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. Gehui Wang, E-mail : ghwang@geo.ecnu.edu.cn, or wanggh@ieecas.cn
Prof. Renyi Zhang, E-mail: renyi-zhang@tamu.edu

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, in contrast to aqueous oxalic acid particles with significant sulfate production. 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.

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

84 severe haze events in China using the thermodynamic model (Cheng et al., 2016; Guo et al.,
85 2017; Liu et al., 2017). For example, Cheng et al. (2016) estimated a pH range of 5.4 to 6.2 using
86 a thermodynamic model (ISORROPIA-II) in Beijing. On the basis of their estimated pH and the
87 previous experimental rates of SO_2 oxidation by NO_2 and the Henry's Law constants for sulfur
88 dioxide (SO_2), bisulfite (HSO_3^-), and sulfite (SO_3^{2-}) from the literature (Lee and Schwartz, 1983;
89 Clifton et al., 1988; Seinfeld and Pandis, 2006), the authors derived a sulfate production rate and
90 concluded that reactive nitrogen chemistry in aerosol water explained the sulfate formation
91 during polluted periods in Beijing. In contrast, other recent studies by Guo et al. (2017) and Liu
92 et al. (2017) adopted the similar method as Cheng et al. (2016), but reported significantly
93 different values of pH and the sulfate formation rates by the aqueous SO_2 oxidation by NO_2 in
94 China. Those two later studies determined a pH range of 3.0-4.9 and suggested that fine particles
95 were moderately acidic and the aqueous SO_2 oxidation by NO_2 was unimportant during severe
96 wintertime haze periods in China.
97 In this article, we conducted laboratory measurements of the hygroscopicity for oxalic acid
98 particles and particle growth of ammonium sulfate particles upon exposure to SO_2, NO_2, and
99 NH_3 at high RH conditions, in order to evaluate the dominant factors regulating the aqueous
100 oxidation of SO_2 by NO_2. In addition, field measurements of chemical compositions of water-
101 soluble fraction for fine PM (including oxalic acid) in Beijing, Hebei Province, and Xi'an of
102 China were performed during the winter haze episodes, showing significantly enriched water-
103 soluble organic matter (WSOM). The implications for the multi-aerosol chemical compositions
104 on the pH value and sulfate production during winter pollution periods in China are discussed.

105 **2. Methods**

106 **2.1 Aqueous phase oxidation of SO_2 by NO_2 in an environmental chamber**

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

2.2 Measurement of hygroscopic growth factor of oxalic acid

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

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

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

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. During the sampling periods temperatures were -6.0±4.0 ^{o}C (-15–1.0^{o}C), -4.0±3.0 ^{o}C (-12–2.0^{o}C) and 1.6±4.4 ^{o}C (-5.4–15^{o}C) in Beijing, Hebei Province and Xi'an, respectively, while relative humidity at the three sites (RH) were 37±18% (16–87%),46±21% (16–87%) and 59± 21% (15–95%), respectively. Previous observations showed that coal combustion, biomass burnings and vehicle exhausts are the three major sources of $PM_{2.5}$ during winter in North China including Beijing, Hebei Province and Xi'an (Li et al., 2016; Zhang et al., 2015).

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

To gain an insight into such a difference in the size growth between $(NH_4)_2SO_4$ and oxalic acid particles, we measured the hygroscopic growth of oxalic acid particles. Figure 2 displays the measured hygroscopic growth factor (HGF) of oxalic acid, showing an exponential increase with an increase in RH. The measured HGF value is close to unity at RH < 40% and increases from 1.1 at RH = 60% to 1.5 at RH = 90%. Our measured HGF for oxalic acid is consistent with the previous studies by Prenni et al. (2001) and Mikhailov et al. (2009); all of which were measured

by using a hygroscopicity tandem differential mobility analyzer (HTDMA) system. On the other hand, another earlier experimental study showed little growth for oxalic acid particles under high RH conditions by using an electrodynamic balance (EDB) system (Peng et al., 2001). The different HGF measured for oxalic acid is most likely due to the different accuracies of the two types of methods for the hygroscopicity measurement. The measurements of HGF also provide information on the particle phase-state. As evident from Figure 2, oxalic acid particles mainly exist in a non-aqueous phase at RH < 40% but in the aqueous phase at RH > 60%.

Our present experiments of aqueous oxidation of SO_2 by NO_2 were performed at similar conditions as those by Wang et al. (2016), i.e., with comparable concentrations for SO_2, NO_2, 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 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 expected to be less acidic than ammonium sulfate, because for a bulk solution the pH value of 0.1 M ammonium oxalate is 6.5 and 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

199 SO_4^{2-}, which is consequently neutralized by NH_3 to produce $(NH_4)_2SO_4$. The resulting aqueous
200 ammonium oxalate/$(NH_4)_2SO_4$ particles, which is internally mixed, exhibit a lower acidity than
201 that of pure $(NH_4)_2SO_4$ particles, responsible for a significant growth in the dry particle size and
202 sulfate formation for the previous experiments by Wang et al. (2016).

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

210 **3.2 Field measurements of WSOM in China**

211 Atmospheric measurements have shown that the occurrence of severe haze episodes in
212 China is accompanied with high RH conditions and $PM_{2.5}$ particles consist of large amounts of
213 secondary organic and inorganic compounds. We present additional field measurements of the
214 chemical composition of $PM_{2.5}$ in Beijing, Hebei Province, and Xi'an of China. Figure 3 shows
215 that the wintertime $PM_{2.5}$ samples collected at the three locations. It is evident that WSOM is
216 considerably enriched and their concentrations are comparable to those of the total inorganic ions
217 (Figure 3a and b). For example, the mass concentration of WSOM ranges from 10 to 60 μg m^{-3}
218 in Beijing and Hebei Province during the winter of 2016 and from 10 to 180 μg m^{-3} in Xi'an
219 during the winter of 2012 (Figure 3c and d, respectively). Compared to those in Beijing and
220 Hebei Province, the more abundant WSOM in Xi'an was caused by more emissions from
221 biomass burning for house heating (Li et al., 2016). As seen in Figure 3c–f, the variation of

WSOM displays a temporal pattern similar to that of oxalic acid, with a linear correlation coefficient of 0.79, 0.88 and 0.72 in Beijing, Hebei Province, and Xi'an, respectively (Figure 3e and f). The mass concentration of oxalic acid in fine PM during the haze episodes is about 500 ng m^{-3} in Beijing and Hebei Province (Figure 3e) and more than 2000 ng m^{-3} in Xi'an (Figure 3f). Hence, our field measurements indicate that oxalic acid represents one of the most abundant WSOM in the aerosol-phase. Oxalic acid is a secondary product formed from the aqueous-phase oxidation of water-soluble organic precursors and ubiquitously exists in the troposphere. Like other pollutants, oxalic acid has been also shown to occur with large abundance in China (Wang et al., 2012; Cheng et al., 2013; Meng et al., 2014; Kawamura and Bikkina, 2016). As shown in Figure 3g and h, during the field observation periods sulfate at the three sites showed a temporal variation pattern similar to that of oxalic acid with a robust linear correlation (r^2=0.67, 0.84 and 0.61 in Xi'an, Beijing and Hebei Province, respectively). Such a correlation was also reported by other researchers (Wang et al, 2017, Yu et al, 2005), suggesting the cooccurrence and internally mixing state of both compounds in the atmosphere. In addition, the previous field measurements also revealed that WSOM in China is not only enriched in carboxylic acids (including oxalic acid) but also in other organic species, including carbonyls, amines, and water-soluble nitrogen-containing organic compounds (Wang et al., 2010, 2013; 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.

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 (Fig. 4c-f). Guo et al. (2017) only compared the liquid NH_4^+ and NO_3^- predicted by the model under the stable mode with the field measured aerosols composed of both liquid and solid compounds, and thus 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 model code errors (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 in China. The SO_2 uptake coefficient on oxalic acid particles in the laboratory reaction chamber is $8.3\pm5.7x10^{-5}$ (Wang et al., 2016) under the humid conditions and similar to that ($4.5\pm1.1 \times 10^{-5}$) (Wang et al., 2016) observed in Beijing during the haze period of 2015. The results of the SO_2 uptake coefficients determined by Wang et al. (2016) are also consistent with the modeling studies in quantification of the sulfate formation using atmospheric models in the country (e.g., Wang et al., 2014), indicating the applicability of their proposed mechanism to haze conditions in China. 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 production on fine particles is dependent on the particle hygroscopicity, phase-state, and acidity,

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

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

Acknowledgements

Financial support for this work was provided by National Key R&D Plan (Quantitative Relationship and Regulation Principle between Regional Oxidation Capacity of Atmospheric and Air Quality (No. 2017YFC0210000), the China National Natural Science Funds for

Distinguished Young Scholars (No.41325014), the program from National Nature Science Foundation of China (No. 41773117). This work was also supported by the Robert A. Welch Foundation (Grant A-1417) W.M.-O. was supported by the National Science Foundation Graduate Research Fellowship Program.

References

Cheng, C., Wang, G., Zhou, B., Meng, J., Li, J., Cao, J., and Xiao, S.: Comparison of dicarboxylic acids and related compounds in aerosol samples collected in Xi'an, China during haze and clean periods, Atmospheric Environment, 81(0), 443-449, 2013.

Cheng, C., Wang, G., Meng, J., Wang, Q., Cao, J., Li, J., and Wang, J.: Size-resolved airborne particulate oxalic and related secondary organic aerosol species in the urban atmosphere of Chengdu, China, Atmospheric Research, 161–162, 134-142, 2015.

Cheng, Y., Zheng, G., Wei, C., Mu, Q., Bo Zheng, Wang, Z., Gao, M., Zhang, Q., He, K., Carmichae, G., Pöschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Science Advances, 2, e1601530, 2016.

Clegg, S.L., Qiu, C., Zhang, R.: The deliquescence behaviour, solubilities, and densities of aqueous solutions of five methyl- and ethyl-aminium sulphate salts, Atmospheric Environment, 73, 1-14, 2013.

Clifton, C. L., Altstein, N., and Huie, R. E.: Rate constant for the reaction of nitrogen dioxide with sulfur(IV) over the pH range 5.3-13, Environmental Science & Technology, 22, 586-589, 1988.

Dong, X. L., Liu, D. M., and Gao, S. P.: Seasonal variations of atmospheric heterocyclic aromatic amines in Beijing, China, Atmospheric Research, 120, 287-297, 2013.

Fountoukis, C., and Nenes, A.: ISORROPIA II: A computationally efficient thermodynamic equilibrium model for K^+-Ca^{2+}-Mg^2+-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosols, Atmospheric Chemistry and Physics, 7, 4639-4659, 2007.

Gomez-Hernandez, M., McKeown, M., Secrest, J., Marrero-Ortiz, W., Lavi, A., Rudich, Y., Collins, D. R., and Zhang, R.: Hygroscopic characteristics of alkylaminium carboxylate Aerosols, Environmental Science & Technology, 50, 2292-2300, 2016.

Guo, H., Weber, R. J., and Nenes, A.: High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Scientific Reports, 7, 12109, doi:12110.11038/s41598-12017-11704-12100, 2017.

Guo, H., Liu, J., Froyd, K. D., Roberts, J. M., Veres, P. R., Hayes, P. L., Jimenez, J. L., Nenes, A., and Weber, R. J.: Fine particle pH and gas–particle phase partitioning of inorganic species in Pasadena, California, during the 2010 CalNex campaign, Atmospheric Chemistry and Physics, 17, 5703-5719, 2017.

Guo, S., Hu, M., Zamora, M. L., Peng, J. F., Shang, D. J., Zheng, J., Du, Z. F., Wu, Z., Shao, M., Zeng, L. M., Molina, M. J., and Zhang, R. Y.: Elucidating severe urban haze formation in China, Proceedings of the National Academy of Sciences of the United States of America, 111, 17373-17378, 2014.

Hung, H.-M., and Hoffman, M. R.: Oxidation of gas-phase SO2 on the surfaces of acidic microdroplets: Implications for sulfate and sulfate radical anion formation in the atmospheric liquid phase, Environmental Science & Technology, 49, 13768-13776, 2015.

Kawamura, K., and Bikkina, S.: A review of dicarboxylic acids and related compounds in atmospheric aerosols: Molecular distributions, sources and transformation, Atmospheric Research, 170, 140-160, 2016.

Khalizov, A.F., Zhang, R., Zhang, D. Xue, H., Pagels, J., and McMurry, P.H.: Formation of highly hygroscopic aerosols upon internal mixing of airborne soot particles with sulfuric acid vapor, Journal of Geophysical Research-Atmospheres, 114, D05208, doi:10.1029/2008JD010595, 2009.

Lee, Y. N., and Schwartz, S. E.: Kinetics of oxidation of aqueous sulfur (IV) by nitrogen dioxide, in Precipitation scavenging, dry deposition, and resuspension, edited by H. R. Pruppacher, R. G. Semmon and W. G. N. Slinm, Elsevier, New York, 1983.

Li, J., Wang, G., Ren, Y., Wang, J., Wu, C., Han, Y., Zhang, L., Cheng, C., and Meng, J.: Identification of chemical compositions and sources of atmospheric aerosols in Xi'an, inland China during two types of haze events, Science of the Total Environment, 566-567, 230-237, 2016..

Li, L., Hoffmann, M. R., and Colussi, A. J.: The role of nitrogen dioxide in the production of sulfate during Chinese haze-aerosol episodes, Environmental Science & Technology 52, DOI: 10.1021/acs.est.7b05222, 2018.

Liu, F., Bi, X., Zhang, G., Peng, L., Lian, X., Lu, H., Fu, Y., Wang, X., Peng, P. a., and Sheng, G.: Concentration, size distribution and dry deposition of amines in atmospheric particles of urban Guangzhou, China, Atmospheric Environment, 171, 279-288, 2017.

Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in Northern China, Geophysical Research Letters, 44, 5213-5221 ,doi: 5210.1002/2017GL073210, 2017.

Meng, J., Wang, G., Li, J., Cheng, C., Ren, Y., Huang, Y., Cheng, Y., Cao, J., and Zhang, T.: Seasonal characteristics of oxalic acid and related SOA in the free troposphere of Mt. Hua, central China: Implications for sources and formation mechanisms, Science of the Total Environment, 493, 1088-1097, 2014.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Poeschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmospheric Chemistry and Physics, 9, 9491-9522, 2009.

Pagels, J., McMurry, P.H., Khalizov, A.F., and Zhang, R.: Processing of soot by controlled sulphuric acid and water condensation—Mass and mobility relationship, Aerosol Science & Technology, 43, 629–640, 2009.

Peng, J., Hu, M., Guo, S., Du, Z., Zheng, J., Shang, D., Zamora, M.L., Zeng, L., Shao, M., Wu, Y., Zheng, J., Wang, Y., Glen, C.R., Collins, D.R., Molina, M.J., and Zhang, R.: Markedly enhanced absorption and direct radiative forcing of black carbon under polluted urban environments, Proceedings of the National Academy of Sciences of the United States of America, 113, 4266–4271, 2016.

Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multifunctional acids: measurements and UNIFAC predictions, Environmental Science & Technology, 35, 4495-4501, 2001.

Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Sherman, D. E., Russell, L. M., and Ming, Y.: The effects of low molecular weight dicarboxylic acids on cloud formation, Journal of Physical Chemistry A, 105, 11240-11248, 2001.

Qiu, Q., Wang, L., Lal, V., Khalizov, A.F., and Zhang, R.: Heterogeneous chemistry of Alkylamines on Ammonium Sulfate and Ammonium Bisulfate, Environmental Science & Technology, 45, 4748–4755, 2011.

Qiu, C., and Zhang, R.: Physiochemical Properties of Alkylaminium Sulfates: Hygroscopicity, Thermostability, and Density, Environmental Science & Technology, 46, 4474-4480, 2012.

Qiu, C., and Zhang, R. Y.: Multiphase chemistry of atmospheric amines, Physical Chemistry Chemical Physics, 15(16), 5738-5752, 2013.

Seinfeld, J. H., and Pandis, S. N., *Atmospheric Chemistry and Physics: From Air Pollution to*

Climate Change, 2nd ed., John Wiley & Sons, Hoboken, NJ, 2006.
Silvern, R.F., Jacob, D.J., Kim, P.S., Marais, E.A., Turner, J. R., Campuzano-Jost, P., and Jimenez, J. L. Inconsistency of ammonium–sulfate aerosol ratios with thermodynamic models in the eastern US: a possible role of organic aerosol, Atmospheric Chemistry and Physics, 17, 5107–5118, 2017.
Song, S., Gao, M., Xu, W., Shao, J., Shi, G., Wang, S., Wang, Y., Sun, Y., and McElroy, M. B.: Fine particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atmospheric Chemistry and Physics Discussions, https://doi.org/10.5194/acp-2018-6, 2018.
Sun, Y. L., Wang, Z. F., Fu, P. Q., Yang, T., Jiang, Q., Dong, H. B., Li, J., and Jia, J. J.: Aerosol composition, sources and processes during wintertime in Beijing, China, Atmospheric Chemiatry and Physics, 13(9), 4577-4592, 2013.
Wang, G., Xie, M., Hu, S., Tachibana, E., and Kawamura, K.: Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: Implications for dust and coal burning emission and secondary aerosol formation, Atmospheric Chemistry and Physics, 10, 6087-6096, 2010.
Wang, G., Kawamura, K., Umemoto , N., Xie, M., Hu, S., and Wang, Z.: Water-soluble organic compounds in PM2.5 and size-segregated aerosols over Mt. Tai in North China Plain, Journal of Geophysical Research-Atmospheres, 114, D19208, dio.19210.11029/12008JD011390, 2009.
Wang, G., Kawamura, K., Cao, J., Zhang, R., Cheng, C., Li, J., Zhang, T., Liu, S., and Zhao, Z.: Molecular distribution and stable carbon isotopic composition of dicarboxylic acids, ketocarboxylic acids and a-dicarbonyls in size-resolved atmospheric particles from Xi'an city, China, Environmental Science & Technology, 46, 4783-4791, 2012.
Wang, G., Zhang, R., Zamora, M. L., Gomez, M. E., Yang, L., Hu, M., Lin, Y., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Wang, J., Marrero-Ortiz, W., Tian, P., Secrest, J., Peng, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent Sulfate Formation from London Fog to Chinese Haze, Proceedings of National Academy of Science of United States of America, 113(48), 13630-13635, doi/13610.11073/pnas.1616540113, 2016.
Wang, G. H., Niu, S. L., Liu, C., and Wang, L. S.: Identification of dicarboxylic acids and aldehydes of PM10 and PM2.5 aerosols in Nanjing, China, Atmospheric Environment, 36(12), 1941-1950, 2002.
Wang, G. H., Kawamura, K., Watanabe, T., Lee, S. C., Ho, K. F., and Cao, J. J.: Heavy loadings and source strengths of organic aerosols in China, Geophysical Research Letters, 33, L22801, doi:22810.21029/22006GL027624, 2006.
Wang, G. H., Zhou, B. H., Cheng, C. L., Cao, J. J., Li, J. J., Meng, J. J., Tao, J., Zhang, R. J., and Fu, P. Q.: Impact of Gobi desert dust on aerosol chemistry of Xi'an, inland China during spring 2009: differences in composition and size distribution between the urban ground surface and the mountain atmosphere, Atmospheric Chemistry and Physics, 13(2), 819-835, 2013.
Wang, J., Wang, G., Gao, J., Wang, H., Ren, Y., Li, J., Zhou, B., Wu, C., Zhang, L., Wang, S., and Chai, F.: Concentrations and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before, during, and after the 2014 APEC, Atmospheric Chemistry

and Physics, 17(2), 981-992, 2017.
Wang, L., Lal, V., Khalizov, A.F., and Zhang, R.: Heterogeneous chemistry of alkylamines with sulfuric acid: Implications for atmospheric formation of alkylaminium sulfates, Environmental Science & Technology, 44, 2461–2465, 2010a.
Wang, L., Khalizov, A.F., Zheng, J., Xu, W., Lal, V., Ma, Y., and Zhang, R.: Atmospheric nanoparticles formed from heterogeneous reactions of organics, Nature Geoscience, 3, 238-242, 2010b.
Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B., He, K., Duan, F., Zhan, Q., Philip, S., and Xie1, Y.: Enhanced sulfate formation during China's severe winter haze episode in January 2013 missing from current models, Journal Geophysical Research-Atmospheres, 119(17), 10425-10440, doi:10410.11002/12013JD021426, 2014.
Wexler, A.S., and Clegg, S. L.: Atmospheric aerosol models for systems including the ions H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, Br^- and H_2O. Journal of Geophysical Research, 107 (D14), 4207, doi:10.1029/2001JD000451, 2002.
Yao, L., Wang, M.-Y., Wang, X.-K., Liu, Y.-J., Chen, H.-F., Zheng, J., Nie, W., Ding, A.-J., Geng, F.-H., Wang, D.-F., Chen, J.-M., Worsnop, D. R., and Wang, L.: Detection of atmospheric gaseous amines and amides by a high-resolution time-of-flight chemical ionization mass spectrometer with protonated ethanol reagent ions, Atmospheric Chemistry and Physics, 16(22), 14527-14543, 2016.
Yu, J. Z., Huang, X. F., Xu, J. H., and Hu, M.: When aerosol sulfate goes up, so does oxalate: Implication for the formation mechanisms of oxalate, Environmental Science & Technology, 39(1), 128-133, 2005.
Zhang, R., Wang, G., Guo, S., Zamora, M. L., Ying, Q., Lin, Y., Wang, W., Hu, M., and Wang, Y.: Formation of urban fine particulate matter, Chemical Reviews, 115, 3803-3855, doi:3810.1021/acs.chemrev.3805b00067, 2015.
Zhang, H., Chen, S., Zhong, J., Zhang, S., Zhang, Y., Zhang, X., Li, Z., and Zeng, X.C.: Formation of aqueous-phase sulfate during the haze period in China: Kinetics and atmospheric implications, Atmospheric Environment, 177, 93-99, 2018.
Zheng, J., Ma, Y., Chen, M., Zhang, Q., Wang, L., Khalizov, A. F., Yao, L., Wang, Z., Wang, X., and Chen, L.: Measurement of atmospheric amines and ammonia using the high resolution time-of-flight chemical ionization mass spectrometry, Atmospheric Environment, 102, 249-259, 2015.

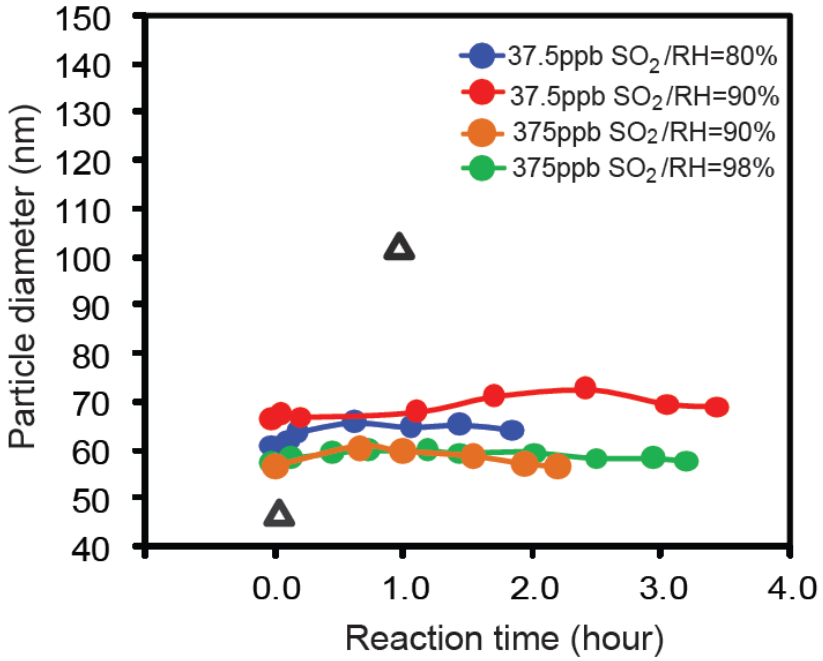

Figure 1**.** Size evolution of ammonium sulfate (circle dots) and oxalic acid (black triangles) particles after exposure to SO_2, NO_2, and NH_3 at different RH levels. Variations in mobility diameter (D_p) of the particles as a function of reaction time. The symbols with different colors denote measurements with exposure to different SO_2, NO_2 and NH_3 concentrations and RH levels. For the ammonium sulfate particles exposure experiment, two levels of SO_2 were used,, which are 37.5 ppb and 375 ppb, respectively, while the NO_2 concentration is 375 ppb, and the NH_3 concentration is 500 ppb. For the oxalic acid particles exposure experiment, the SO_2 concentration is 250 ppb, the NO_2 concentration is 250 ppb, and the NH_3 concentration is 1 ppm (The data of oxalic acid growth are cited from the previous study by Wang et al (2016)).

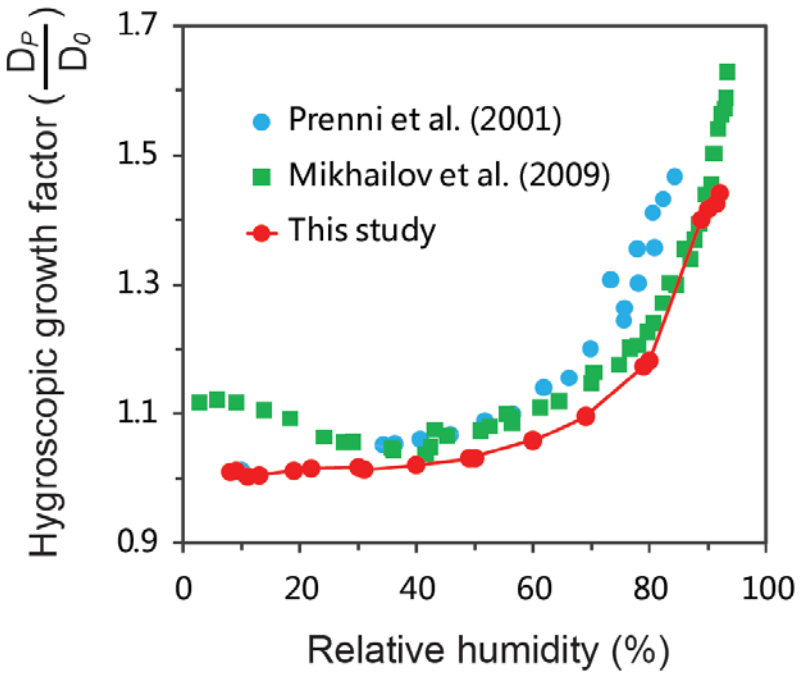

Figure 2. Measured hygroscopic growth factor (HGF) of oxalic acid particles at different RH conditions. D_p is the particle diameter at an elevated RH, and D_0 (100nm) is the initial diameter of oxalic acid particles at RH = 8%.

.

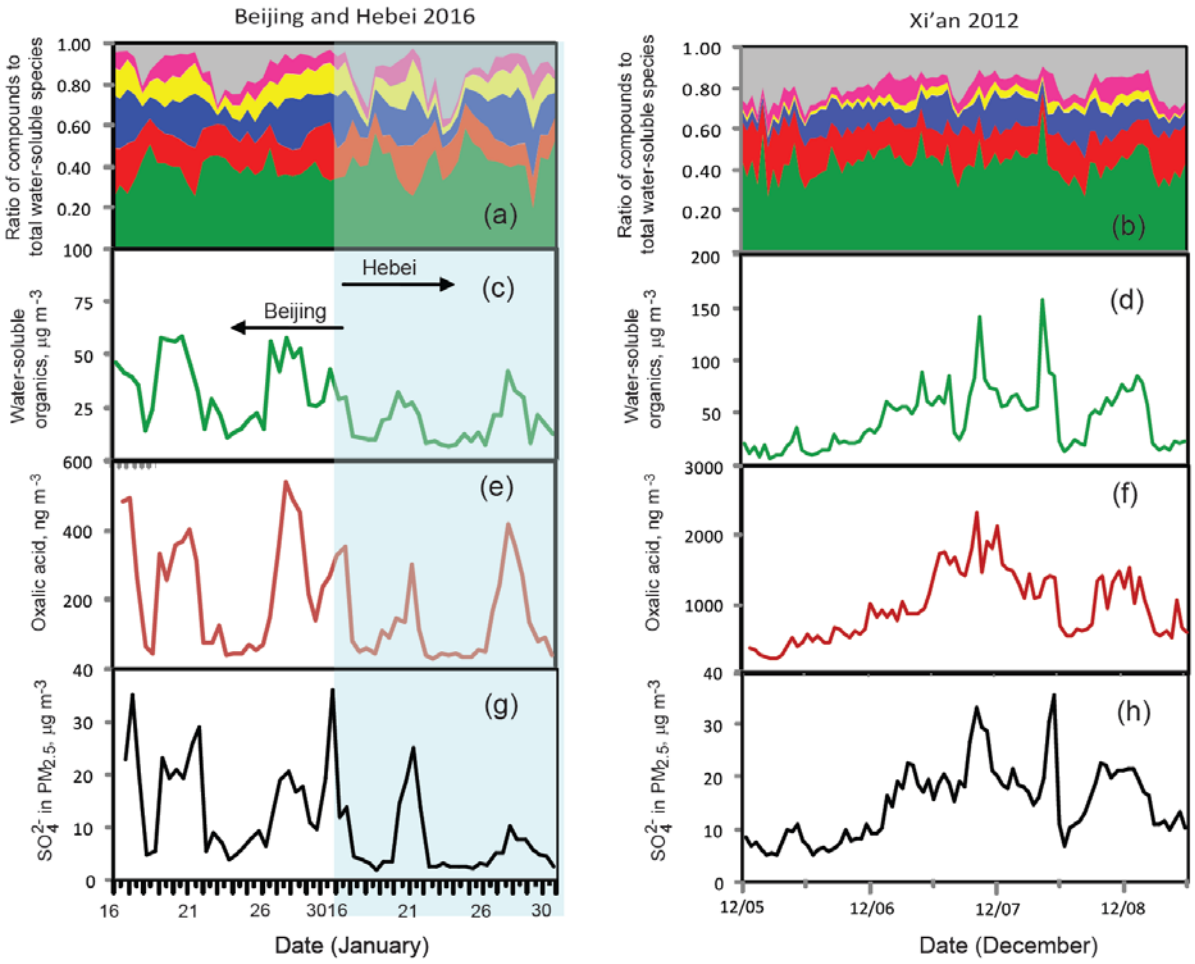

Figure 3. Measurements of water-sluble organic matter (WSOM) of $PM_{2.5}$ collected in Beijing and Hebei Province during the winter of 2016 (left panels: a, c,e and g) and in Xi'an during the winter of 2012 (right panels: b, d , f and h). In (a) and (b), the green, red, blue, yelow, pink, and gray colors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

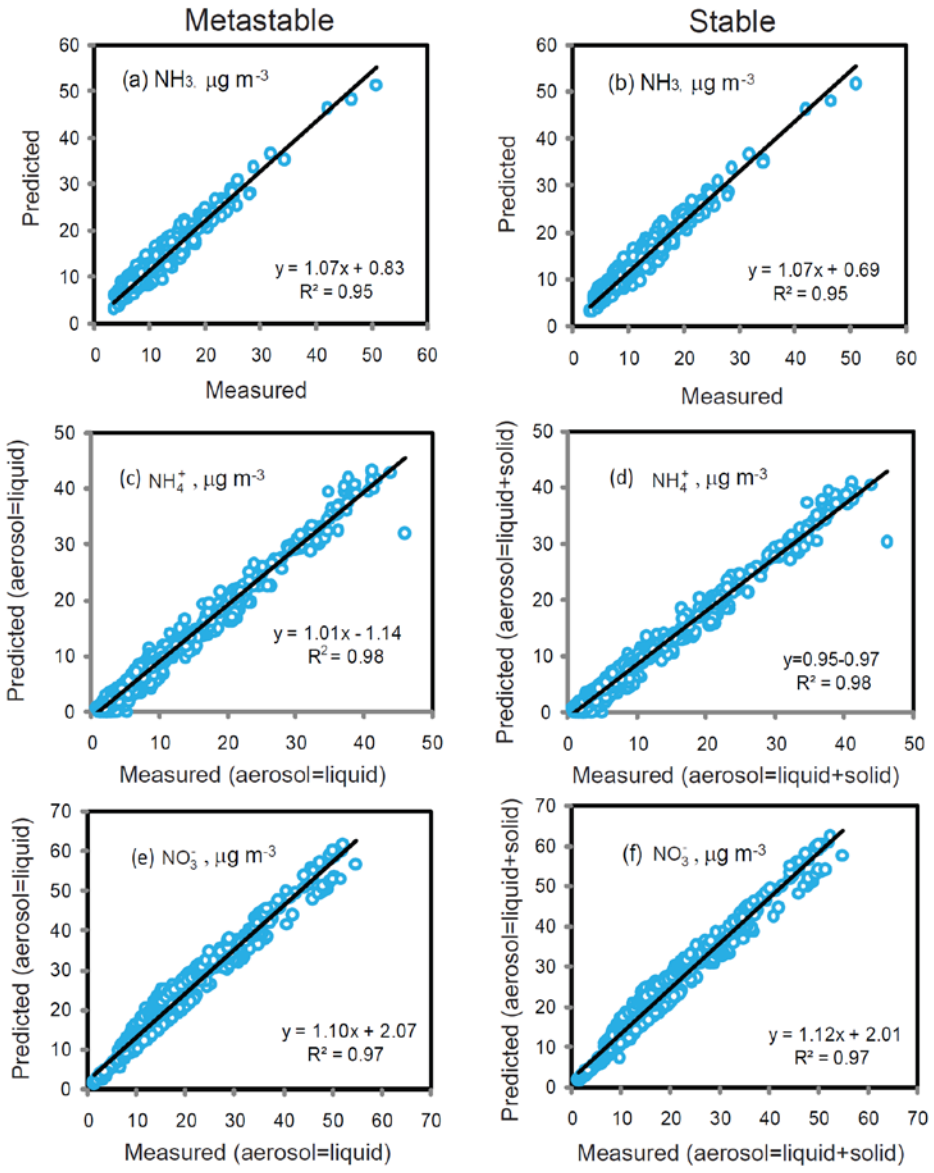

Figure 4. Comparison of measured NH_3, NH_4^+, and NO_3^- concentrations with those predicted by ISORROPIA-II model using the forward mode under the metastable (left panels) and stable assumptions (right panels).