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

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Abstract. Ammonia in the atmosphere is essential for the formation of fine particles that impact air quality and climate. Despite extensive prior research to disentangle the relationship between ammonia and haze pollution, the role of ammonia in haze formation in the high ammonia emitted regions is still not well understood. Aiming to better understand secondary inorganic aerosol (SNA) formation mechanisms under high ammonia conditions, one-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 that ammonia gas-particle conversion ratio (ACR), as opposed to ammonia concentrations, plays a critical role in SNA formation during the haze period. By assessing the effects of various parameters, including temperature (T), aerosol water content (AWC), aerosol pH, and activity coefficient, it seems that AWC plays predominant regulating roles for ACR. We propose a self-amplifying feedback mechanism associated with ACR for the formation of SNA, which is consistent with diurnal variations of ACR, AWC, and SNA. Our results imply that reduction of ammonia emissions alone may not reduce SNA effectively at least in rural agricultural sites in China.

1 Introduction

Gas-phase ammonia (NH_3) in the environment not only fuel the eutrophication and acidification of ecosystems, but also play key roles in atmospheric chemistry. NH_3 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, 1995;Kirkby et al., 2011). Prior studies suggest that the SO_2 oxidation can be enhanced by the presence of NH_3 (Turšič et al., 2004;Wang et al., 2016;Benner et al., 1992). High levels of NH_3 can also promote SOA formation (Na et al., 2007;Ortiz-Montalvo et al., 2013). As the main alkaline species in the atmosphere, NH_3 are expected to affect the acidity of clouds (Wells et al., 1998), fine particles (Liu et al., 2017;Guo et al., 2017b), and wet deposition (ApSimon et al., 1987) by neutralizing acidic species. The neutralized ammonium (NH_4^+) exclusively contribute to

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aerosol hygroscopicity especially in hazy periods (Liu et al., 2017;Ye et al., 2011). Serving as efficient catalysts for aerosol aldol condensation, ammonium has also been proved to contribute to radiative forcing (Noziere et al., 2010;Park et al., 2014). Most importantly, ammonium is among the major secondary inorganic aerosols (i.e., sulfate SO_4^{2-}, nitrate NO_3^-, and ammonium NH_4^+, denoted as SNA), which typically rivals the organics and can make up more than 50% of $PM_{2.5}$ mass loadings (Wang et al., 2015a;Sun et al., 2014;Huang et al., 2014;Plautz, 2018;Schiferl et al., 2014). Despite the significant importance of SNA in hazy periods, its formation mechanism responsible, particularly the role of NH_3, remains highly controversial. Cheng et al. (2016) and Wang et al. (2016), for example, suggested that the near-neutral acidity, resulting from the NH_3 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 NH_3. These findings collectively imply that the fundamental role of NH_3 in regulating aerosol acidity is still ambiguous, thus altering the SNA formation mechanism (Seinfeld and Pandis, 2012).

NH_3 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 NH_3 emissions in China (Zhang et al., 2018;Kang et al., 2016;Huang et al., 2011). Globally, NH_3 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 NH_3 emissions has not been targeted a priority in most countries. For example, even though stringent mitigation targets have been set for SO_2 and NO_x in China's 13th Five-Year Plan (2016-2020), slashing NH_3 emissions is not yet a prime concern in China. The sustained increase of NH_3 has been observed from the space (Warner et al., 2017) and reported to deflect the mitigation efforts of SO_2 and NO_x emissions in East China (Fu et al., 2017).

Although agricultural NH_3 emission has been the subject of extensive research, previous studies have focused on densely populated or urban areas, where NH_3 was mostly "aged" and transformed to NH_4^+ downwind (Chang et al., 2016). Varying in location and time, the typical mass concentrations of NH_3 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 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., 2011;Pan et al., 2018). Numerous studies highlighted the importance of NH_3 emissions from agricultural areas (Meng et al., 2018;Shen et al., 2011;Robarge et al., 2002;Wang et al., 2013;Nowak et al., 2012;Zhang et al., 2017;Warner et al., 2017), but the gas-particle conversion of agricultural NH_3 in rural regions and its subsequent impact on SNA formation, has scarcely been reported and remains poorly understood.

In this study, we provide observational constraints on the abnormally high agricultural NH_3 emission at a rural site. We report our findings on the influence of NH_3 gas-particle conversion ratio on SNA formation and discuss the decisive factors driving the NH_3 gas-particle conversion ratio (ACR).

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2 Methods

2.1 Observation site

Field measurements of gases and fine particles were conducted over the course of a year from March 2017 to February 2018 at the Dongtan Wetland Park (31°32′ N, 121°58′ E; altitude: 12 m a.s.l.), which is approximately 50 km northeast of downtown Shanghai. The sampling site, illustrated in Figure 1, was located on the east side of the 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% ± 19% and the yearly average 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 NH_3 emissions in China (Fan et al., 2011), with an increasing use especially in East-Central China (Yang and Fang, 2015), where rice/wheat intercropping (similar to those in Chongming) was applied. Based on a 2011 agricultural NH_3 emission inventory in Shanghai, Chongming has the largest nitrogen fertilizer consumption among all the districts in Shanghai (Fang et al., 2015). According to the Multi-resolution Emission Inventory for China (MEIC, www.meicmodel.org) in 2016, nearly 94% of NH_3 in Chongming came from the agricultural sector, accounting for 14% of the total NH_3 emissions in Shanghai. In comparison, Chongming contributes only 6% and 5% of the total NO_x and SO_2 emissions in Shanghai, respectively (Table S1). With the most intensive agriculture and 34% of arable farmland area in Shanghai (Wen et al., 2011), atmospheric ammonium aerosols over the Chongming island are mostly of agricultural origin. Therefore, this site is ideal for investigating the role of agricultural emissions of NH_3 in haze formation.

2.2 Measurements

Water-soluble samples of both gases (NH_3, SO_2, HCl, HNO_2, and HNO_3) and particles (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) were measured hourly using MARGA (Monitor for AeRosols and Gases in Air, ADI 2080, Metrohm Applikon B.V., Netherlands). Online sampling was conducted from March 2017 to February 2018 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 m^3 h^{-1} and passed through either a wet rotating denuder (gases) or a steam jet aerosol collector (aerosols). Subsequently, the aqueous samples were analyzed with ion chromatography. Meanwhile, $PM_{2.5}$ and gaseous pollutants (SO_2, NO_2, O_3, and CO) were monitored by co-located instruments. Mass loadings of $PM_{2.5}$ was determined by a Tapered Element Oscillating Microbalance coupled with Filter Dynamic Measurement System (TEOM 1405-F). SO_2 mass concentrations were analyzed by Pulsed Fluorescence SO_2 Analyzer (Thermo Fisher Scientific, Model 43i). NO_2 mass concentrations were analyzed by Chemiluminescence NO-NO_2-NO_x Analyzer (Thermo Fisher Scientific, Model 42i). O_3 mass concentrations were analyzed by UV Photometric Ozone Analyzer (Thermo Fisher Scientific, Model 49i). CO mass concentrations were analyzed by Gas Filter Correlation CO Analyzer (Thermo Fisher Scientific, Model 48i). The QA/QC of these instruments were managed by professional staff in Shanghai Environmental Monitoring Center (SEMC) according to the Technical Guideline of Automatic Stations of Ambient Air Quality in Shanghai (HJ/T193-2005).

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2.3 ISORROPIA-II modelling

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 averaged measurements of Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, NH_3, NH_4^+, HNO_3, NO_3^-, HCl, and Cl^-, along with RH and T. The molality based pH was a default output in the model. The model showed a good performance when predicting NH_3-NH_4^+ partitioning (Figure 2).

3 Results and Discussion

3.1 NH_3 levels and its link to secondary inorganic aerosol

Figure 3 shows that the mean concentration of NH_3 at Chongming (CM: 17.0 ± 4.2 μg m^{-3}) is more than three times higher than an urban site in Shanghai (PD: 2.5 ± 0.9 μg m^{-3}) and a representative regional transport region (DL: 4.6 ± 2.0 μg m^{-3}) in the Yangtze River Delta. The level of NH_3 at Chongming is even close to that observed inside a typical dairy farm (JS: 19.4 ± 12.6 μg m^{-3}), which is dominated by livestock emissions. Thus, it is interesting to investigate how the formation of secondary inorganic aerosols is impacted by this abnormally high level of NH_3.

Figure 4 indicates the response of SNA (sulfate, nitrate, and ammonium) mass concentrations to NH_3 is nonlinear. Higher NH_3 sometimes correspond to even lower SNA mass concentrations. Statistically, the average SNA concentration in each bin of NH_3 doesn't show significant difference. This is at odds with the traditional view that 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., NH_3), the ambient condition (e.g., RH and T), and acid precursors (i.e., SO_2 and NO_x) whether favor the conversion of precursors into particles or not is equally important, if not higher. For example, the urban areas show higher SNA levels than the rural region while lower NH_3 mixing ratio was observed (Wu et al., 2016;Wang et al., 2015b). Previous field measurements suggest that rural NH_4^+ levels are more sensitive to acidic gases than to the NH_3 availability (Shen et al., 2011;Robarge et al., 2002). Therefore, the level of NH_3 concentration is not the determining factor for the formation of secondary inorganic aerosols.

3.2 The role of ammonia gas-particle conversion ratio

In this regard, we further investigate the relationship between the ammonia gas-particle conversion ratio (ACR, 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 averaged $PM_{2.5}$ 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 ACR. Higher ACR results in higher SNA concentrations. In addition, under the same ACR conditions, higher NH_3 promotes stronger formation of SNA. Thus, NH_3 and ACR collectively determine the haze formation potential. The level of NH_3 can be regarded as a proxy of NH_3 emission intensity, which is source dependent. As for ACR, it represents the relative abundance of gaseous NH_3 and particulate ammonium. The shift between the two phases is controlled by various factors such as the ambient environmental conditions. Previous study shows that elevated RH and acidic gas levels favor the shift

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of NH_3 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 ACR values coincide with heightened RH, SO_2, and NO_x.

Based on the above results, elucidation of the driving factors determining ACR is of great importance to explore the formation mechanism of haze. Theoretically, ACR is determined by NH_3, NH_4^+, and the equilibrium between NH_3 and NH_4^+. Assuming NH_3 and NH_4^+ are in thermodynamic equilibrium, the following equation can be obtained.

$$H^+ + NH_{3(g)} \leftrightarrow NH_4^+ \quad \text{(R1)}$$

The equilibrium constant $H^*_{NH_3}$ is equal to the Henry's constant of NH_3 divided by the acid dissociation constant for NH_4^+ (Clegg et al., 1998b). $H^*_{NH_3}$ is calculated by the following equation:

$$\ln(H^*_{NH_3}) = 25.393 - 10373.6(1/T_r - 1/T) + 4.131(T_r/T - (1 + \ln(T_r/T))) \quad \text{(Eq. 1)}$$

here, T_r is the reference temperature of 298. 15 K. ACR can be analytically calculated as detailed in Guo et al.(2017a) via the following equation:

$$\text{ACR} = \frac{[NH_4^+]}{[NH_x]} \cong \frac{\frac{\gamma_{H^+}10^{-pH}}{\gamma_{NH_4^+}} H^*_{NH_3} W_i RT \times 0.987 \times 10^{-14}}{1 + \frac{\gamma_{H^+}10^{-pH}}{\gamma_{NH_4^+}} H^*_{NH_3} W_i RT \times 0.987 \times 10^{-14}} \quad \text{(Eq. 2)}$$

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

In Figure 6, ACR curve (The "S" shape curve, referred to as "S Curve" hereafter) is plotted against pH based on the average T (10°C), AWC (100 μg m^{-3}), and $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$ (2.4) during the haze period. Observation-based ACR as a function of pH with varying T and AWC is also shown. Clearly, the observational ACR data points are relatively well constrained by the theoretical equation, suggestive of reasonable judgement that ACR is controlled by T, AWC, pH, and $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$. Under the condition of average pH (4.6 ± 0.3) during the winter haze period, the "S curve" derives ACR of 0.2, around half of the average measured ACR (0.4 ±0.1). Regional and long-range transport of aerosol pollutants from northern China during the cold season (Xu et al., 2018) may have increased NH_4^+, yet NH_3 remains little unaffected because of its limited transport distance (Asman et al., 1998). The transport effect cannot be predicted by the theoretical equation and this should partly explain the divergence between the calculated and observed ACR. Earlier works have also 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 the underestimation of ACR 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 AWC in the southeast USA (Guo et al., 2015), thus ACR would be enhanced by including organic aerosol. To quantitatively determine which parameter dominates the ACR, the impact on ACR from individual variable (i.e. T,

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AWC, pH, and $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$) during the haze period in winter is assessed (Figure 7). From a theoretical perspective, the decrease of pH and T, and increase of AWC and $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$ would raise ACR. For instance, in summertime, the lower ACR (Figure 4) are mainly due to higher T that shift the equilibrium to the gas phase, thus higher NH_3 (40 ± 8 μg m^{-3}) while lower NH_4^+ was observed. Likewise, in wintertime, the lower T facilitates the residence of NH_4^+ in the particle phase than the gas phase (NH_3: 20 ± 4 μg m^{-3}), resulting in higher ACR.

On the basis of "S curve" (Figure 7), each 0.1 unit change of ACR can be caused by approximate 5 ℃, 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 narrow range during the winter haze period (Table 1), suggesting the variation of these parameters shouldn't result in the significant change of ACR. On the contrary, AWC fluctuates greatly during the study period (Table 1). Therefore, AWC should be the key factor regulating ACR. 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). AWC has been known to promote secondary aerosol formation by providing aqueous medium for uptake of reactive gases, gas to particle partitioning, and the subsequent chemical processing (McNeill, 2015;McNeill et al., 2012;Tan et al., 2009;Xu et al., 2017b).

The winter haze pH in this study were ~3 units higher than that of the southeastern United States summer campaign (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 NH_3-rich conditions are prevalent. AWC may act as the major factor, because greater AWC dilute the $[H^+]$ and raise the pH. The AWC during the haze period (82 ± 105 μg m^{-3}) were much higher than those during the non-haze period (32 ± 41 μg m^{-3}).

3.3 A possible self-amplifying feedback mechanism

Given that AWC is a function of RH and SNA, a conceptual model of how AWC control ACR can be illustrated by a self-amplifying feedback loop (Figure 8). Formation of SNA is initiated by gas-particle conversion of NH_3. Under certain meteorological conditions such as high RH and shallow planetary boundary layer, SNA is subject to uptake moisture and result in the increases of AWC. Based on the discussions above, the increase of AWC would further raise ACR, leading to more efficient transformation of NH_3 as SNA.

Figure 9 shows the yearly average diurnal variation of ACR, AWC, SNA along with T and RH. Apparently, SNA tracked well with ACR and AWC, especially over nighttime. The not well-correlated track between SNA and AWC and ACR during the daytime (8:00-16:00) can be ascribed to the photochemical reactions that lead to SNA formation. The good correlation between SNA and AWC and ACR demonstrated in figure 9 support the proposed self-amplifying feedback loop in SNA formation.

4 Conclusion

Our results demonstrate that ACR, rather than NH_3 concentrations, plays a critical role in driving haze formation in the agricultural NH_3 emitted regions. Based on the "S curve" calculation, we have unraveled that AWC is the major

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factor controlling ACR. Upon analyzing the cross-correlations between AWC, ACR and SNA, we proposed a self-amplifying feedback mechanism of SNA formation that associated with AWC and ACR. This positive feedback cycle is likely to occur in other rural regions, where high agricultural NH_3 emissions are prevalent.

We have shown that high NH_3 concentrations may not necessarily lead to strong SNA formation, particularly in the agriculture intensive areas, e.g. the North China Plain (NCP) and the extensive farming lands in Eastern China where the high NH_3 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 NH_3 from the agricultural sector and 15% mitigation of NO_x and SO_2 emissions was achieved, a recent study has demonstrated that only when aerosol pH drops below 3.0, the NH_3 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 NH_3 only may not be an effective solution to tackle air pollution in these regions.

Data availability.

The data presented in this paper are available upon request from the corresponding author (huangkan@fudan.edu.cn).

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.

Competing interests.

The authors declare that they have no conflict of interest.

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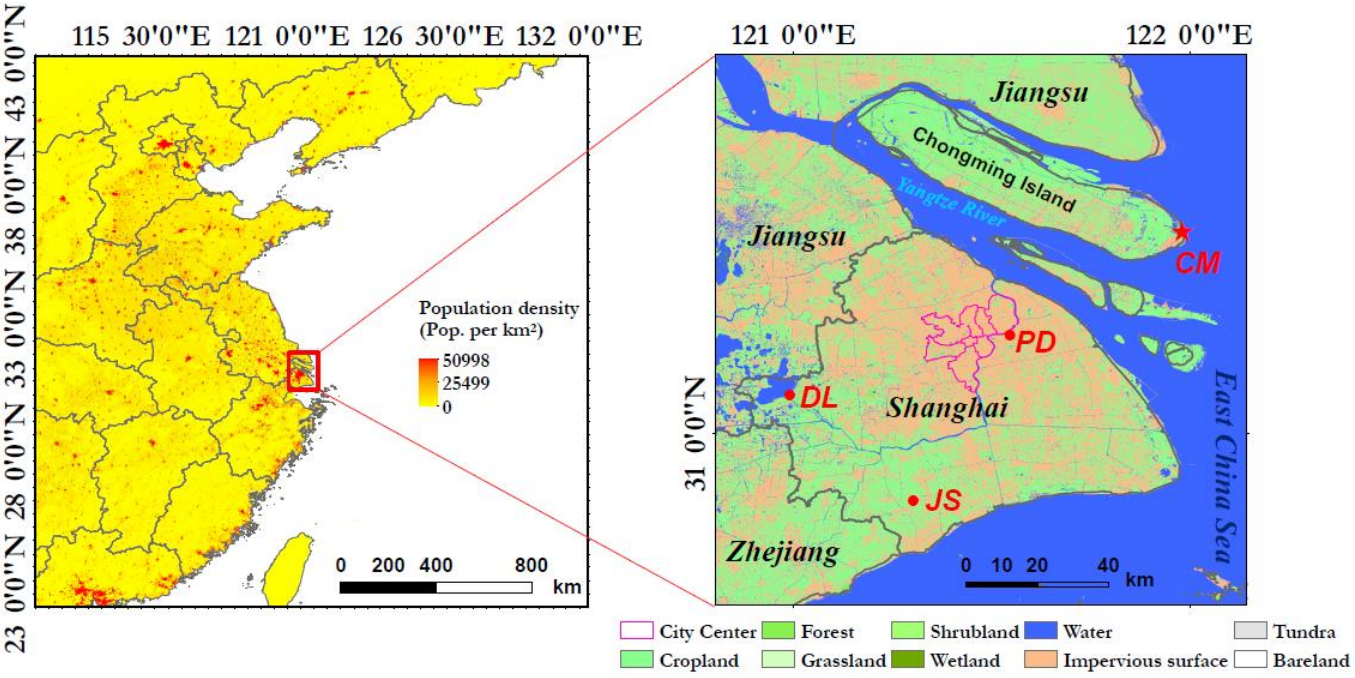

Figure 1: Location of the sampling site. Population density is color-coded in the left panel. The right panel shows the land cover in Shanghai (adapted from Peng et al.(2018)). CM (Chongming) is the sampling site on Chongming island. JS (Jinshan) represents the source emission from a dairy farm in rural Shanghai. DL (Dianshan Lake) represents a regional transport region in the Yangtze River Delta. PD (Pudong) represents the urban site.

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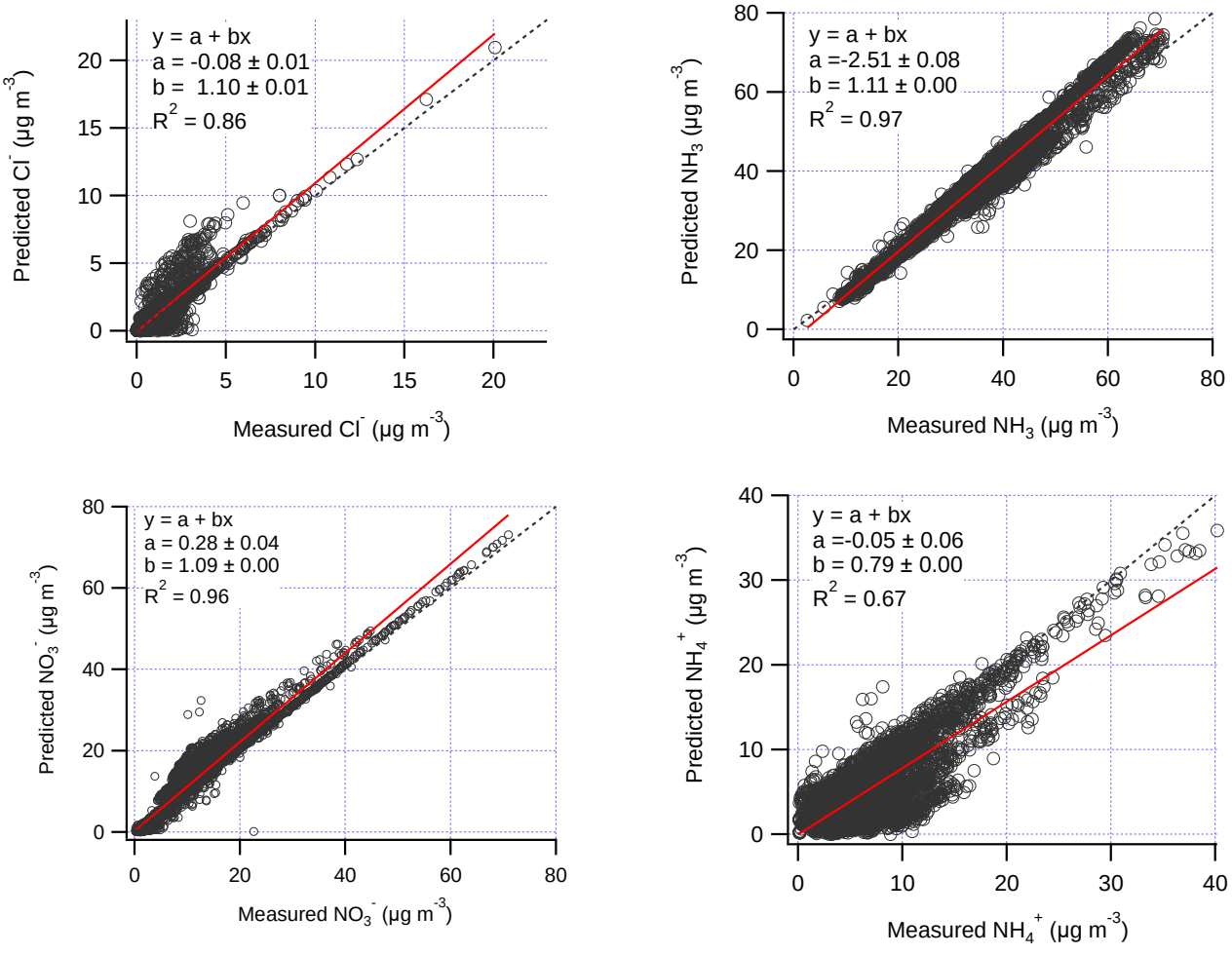

Figure 2: Comparison of predicted and measured Cl^-, NO_3^-, NH_3, NH_4^+. Orthogonal distance regression (ODR) fits with ±1σ are shown.

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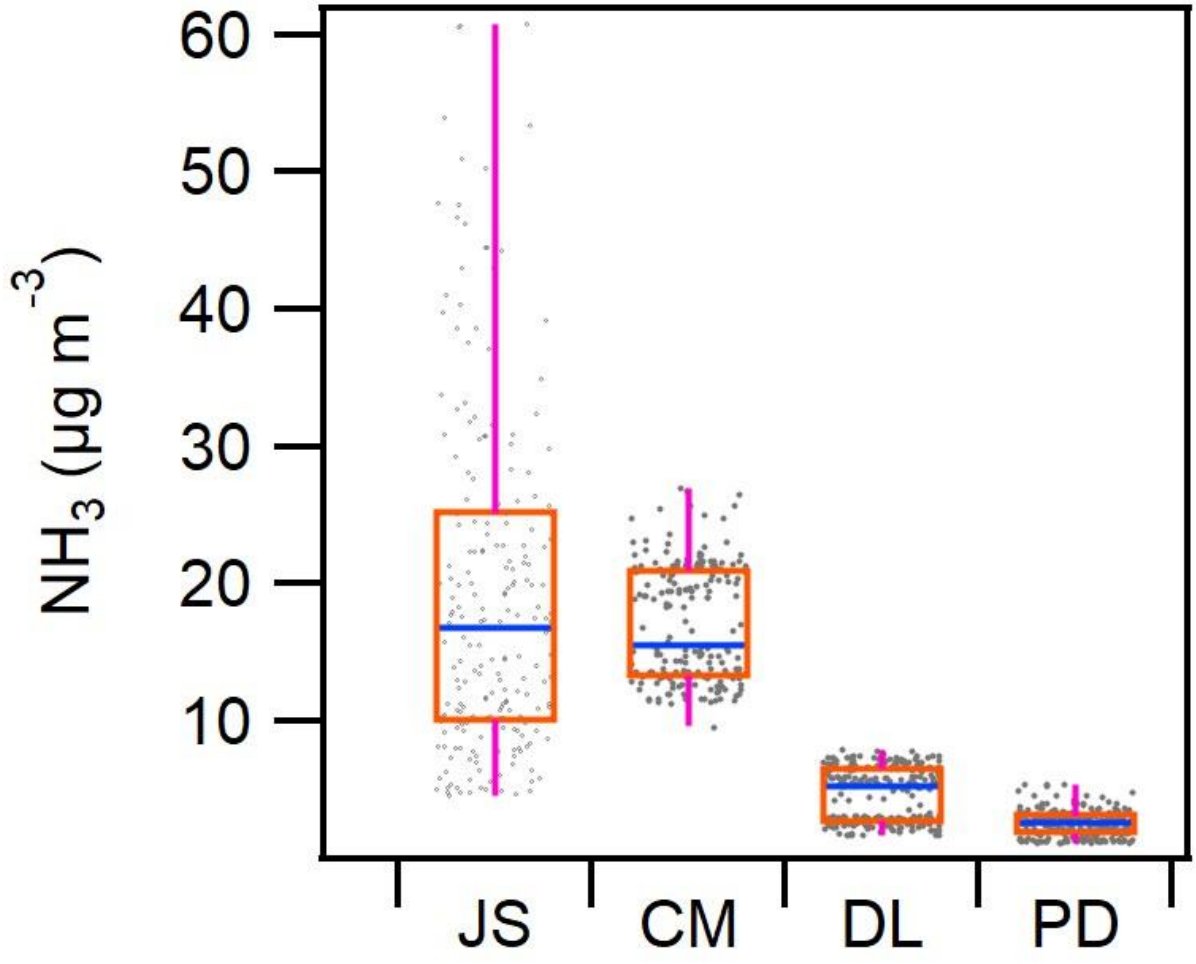

Figure 3: NH_3 at different sampling site over the same period (From Jan 18 to 27 of 2018). The locations of all sites are shown in Figure 1. Scattered dots indicate raw data points.

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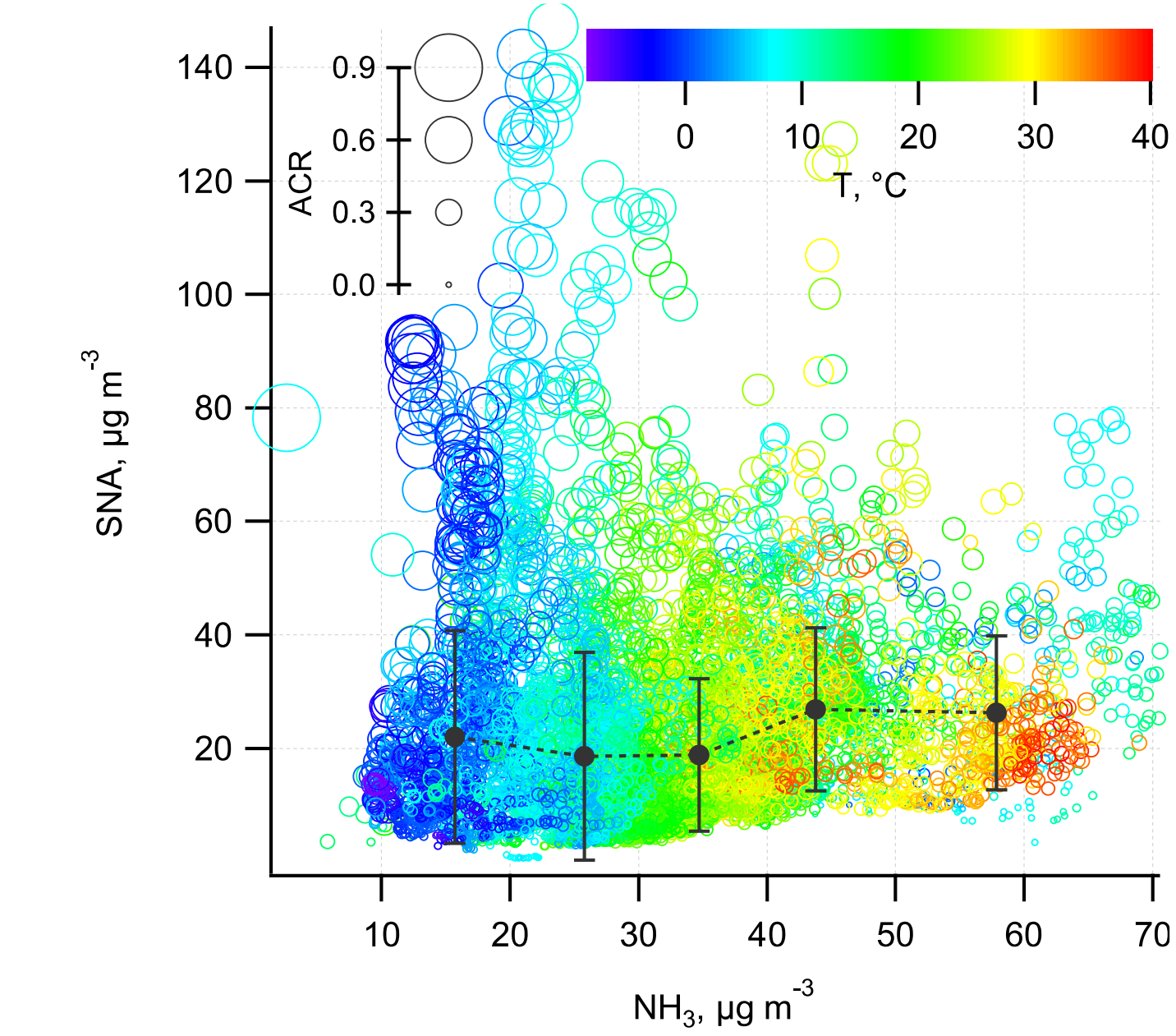

Figure 4: Secondary inorganic aerosol mass concentration in $PM_{2.5}$ (SNA refers to sulfate, nitrate, and ammonium) as a function of NH_3. The sizes of the void circles are scaled to the ACR and colored by T. The SNA concentrations in black filled circles are binned and averaged according to the NH_3 mass concentration of each 10 μg m^{-3}. Error bars represent one standard deviation (±1σ).

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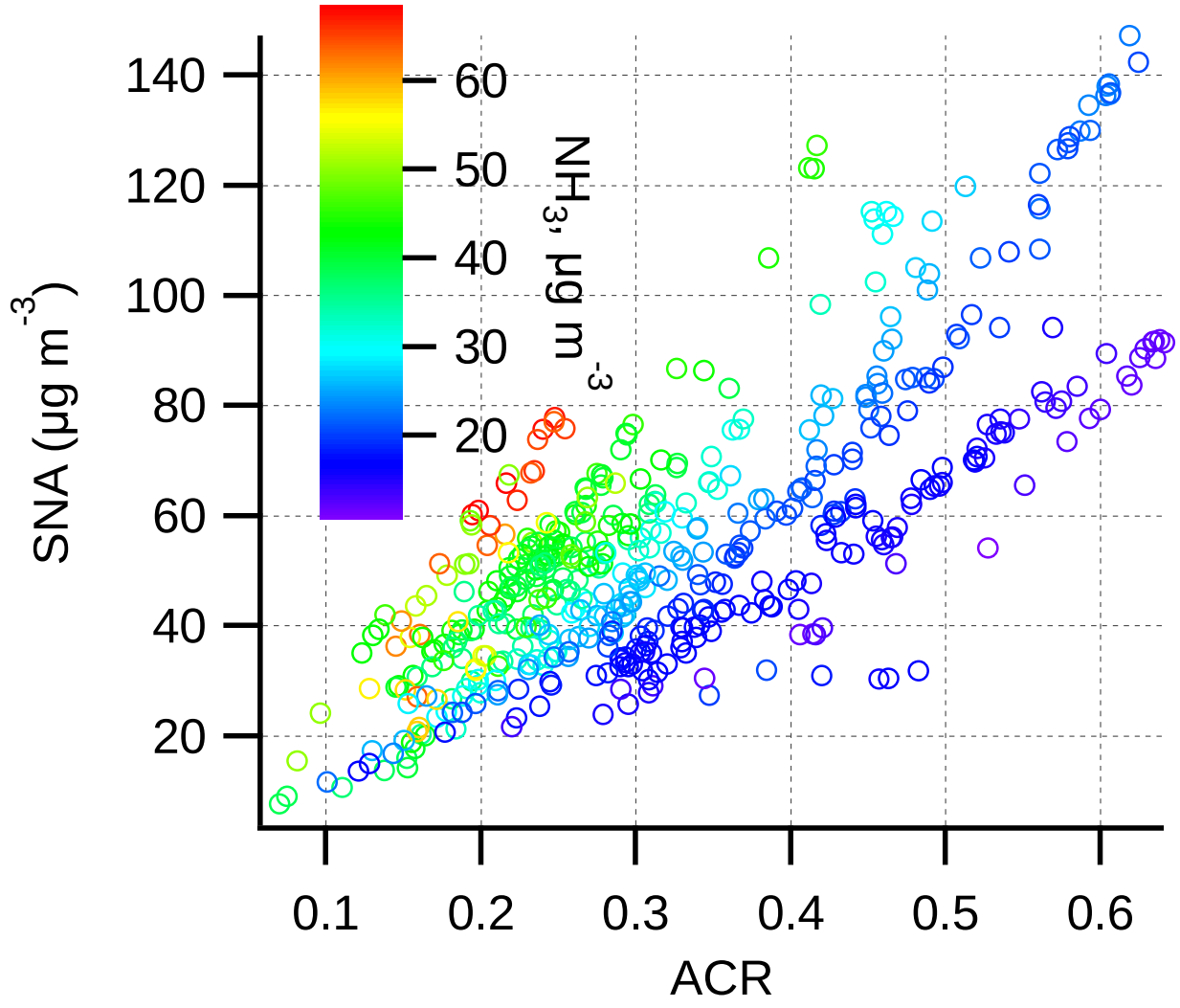

Figure 5: SNA mass concentration in $PM_{2.5}$ as a function of ACR during the haze period. The circles are colored by the NH_3 mass concentration.

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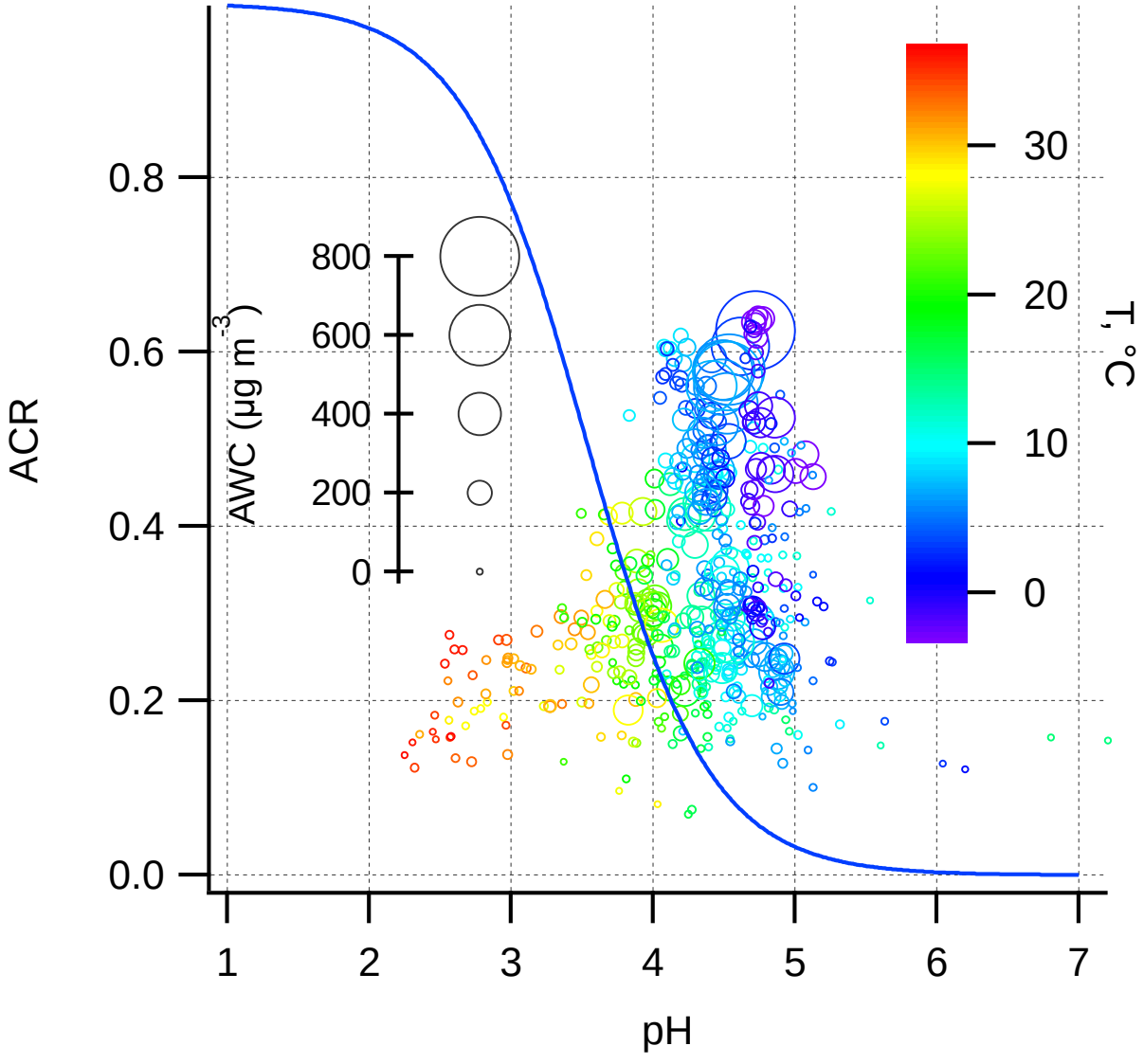

Figure 6: ACR as a function of pH during the haze period. The sizes of the void circles are scaled to AWC and colored by T. The blue curve was calculated based on the average T (10 °C), AWC (100 μg m^{-3}), and activity coefficients ratio of $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$ respectively. The average $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$ for the haze period is 2.4 ± 2.0 (±1σ).

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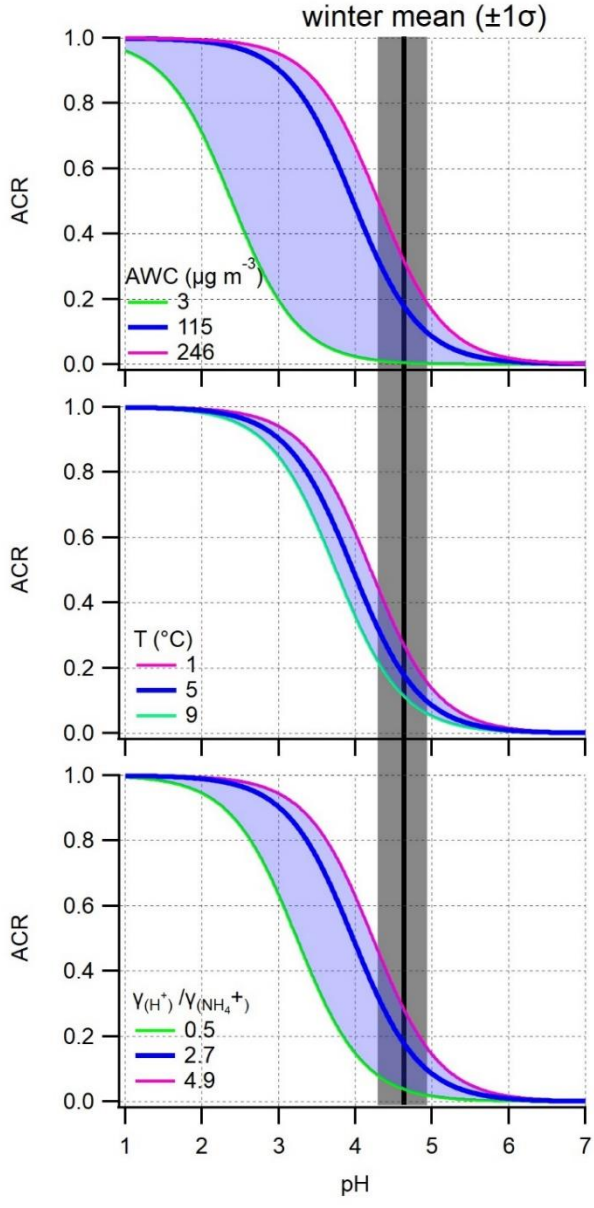

Figure 7: ACR as a function of pH during the winter haze period. Other variables are held constant at the average value during the winter haze period, while varying only the AWC, T, activity coefficients ratio of $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$, respectively. Shaded dark areas indicate the winter haze average pH together with one standard deviation (± 1σ). Shaded blue areas represent the curve corresponding to average ± 1σ, note that for AWC average - 1σ yield a negative value, thus the minimum mass concentration (3 μg m^{-3}) was used.

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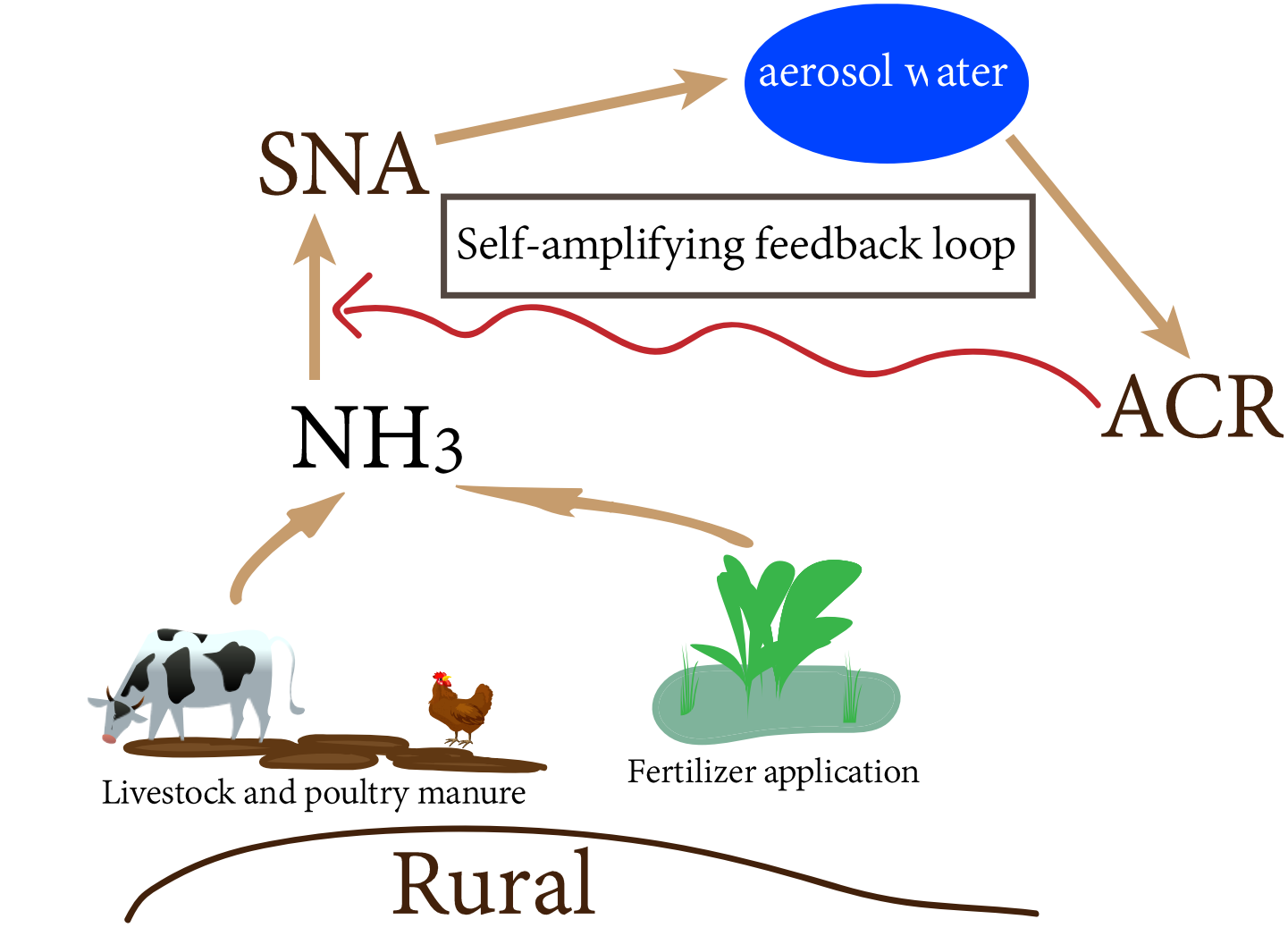

Figure 8: Schematic of self-amplifying feedback loop for SNA formation.

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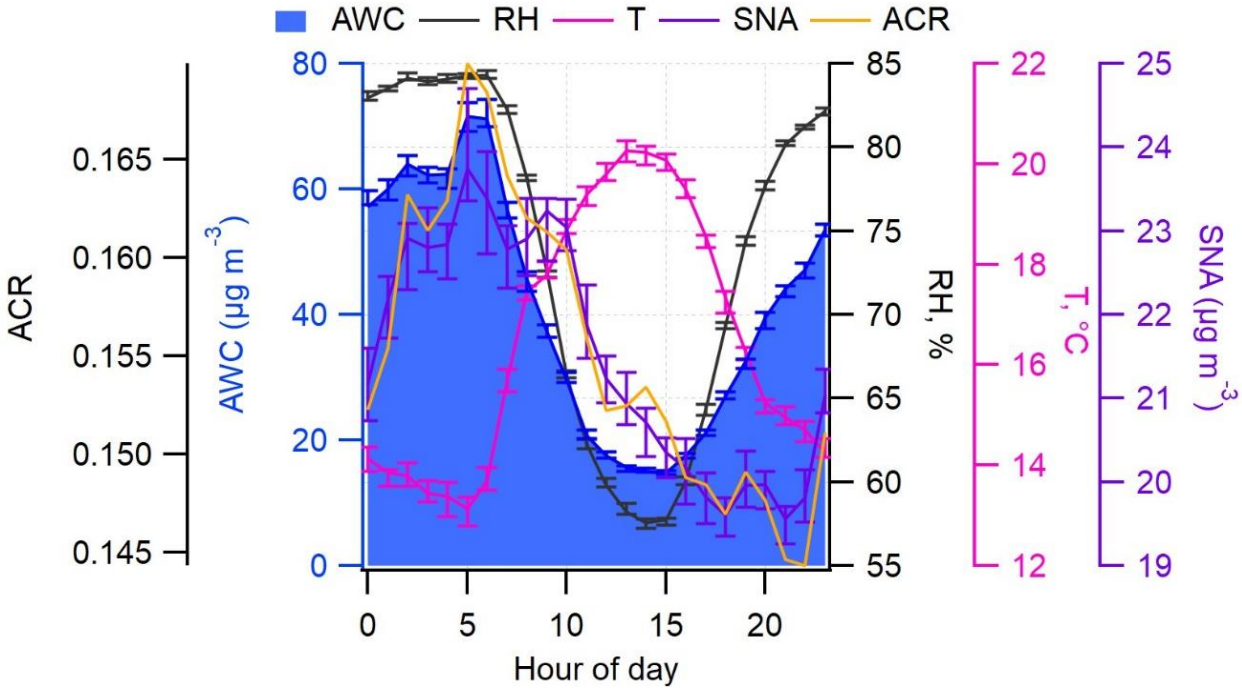

Figure 9: Annual mean diurnal pattern of ACR, AWC, SNA, T, and RH.

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Table 1: The summer and winter average (±1σ) ACR, pH, T, activity coefficients ratio of $\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$, and NH_3 (μg m^{-3}) during the haze period.

	ACR	AWC	pH	NH_3	$\frac{\gamma_{H^+}}{\gamma_{NH_4^+}}$	T
summer	0.2 ±0.1	79 ±73	3.4 ±0.5	40 ±8	1.8 ±1.7	29 ±5
winter	0.4 ±0.1	115 ±131	4.6 ±0.3	20 ±4	2.7 ±2.2	5 ±4