Importance of Gas-Particle Partitioning of Ammonia in Haze Formation in the Rural Agricultural Environment

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13 Abstract. Ammonia in the atmosphere is essential for the formation of fine particles that impact air quality and 14 climate. Despite extensive prior research to disentangle the relationship between ammonia and haze pollution, the 15 role of ammonia in haze formation in the high ammonia emitted regions is still not well understood. Aiming to 16 better understand secondary inorganic aerosol (SNA) formation mechanisms under high ammonia conditions, one-17 year hourly measurement of water-soluble inorganic species (gas and particle) was conducted in a rural supersite in Shanghai. Exceedingly high levels of agricultural ammonia, constantly around 30 ug m⁻³, were observed. We find 18 19 that gas-particle partitioning of ammonia ($\epsilon(NH_{A}^{+})$), as opposed to ammonia concentrations, plays a critical role in 20 SNA formation during the haze period. By assessing the effects of various parameters, including temperature (T), 21 aerosol water content (AWC), aerosol pH, and activity coefficient, it seems that AWC plays predominant regulating roles for $\varepsilon(NH_4^+)$. We propose a self-amplifying feedback mechanism associated with $\varepsilon(NH_4^+)$ for the formation 22 of SNA, which is consistent with diurnal variations of $\varepsilon(NH_4^+)$, AWC, and SNA. Our results imply that reduction 23

24 of ammonia emissions alone may not reduce SNA effectively at least in rural agricultural sites in China.

25 1 Introduction

Gas-phase ammonia (NH₃) in the environment not only fuel the eutrophication and acidification of ecosystems, but also play key roles in atmospheric chemistry. NH₃ has been known to promote new particle formation both in the initial homogeneous nucleation and subsequent growth (Ball et al., 1999;Zhang et al., 2011;Coffman and Hegg,

29 1995; Kirkby et al., 2011). Prior studies suggest that the SO_2 oxidation can be enhanced by the presence of NH_3

- 30 (Turšič et al., 2004; Wang et al., 2016; Benner et al., 1992). High levels of NH₃ can also promote SOA formation (Na
- 31 et al., 2007;Ortiz-Montalvo et al., 2013). As the main alkaline species in the atmosphere, NH₃ are expected to affect

32 the acidity of clouds (Wells et al., 1998), fine particles (Liu et al., 2017;Guo et al., 2017b), and wet deposition

- 33 (ApSimon et al., 1987) by neutralizing acidic species. The neutralized ammonium (NH₄⁺) exclusively contribute to
- 34 aerosol hygroscopicity especially in hazy periods (Liu et al., 2017;Ye et al., 2011). Serving as efficient catalysts for
- 35 aerosol aldol condensation, ammonium has also been proved to contribute to radiative forcing (Noziere et al.,
- 36 2010; Park et al., 2014). Most importantly, ammonium is among the major secondary inorganic aerosols (i.e., sulfate

- 37 SO₄²⁻, nitrate NO₃⁻, and ammonium NH₄⁺, denoted as SNA), which typically rivals the organics and can make up
- 38 more than 50% of PM_{2.5} mass loadings (Wang et al., 2015a;Sun et al., 2014;Huang et al., 2014;Plautz, 2018;Schiferl
- 39 et al., 2014). Despite the significant importance of SNA in hazy periods, its formation mechanism responsible,
- 40 particularly the role of NH₃, remains highly controversial. Cheng et al. (2016) and Wang et al. (2016), for example,
- 41 suggested that the near-neutral acidity, resulting from the NH₃ rich atmosphere, is vital for SNA formation. While
- Liu et al. (2017) and Guo et al. (2017b) demonstrated that the close to neutral state is unlikely even under conditions of excess NH₃. These findings collectively imply that the fundamental role of NH₃ in regulating aerosol acidity is
- still ambiguous, thus altering the SNA formation mechanism (Seinfeld and Pandis, 2012).
- NH₃ emission sources include agricultural practices, on-road vehicles(Chang et al., 2016;Sun et al., 2016) and biomass burning (Lamarque et al., 2010;Paulot et al., 2017). Recent field measurements and modeling works reveal that agricultural practices (i.e., animal manure and fertilizer application) contribute to 80-90% of total NH₃ emissions in China (Zhang et al., 2018;Kang et al., 2016;Huang et al., 2011). Globally, NH₃ emissions are projected to continue to rise along with increasing demand of chemical fertilizers due to the growing human population (Erisman et al., 2008;Stewart et al., 2005) and in part because limiting NH₃ emissions has not been targeted a priority in most countries. For example, even though stringent mitigation targets have been set for SO₂ and NO_x in
- 52 China's 13th Five-Year Plan (2016-2020), slashing NH₃ emissions is not yet a prime concern in China. The
- 53 sustained increase of NH₃ has been observed from the space (Warner et al., 2017) and reported to deflect the
- 54 mitigation efforts of SO_2 and NO_x emissions in East China (Fu et al., 2017).
- 55 Although agricultural NH₃ emission has been the subject of extensive research, previous studies have focused on
- 56 densely populated or urban areas, where NH₃ was mostly "aged" and transformed to NH₄⁺ downwind (Chang et al.,
- 57 2016). Varying in location and time, the typical mass concentrations of NH₃ are on the order of several micrograms
- per cubic meter(Yao et al., 2006;Gong et al., 2013;Robarge et al., 2002;Chang et al., 2016;Phan et al., 2013), with
- 59 extremely high levels up to more than 20 μg m⁻³ in the rural area of North China Plain(Meng et al., 2018;Shen et al.,
- 60 2011;Pan et al., 2018). Numerous studies highlighted the importance of NH₃ emissions from agricultural areas
- 61 (Meng et al., 2018;Shen et al., 2011;Robarge et al., 2002;Wang et al., 2013;Nowak et al., 2012;Zhang et al.,
- 62 2017;Warner et al., 2017), but the gas-particle conversion of agricultural NH₃ in rural regions and its subsequent
- 63 impact on SNA formation, has scarcely been reported and remains poorly understood.
- 64 In this study, we provide observational constraints on the abnormally high agricultural NH₃ emission at a rural site.
- 65 We report our findings on the influence of $\varepsilon(NH_4^+)$ on SNA formation and discuss the decisive factors driving the

66 $\epsilon(NH_4^+)$.

67 2 Methods

68 **2.1 Observation site**

69 Field measurements of gases and fine particles were conducted over the course of a year from March 2017 to

70 February 2018 at the Dongtan Wetland Park (31°32' N, 121°58' E; altitude: 12 m a.s.l.), which is approximately 50

71 km northeast of downtown Shanghai. The sampling site, illustrated in Figure 1, was located on the east side of the

72 Chongming island, which is the largest eco-friendly island in China and the least developed district of Shanghai. The

- annual mean relative humidity (RH) is $78\% \pm 19\%$ and the yearly mean temperature (T) is 16.3 ± 9.9 °C. Although Chongming shares limited industrial and vehicle emissions compared to urban Shanghai, the level of fine particles on this island is slightly higher than the urban site (Figure S1). The overuse of nitrogen fertilizer has long been a large agricultural source of NH₃ emissions in China (Fan et al., 2011), with an increasing use especially in East-
- 77 Central China (Yang and Fang, 2015), where rice/wheat intercropping (similar to those in Chongming) was applied.
- 78 Based on a 2011 agricultural NH₃ emission inventory in Shanghai, Chongming has the largest nitrogen fertilizer
- 79 consumption among all the districts in Shanghai (Fang et al., 2015). According to the Multi-resolution Emission
- 80 Inventory for China (MEIC, <u>www.meicmodel.org</u>) in 2016, nearly 94% of NH₃ in Chongming came from the
- 81 agricultural sector, accounting for 14% of the total NH3 emissions in Shanghai. In comparison, Chongming
- 82 contributes only 6% and 5% of the total NO_x and SO_2 emissions in Shanghai, respectively (Table S1). With the most
- 83 intensive agriculture and 34% of arable farmland area in Shanghai (Wen et al., 2011), atmospheric ammonium
- 84 aerosols over the Chongming island are mostly of agricultural origin. Therefore, this site is ideal for investigating
- 85 the role of agricultural emissions of NH₃ in haze formation.

86 2.2 Measurements

- 87 Water-soluble samples of both gases (NH₃, SO₂, HCl, HNO₂, and HNO₃) and particles (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺,
- 88 Cl⁻, NO₃⁻, and SO₄²⁻) were measured hourly using MARGA (Monitor for AeRosols and Gases in Air, ADI 2080,
- 89 Metrohm Applikon B.V., Netherlands). Online sampling was conducted from March 2017 to February 2018
- 90 following the description in Kong et al. (2014). Briefly, air was drawn into a PM_{2.5} cyclone inlet with a flow rate of 1
- 91 m³ h⁻¹ and passed through either a wet rotating denuder (gases) or a steam jet aerosol collector (aerosols).
- 92 Subsequently, the aqueous samples were analyzed with ion chromatography. Meanwhile, mass loadings of PM_{2.5}
- 93 was determined by a Tapered Element Oscillating Microbalance coupled with Filter Dynamic Measurement System
- 94 (TEOM 1405-F). The QA/QC of these instruments were managed by professional staff in Shanghai Environmental
- 95 Monitoring Center (SEMC) according to the Technical Guideline of Automatic Stations of Ambient Air Quality in
- 96 Shanghai (HJ/T193-2005).

97 2.3 ISORROPIA-II modelling

98 The thermodynamic model ISORROPIA II (Fountoukis and Nenes, 2007) was used to predict the aerosol water

- content and pH. ISORROPIA was constrained in forward metastable mode by hourly mean measurements of Na⁺,
 K⁺, Mg²⁺, Ca²⁺, SO4²⁻, NH₃, NH₄⁺, HNO₃, NO₃⁻, HCl, and Cl⁻, along with RH and T. The molality based pH was a
- 101 default output in the model. The model showed a good performance when predicting NH₃-NH₄⁺ partitioning (Figure
- 102 S2).

103 **3 Results and Discussion**

104 **3.1 Overview of 1 year continuous measurements at Chongming**

Figure 2 shows the time-series of hourly water-soluble $PM_{2.5}$ species during the study period. The mean concentration of NO_3^- , SO_4^{2-} , NH_4^+ and CI^- over the entire study period was 8.4 µg m⁻³, 6.3 µg m⁻³ and

- 107 1.2 µg m⁻³. The haze period was defined as hourly mean PM_{2.5} mass loadings higher than 75 µg m⁻³ and the rest was
- 108 non-haze periods. Table 1 gives the statistical summary of major aerosols during the haze and non-haze period.
- 109 Clearly, the mass concentration of major PM_{2.5} species (NO₃⁻, SO₄²⁻, NH₄⁺ and Cl⁻) increased during the haze
- 110 period compared to those during the non-haze period. However, the concentration of NH₃ showed no significant
- 111 change during these two periods. The mean mass concentration of SNA (sulfate, nitrate, and ammonium) was 49.0
- 112 μ g m⁻³, contributing to about 50.0 % of total PM_{2.5} mass.

113 **3.2** NH₃ levels and its link to secondary inorganic aerosol

- Figure 3 shows that the mean concentration of NH₃ at Chongming (CM: $17.0 \pm 4.2 \ \mu g \ m^{-3}$) was more than three
- times higher than an urban site in Shanghai (PD: $2.5 \pm 0.9 \ \mu g \ m^{-3}$) and a representative regional transport region
- 116 (DL: $4.6 \pm 2.0 \ \mu g \ m^{-3}$) in the Yangtze River Delta. The level of NH₃ at Chongming was even close to that observed
- 117 inside a typical dairy farm (JS: $19.4 \pm 12.6 \ \mu g \ m^{-3}$), which was dominated by livestock emissions. Thus, it is 118 interesting to investigate how the formation of secondary inorganic aerosols is impacted by this abnormally high 119 level of NH₃.
- 120 Figure 4 indicates the response of SNA (sulfate, nitrate, and ammonium) mass concentrations to NH₃ is nonlinear. Higher NH₃ sometimes correspond to even lower SNA mass concentrations. Statistically, the mean SNA 121 122 concentration in each bin of NH₃ doesn't show significant difference. This is at odds with the traditional view that 123 higher concentrations of precursors usually result in elevated inorganic aerosols (Nowak et al., 2010). Although the abundance of SNA is related to the alkaline gaseous precursor (e.g., NH₃), the ambient condition (e.g., RH and T), 124 125 and acid precursors (i.e., SO_2 and NO_x) whether favor the conversion of precursors into particles or not is equally 126 important, if not higher. For example, the urban areas show higher SNA levels than the rural region while lower 127 NH₃ mixing ratio was observed (Wu et al., 2016;Wang et al., 2015b). Previous field measurements suggest that rural 128 NH_4^+ levels were more sensitive to acidic gases than to the NH_3 availability (Shen et al., 2011; Robarge et al., 2002). 129 Therefore, the level of NH₃ concentration is not the determining factor for the formation of secondary inorganic 130 aerosols.

131 **3.3 The role of \varepsilon(NH_4^+)**

- 132 In this regard, we further investigate the relationship between the gas-particle partitioning of ammonia ($\epsilon(NH_4^+)$),
- defined as the molar ratio between particle phase ammonia (NH_4^+) and total ammonia ($NH_x = NH_3 + NH_4^+$)) and SNA during the haze period. The haze period is defined as hourly mean PM_{2.5} mass loadings higher than 75 µg m⁻³.
- As shown in Figure 5, it is obvious that SNA in PM_{2.5} is almost linearly correlated with $\varepsilon(NH_4^+)$. Higher $\varepsilon(NH_4^+)$
- results in higher SNA concentrations. In addition, under the same $\varepsilon(NH_4^+)$ conditions, higher NH₃ promotes
- 137 stronger formation of SNA. Thus, NH₃ and $\varepsilon(NH_4^+)$ collectively determine the haze formation potential. The level
- 138 of NH₃ can be regarded as a proxy of NH₃ emission intensity, which is source dependent. As for $\varepsilon(NH_4^+)$, it
- 139 represents the relative abundance of gaseous NH₃ and particulate ammonium. The shift between the two phases is
- 140 controlled by various factors such as the ambient environmental conditions. Previous study shows that elevated RH
- 141 and acidic gas levels favor the shift of NH₃ towards the particulate phase at an urban site, thereby a lower

- $[NH_3]:[NH_4^+]$ ratio was observed (Wei et al., 2015). In this study, it is also observed that higher $\varepsilon(NH_4^+)$ values 142
- 143 coincide with heightened RH, SO₂, and NO_x.
- Based on the above results, elucidation of the driving factors determining $\varepsilon(NH_4^+)$ is of great importance to explore 144
- the formation mechanism of haze. Theoretically, $\varepsilon(NH_4^+)$ is determined by NH₃, NH₄⁺, and the equilibrium 145
- between NH₃ and NH₄⁺. Assuming NH₃ and NH₄⁺ are in thermodynamic equilibrium, the following equation can be 146
- 147 obtained.

- $H^+ + NH_{3(g)} \leftrightarrow NH_4^+$ 148 (R1)
- The equilibrium constant $H_{NH_3}^*$ is equal to the Henry's constant of NH₃ divided by the acid dissociation constant for 149
- NH_{4^+} (Clegg et al., 1998). $\epsilon(NH_4^+)$ can be analytically calculated as detailed in Guo et al.(2017a) via the following 150 151 equation:
- $\varepsilon(NH_4^+) = \frac{[NH_4^+]}{[NH_x]} \cong \frac{\frac{\gamma_{H^+10}^{-pH}}{\gamma_{NH_4^+}} H_{NH_3}^* W_i RT \times 0.987 \times 10^{-14}}{1 + \frac{\gamma_{H^+10}^{-pH}}{\gamma_{NH_4^+}}} H_{NH_3}^* W_i RT \times 0.987 \times 10^{-14}}$ (Eq. 1) 152

153 here, $[NH_4^+]$ is the molar concentration of NH₄⁺ (mole m⁻³). γ is the activity coefficient, which is extracted from the ISORROPIA II model to account for the non-ideality solution effect. $H_{NH_3}^*$ (atm⁻¹) represents the molality-based 154 155 equilibrium constant, which is T dependent and can be determined using equation (12) in Clegg et al.(1998). Wi (µg m⁻³) is the aerosol water content predicted by ISORROPIA-II. R (J/mole/K) is the universal gas constant. T (K) is 156 ambient temperature and 0.987×10^{-14} is the conversion multiplication factors from atm and μg to SI units. 157

- In Figure 6, $\varepsilon(NH_4^+)$ curve (The "S" shape curve, referred to as "S Curve" hereafter) is plotted against pH based on 158 the mean T (10°C), AWC (100 µg m⁻³), and $\frac{\gamma_{H^+}}{\gamma_{NH^+}}$ (2.4) during the haze period. Observation-based $\varepsilon(NH_4^+)$ as a 159
- function of pH with varying T and AWC is also shown. Clearly, the observational $\varepsilon(NH_4^+)$ data points are 160 relatively well constrained by the theoretical equation, suggestive of reasonable judgement that $\varepsilon(NH_4^+)$ is 161 controlled by T, AWC, pH, and $\frac{\gamma_{H^+}}{\gamma_{NH_{4}^+}}$. Under the condition of mean pH (4.6 ± 0.3) during the winter haze period, the 162
- "S curve" derives $\varepsilon(NH_4^+)$ of 0.3, around 3/4 of the mean measured $\varepsilon(NH_4^+)$ (0.4 ± 0.1). Earlier works have also 163 164 observed higher particle phase fraction than the henry's law constants predicted for water soluble aerosol components (Arellanes et al., 2006;Hennigan et al., 2008;Shen et al., 2018). Another possible factor contributing to
- 166 the underestimation of $\varepsilon(NH_4^+)$ is the unaccounted effect from organic species, whose role in driving the SNA
- formation is thought to be significant (Silvern et al., 2017). The organics have been found to account for 35% of 167
- 168 AWC in the southeast USA (Guo et al., 2015), thus $\varepsilon(NH_{4}^{+})$ would be enhanced by including organic aerosol.
- 169 Since the mass concentration of organic aerosol was not available in this study, we did a sensitivity analysis via
- 170 increasing the AWC by 10, 20 to 90 μ g m⁻³ as shown in Figure 7. The pH was not re-calculated using the new AWC
- 171 because the co-existed organic aerosol altered pH in a complex way (Battaglia Jr et al., 2019; Wang et al., 2018; Pye 172 et al., 2020). For example, some organic acids increase aerosol acidity thus decrease pH, whereas organic basics
- 173 (e.g., amines) raise aerosol pH. We found that the best agreement between the predicted and measured $\varepsilon(NH_4^+)$ was
- achieved when we increase the AWC by roughly 90 μ g m⁻³, suggesting a nearly 48% of AWC contributed by the 174

- 175 organics. This result falls in the range from a recent report in North China that organics contribute to $30\% \pm 22\%$ of
- 176 AWC (Jin et al., 2020), and slightly higher than those southeastern United States sites that organic aerosol-related
- 177 water accounting for about 29 to 39% of total water (Guo et al., 2015) and those in the eastern Mediterranean that
- about 27.5% of total aerosol water resulted from organics (Bougiatioti et al., 2016). To quantitatively determine
- 179 which parameter dominates the $\varepsilon(NH_4^+)$, the impact on $\varepsilon(NH_4^+)$ from individual variable (i.e. T, AWC, pH, and
- 180 $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$) during the haze period in winter is assessed (Figure 8). From a theoretical perspective, the decrease of pH and
- 181 T, and increase of AWC and $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$ would raise $\varepsilon(NH_4^+)$. For instance, in summertime, the lower $\varepsilon(NH_4^+)$ (Figure 4)
- are mainly due to higher T that shift the equilibrium to the gas phase, thus higher NH₃ ($40 \pm 8 \ \mu g \ m^{-3}$) while lower
- 183 NH_4^+ was observed. Likewise, in wintertime, the lower T facilitates the residence of NH_4^+ in the particle phase than
- 184 the gas phase (NH₃: $20 \pm 4 \,\mu g \, m^{-3}$), resulting in higher $\varepsilon(NH_4^+)$.
- 185 On the basis of "S curve" (Figure 8), each 0.1 unit change of $\varepsilon(NH_4^+)$ can be caused by approximate 5 °C, 75 µg m⁻
- ³, 0.3, and 2 units change of T, AWC, pH, and $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$, respectively. Actually, T, pH, and $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$ are within a relatively
- 187 narrow range during the winter haze period (Table 2), suggesting the variation of these parameters shouldn't result
- in the significant change of $\varepsilon(NH_4^+)$. On the contrary, AWC fluctuates greatly during the study period (Table 2).
- 189 Therefore, AWC should be the key factor regulating $\varepsilon(NH_4^+)$. It is well established that AWC is a function of RH
- and atmospheric aerosol compositions (Pilinis et al., 1989; Wu et al., 2018; Nguyen et al., 2016; Hodas et al., 2014).
- 191 AWC has also been known to promote secondary organic aerosol formation by providing aqueous medium for
- 192 uptake of reactive gases, gas to particle partitioning, and the subsequent chemical processing (McNeill,
- 193 2015;McNeill et al., 2012;Tan et al., 2009;Xu et al., 2017b).
- 194 The winter haze pH in this study were \sim 3 units higher than that of the southeastern United States summer campaign
- 195 (Nah et al., 2018; Guo et al., 2015; Guo et al., 2017a; Xu et al., 2017a), but close to that of 3.7 in rural Europe (Guo et
- al., 2018) and 4.2 in North China Plain (Liu et al., 2017), where NH₃-rich conditions are prevalent. AWC may act as
- 197 the major factor, because greater AWC dilute the $[H^+]$ and raise the pH. The AWC during the haze period (82 ± 105
- 198 μ g m⁻³) were much higher than those during the non-haze period (32 ± 41 μ g m⁻³).

199 **3.4 A possible self-amplifying feedback mechanism**

- 200 Given that AWC is a function of RH and SNA, a conceptual model of how AWC control $\varepsilon(NH_4^+)$ can be illustrated
- by a self-amplifying feedback loop (Figure 9). Formation of SNA is initiated by gas-particle conversion of NH₃.
 Under certain meteorological conditions such as high RH and shallow planetary boundary laver, SNA is subject to
- 203 uptake moisture and result in the increases of AWC. The enhanced aerosol water dilutes the vapor pressure of semi-
- volatile species (i.e., nitrate, ammonium and chloride) above the particle and driving semi-volatile species continue
- 205 to condense (Topping et al., 2013). Based on the discussions above, the increase of AWC would further raise
- 206 $\epsilon(NH_4^+)$, leading to more efficient transformation of NH₃ as SNA.
- 207 Figure 10 shows the yearly mean diurnal variation of $\varepsilon(NH_4^+)$, AWC, SNA along with T and RH. Apparently, SNA
- 208 tracked well with $\varepsilon(NH_4^+)$ and AWC, especially over nighttime. The not well-correlated track between SNA and

- AWC and $\varepsilon(NH_4^+)$ during the daytime (8:00-16:00) can be ascribed to the photochemical reactions that lead to
- 210 SNA formation. The good correlation between SNA and AWC and $\varepsilon(NH_4^+)$ demonstrated in Figure 10 support the
- 211 proposed self-amplifying feedback loop in SNA formation.

212 4 Conclusion

- Our results demonstrate that $\varepsilon(NH_4^+)$, rather than NH₃ concentrations, plays a critical role in driving haze formation 213 214 in the agricultural NH3 emitted regions. Based on the "S curve" calculation, we have unraveled that AWC is the major factor controlling $\varepsilon(NH_4^+)$. Upon analyzing the cross-correlations between AWC, $\varepsilon(NH_4^+)$ and SNA, we 215 proposed a self-amplifying feedback mechanism of SNA formation that associated with AWC and $\varepsilon(NH_4^+)$. This 216 217 positive feedback cycle is likely to occur in other rural regions, where high agricultural NH₃ emissions are prevalent. 218 We have shown that high NH₃ concentrations may not necessarily lead to strong SNA formation, particularly in the 219 agriculture intensive areas, e.g. the North China Plain (NCP) and the extensive farming lands in Eastern China 220 where the high NH₃ levels are still unregulated and increasing (Meng et al., 2018; Warner et al., 2017). Although Liu
- et al.(2019) have predicted that $PM_{2.5}$ can be slashed by 11-17% when 50% reduction in NH₃ from the agricultural
- sector and 15% mitigation of NO_x and SO_2 emissions was achieved, a recent study has demonstrated that only when
- 223 aerosol pH drops below 3.0, the NH₃ reduction would have expected mitigation effects (Guo et al., 2018). The
- winter haze pH (4.6 ± 0.3) in this study was mostly between 4-5. Our results thus imply that NH₃ only may not be an
- 225 effective solution to tackle air pollution in these regions.
- 226 Data availability.
- 227 The data presented in this paper are available upon request from the corresponding author 228 (huangkan@fudan.edu.cn).
- 229 Author contributions.
- JX and KH conceived the study. JX, JC, and KH performed data analysis and wrote the paper. All authors contributed to the review of the manuscript.
- 232 *Competing interests.*
- 233 The authors declare that they have no conflict of interest.
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Figure 1: Location of the sampling site. Population density is color-coded in the left panel. The right panel shows the land cover in Shanghai (adapted from Peng et al.(2018)). CM (Chongming) is the sampling site on Chongming island. JS (Jinshan) represents the source emission from a dairy farm in rural Shanghai. DL (Dianshan Lake) represents a regional transport region in the Yangtze River Delta. PD (Pudong) represents the urban site.



Figure 2: Time series of $PM_{2.5}$ species during the study period. The mass fraction of major $PM_{2.5}$ species is shown in the inserted pie chart.



Figure 3: NH₃ at different sampling site over the same period (From Jan 18 to 27 of 2018). The locations of all sites are shown in Figure 1. Scattered dots indicate raw data points.



Figure 4: Secondary inorganic aerosol mass concentration in PM_{2.5} (SNA refers to sulfate, nitrate, and ammonium) as a function of NH₃. The sizes of the void circles are scaled to the $\varepsilon(NH_4^+)$ and colored by T. The number of data points in each NH₃ concentration bin is also shown.



Figure 5: SNA mass concentration in PM_{2.5} as a function of $\varepsilon(NH_4^+)$ during the haze period. The circles are colored by the NH₃ mass concentration.



Figure 6: $\varepsilon(NH_4^+)$ as a function of pH during the haze period. The sizes of the void circles are scaled to AWC and colored by T. The blue curve was calculated based on the mean T (10 °C), AWC (100 µg m⁻³), and activity coefficients ratio of $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$ respectively. The mean $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$ for the haze period is 4.0 ± 2.6 (±1 σ).





Figure 7: Comparison of predicted and measured $\varepsilon(NH_4^+)$. Note the predicted $\varepsilon(NH_4^+)$ was analytically calculated using the equation 2 with input (i.e., pH, AWC, $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$) taken from ISORROPIA II prediction and the AWC has been increased by 10, 20 to 90 µg m⁻³ while other inputs fixed. Orthogonal distance regression (ODR) fits line (red) and y=x line (dashed orange) was shown for the clarity of the figure.



Figure 8: $\varepsilon(NH_4^+)$ as a function of pH during the winter haze period. Other variables are held constant at the mean value during the winter haze period, while varying only the AWC, T, activity coefficients ratio of $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$, respectively.

485 Shaded dark areas indicate the winter haze mean pH together with one standard deviation ($\pm 1\sigma$). The areas between the green and red line represent the curve corresponding to mean $\pm 1\sigma$, note that for AWC mean - 1σ yield a negative value, thus the minimum mass concentration (3 µg m⁻³) was used.



490 Figure 9: Schematic of self-amplifying feedback loop for SNA formation.



Figure 10: Annual mean diurnal pattern of $\epsilon(NH_4^+)$, AWC, SNA, T, and RH.

Table 1. Statistical summary on mass concentrations of PM_{2.5} species and NH₃.

| Unit: µg m ⁻³ | PM _{2.5} | SO4 ²⁻ | NO ₃ - | Cl- | $\mathrm{NH_{4}^{+}}$ | NH ₃ |
|--------------------------|-------------------|-------------------|-------------------|-------------|-----------------------|-----------------|
| non-haze | 28.5 ± 16.9 | 5.6 ± 3.6 | 6.9 ± 6.6 | 1.1 ± 0.9 | 5.6 ± 3.3 | 32.2 ± 11.6 |
| haze | 98.3 ± 37.2 | 13.3 ± 7.7 | 23.1 ± 14.5 | 2.2 ± 1.9 | 13.2 ± 6.6 | 32.3 ± 13.5 |

500 Table 2: The summer and winter mean (±1 σ) $\epsilon(NH_4^+)$, pH, T, activity coefficients ratio of $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$, and NH₃ (µg m⁻³)

| during t | he haze | period. |
|----------|---------|---------|
|----------|---------|---------|

| | $\epsilon(NH_4^+)$ | AWC | рН | NH3 | $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$ | Т |
|--------|--------------------|-------------|--------------|-----------|--|----------|
| summer | 0.2 ± 0.1 | 79 ± 73 | 3.4 ± 0.5 | 40 ± 8 | 1.9 ± 0.9 | 29 ± 5 |
| winter | 0.4 ± 0.1 | 115 ± 131 | 4.6 ± 0.3 | 20 ± 4 | 4.0 ± 4.7 | 5 ± 4 |