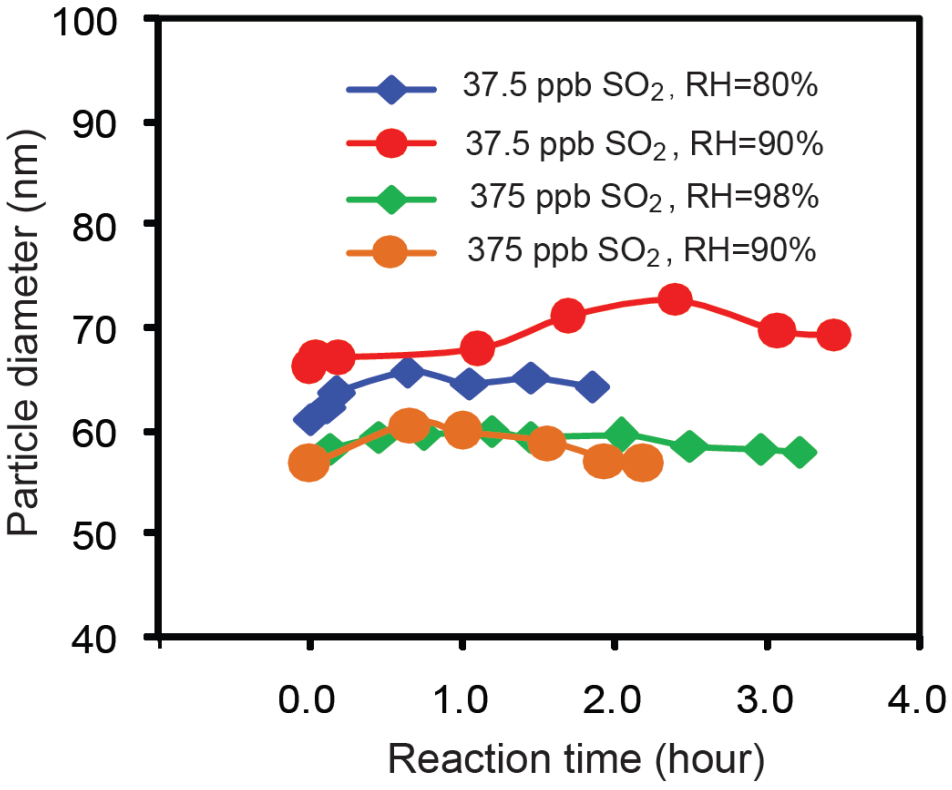

Figure 1. Size evolution of ammonium sulfate particles after exposure to SO_2, NO_2, and NH_3 at different RH levels. Variations in mobility diameter (D_p) of ammonium sulfate particles as a function of reaction time. The symbols with different colors denote measurements with exposure to different SO_2 concentrations and RH levels. In all cases, the NO_2 concentration is 375 ppb, and the NH_3 concentration is 500 ppb.

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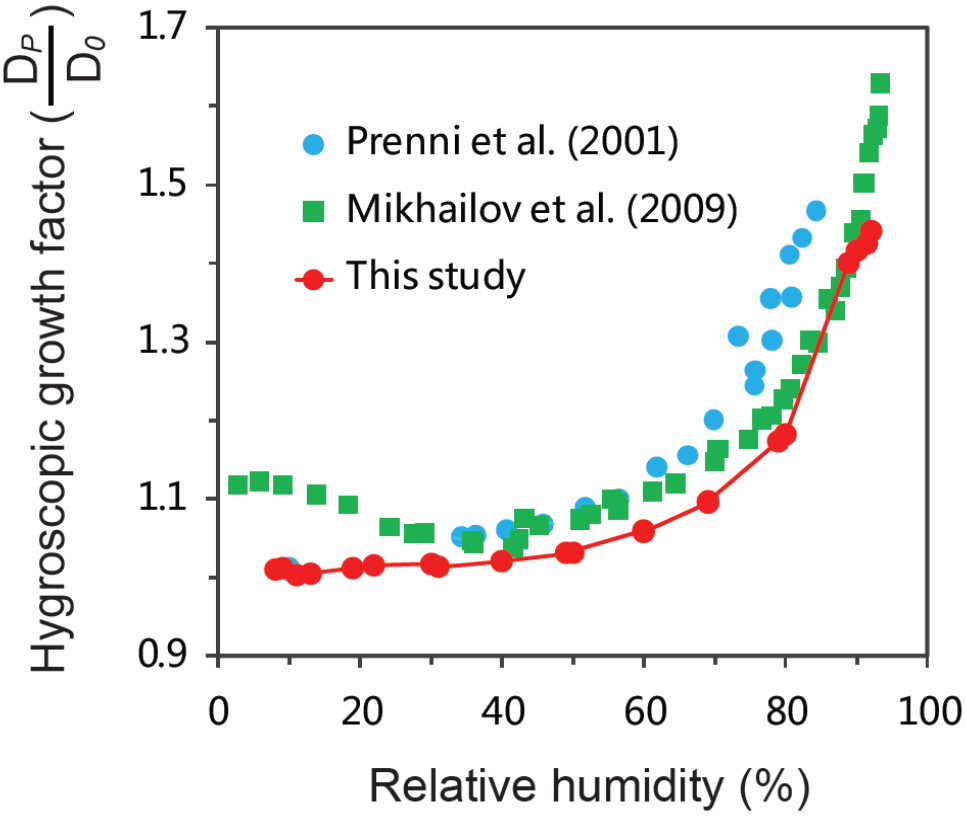

Figure 2. Measured hygroscopic growth factor (HGF) of oxalic acid particles at different RH conditions. D_p is the particle diameter at an elevated RH, and D_0 (100nm) is the initial diameter of oxalic acid particles at RH = 8%.

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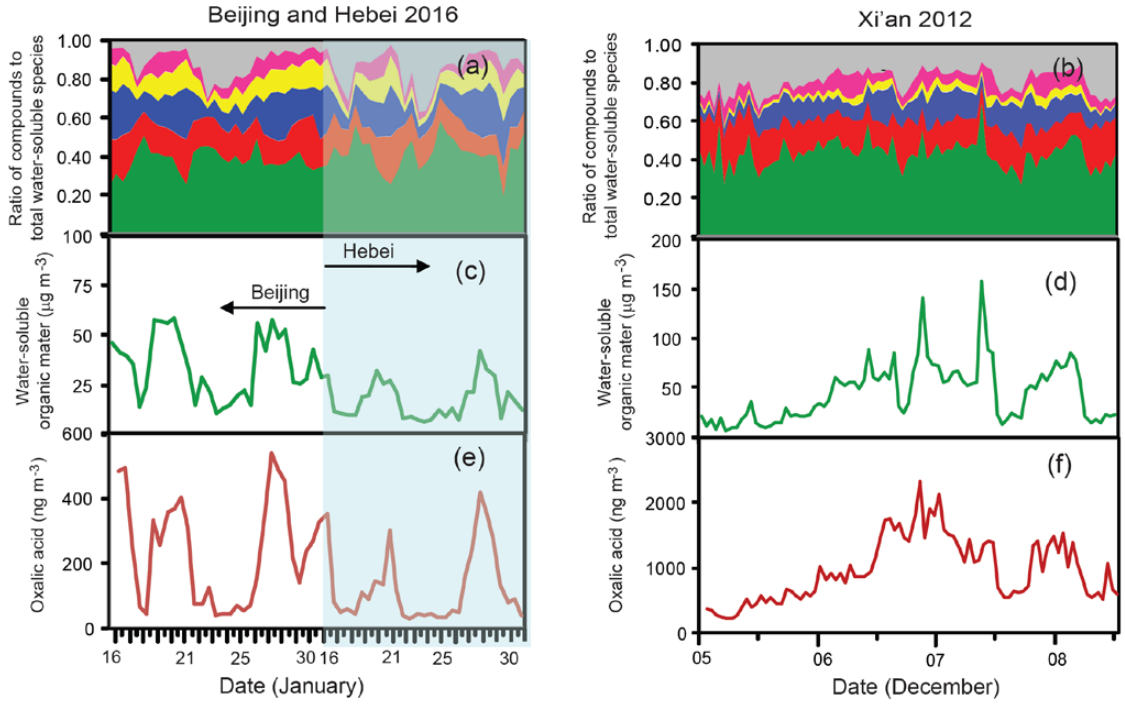

Figure 3. Measurements of water-sluble organic matter (WSOM) of $PM_{2.5}$ collected in Beijing and Hebei Province during the winter of 2016 (left panels: a, c and e) and in Xi'an during the winter of 2012 (right panels: b, d and f). In (a) and (b), the green, red, blue, yelow, pink, and gray colors represent WSOM, sulfate, nitrate, ammonium, chloride, and the others (i.e., the sum of $Na^+ + Ca^{2+} + Mg^{2+} + K^+$), respectively.

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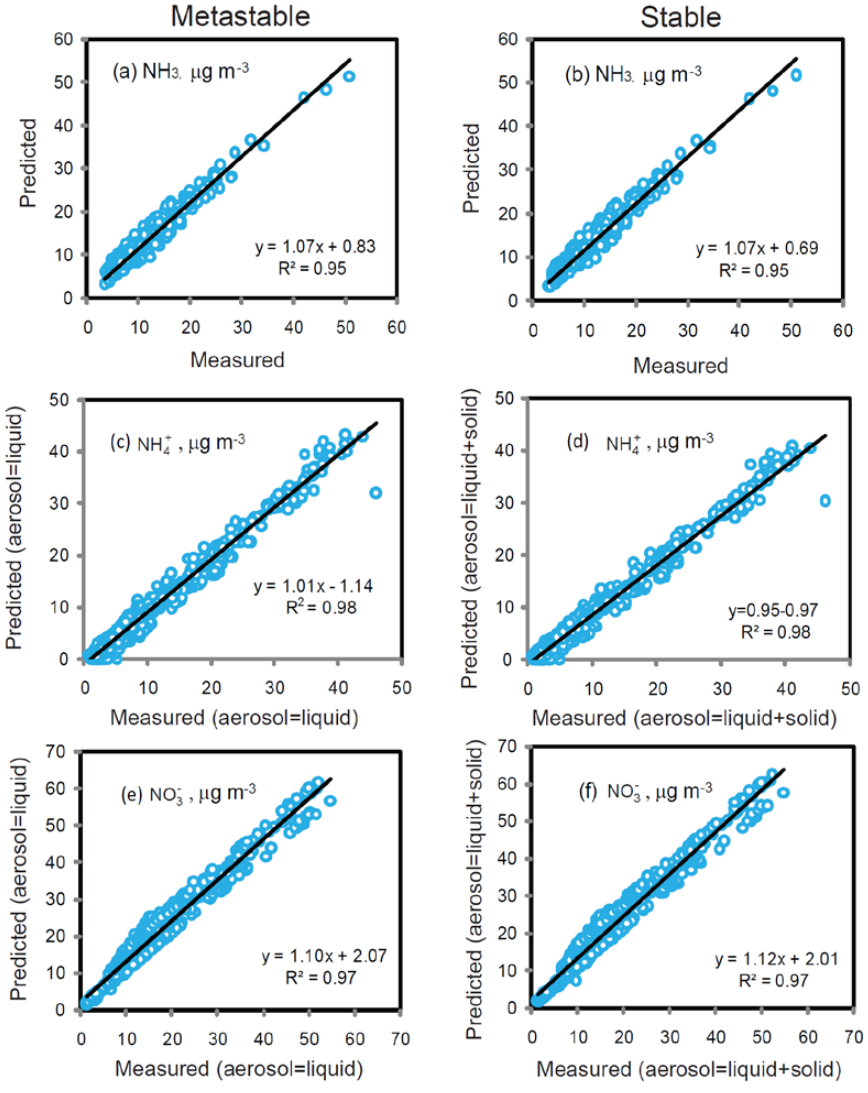

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538 Figure 4. Comparison of measured NH_3, NH_4^+, and NO_3^- concentrations with those predicted by
539 ISORROPIA-II model using the forward mode under the metastable (left panels) and stable
540 assumptions (right panels).
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