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 most cities increased significantly during the polluted days, while relatively weak aminium outbreaks during the polluted days occurred 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 influencing factors require further mechanistic research.

Keywords: Aminiums, $PM_{2.5}$ pollution, Aerosol acidity, Spatiotemporal variations, Formation mechanism

1. Introduction

Low-molecular-weight amines are ubiquitous and important in the gaseous and particulate phases (Nielsen et al., 2012; Ge et al., 2011a; Berta et al., 2023). More than 150 amines have been identified in the atmosphere (Ge et al., 2011a). The most abundant and frequently reported amines in field observations are typically C1–C6 alkylamines including dimethylamine, monomethylamine, trimethylamine, diethylamine, ethylamine, 1-propanamine, and 1-butanamine (Yang et al., 2023b; Liu et al., 2023). Amines can participate in various chemical and physical processes in the atmosphere, promoting the formation and growth of new particles and contributing to the production of secondary organic aerosols (Yao et al., 2018; Tong et al., 2020; Møller et al., 2020). Amines are thus considered to have a direct or indirect impact on air quality (Li et al., 2019; Tao et al., 2016; Shen et al., 2023). Air pollution (e.g., haze) caused by high levels of atmospheric fine particles ($PM_{2.5}$) has received considerable attention in China over the past decade due to rapid industrialization and urbanization (Liu et al., 2022b; Liu et al., 2022c). Evidently, controlling the emission strength of amine sources and understanding the transformation of atmospheric amines can effectively reduce air pollution in cities.

The main sources of atmospheric amines during the air pollution period in cities in China are typically fossil fuel combustion and biomass burning rather than agricultural emissions (Feng et al., 2022; Liu et al., 2022c; Wang et al., 2022; Shen et al., 2017; Ho et al., 2016; Chang et al., 2022). Owing to the water solubility and alkalinity of amines, low-molecular-weight amines in $PM_{2.5}$ during the air pollution period are mainly present in the form of amine salts (i.e., aminiums) via the gas-to-particle partitioning of gaseous amines and subsequent acid-base chemistry (Zhang et al., 2021; Liu et al., 2022a; Ge et al., 2011a; Xie et al., 2018). It should be noted that organic amines (e.g., dimethylamine and trimethylamine) in nanoparticles (<200 nm) may also be largely present in the organic phase (Xie et al., 2018). In addition, oxidative degradation of higher-molecular-weight amines and displacement reactions are also potential formation pathways of aminiums in $PM_{2.5}$ (Tao et al., 2021; Qiu and Zhang, 2013; Tong et al., 2020). Although previous observational studies have investigated the compositions, concentrations, sources, and formation processes of low-molecular-weight aminiums in the particle phase in urban areas of Shanghai (Liu et al., 2023), Guangzhou (Shu et al., 2023), Qingdao (Liu et al., 2022c), Xuzhou (Yang et al., 2023b), China, there has been relatively little focus on the association between $PM_{2.5}$ and amine outbreaks. A recent study conducted in Wangdu County, Hebei Province, China has suggested that amines exhibited outbreak characteristics during the haze episode (Feng et al., 2022). Climate and air pollution conditions can vary greatly from city to city due to the vastness of China. However, it is poorly understood how the characteristics and formation processes of low-molecular-weight aminiums in $PM_{2.5}$ vary between clean and polluted days in different cities in China, which may hinder the further assessment of the environmental impacts of amines with regional differences.

In winter in China, air pollution episodes are more frequent compared to other seasons. Thus, we present the measurements of aminiums in $PM_{2.5}$ collected from 11 different Chinese cities during the winter (2017–2018). The aims of this study are (1) to investigate the spatial differences in the compositions and concentrations of aminiums in $PM_{2.5}$, with a focus on the difference between them on clean days and polluted days, and (2) to understand the key factors controlling the formation of aminiums in $PM_{2.5}$ in different cities.

2. Materials and Methods

2.1. Site Description and Sample Collection

A total of eleven urban sites were selected for aerosol sample collection, including Beijing (BJ; 116.41°E, 40.04°N), Taiyuan (TY; 112.58°E, 37.80°N), Xi'an (XA; 108.98°E, 34.25°N), Lanzhou (LZ; 103.73°E, 36.11°N), Haerbin (HEB, i.e., Harbin; 126.64°E, 45.77°N), Wulumuqi (WLMQ, i.e., Urumqi; 87.75°E, 43.86°N), Chengdu (CD; 104.14°E, 30.68°N), Guiyang (GY; 106.73°E, 26.58°N), Guangzhou (GZ; 113.35°E, 23.18°N), Wuhan (WH; 114.36°E, 30.55°N), and Hangzhou (HZ; 120.16°E, 30.30°N) sites (**Figure S1**). HZ and GZ are megacities situated in the

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) .

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 described in our recent publication (Liu et al., 2023). It should be noted that we did not consider the impact of continuous aging of aminiums collected on the filter on the measurement results. This is mainly due to the following reasons. The $PM_{2.5}$ samples investigated in this study are all acidic (**Tables S1–S3**), promoting the protonation of amino groups. The protonated amino group is difficult to undergo oxidation by oxidants (e.g., hydroxyl radicals and ozone) (Nielsen et al., 2012).

Another filter cut was extracted with Milli-Q water to measure the concentrations of inorganic ions (e.g., NO_3^-, SO_4^{2-}, NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+}) and organic acids (e.g., acetic acid, formic acid, succinic acid, oxalic acid, glutaric acid, and methanesulfonic acid) (Xu et al., 2022a; Xu et al., 2023; Liu et al., 2023; Lin et al., 2023). These inorganic ions were quantified via an ion chromatograph system (Dionex Aquion, Thermo Scientific, USA).

2.3. Parameter calculation

The thermodynamic model (ISORROPIA-II) was used for the prediction of the mass concentration of aerosol liquid water (ALW) and the pH value, which was detailed in our previous studies (Xu et al., 2022b; Xu et al., 2020; Xu et al., 2023). The ventilation coefficient (VC) can be used as an indicator to assess the state of atmospheric dilution of pollutant concentrations (Gani et al., 2019). It is calculated by multiplying the wind speed by the planetary boundary layer height (PBLH) (Yang et al., 2023a).

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., 2011b), implying that the potential of MMA, DMA, and EA to be partitioned into aqueous particles was weaker compared to DEA. Additionally, the gaseous forms of these determined aminiums typically have strong alkalinity (Ge et al., 2011b). The aerosol samples in this study were all acidic (**Tables S1–S3**). Thus, these results imply that the increased emissions of MMA and DMA may partially explain the higher abundance of MMAH$^+$ and DMAH$^+$ in PM$_{2.5}$ in these investigated cities during winter.

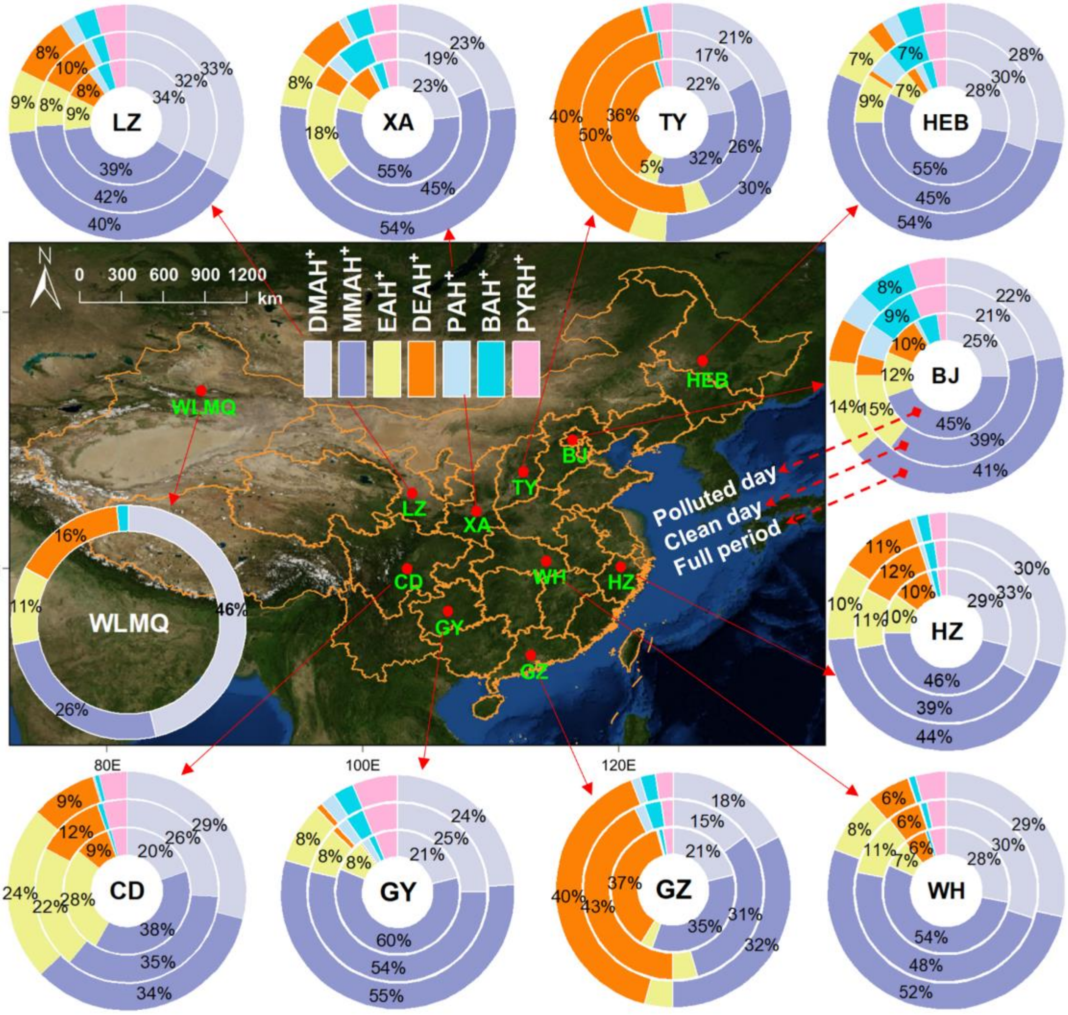

Figure 1. Average percentage distributions of various aminiums in $PM_{2.5}$ collected in different cities in China during winter. The map was obtained from ©MeteoInfoMap (version 3.3.0) (Chinese Academy of Meteorological Sciences, China).

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 addition, the proportions of MMAH$^+$ (solubility of 23.76 mol kg^{-1} for aminium chloride form (Ge et al., 2011b)) and DMAH$^+$ (solubility of 44.80 mol kg^{-1} for aminium chloride form (Ge et al., 2011b)) tended to further increase from the clean days to the polluted days, while that of DEAH$^+$ with relatively low solubility (solubility of 20.52 mol kg^{-1} for aminium chloride form (Ge et al., 2011b)) showed a decreasing trend, especially in TY and GZ (where DEAH$^+$ was dominant). The concentrations of ALW in $PM_{2.5}$ were generally much higher on polluted days than on clean days, especially in the northern cities (**Tables S1–S3**). Clearly, liquid-phase processes likely played an important role in the formation of aminiums on polluted days.

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

Figure 2 shows the average concentration distributions of various aminiums in $PM_{2.5}$ collected in different cities in China during winter, focusing on the difference between their concentrations on clean days and polluted days. The concentrations of total aminiums (TA) in TY ranged from 17.50 to 149.00 ng m^{-3}, with an average of 56.90 ± 41.81 ng m^{-3}. This average TA level was the highest among all the cities investigated. The average concentration of TA in WLMQ was found to be the lowest (4.16 ± 1.24 ng m^{-3}), with a range of 2.10–6.50 ng m^{-3}. As previously mentioned, WLMQ is a vast city with a lower population density and less developed industries compared to the more developed northern and coastal cities in China. Additionally, this region is surrounded by barren mountains and sandy land (Ma et al., 2024) (**Figure 2**). Apparently, the weak amine emission intensity appears to be responsible for the low levels of aminiums in the WLMQ.

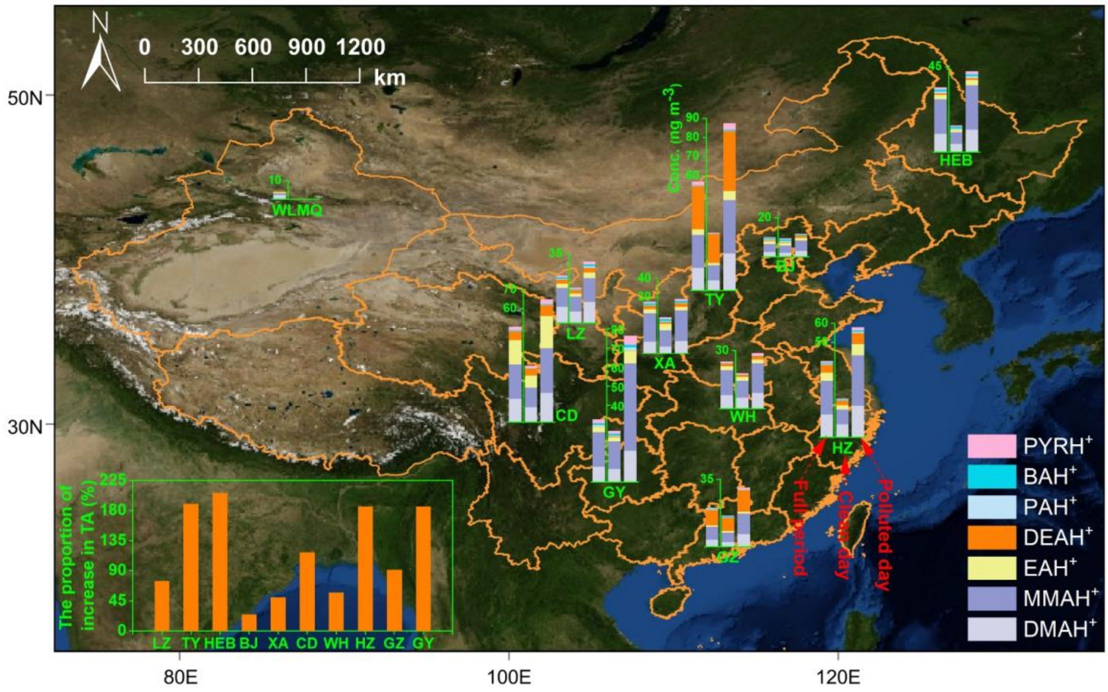

Figure 2. Average concentration distributions of various aminiums in $PM_{2.5}$ collected in different cities in the winter in China. The stacked bar chart from left to right indicates the data for the full sampling period, the clean day, and the polluted day in turn. The column chart in the bottom left 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 within the observation ranges reported in previous studies (1.49 ng m^{-3} – 329.80 ng m^{-3}) (**Table S4**) (Ho et al., 2016; Liu et al., 2023; Shen et al., 2017; Huang et al., 2016; Choi et al., 2020; Liu et al., 2018; Shu et al., 2023). $MMAH^+$, as the dominant aminium species in most of cities, showed the highest (18.33 ± 12.82 ng m^{-3}) and lowest (1.07 ± 0.55 ng m^{-3}) average concentrations in HEB and WLMQ, respectively. $DEAH^+$ was the most abundant aminium species in TY and GZ, with average concentrations of 22.62 ± 17.62 ng m^{-3} and 8.16 ± 4.65 ng m^{-3}, respectively (**Tables S1** and **S3**). Two previous studies conducted in the GZ area in winter (2021 and 2015–2016) showed similar average $DEAH^+$ (~ 7 ng m^{-3}) levels to this study (Liu et al., 2022b; Shu et al., 2023). However, $DEAH^+$ was not identified as the dominant aminium component in those two previous studies. Furthermore, lower aminium concentrations (< 8 ng m^{-3}) were generally found in most of the marine and polar regions (Dall'osto et al., 2019; Corral et al., 2022). In general, the concentration and composition of aminiums vary spatially, which may be attributed to spatial differences in amine sources, emission intensities, and the main factors affecting aminium formation.

The average concentrations of TA in all the investigated cities exhibited a similar variation pattern from clean to polluted days, which was characterized by higher levels on polluted days (**Figure 2**). Specifically, the average aminium concentration showed an increase of up to 206% in HEB during the polluted period. TA concentrations in LZ, TY, CD, HZ, and GZ also increased greatly by 91% (in GZ) −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.

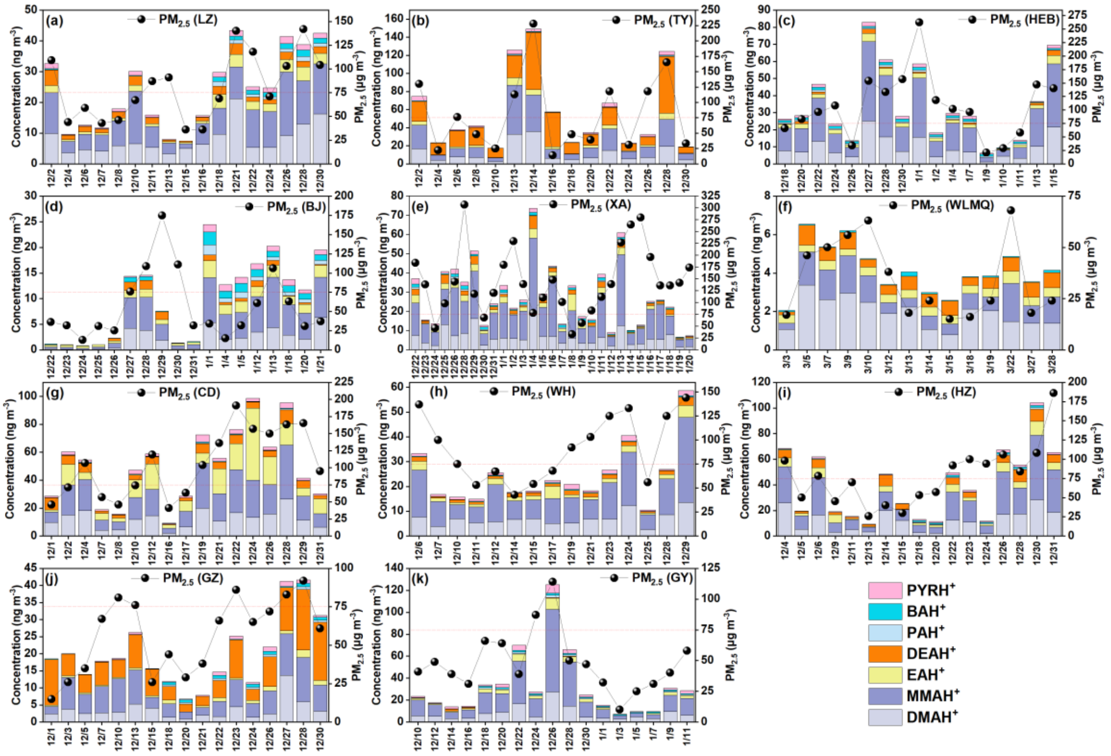

Figure 3. Temporal variations in the mass concentrations of aminiums and PM$_{2.5}$ observed at the (a) LZ, (b) TY, (c) HEB, (d) BJ, (e) XA, (f) WLMQ, (g) CD, (h) WH, (i) HZ, (j) GZ, and (k) GY sites.

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–S3**); moreover, there was no significant change in the atmospheric oxidation (indicated by O_x levels ($O_x = O_3 + NO_2$)) of polluted and clean days in XA (higher O_x level during clean days) and BJ. In particular, the protonated amino group has been suggested to be difficult to undergo oxidation by hydroxyl radicals and ozone (Nielsen et al., 2012). Accordingly, atmospheric oxidation and temperature may not be the main factors affecting changes in aminium concentrations from clean to polluted days. Furthermore, the insignificant correlation between aminiums and acidic components in XA and BJ suggests that other factors affecting aminium formation must be considered.

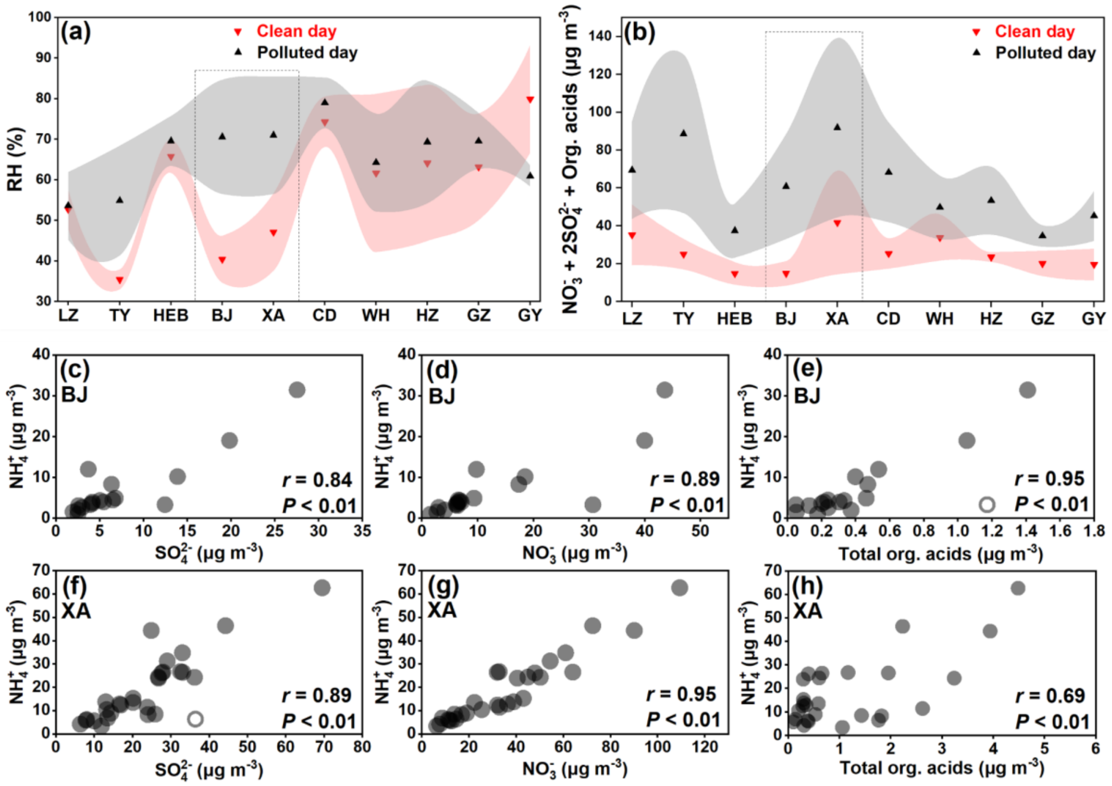

Figure 5. The values of (**a**) RH and the concentrations of (**b**) major acidic components (expressed as $NO_3^- + 2SO_4^{2-}$ + total organic acids) on clean and polluted days in different cities. The triangle and the shaded area represent the mean value and the associated standard deviation, respectively. 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 to be lower in XA and BJ, especially on the polluted days, which was similar to the characteristics of the TA/($NH_3 + NH_4^+$) ratios (**Figure S4**). The sensitivity analysis of the TA/NH_4^+ ratio (the lowest in XA and BJ) to NH_4^+ changes (**Figures 6b,c** and **Figure S5**) suggests that when TA/NH_4^+ >2, the NH_4^+ concentrations in XA and BJ remained at a relatively low level (less than 6 μg m^{-3} and 15 μg m^{-3} in BJ and XA, respectively) with the increase of TA/NH_4^+ ratio, indicating that the formation of aminiums was not limited by ammonia at low amine and ammonium levels (in this case, TA was significantly ($P < 0.01$) correlated with NH_4^+). When TA/NH_4^+ < 2, the formation of aminiums may be constrained by higher amine and ammonium levels, which can also be supported by the insignificant ($P > 0.05$) correlation between TA and NH_4^+ in this case. In contrast, the distributions of the ratios of TA to NH_4^+ in other cities were mainly in regions greater than 2 (**Figure S5**). The TA concentrations were thus significantly positively correlated with ammonium in these cities (excepting BJ and XA) (**Figure 4**). A recent study on the uptake of marine aerosol DMA by acidic aerosols has found that the concentrations of particle $DMAH^+$ generally decreased with increasing atmospheric ammonia concentrations (Chen et al., 2022a); moreover, these researchers proposed the possibility that aminiums can be displaced by ammonia in a high ammonia environment. Accordingly, high atmospheric ammonia levels can indeed constrain the conversion of amines to aminiums, even if the aerosol is acidic. In addition, due to the lower VC values (**Tables S1–S3**) on polluted days compared to clean days, the atmospheric amines were less able to diffuse on polluted days. This may result in an accumulation of aminiums on polluted days via acid-base chemistry. However, a large decrease in average TA/NH_4^+ and TA/($NH_3 + NH_4^+$) ratios from clean to polluted days occurred in XA (*t*-Test, $P < 0.05$) (**Figure 6a**, **Figure S4,** and **Table S1–S3**), followed by BJ. These results indicate that the uptake of amines on acidic particles relative to that of ammonia was significantly reduced from clean to polluted days in XA. It should be noted that this reduced case may also occur in BJ, while it is statistically insignificant. Presumably, the aminiums/ammonium ratio was likely an important indicator to reveal the competitive uptake of ammonia against amines on acidic aerosols, or the displacement of aminiums by ammonia in a high ammonia environment. Thus, this study provides a special field case that emphasizes the potential suppression of ammonia on aminium outbreaks during the polluted days.

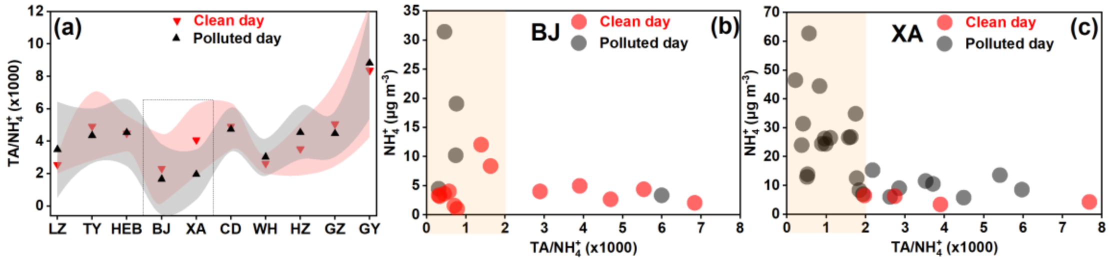

Figure 6. The (**a**) average ratio of TA to NH_4^+ on clean and polluted days in different cities. The triangle and the shaded area represent the mean value and the associated standard deviation, respectively. Scatterplots of the mass concentration of NH_4^+ with the ratio of TA to NH_4^+ at the (**b**) BJ and (**c**) XA sites.

4. Conclusions and atmospheric implications

The concentrations, compositions, and temporal and spatial variations of aminiums in $PM_{2.5}$ in 11 different Chinese cities during the winter were systematically investigated to reveal the key factors affecting the aminium outbreak during the polluted days. Specifically, $MMAH^+$ was the dominant species among the aminiums investigated in $PM_{2.5}$ in most cities, including LZ, XA, HEB, BJ, WLMQ, HZ, WH, CD, and GY, followed by $DMAH^+$. In contrast, $DEAH^+$ was found to be the most abundant aminium species in TY and GZ, followed by $MMAH^+$ and $DMAH^+$. This result can be attributed to the fact that the main sources of amines in TY and GZ were significantly different from those in other cities. However, due to the lack of amine emission inventories and sufficient tracers in these investigated cities, this study did not provide a detailed analysis of the specific sources of amines in these investigated cities.

We found that the concentrations of TA and major aminiums in all cities showed a similar pattern of variation from the clean days to the polluted days, which was characterized by higher levels on the polluted days. However, the lowest percentage increase in TA concentration during the polluted days was found in XA (50%) and BJ (25%). Moreover, the concentrations of TA in XA and BJ were insignificantly ($P > 0.05$) correlated with those of $PM_{2.5}$ and the main acidic components in $PM_{2.5}$. However, the significant correlations of TA with $PM_{2.5}$ and the main acidic components were observed in other cities. Thus, acid-base chemistry was strongly associated with the formation of aminiums in $PM_{2.5}$ in all cities with the exception of XA and BJ. The concentrations of NH_4^+ were significantly ($P < 0.01$) correlated with those of the acidic components in XA and BJ, indicating that the acidity of the particles was sufficient for the uptake of ammonia to form ammonium at these two sites. Further, based on the sensitivity analysis of the TA/NH_4^+ ratio (the lowest in XA and BJ) to NH_4^+ changes as well as excluding the effects of ALW and atmospheric oxidation, we proposed a possibility about the competitive uptake of ammonia against amines on acidic aerosols in the ambient atmosphere in XA and BJ. This consideration may explain the insignificant acid-dependent aminium formation in XA and BJ. The main finding of this study has been illustrated in a diagram (**Figure 7**).

In general, this study has preliminarily explored the characteristics of aminiums, ammonium, and $PM_{2.5}$ from the clean days to the polluted days according to the observational data from 11 different Chinese cities, highlighting the possibility of the competitive uptake of ammonia versus amines on acidic aerosols, or the displacement of aminiums by ammonia under a high ammonia condition. Although a recent study has also demonstrated the possibility of individual aminium being displaced by ammonia in an environment of high ammonia level (Chen et al., 2022a), the uptake of amines on particles to form aminiums and the mechanisms of relevant influencing factors are still not fully understood. This is because acidity, environmental ammonia and amine content, temperature, and liquid-phase reactions all affect the uptake of amines, although acid-base neutralization of amines seems to be the most important pathway for amine uptake. Furthermore, if the uptake of amines is significantly constrained by the aforementioned factors, the traditional source apportionment methods using correlation analysis between particle aminiums and tracers will have significant uncertainty due to the weakened partitioning of the amines into the particle phase (i.e., causing insignificant correlations between aminiums and indicators). Further laboratory validation experiments are required to substantiate this inference. In addition, it is essential to conduct prolonged observational research in settings with elevated ammonia levels and depleted amine concentrations in the near future.

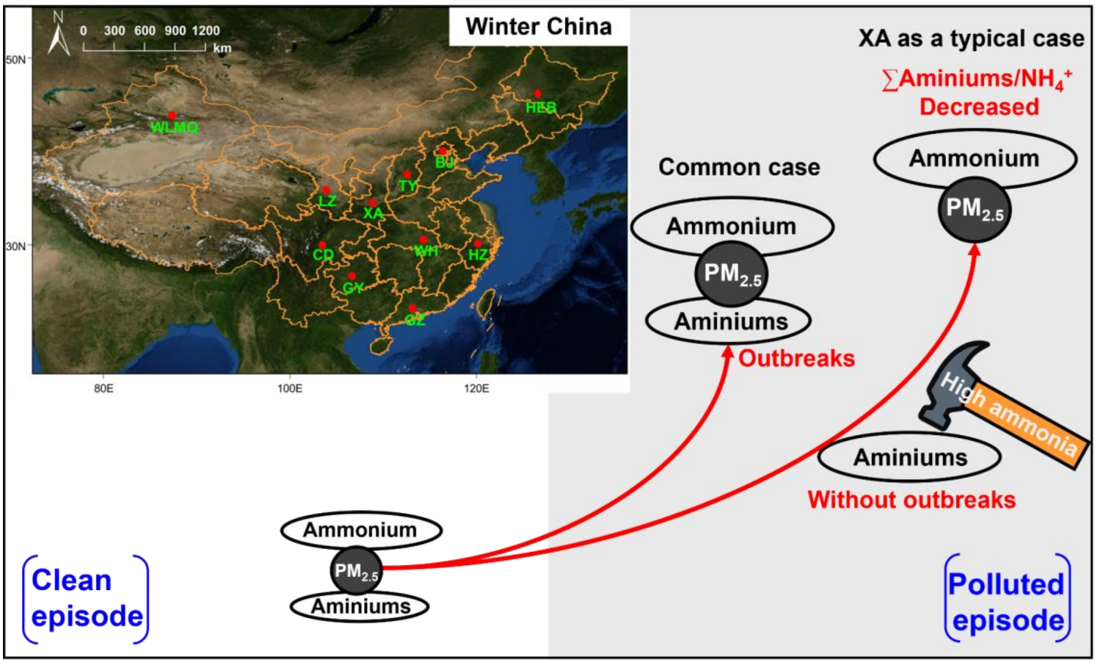

Figure 7. Conceptual illustration showing the characteristics of aminiums, ammonium, and $PM_{2.5}$ from the clean days to the polluted days. The map was obtained from ©MeteoInfoMap (version 3.3.0) (Chinese Academy of Meteorological Sciences, China).

Data availability. The data in this study are available at https://doi.org/10.5281/zenodo.11102019 (Xu et al., 2024).

Supplement. Four tables (Tables S1−S4) and five extensive figures (Figures S1−S5) are provided in the Supplement. The supplement related to this article is available online.

Author contributions. YX and HYX designed the study. YX, YJM, QBS, HWX, and HX performed field measurements and sample collection; TL performed chemical analysis; YX performed data analysis; YX wrote the original manuscript; and YX, HYX, and CQL reviewed and edited the manuscript.

Competing interests. The contact author has declared that none of the authors has any competing interests.

Acknowledgements. The authors are very grateful to the editor and the anonymous referees for the kind and valuable comments that improved the paper.

Financial support. This study has been kindly supported by the National Natural Science Foundation of China (grant no. 42303081) (Yu Xu) and the Shanghai Sailing Program of Shanghai Science and Technology Commission (grant no. 22YF1418700) (Yu Xu).

Review statement. This paper was edited by Roya Bahreini and reviewed by three anonymous referees.

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