Measurement report: Occurrence of aminiums in PM$_{2.5}$ during winter in China: aminium outbreak during polluted episodes and potential constraints

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Abstract: Amines and aminiums play an important role in particle formation, liquid-phase reactions, and climate change, attracting considerable attention over the years. Here, we investigated the concentrations and compositions of aminiums in $PM_{2.5}$ in 11 Chinese cities during the winter, focusing on the characteristics of aminiums during the polluted days and the key factors influencing aminium outbreak. Monomethylaminium was the dominant aminium species in most cities except Taiyuan and Guangzhou, followed by dimethylaminium. Diethylaminium dominated the total aminiums in Taiyuan and Guangzhou. Thus, the main amine sources in Taiyuan and Guangzhou were significantly different from those in other cities. The concentrations of the total aminiums (TA) in all cities increased significantly during the polluted days, with weak aminium outbreaks in Xi'an and Beijing. Additionally, the concentrations of TA in Xi'an and Beijing were insignificantly correlated with those of $PM_{2.5}$ and the major acidic aerosol components, while the opposite pattern was observed in 9 other cities. Thus, acid-base chemistry was significantly associated with the formation of aminiums in $PM_{2.5}$ in all cities except Xi'an and Beijing. Based on the sensitivity analysis of the aminiums/ammonium ratio to ammonium changes as well as excluding the effects of relative humidity and atmospheric oxidation, we proposed the possibility of the competitive uptake of ammonia versus amines on acidic aerosols or the displacement of aminiums by ammonia in Xi'an and Beijing (constraining aminium outbreaks). Overall, this study deepens the understanding of the spatiotemporal differences in aminium characteristic and formation in China. However, the uptake of amines on particles to form aminiums and the relevant

47   influencing factors require further mechanistic research.

48

49   **Keywords:** Aminiums, PM$_{2.5}$ pollution, Aerosol acidity, Spatiotemporal variations,

50   Formation mechanism

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1. Introduction

54   Low-molecular-weight amines are ubiquitous and important in the gaseous and

55   particulate phases (Nielsen et al., 2012; Ge et al., 2011a; Berta et al., 2023). More

56   than 150 amines have been identified in the atmosphere (Ge et al., 2011a). The most

57   abundant and frequently reported amines in field observations are typically C1–C6

58   alkylamines   including   dimethylamine,   monomethylamine,   trimethylamine,

59   diethylamine, ethylamine, 1-propanamine, and 1-butanamine (Yang et al., 2023b; Liu

60   et al., 2023). Amines can participate in various chemical and physical processes in the

61   atmosphere, promoting the formation and growth of new particles and contributing to

62   the production of secondary organic aerosols (Yao et al., 2018; Tong et al., 2020;

63   Møller et al., 2020). Amines are thus considered to have a direct or indirect impact on

64   air quality (Li et al., 2019; Tao et al., 2016; Shen et al., 2023). Air pollution (e.g.,

65   haze) caused by high levels of atmospheric fine particles (PM$_{2.5}$) has received

66   considerable attention in China over the past decade due to rapid industrialization and

67   urbanization (Liu et al., 2022b; Liu et al., 2022c). Evidently, controlling the emission

68   strength of amine sources and understanding the transformation of atmospheric

69   amines can effectively reduce air pollution in cities.

70   The main sources of atmospheric amines during the air pollution period in cities

71   in China are typically fossil fuel combustion and biomass burning rather than

72   agricultural emissions (Feng et al., 2022; Liu et al., 2022c; Wang et al., 2022; Shen et

73   al., 2017; Ho et al., 2016; Chang et al., 2022). Owing to the water solubility and

74   alkalinity of amines, low-molecular-weight amines in $PM_{2.5}$ during the air pollution

75   period are mainly present in the form of amine salts (i.e., aminiums) via the gas-to-

76   particle partitioning of gaseous amines and subsequent acid-base chemistry (Zhang et

77   al., 2021; Liu et al., 2022a; Ge et al., 2011a; Xie et al., 2018). It should be noted that

78   organic amines (e.g., dimethylamine and trimethylamine) in nanoparticles (<200 nm)

79   may also be largely present in the organic phase (Xie et al., 2018). In addition,

80   oxidative degradation of higher-molecular-weight amines and displacement reactions

81   are also potential formation pathways of aminiums in $PM_{2.5}$ (Tao et al., 2021; Qiu and

82   Zhang, 2013; Tong et al., 2020). Although previous observational studies have

83   investigated the compositions, concentrations, sources, and formation processes of

84   low-molecular-weight aminiums in the particle phase in urban areas of Shanghai (Liu

85   et al., 2023), Guangzhou (Shu et al., 2023), Qingdao (Liu et al., 2022c), Xuzhou

86   (Yang et al., 2023b), China, there has been relatively little focus on the association

87   between $PM_{2.5}$ and amine outbreaks. A recent study conducted in Wangdu County,

88   Hebei Province, China has suggested that amines exhibited outbreak characteristics

89   during the haze episode (Feng et al., 2022). Climate and air pollution conditions can

90   vary greatly from city to city due to the vastness of China. However, it is poorly

91 understood how the characteristics and formation processes of low-molecular-weight

92 aminiums in $PM_{2.5}$ vary between clean and polluted days in different cities in China,

93 which may hinder the further assessment of the environmental impacts of amines with

94 regional differences.

95 In winter in China, air pollution episodes are more frequent compared to other

96 seasons. Thus, we present the measurements of aminiums in $PM_{2.5}$ collected from 11

97 different Chinese cities during the winter (2017–2018). The aims of this study are (1)

98 to investigate the spatial differences in the compositions and concentrations of

99 aminiums in $PM_{2.5}$, with a focus on the difference between them on clean days and

100 polluted days, and (2) to understand the key factors controlling the formation of

101 aminiums in $PM_{2.5}$ in different cities.

102

103 **2. Materials and Methods**

104 **2.1. Site Description and Sample Collection**

105 A total of eleven urban sites were selected for aerosol sample collection,

106 including Beijing (BJ; 116.41°E, 40.04°N), Taiyuan (TY; 112.58°E, 37.80°N), Xi'an

107 (XA; 108.98°E, 34.25°N), Lanzhou (LZ; 103.73°E, 36.11°N), Haerbin (HEB, i.e.,

108 Harbin; 126.64°E, 45.77°N), Wulumuqi (WLMQ, i.e., Urumqi; 87.75°E, 43.86°N),

109 Chengdu (CD; 104.14°E, 30.68°N), Guiyang (GY; 106.73°E, 26.58°N), Guangzhou

110 (GZ; 113.35°E, 23.18°N), Wuhan (WH; 114.36°E, 30.55°N), and Hangzhou (HZ;

111 120.16°E, 30.30°N) sites (**Figure S1**). HZ and GZ are megacities situated in the

112 Yangtze River Delta (YRD) and Pearl River Delta (PRD) regions respectively, both of

which have developed economies. WH is located in the central region of China. CD

and GY are representative cities in southwest China. LZ, XA, TY, BJ, and HEB are

cities in northern China. WLMQ, located in northwest China, is the largest inland city

farthest from the ocean in the world. Obviously, the varying geographical locations

and economic development levels of different cities lead to different air pollution and

climate conditions between them.

PM$_{2.5}$ sampling in most cities was conducted on the rooftops of buildings (4–6

floors in total) using a high-volume air sampler (Series 2031, Laoying, China) from

December 1, 2017 to January 21, 2018 (winter). Specifically, the sampling periods in

LZ, TY, HEB, BJ, XA, WLMQ, CD, WH, HZ, GZ, and GY were Dec. 2–30, 2017,

Dec. 2–30, 2017, Dec. 18, 2017 – Jan. 15, 2018, Dec. 22, 2017 – Jan. 21, 2018, Dec.

22, 2017 – Jan. 20, 2018, Mar. 3–28, 2018, Dec. 1 – 31, 2017, Dec. 6–29, 2017, Dec.

4–31, 2017, Dec. 1–30, 2017, and Dec. 10, 2017 – Jan. 11, 2018, respectively (**Tables**

S1-S3). At each site, PM$_{2.5}$ was sampled once every one to two days for ~24 hours on

prebaked quartz fiber filters (500 °C for 8 hours). Moreover, two random blank filters

were collected. The total number of PM$_{2.5}$ samples at each sampling site was shown in

Tables S1-S3. All samples were stored at –30 °C. Meteorological data such as

precipitation, wind speed, temperature, and relative humidity (RH), as well as

concentrations of various pollutants were recorded during the sampling campaigns

from the adjacent environmental monitoring stations. Sampling periods were

classified as either clean or polluted days based on a daily average PM$_{2.5}$ mass

concentration of 75 μg m^{-3} (Zhang and Cao, 2015) .

135

2.2. Chemical Analysis

The extraction of low-molecular-weight aminiums in the filter samples was carried out using the method described in our recent publication (Liu et al., 2023) and in a previous study (Liu et al., 2017). Briefly, the sample was filtered using a 0.22 μm Teflon syringe filter (CNW Technologies GmbH) after extraction with Milli-Q water (~18.2 MΩ cm). The aminiums in the extracts that underwent pH regulation were derivatized using 0.1 mL of benzenesulfonyl chloride (BSC). The tube containing the derivatives was sealed and agitated for 30 minutes. To remove excess derivatization reagents, the extracts were agitated again for 30 minutes at 80°C after adding NaOH solution (0.5 mL of 10 mol L^{-1}). Once the mixed solution had cooled down, it was acidified with a solution of HCl to adjust the pH to 5.5. A further extraction of derivatives was carried out by adding dichloromethane. It is important to mention that the organic phase was treated with Na_2CO_3 solution and anhydrous Na_2SO_4 sequentially. A stream of nitrogen gas was used to concentrate the organic extracts. Finally, the sample was analyzed using GC-MS after adding dichloromethane and hexamethylbenzene. Dimethylaminium ($DMAH^+$), monomethylaminium ($MMAH^+$), diethylaminium ($DEAH^+$), ethylaminium (EAH^+), propylaminium (PAH^+), butylaminium (BAH^+), and pyrrolidinium ($PYRH^+$) were quantified. Aminium recoveries varied between 73% for $DMAH^+$ and 112% for PAH^+. The detection limits of the aminium measurements ranged from 0.8 ng mL^{-1} for $DEAH^+$ to 2.8 ng mL^{-1} for $MMAH^+$. Aminiums are undetectable in the blank. Detailed data quality controls were

157 described in our recent publication (Liu et al., 2023). It should be noted that we did

158 not consider the impact of continuous aging of aminiums collected on the filter on the

159 measurement results. This is mainly due to the following reasons. The $PM_{2.5}$ samples

160 investigated in this study are all acidic (**Tables S1–S3**), promoting the protonation of

161 amino groups. The protonated amino group is difficult to undergo oxidation by

162 oxidants (e.g., hydroxyl radicals and ozone) (Nielsen et al., 2012).

163   Another filter cut was extracted with Milli-Q water to measure the

164 concentrations of inorganic ions (e.g., NO_3^-, SO_4^{2-}, NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+}) and

165 organic acids (e.g., acetic acid, formic acid, succinic acid, oxalic acid, glutaric acid,

166 and methanesulfonic acid) (Xu et al., 2022a; Xu et al., 2023; Liu et al., 2023; Lin et

167 al., 2023). These inorganic ions were quantified via an ion chromatograph system

168 (Dionex Aquion, Thermo Scientific, USA).

169

170 **2.3. Parameter calculation**

171   The thermodynamic model (ISORROPIA-II) was used for the prediction of the

172 mass concentration of aerosol liquid water (ALW) and the pH value, which was

173 detailed in our previous studies (Xu et al., 2022b; Xu et al., 2020; Xu et al., 2023).

174 The ventilation coefficient (VC) can be used as an indicator to assess the state of

175 atmospheric dilution of pollutant concentrations (Gani et al., 2019). It is calculated by

176 multiplying the wind speed by the planetary boundary layer height (PBLH) (Yang et

177 al., 2023a).

178

3. Results and discussion

3.1. Compositions of aminiums in PM$_{2.5}$ in China during winter

Figure 1 shows the average percentage distributions of various aminiums in PM$_{2.5}$ collected in different cities in China during winter, with a comparison between their mass fractions on clean and polluted days. MMAH$^+$ was the predominant species among the aminiums investigated in PM$_{2.5}$ in most cities in northern China, including LZ, XA, HEB, BJ, and WLMQ. MMAH$^+$ and DMAH$^+$ (as the second most abundant species) constituted over 63% of the total aminium concentrations in those northern cities. The relatively minor species, including DEAH$^+$, EAH$^+$, PAH$^+$, BAH$^+$, and PYRH$^+$, contributed between 1% and 18% of the total aminium concentrations. The predominance of MMAH$^+$ was also found in cities in the YRD (HZ), central (WH), and southwestern (CD and GY) China, closely followed by DMAH$^+$. Previous studies conducted in Xi'an (winter, China) (Ho et al., 2015), Beijing (winter, China) (Wang et al., 2022; Ho et al., 2016), Nanjing (winter, China) (Liu et al., 2023) Shanghai (winter, China) (Liu et al., 2023), Xiamen (winter, China) (Ho et al., 2016), Hong Kong (winter, China) (Ho et al., 2016), and Arabian Sea (autumn and winter) (Gibb et al., 1999), as well as at mountain (autumn, Nanling, China) (Liu et al., 2018) and background (winter, Puding, China) (Liu et al., 2023) sites have suggested that the mass concentration fraction of MMAH$^+$ was highest in the measured aerosol amine salts. The Henry's constants of MMA (3.65×10^1 mol kg^{-1} atm^{-1}), DMA (3.14×10^1 mol kg^{-1} atm^{-1}), and EA (3.55×10^1 mol kg^{-1} atm^{-1}) are relatively lower than those of the other amines investigated (e.g., 1.32×10^2 mol kg^{-1} atm^{-1} for DEA) (Ge et al.,

201 2011b), implying that the potential of MMA, DMA, and EA to be partitioned into

202 aqueous particles was weaker compared to DEA. Additionally, the gaseous forms of

203 these determined aminiums typically have strong alkalinity (Ge et al., 2011b). The

204 aerosol samples in this study were all acidic (**Tables S1–S3**). Thus, these results imply

205 that the increased emissions of MMA and DMA may partially explain the higher

206 abundance of MMAH$^+$ and DMAH$^+$ in PM$_{2.5}$ in these investigated cities during winter.

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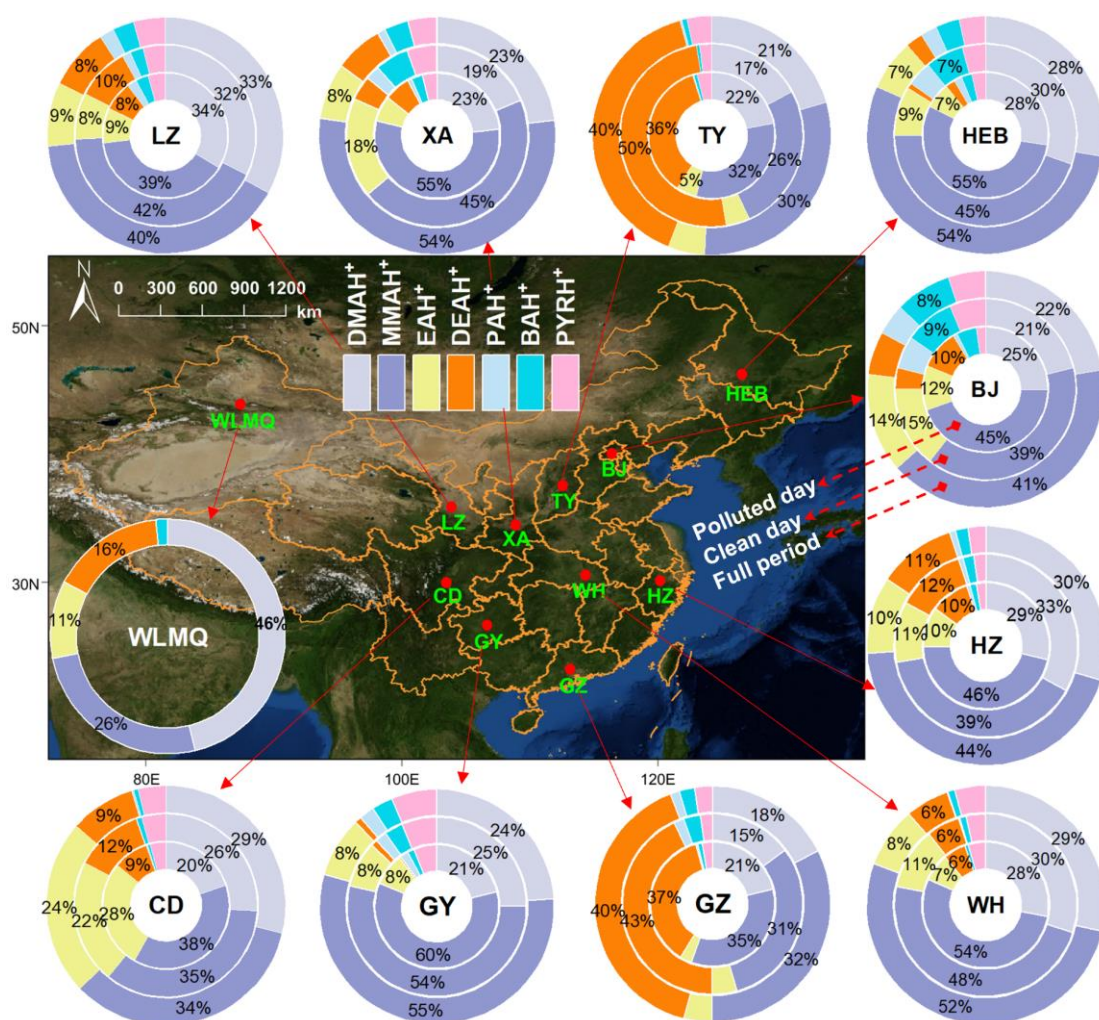
208

209 **Figure 1.** Average percentage distributions of various aminiums in PM$_{2.5}$ collected in

210 different cities in China during winter. The map was obtained from $^{©}$MeteoInfoMap

211 (version 3.3.0) (Chinese Academy of Meteorological Sciences, China).

212

In another northern city (i.e., TY), $DEAH^+$ was the most abundant aminium species (40% of the total aminium concentrations), followed by $MMAH^+$ (30%) and $DMAH^+$ (21%). The composition characteristic of aminiums in the city of GZ (PRD area) was similar to that observed in TY (**Figure 1**). Anthropogenic emissions, including vehicle exhaust and industrial production are considered to be the main contributors to aerosol $DEAH^+$ in urban areas (Chen et al., 2022b; Chen et al., 2019; Yang et al., 2023b; Chang et al., 2022). A recent study has suggested that ethanol gasoline vehicles can emit a large amount of ethyl-amines, leading to the outbreak of $DEAH^+$ during the haze episodes in Hebei Province (North China) (Feng et al., 2022). Thus, the relative emission strength of anthropogenic DEA in the investigated amines was probably higher in TY (an inland city with application of ethanol gasoline vehicles) than in other cities. In addition, previous studies have suggested that aerosol $DEAH^+$ can also be largely derived from marine emissions (Facchini et al., 2008; Dall'osto et al., 2019). Since GZ is a developed coastal city, local aerosol aminiums may be influenced by large gaseous DEA inputs from both local industrial production and marine sources.

The mass concentration fractions of aminiums on clean and polluted days were also compared (**Figure 1**). The dominant aminium species (i.e., $MMAH^+$, $DMAH^+$, or $DEAH^+$) in $PM_{2.5}$ in all cities were not replaced by other aminiums from the clean days to the polluted days. This likely suggests that the main sources of atmospheric gas-phase amines in the cities did not change significantly on the polluted days. In

234 addition, the proportions of $MMAH^+$ and $DMAH^+$ tended to further increase from the

235 clean days to the polluted days, while that of $DEAH^+$ with relatively low solubility

236 showed a decreasing trend, especially in TY and GZ (where $DEAH^+$ was dominant).

237 The concentrations of ALW in $PM_{2.5}$ were generally much higher on polluted days

238 than on clean days, especially in the northern cities (**Tables S1–S3**). Clearly, liquid-

239 phase processes likely played an important role in the formation of aminiums on

240 polluted days.

241

242 **3.2. Aminium concentrations and their linkage with $PM_{2.5}$ variations**

243   **Figure 2** shows the average concentration distributions of various aminiums in

244 $PM_{2.5}$ collected in different cities in China during winter, focusing on the difference

245 between their concentrations on clean days and polluted days. The concentrations of

246 total aminiums (TA) in TY ranged from 17.50 to 149.00 ng m^{-3}, with an average of

247 56.90 $\pm$ 41.81 ng m^{-3}. This average TA level was the highest among all the cities

248 investigated. The average concentration of TA in WLMQ was found to be the lowest

249 (4.16 $\pm$ 1.24 ng m^{-3}), with a range of 2.10–6.50 ng m^{-3}. As previously mentioned,

250 WLMQ is a vast city with a lower population density and less developed industries

251 compared to the more developed northern and coastal cities in China. Additionally,

252 this region is surrounded by barren mountains and sandy land (Ma et al., 2024)

253 (**Figure 2**). Apparently, the weak amine emission intensity appears to be responsible

254 for the low levels of aminiums in the WLMQ.

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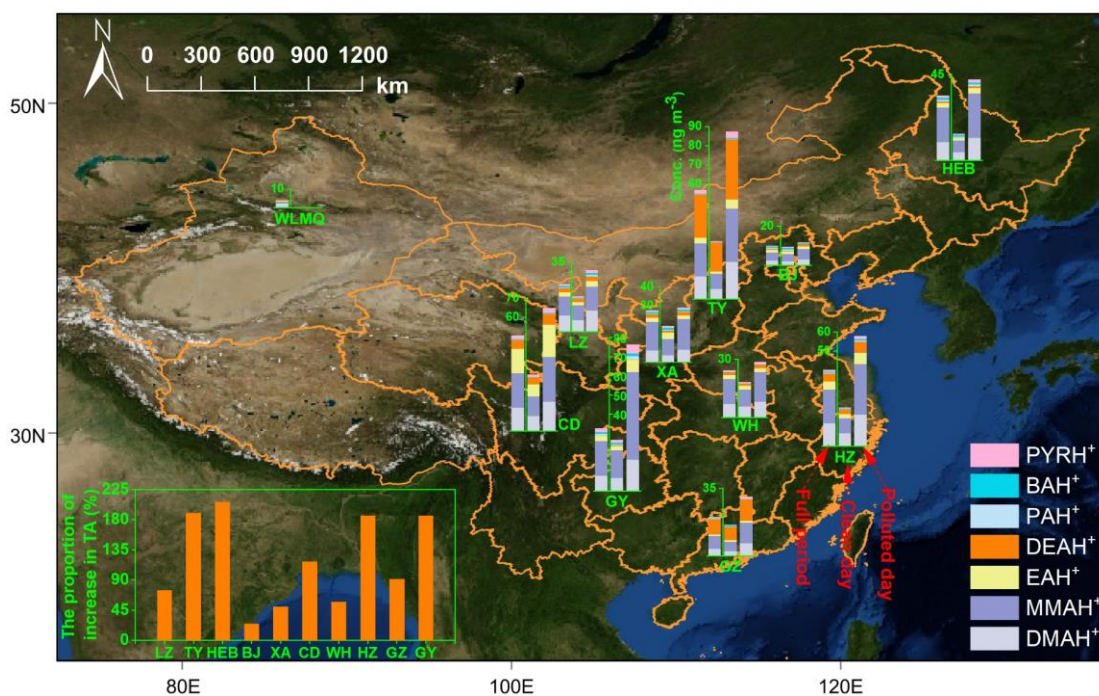
Figure 2. Average concentration distributions of various aminiums in PM$_{2.5}$ collected in different cities in the winter in China. The stacked bar chart from left to right indicates the data for the full sampling period, the clean day, and the polluted day in turn. The column chart in the bottom left corner shows the proportion of the increase in TA concentration from the clean days to the polluted days. The map was obtained from ©MeteoInfoMap (version 3.3.0) (Chinese Academy of Meteorological Sciences, China).

Table S4 provides an overview of the aminiums detected in atmospheric fine particles detected in different seasons and regions. The ranges of average TA concentrations in the northern cities (i.e., HEB, BJ, TY, XA, LZ, and WLMQ) generally overlapped with those measured in the coastal (GZ and HZ), central (WH), and southwestern (CD and GY) cities in this study (**Tables S1–S3**). Moreover, the average TA concentrations investigated here (4.16 ng m^{-3} – 56.90 ng m^{-3}) were also

271 within the observation ranges reported in previous studies (1.49 ng m^{-3} – 329.80 ng m^{-3}

272 ^{3}) (**Table S4**) (Ho et al., 2016; Liu et al., 2023; Shen et al., 2017; Huang et al., 2016;

273 Choi et al., 2020; Liu et al., 2018; Shu et al., 2023). MMAH^{+}, as the dominant

274 aminium species in most of cities, showed the highest (18.33 ± 12.82 ng m^{-3}) and

275 lowest (1.07 ± 0.55 ng m^{-3}) average concentrations in HEB and WLMQ, respectively.

276 DEAH^{+} was the most abundant aminium species in TY and GZ, with average

277 concentrations of 22.62 ± 17.62 ng m^{-3} and 8.16 ± 4.65 ng m^{-3}, respectively (**Tables**

278 **S1** and **S3**). Two previous studies conducted in the GZ area in winter (2021 and 2015–

279 2016) showed similar average DEAH^{+} (~ 7 ng m^{-3}) levels to this study (Liu et al.,

280 2022b; Shu et al., 2023). However, DEAH^{+} was not identified as the dominant

281 aminium component in those two previous studies. Furthermore, lower aminium

282 concentrations (< 8 ng m^{-3}) were generally found in most of the marine and polar

283 regions (Dall'osto et al., 2019; Corral et al., 2022). In general, the concentration and

284 composition of aminiums vary spatially, which may be attributed to spatial differences

285 in amine sources, emission intensities, and the main factors affecting aminium

286 formation.

287 The average concentrations of TA in all the investigated cities exhibited a similar

288 variation pattern from clean to polluted days, which was characterized by higher

289 levels on polluted days (**Figure 2**). Specifically, the average aminium concentration

290 showed an increase of up to 206% in HEB during the polluted period. TA

291 concentrations in LZ, TY, CD, HZ, and GZ also increased greatly by 91% (in GZ)

292 −190% (in TY). It seems that PM$_{2.5}$ pollution can be accompanied by an outbreak of

aminiums. In contrast, a relatively small percentage increase in TA concentration

during the polluted days was found in WH (57%), XA (50%), and BJ (25%). To

further explore the linkage between changes in $PM_{2.5}$ and fluctuations in aminiums,

the temporal variations in the mass concentrations of aminiums and $PM_{2.5}$ were

compared across various cities (**Figure 3**). The concentrations of total and major

aminiums in LZ, TY, HEB, WLMQ, CD, WH, HZ, GZ, and GY showed a temporal

variation highly similar to that of $PM_{2.5}$, as indicated by a significant correlation

between TA and $PM_{2.5}$ in these cities ($r = 0.61–0.85$, $P < 0.05$). However, high levels

of $PM_{2.5}$ can correspond to low levels of aminiums in XA (e.g., Dec. 29 and Jan. 2,

14, 15, and 16) and BJ (e.g., Dec. 28, 30). The correlations between TA and $PM_{2.5}$ in

these two cities were also insignificant ($P > 0.05$). These results suggest that the

formation of aminiums in XA and BJ during the polluted period may be constrained

by some special factors, which will be discussed in the following discussion.
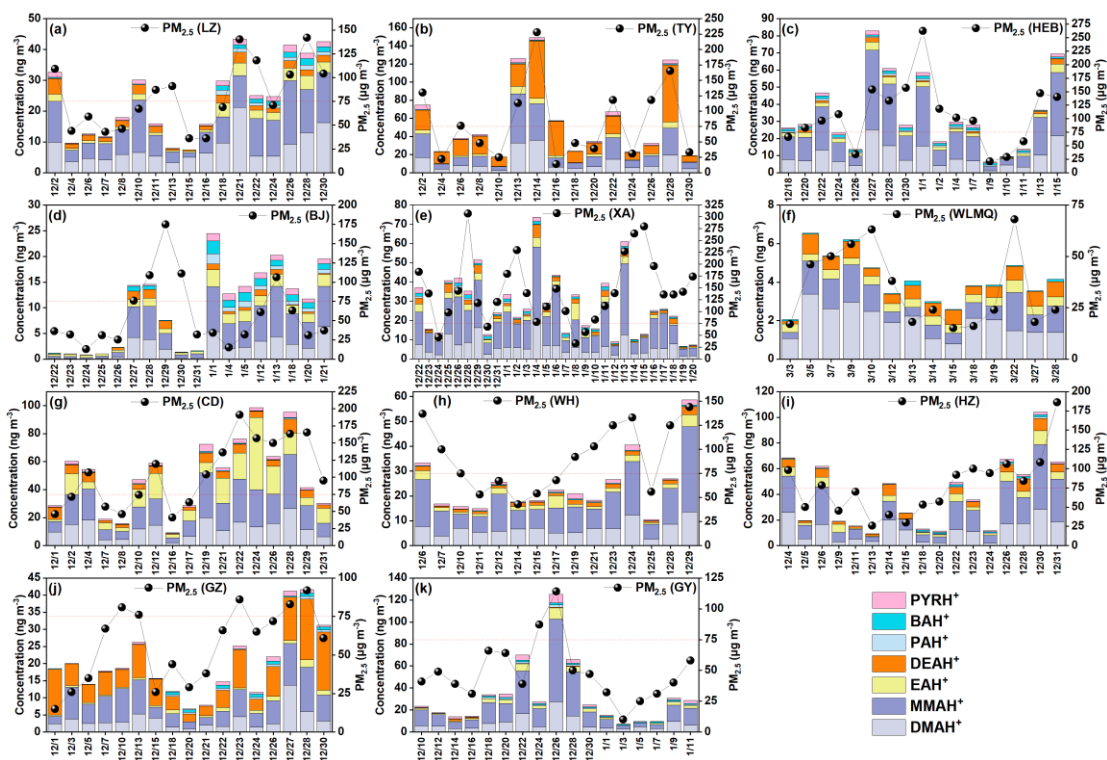
Figure 3. Temporal variations in the mass concentrations of aminiums and PM$_{2.5}$ observed at the (a) LZ, (b) TY, (c) HEB, (d) BJ, (e) XA, (f) WLMQ, (g) CD, (h) WH, (i) HZ, (j) GZ, and (k) GY sites.

3.3. Formation of aminiums and potential ammonia suppression in aminium outbreaks

It is well documented that aminiums in PM$_{2.5}$ can be formed mainly via the uptake of their gaseous form (i.e., amines) by aqueous particles, followed by acid-base neutralization reactions (Ge et al., 2011b; Xie et al., 2018; Sauerwein and Chan, 2017; Qiu and Zhang, 2013; Liu et al., 2023). Clearly, the formation of particle-phase aminiums was closely associated with the origins of the corresponding gas-phase amines (as precursors of aminiums). We found that TA and major aminiums (e.g., MMAH$^+$, DMAH$^+$, and DEAH$^+$) showed a significant positive correlation ($P < 0.05$)

with either SO_2, NO_2, or K^+ (as indicators of fuel combustion and biomass burning

(Tian et al., 2020; Liu et al., 2023; Kunwar and Kawamura, 2014)) in LZ, TY, HEB,

BJ, WLMQ, CD, WH, HZ, GZ, and GY (**Figure 4** and **Figure S2**). Thus, although

lacking sufficient indicators (e.g., biogenic source traces) to trace the source of

amines, our results can at least indicate that fossil fuel combustion or biomass burning

may be important contributors to atmospheric amines in most of the investigated cities

during the winter. This consideration was also supported by previous studies about the

potential source analysis of aerosol aminiums in Guangzhou, Xuzhou, and Wulumuqi

during the winter (Yang et al., 2023b; Shu et al., 2023; Ma et al., 2024). In contrast,

the concentrations of TA in XA were weakly correlated ($P > 0.05$) with those of K^+,

SO_2, and NO_2. Several studies conducted in XA have suggested that aerosol nitrogen-

containing organic compounds can be largely derived from fossil fuel combustion and

biomass burning (Zhang et al., 2023a; Zhang et al., 2023b; He et al., 2023; Yang et al.,

2024). Moreover, the traditional method of identifying amine sources through

correlation analysis (Berta et al., 2023; Liu et al., 2022b; Liu et al., 2022a; Huang et

al., 2022; Corral et al., 2022) can also have significant uncertainties, as implied by the

following two cases. First, the uptake of amines by aerosol particles might be

constrained by low ALW concentration, weak particle acidity, or high ammonia levels

(Liu et al., 2022b; Chen et al., 2022a; Ge et al., 2011b; Sauerwein and Chan, 2017;

Chan and Chan, 2013; Wang et al., 2010). Second, amines might be largely

decomposed by atmospheric oxidants (e.g., hydroxyl radical and ozone) (Nielsen et

al., 2012; Qiu and Zhang, 2013). Thus, the abovementioned weak correlations

between aminiums and indicators in XA cannot definitely indicate that the

contributions of fossil fuel combustion and biomass burning to amines in XA were

insignificant. Presumably, the prerequisite for amine source apportionment using the

correlation between aminiums and indicators is that the gas-phase amines can be

largely converted into aminiums in $PM_{2.5}$ through secondary processes without the

influence of constrained factors. To further explore this issue, the following discussion

focuses on the main factors affecting the formation of aminiums in particles.

Figure 4. Diagrams presenting correlations between the concentrations of TA and

other parameters at (**a–c**) different sites. The colors of the different solid circles

indicate different correlation coefficients r. The size of the solid circle indicates the

significance of the correlation between the two corresponding parameters: the larger

circle indicates that the correlation is more significant, while the symbol "×" indicates

that the P-value is greater than 0.05.

The concentrations of TA in LZ, TY, HEB, WLMQ, CD, WH, HZ, GZ, and GY

showed significant positive correlations ($P < 0.01$) with those of the acidic

components (e.g., NO_3^-, SO_4^{2-}, organic acids, and acidity (expressed as $[(NO_3^- +$

$2SO_4^{2-}) – NH_4^+]$ (Feng et al., 2022)), whereas an insignificant correlation ($P > 0.05$)

was found between them in BJ and XA (**Figure 4** and **Figure S3**). Thus, acid-base

chemistry was tightly associated with the formation of aminiums in $PM_{2.5}$ at all sites

excepting BJ and XA. A recent laboratory study has suggested that amines can be

neutralized by H_3O^+ to form aminiums within picoseconds under conditions of high

concentrations of particle sulfuric acid (Zhang et al., 2021). In addition, it has also

been found that organic acids (e.g., formic acid) are able to participate in the

nucleation of methanesulfonic acid–methylamine through an acid-base reaction

(Zhang et al., 2022). The particles are acidic (especially on polluted days) at all study

sites, with an average pH value ranging from 2.4 to 5.7 (**Tables S1–S3**). Amines can

also partition into the particles by direct dissolution under high RH conditions (Ge et

al., 2011b). Significantly increased RH values (i.e., high ALW) (**Figure 5a**) and acidic

components (**Figure 5b**) on polluted days were also observed in XA and BJ.

Nevertheless, the insignificant correlation between aminiums and acidic components

and ALW concentrations in XA and BJ, together with a relatively small proportional

increase in aminiums (**Figure 2**) from clean to polluted days at these two sites suggest

that besides acidity and RH, there were other key factors affecting aminium formation

in XA and BJ. As we know, the oxidative degradation of amines is one of the main

pathways for the removal of atmospheric amines (Qiu and Zhang, 2013; Murphy et

al., 2007). Furthermore, for atmospheric oxidants (e.g., hydroxyl radical) reacting

with low-molecular-weight alkylamines, a negative temperature dependence of the

rate coefficients has been reported (Nielsen et al., 2012). However, the winter air

temperature in northern China was relatively low (< 0 °C in XA and BJ) (**Tables S1–**

384   **S3**); moreover, there was no significant change in the atmospheric oxidation

385   (indicated by O_x levels ($O_x = O_3 + NO_2$)) of polluted and clean days in XA (higher O_x

386   level during clean days) and BJ. In particular, the protonated amino group has been

387   suggested to be difficult to undergo oxidation by hydroxyl radicals and ozone

388   (Nielsen et al., 2012). Accordingly, atmospheric oxidation and temperature may not

389   be the main factors affecting changes in aminium concentrations during clean and

390   polluted days. Furthermore, the insignificant correlation between aminiums and acidic

391   components in XA and BJ suggests that other factors affecting aminium formation

392   must be considered.

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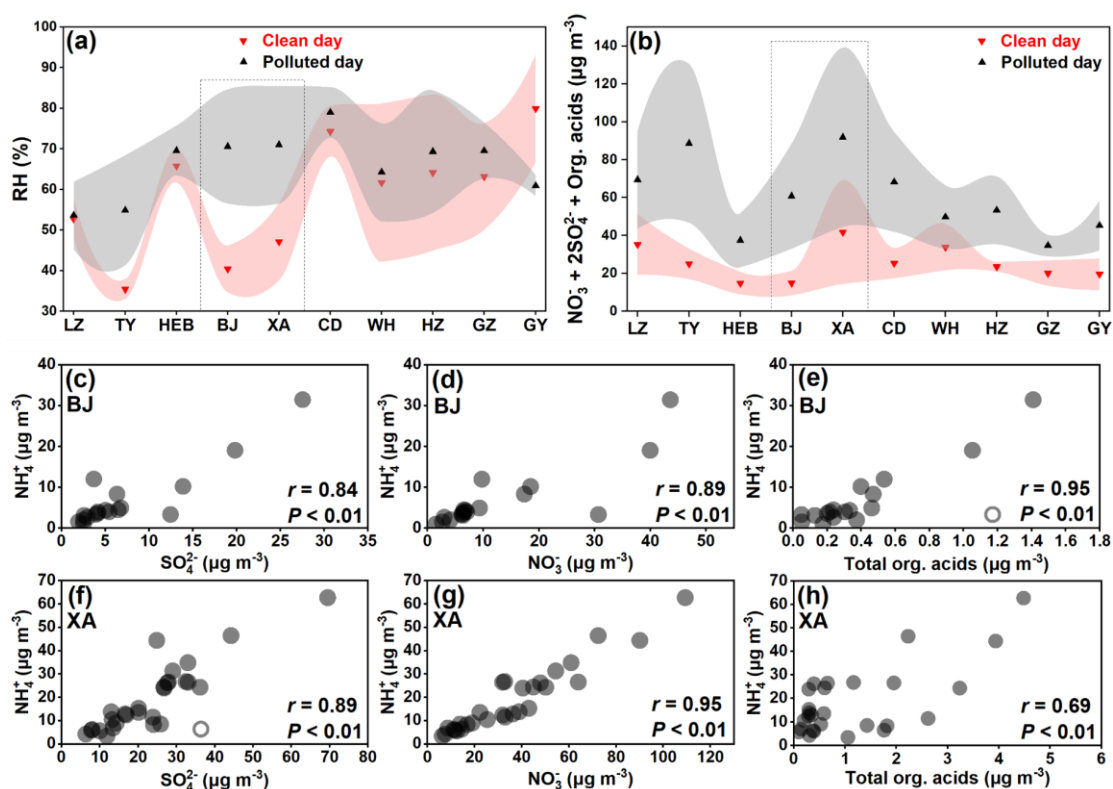
395   **Figure 5.** The values of (**a**) RH and the concentrations of (**b**) major acidic

396   components (expressed as $NO_3^- + 2SO_4^{2-}$ + total organic acids) on clean and polluted

397   days in different cities. The triangle and the shaded area represent the mean value and

the associated standard deviation, respectively. The correlations of NH_4^+ with the

concentrations of NO_3^-, SO_4^{2-}, and total organic acids at (**c–e**) BJ and (**f–h**) XA. Open

circles represent outliers.

Furthermore, we found that the concentrations of NH_4^+ were strongly ($P < 0.01$)

correlated with those of acidic components in XA and BJ (**Figures 5c–h**). This

indicates that the acidity of the particles was sufficient for the uptake of ammonia to

form ammonium at these two study sites. Typically, the concentration of ammonia in

the atmosphere is 1 to 3 orders of magnitude higher than that of low-molecular-weight

alkylamines (Zheng et al., 2015; You et al., 2014; Yao et al., 2016; Wang et al., 2010).

The uptake coefficient of alkylamines on acidic particles is lower than that of

ammonia (Wang et al., 2010); moreover, Wang et al. (2010) proposed that fresh

H_2SO_4 particles can be overwhelmingly neutralized by ammonia when both amines

and ammonia are present in the air. In particular, although the strong acidic condition

was conducive to the formation of aminiums, amines and ammonia may compete for

uptake into acidic aerosol particles (Chen et al., 2022a). Thus, the constraint of

ammonia on amine uptake at much higher ammonia levels than amine levels may be a

possible explanation for the insignificant acid-dependent aminium formation in XA

and BJ (**Figures 4a,b**).

To further explore the role of ammonia (or ammonium) in aminium formation,

the average ratios of TA to NH_4^+ on clean and polluted days in different cities were

examined (**Figure 6a** and **Table S1–S3**). The average ratios of TA to NH_4^+ were found

420   to be lower in XA and BJ, especially on the polluted days, which was similar to the

421   characteristics of the $TA/(NH_3 + NH_4^+)$ ratios (**Figure S4**). The sensitivity analysis of

422   the TA/NH_4^+ ratio (the lowest in XA and BJ) to NH_4^+ changes (**Figures 6b,c** and

423   **Figure S5**) suggests that when $TA/NH_4^+ > 2$, the NH_4^+ concentrations in XA and BJ

424   remained at a relatively low level (less than 6 μg m^{-3} and 15 μg m^{-3} in BJ and XA,

425   respectively) with the increase of TA/NH_4^+ ratio, indicating that the formation of

426   aminiums was not limited by ammonia at low amine and ammonium levels (in this

427   case, TA was significantly ($P < 0.01$) correlated with NH_4^+). When $TA/NH_4^+ < 2$, the

428   formation of aminiums may be constrained by higher amine and ammonium levels,

429   which can also be supported by the insignificant ($P > 0.05$) correlation between TA

430   and NH_4^+ in this case. In contrast, the distributions of the ratios of TA to NH_4^+ in other

431   cities were mainly in regions greater than 2 (**Figure S5**). The TA concentrations were

432   thus significantly positively correlated with ammonium in these cities (excepting BJ

433   and XA) (**Figure 4**). A recent study on the uptake of marine aerosol DMA by acidic

434   aerosols has found that the concentrations of particle $DMAH^+$ generally decreased

435   with increasing atmospheric ammonia concentrations (Chen et al., 2022a); moreover,

436   these researchers proposed the possibility that aminiums can be displaced by

437   ammonia in a high ammonia environment. Accordingly, high atmospheric ammonia

438   levels can indeed constrain the conversion of amines to aminiums, even if the aerosol

439   is acidic. In addition, due to the lower VC values (**Tables S1–S3**) on polluted days

440   compared to clean days, the atmospheric amines were less able to diffuse on polluted

441   days. This may result in an accumulation of aminiums on polluted days via acid-base

442   chemistry. However, a large decrease in average TA/NH_4^+ and $TA/(NH_3 + NH_4^+)$ ratios

443   from clean to polluted days occurred in XA (*t*-Test, $P < 0.05$) (**Figure 6a**, **Figure S4,**

444   and **Table S1–S3**), followed by BJ. These results indicate that the uptake of amines on

445   acidic particles relative to that of ammonia was significantly reduced from clean to

446   polluted days in XA and BJ. Presumably, the aminiums/ammonium ratio was likely an

447   important indicator to reveal the competitive uptake of ammonia against amines on

448   acidic aerosols, or the displacement of aminiums by ammonia in a high ammonia

449   environment. Thus, this study provides a special field case that emphasizes the

450   potential suppression of ammonia on aminium outbreaks during the polluted days.

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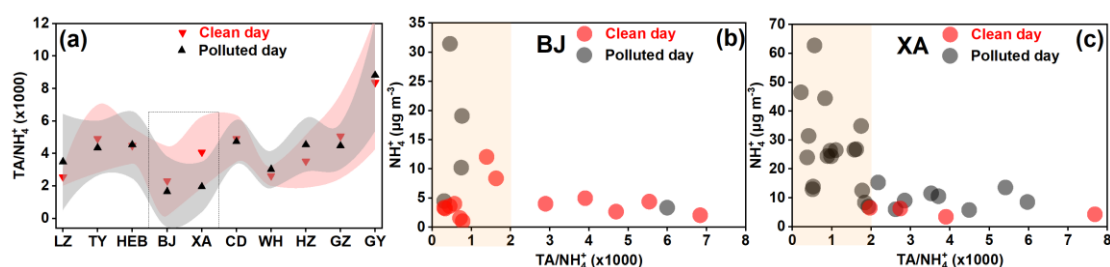
453   **Figure 6.** The (**a**) average ratio of TA to NH_4^+ on clean and polluted days in different

454   cities. The triangle and the shaded area represent the mean value and the associated

455   standard deviation, respectively. Scatterplots of the mass concentration of NH_4^+ with

456   the ratio of TA to NH_4^+ at the (**b**) BJ and (**c**) XA sites.

457

458   **4. Conclusions and atmospheric implications**

459   The concentrations, compositions, and temporal and spatial variations of

460   aminiums in PM$_{2.5}$ in 11 different Chinese cities during the winter were systematically

461   investigated to reveal the key factors affecting the aminium outbreak during the

462 polluted days. Specifically, MMAH$^+$ was the dominant species among the aminiums

463 investigated in PM$_{2.5}$ in most cities, including LZ, XA, HEB, BJ, WLMQ, HZ, WH,

464 CD, and GY, followed by DMAH$^+$. In contrast, DEAH$^+$ was found to be the most

465 abundant aminium species in TY and GZ, followed by MMAH$^+$ and DMAH$^+$. This

466 result can be attributed to the fact that the main sources of amines in TY and GZ were

467 significantly different from those in other cities. However, due to the lack of amine

468 emission inventories and sufficient tracers in these investigated cities, this study did

469 not provide a detailed analysis of the specific sources of amines in these investigated

470 cities.

471   We found that the concentrations of TA and major aminiums in all cities showed

472 a similar pattern of variation from the clean days to the polluted days, which was

473 characterized by higher levels on the polluted days. However, the lowest percentage

474 increase in TA concentration during the polluted days was found in XA (50%) and BJ

475 (25%). Moreover, the concentrations of TA in XA and BJ were insignificantly ($P >$

476 0.05) correlated with those of PM$_{2.5}$ and the main acidic components in PM$_{2.5}$.

477 However, the significant correlations of TA with PM$_{2.5}$ and the main acidic

478 components were observed in other cities. Thus, acid-base chemistry was strongly

479 associated with the formation of aminiums in PM$_{2.5}$ in all cities with the exception of

480 XA and BJ. The concentrations of NH$_4^+$ were significantly ($P < 0.01$) correlated with

481 those of the acidic components in XA and BJ, indicating that the acidity of the

482 particles was sufficient for the uptake of ammonia to form ammonium at these two

483 sites. Further, based on the sensitivity analysis of the TA/NH$_4^+$ ratio (the lowest in XA

484 and BJ) to NH_4^+ changes as well as excluding the effects of ALW and atmospheric

485 oxidation, we proposed a possibility about the competitive uptake of ammonia against

486 amines on acidic aerosols in the ambient atmosphere in XA and BJ. This

487 consideration may explain the insignificant acid-dependent aminium formation in XA

488 and BJ. The main finding of this study has been illustrated in a diagram (**Figure 7**).

489   In general, this study has preliminarily explored the characteristics of aminiums,

490 ammonium, and $PM_{2.5}$ from the clean days to the polluted days according to the

491 observational data from 11 different Chinese cities, highlighting the possibility of the

492 competitive uptake of ammonia versus amines on acidic aerosols, or the displacement

493 of aminiums by ammonia under a high ammonia condition. Although a recent study

494 has also demonstrated the possibility of individual aminium being displaced by

495 ammonia in an environment of high ammonia level (Chen et al., 2022a), the uptake of

496 amines on particles to form aminiums and the impact mechanisms of relevant

497 influencing factors are still not fully understood. This is because acidity,

498 environmental ammonia and amine content, temperature, and liquid-phase reactions

499 all affect the uptake of amines, although acid-base neutralization of amines seems to

500 be the most important pathway for amine uptake. Furthermore, if the uptake of amines

501 is significantly constrained by the aforementioned factors, the traditional source

502 apportionment methods using correlation analysis between particle aminiums and

503 tracers will have significant uncertainty due to the weakened partitioning of the

504 amines into the particle phase (i.e., causing insignificant correlations between

505 aminiums and indicators). Further laboratory validation experiments are required to

506 substantiate this inference. In addition, it is essential to conduct prolonged

507 observational research in settings with elevated ammonia levels and depleted amine

508 concentrations in the near future.

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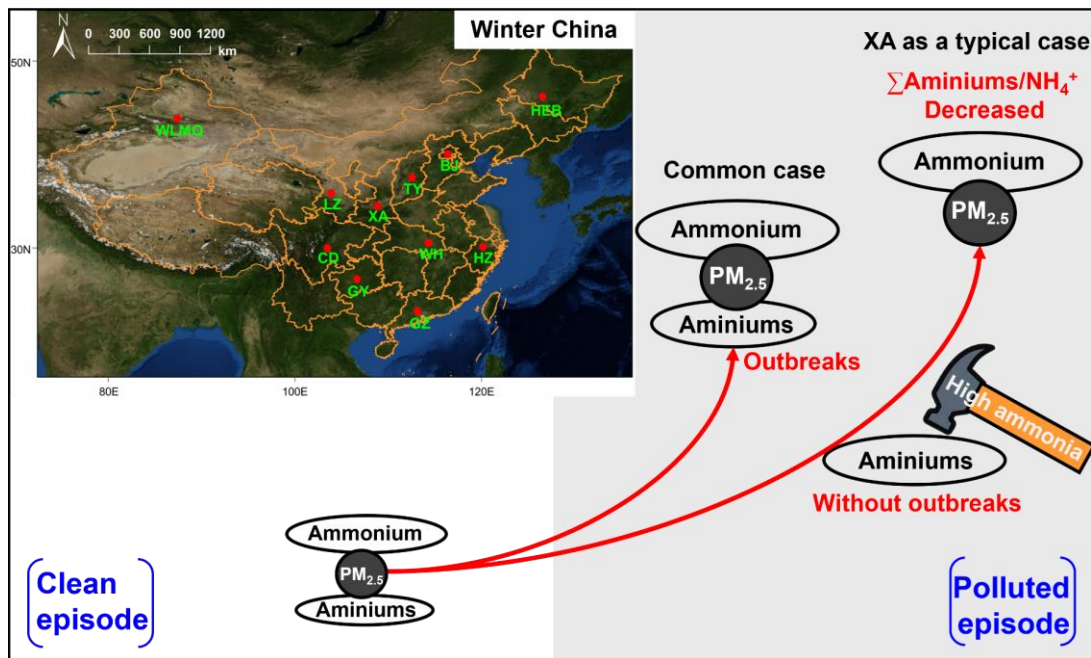
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511 **Figure 7.** Conceptual illustration showing the characteristics of aminiums,

512 ammonium, and $PM_{2.5}$ from the clean days to the polluted days. The map was

513 obtained from ©MeteoInfoMap (version 3.3.0) (Chinese Academy of Meteorological

514 Sciences, China).

515

516 **Data availability.** The data in this study are available at

517 https://doi.org/10.5281/zenodo.11102019 (Xu et al., 2024).

518

519 **Supplement.** Four tables (Tables S1−S4) and five extensive figures (Figures S1−S5)

520 are provided in the Supplement. The supplement related to this article is available

521 online.

522

523 **Author contributions.** YX and HYX designed the study. YX, YJM, QBS, HWX, and

524 HX performed field measurements and sample collection; TL performed chemical

525 analysis; YX performed data analysis; YX wrote the original manuscript; and YX,

526 HYX, and CQL reviewed and edited the manuscript.

527

528 **Competing interests.** The contact author has declared that none of the authors has

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530

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538

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