Measurement report: Exploring the NH₃ behaviours at urban and suburban Beijing: Comparison and implications

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Abstract. Ammonia (NH₃) plays an important role in particulate matter formation; however, few long-term observations with a high temporal resolution have been conducted on the NH₃ concentrations in Beijing. In this study, online ammonia analyzers were used to observe continuously the atmospheric NH₃ concentrations at an urban site and a suburban site in Beijing from January 13, 2018, to January 13, 2019. The average mixing ratio of NH₃ at the urban site was 21 ± 14 ppb (range: 1.6–133 ppb) and that at the suburban site was 22 ± 15 ppb (range: 0.8–199 ppb). The NH₃ mixing ratios at the urban and suburban sites exhibited similar seasonal variations, with high values being observed in the summer and spring and low values being observed in the autumn and winter. The hourly mean NH₃ mixing ratios at the urban site were highly correlated (R = 0.849, P < 0.01) with those at the suburban site. However, the average diurnal variations in the NH₃ mixing ratios at the urban and suburban sites differed significantly, which indicated the different contributions of NH₃ sources and sinks at the urban and suburban sites. In addition to the emission sources, meteorological factors were closely related to the changes in the NH₃ concentrations. For the same temperature (relative humidity) at the urban and suburban sites, the NH₃ mixing ratios increased with the relative humidity (temperature). The relative humidity was the factor with the strongest influence on the NH₃ mixing ratio in different seasons at the two sites. In general, a high wind speed promoted a reduction in the NH₃ mixing ratio. Similar with other primary pollutants in Beijing, the NH₃ mixing ratios were high when winds originated from the south and low when winds originated from the north and northwest.

1. Introduction

Ammonia (NH₃) is the most abundant alkaline trace gas in the atmosphere (Meng et al., 2017). An excessive NH₃ concentration directly harms the ecosystem; causes water eutrophication and soil acidification; and leads to forest soil erosion, biodiversity reduction, and carbon uptake variations (Pearson and Stewart, 1993; Reay et al., 2008; van Breemen et al., 1983). Thus, the NH₃ concentration influences climate change (Charlson et al., 1991; Erisman et al., 2007). NH₃ can react with acidic gases to form ammonium salts, which might significantly influence the mass concentration and composition of particulate matter (Wu et al., 2009). After the implementation of policies such as the 12th Five-Year Plan for the Key Regional Air Pollution Prevention and Control in Key Regions (Ministry of Ecology and Environment of the People’s Republic of China, 2012) and...
the Air Pollution Prevention and Control Action Plan (General Office of the State Council, PRC, 2013), China, especially for Beijing, has been effectively controlling the emission of primary pollutants, such as sulfur dioxide (SO$_2$) and nitrogen oxide (NO$_x$); however, the pollution caused by fine particles is still serious (Krotkov et al., 2016; UN Environment, 2019). Studies have indicated that when the SO$_2$ and NO$_x$ concentrations are reduced to a certain extent, reducing NH$_3$ emissions is the most economical and effective method to decrease the PM$_{2.5}$ concentration (Pinder et al., 2008). In China, the main anthropogenic sources of NH$_3$ are livestock and poultry feces (54%) and fertilizer volatilization (33%) (Huang et al., 2012). Moreover, the atmospheric NH$_3$ concentration in China has increased with the expansion of agricultural activities, control of SO$_2$ and NO$_x$, and increase in temperature (Warner et al., 2017). This increase in the NH$_3$ concentration might weaken the effectiveness of SO$_2$ and NO$_x$ emission control in reducing PM$_{2.5}$ pollution (Fu et al., 2017).

The North China Plain is a region with high NH$_3$ emission (Zhang et al., 2017), and Beijing has one of the highest NH$_3$ concentrations in the world (Chang et al., 2016b; Pan et al., 2018). Compared with studies on pollutants such as SO$_2$ and NO$_x$, considerably fewer studies have been conducted on the NH$_3$ concentration in Beijing. Chang et al. (2016a) collected gaseous NH$_3$ samples during the 2014 APEC summit (October 18 to November 29, 2014) in the Beijing urban area and concluded that the overall contributions of traffic, garbage, livestock, and fertilizers to the NH$_3$ concentration were 20.4%, 25.9%, 24.0%, and 29.7%, respectively. Zhang (2016) measured the NH$_3$ concentrations in urban and rural areas of Beijing from January to July 2014 and found that NH$_3$ concentration in urban areas was approximately 65% higher than that in rural areas. Meng et al. (2011) reported that the highest NH$_3$ concentration in Beijing occurred in summer and the lowest one occurred in winter, and their results indicated traffic to be a significant source of NH$_3$ in urban areas. Zhang et al. (2018) reported the vertical variability of NH$_3$ in urban Beijing based on one-year passive samples in 2016/2017 and concluded that local sources such as traffic emissions were important contributors to urban NH$_3$. Meng et al. (2020) investigated the significant increase in winter NH$_3$ and its contribution to the increasing nitrate in PM$_{2.5}$ from 2009 to 2016, and they also concluded that vehicles exhaust was an important contributor to NH$_3$ in urban Beijing in winter.

Currently, NH$_3$ is not included in the routine environmental monitoring operation in China. Research data on NH$_3$ monitoring, particularly on the synchronous observation of the NH$_3$ concentrations with a high temporal resolution in urban and suburban areas, are relatively scarce. In this study, high-time-resolution observations of NH$_3$ were obtained simultaneously at an urban site and a suburban site in Beijing. The variation characteristics and influencing factors of the NH$_3$ concentration were analyzed with meteorological data to provide a scientific basis for NH$_3$ pollution control in Beijing.

2. Materials and methods

2.1. Measurement sites

From January 2018 to January 2019, continuous and simultaneous observations of the atmospheric NH$_3$ concentration were conducted in an urban area and a suburban in Beijing. The urban site was located on the roof of the Science and Technology Building of Minzu University of China (referred to as the urban site, 39°95′N, 116°32′E, altitude: 102 m) and the suburban
site was in the Changping Meteorological Station (referred to as the suburban site, 40°13′N, 116°13′E, altitude: 77 m), respectively. The suburban site is in the NW direction relative to the urban site and the shortest distance between these two sites is approximately 32 km (Figure 1).

Figure 1. Location of the observation sites and the topography of Beijing city.

2.2. Measurements and data acquisition

NH$_3$ concentration measurements were performed by using two NH$_3$ analyzers (Ammonia Analyzer-Economical, Los Gatos Research Inc., USA), and the minimum detection limit was <0.2 ppb. These analyzers use off-axis integrated cavity output spectroscopy (OA-ICOS) technology, which is a fourth-generation cavity-enhanced absorption technique, to measure the NH$_3$ and water vapor (H$_2$O) concentrations in the atmosphere. The incident laser beam of the OA-ICOS technology deviates from the optical axis, which differs from the traditional coaxial incidence mode. The axial incidence mode of the OA-ICOS technology can increase the optical path, stimulate additional high-order transverse modes, effectively suppress the noise of the cavity mode, reduce the cross interferences and errors due to contaminants existing in the cavity, and improve the detection sensitivity (Baer et al., 2002; Baer et al., 2012). The analyzer method is a quasi-absolute measurement, which theoretically does not require calibration. However, to ensure the comparability of the obtained data with other monitoring data, NH$_3$ standard gas (Beijing AP BAIF Gases Industry Co., Ltd.) was used for comparison measurement before the observation. The obtained concentration was normalized with respect to a reference concentration.
Sample gases were drained through Teflon lines (1/4'OD), which lengths were designed as short as possible (less than 2 m). Particulate matters were filtered by Teflon membranes with a pore size less than 5 μm. Since NH$_3$ easily “sticks” to surfaces (like inside walls of tubes), heated sample lines were suggested by many measurements. However, according our test using certain concentrations of NH$_3$ in the lab, when heating (70°C) was on, there did have a peak lasting several minutes and then deceeding to the normal level in when heating was off. This tells us that heating is not a solution for NH$_3$ sticking. Keeping the relatively stable balance between adsorption and desorption of NH$_3$ in the sampling system are the most important. When tested by different humidity air, only very sharply change of humidity obviously influenced and changed the balance, and a new balance needed tens of minutes to reestablished. In the routine weather conditions, humidity changed in a relatively smoothing way except in a quickly changing weather system, like rainy days. The minute-level data were converted into hourly averages in the data analysis process and the hourly resolution can smoothing the effect to some extent caused by variations in humidity and temperature during the sampling time.

The balancing idea was also used to carry out multiple calibrations on NH$_3$ analyzers. A high mixing ratio (e.g. 400 ppb) of NH$_3$ mixing gases were firstly produced by a dynamic diluter and measured by the NH$_3$ analyzer overnight. After the signals were keeping in stable level, other lower span values were switched in turn. At each span point, the measurement time was lasting at least two hours. Then a linear regression function was obtained with $R^2$ higher than 0.999. Nowadays, NH$_3$ in compressed gas cylinder is also trustworthy, which result is concluded by the comparison with NH$_3$ permeation tube.

Finally, 7645 and 8342 valid hourly mean observations were obtained for the urban (Haidian) and suburban (Changping) sites, respectively. In addition, the urban and suburban meteorological data (temperature, relative humidity, wind direction, and wind speed) during the sampling period were obtained from the Haidian Meteorological Observation Station and Changping Meteorological Station, respectively.

3. Results and discussion

3.1. Overall variations in the NH$_3$ mixing ratios

Fig. 2 displays the time-series variations in the NH$_3$ mixing ratios, temperatures, and relative humidity at the urban and suburban sites in Beijing. At the urban site, the mean ± 1σ, median, maximum, and minimum values of the hourly average NH$_3$ mixing ratio during the observation period were 21 ± 14, 17, 133 and 1.6 ppb, respectively. At the suburban site, the corresponding values were 22 ± 15, 18, 199, and 0.8 ppb, respectively. The annual average NH$_3$ mixing ratio and range of the NH$_3$ mixing ratio at the suburban site were marginally higher than those at the urban site. The variation characteristics of the weekly smoothing data indicated that the NH$_3$ variations and temperature/humidity fluctuations at the two sites were practically consistent, which suggested that both sites were under the influence of similar weather systems. The hourly mean NH$_3$ concentrations at the urban site were significantly correlated ($R = 0.849, P < 0.01$) with those at the suburban site.
Figure 2. Temporal variations in the hourly average NH$_3$ mixing ratios, temperatures (T) and relative humidity (RH) at the urban and suburban stations in Beijing. Continuous thick lines were smoothed with 168 points (7 days) by using the Savitzky–Golay method.

Table 1 showed the comparison of the atmospheric NH$_3$ concentrations (ppb) in different areas. Meng et al. (2011) obtained an average NH$_3$ mixing ratio of 22.8 ± 16.3 ppb for the period 2008-2020 in Beijing urban area, which means there was no significant change in the annual average NH$_3$ mixing ratio from 2018 to 2019 compared with the change in the average NH$_3$ mixing ratio over the past decade. Moreover, the NH$_3$ concentrations at the urban and suburban sites were higher than those in the background areas. The observed NH$_3$ concentrations in Beijing were higher than those in northwest China (Meng et al. 2010) and the Yangtze River Delta region (Chang et al. 2019). For example, the average annual NH$_3$ concentration in the urban area of Shanghai, a mega city in the south of China (31° N), was approximately 50% lower than that in Beijing. This result might be related to the fact that the North China Plain, in which Beijing is located, is one of the most intensive agricultural production regions in China. The differences in the soil properties of Beijing and Shanghai may be another reason because the loss of soil NH$_3$ can increase with an increase in the soil pH (Ju et al., 2009). Shanghai and its surrounding areas are dominated by acidic soil of paddy fields (Zhao et al., 2009), whereas Beijing is dominated by the alkaline soils of dry land (Wei et al., 2013).
Table 1. Comparison of the atmospheric NH$_3$ concentrations (ppb) in different areas.

| Period         | Location   | Methodology                      | Types  | Concentration | Reference                  |
|----------------|------------|----------------------------------|--------|---------------|----------------------------|
| 2018.01-2019.01| Beijing, CN| Online monitor                   | Urban  | 20.8±13.7     | This study                 |
|                |            |                                  | Suburban| 21.9±14.9     |                            |
| 2008.02-2010.07| Beijing, CN| Passive sampler                  | Urban  | 22.8±16.3     | Meng et al., 2011          |
| 2007.01-2010.07|            |                                  | Background| 10.2±10.8    |                            |
| 2014.5-2015.6  | Shanghai, CN| Passive sampler                  | Urban  | 7.8           | Chang et al. 2019          |
|                |            |                                  | Suburban| 6.8           |                            |
| 2006.04-2007.04| Xi’an, CN   | Passive sampler                  | Urban  | 18.6          | Cao et al. 2009            |
|                |            |                                  | Suburban| 20.3          |                            |
| 2017.12-2018.2 | Hebei, CN  | Online monitor                   | Rural  | 16.7±19.7     | He et al. 2020             |
| 2008           | Qinghai, CN| Passive sampler                  | Rural  | 4.1±2.2       | Meng et al. 2010           |
| 2003.7-2011.9  | Toronto, CA| Passive sampler                  | Urban  | 2.3-3.0       | Hu et al. 2014             |
|                |            |                                  | Rural  | 0.1-4         |                            |
| 2016.4-2017.10 | New York, US| Active and passive system       | Urban  | 2.2-3.2       | Zhou et al. 2019           |
|                |            |                                  | Rural  | 0.6-0.8       |                            |
| 2017.12        | Tokyo, JP  | semi-continuous microflow        | Urban  | 4.1           | Osada et al. 2019          |
|                |            | analytical system                |        |               |                            |
| 2013.1-2015.12 | Delhi, IN  | Automatic analyzer              | Urban  | 53.4±14.9     | Saraswati et al., 2019     |

The NH$_3$ mixing ratios in the United States (Edgerton et al., 2007; Nowak et al., 2006; Zhou et al. 2019), Great Britain (Burkhardt et al., 1998), Canada (Hu et al., 2014), and Japan (Osada et al., 2019) were 0.23–13, 1.6–2.3, 0.1–4, and 4.1 ppb, respectively. These NH$_3$ mixing ratios are considerably lower than that in Beijing. However, Delhi, India (Saraswati et al., 2019), exhibited a higher NH$_3$ mixing ratio (53.4±14.9 ppb) than Beijing did. This result might be attributed to the well-developed livestock breeding activities in Delhi. The comparisons indicate that in the past decade, NH$_3$ concentration in Beijing has not changed considerably, but that it is higher than in large cities in other developed countries.

3.2. Seasonal variations

Fig. 2 displays the monthly statistical results for the NH$_3$ mixing ratios at the urban and suburban sites in Beijing. According to the seasonal division standard of China Meteorological Administration, in China, March to May is spring, June to August is summer, September to November is autumn, and December to February is winter. As presented in Fig. 2, the seasonal
variations in the NH$_3$ mixing ratios were very similar at the urban and suburban sites. The NH$_3$ mixing ratios showed high values in the spring and summer and low values in the autumn and winter. The daily mean concentrations fluctuated considerably in the spring, and the highest variations occurred in April. The highest mean NH$_3$ concentrations occurred in July. The highest mean NH$_3$ concentrations at the urban and suburban sites were $42 \pm 17$ ppb and $42 \pm 8.2$ ppb, respectively. The NH$_3$ concentrations fluctuated considerably in July. On average, the NH$_3$ mixing ratios at the urban and suburban sites can be arranged according to season as follows: summer $>$ spring $>$ autumn $>$ winter. The main grain crops in Beijing are corn and wheat. Corn is categorized as spring corn and summer corn, which are sown in April and June, respectively. A large amount of base fertilizer is applied when planting corn, and the topdressing is applied after 2 months. Wheat is sown from September to October, and the topdressing is applied in the following spring. The volatilization of nitrogen fertilizers can cause an increase in the NH$_3$ mixing ratios and fluctuations in fertilization seasons (Zhang et al., 2016). In addition, the NH$_3$ mixing ratios are relatively high in the summer season due to the relatively high temperature in this season. An increase in the temperature can increase the biological activity and thus enhance the NH$_3$ emission. A high temperature is also conducive for the volatilization of the urea and diammonium phosphate applied to crops. Moreover, the equilibrium among ammonium nitrate particles, gaseous NH$_3$, and nitric acid is transferred to the gas phase at high temperature, which increases NH$_3$ concentration (Behera et al., 2013). Sewage treatment, household garbage, golf courses, and human excreta are crucial NH$_3$ sources that are easily neglected (Pu et al., 2020). The relatively low NH$_3$ concentrations in the autumn and winter might be caused by the decrease in NH$_3$ emission in the soil and vegetation, the decrease in the NH$_4$NO$_3$ decomposition capacity at low temperatures, and the reduced human activities caused by a large floating population returning to their native locations outside Beijing during the Spring Festival (Liao et al., 2014). In the spring and summer, the NH$_3$ mixing ratios at the suburban site were higher than those at the urban site, which might be related to the higher agricultural activity around the suburban site. In the autumn and winter, the NH$_3$ mixing ratios at the urban site were marginally higher than those at the suburban site. This result was obtained possibly because in the autumn and winter seasons, the influence of agricultural activities on the NH$_3$ concentration weakened, whereas the influences of other sources (such as traffic sources) on the NH$_3$ concentration were enhanced. According to Wang et al. (2019), the traffic NH$_3$ emission per unit area in Haidian was three times higher than that in Changping. This difference in traffic source emissions might have resulted in higher NH$_3$ concentrations at the urban site than at the suburban site in the autumn and winter.
Figure 3. Monthly statistical variation in the NH$_3$ mixing ratios at the urban and suburban sites in Beijing.

Table 2. NH$_3$ mixing ratios (ppb) measured at the urban and suburban sites in Beijing.

| Site     | Time period | Mean | Standard deviation | Minimum | Median | Maximum |
|----------|-------------|------|--------------------|---------|--------|---------|
| Urban    | Annual      | 21   | 14                 | 1.6     | 17     | 133     |
|          | Spring      | 25   | 16                 | 1.9     | 21     | 101     |
|          | Summer      | 32   | 12                 | 5.0     | 30     | 133     |
|          | Autumn      | 16   | 7.5                | 3.8     | 15     | 41      |
|          | Winter      | 11   | 6.7                | 1.6     | 9.9    | 42      |
| Suburban | Annual      | 22   | 15                 | 0.8     | 18     | 198     |
|          | Spring      | 29   | 16                 | 6.8     | 26     | 180     |
|          | Summer      | 35   | 12                 | 12.1    | 33     | 199     |
|          | Autumn      | 15   | 6.8                | 4.1     | 13     | 55      |
|          | Winter      | 9.2  | 4.5                | 0.8     | 8.4    | 29      |
3.3. Diurnal variations

Figure 4 displays the average diurnal variations in the NH$_3$ and H$_2$O mixing ratios in different seasons at the urban and suburban sites in Beijing. NH$_3$ exhibited different diurnal behaviors in different seasons.

In the spring, the average diurnal variations in the NH$_3$ mixing ratio were similar at the urban and suburban sites. The NH$_3$ mixing ratio began to increase in the morning, reached its maximum value at 16:00, and then decreased gradually. The lowest mixing ratios at the urban and suburban sites occurred at 03:00 and 09:00, respectively. The NH$_3$ mixing ratio began to increase earlier at the urban site than at the suburban site. This result was obtained possibly due to the increased NH$_3$ emission at the urban site due to traffic in the morning rush hours. On average, the mixing ratio of NH$_3$ was considerably higher at the suburban site than that at the urban site, with an average difference of 4.1 ppb and a maximum difference of 6.1 ppb in the NH$_3$ mixing ratios of the sites. The average fluctuation in the NH$_3$ mixing ratio at the suburban site was 5.3 ppb, which was higher than that (2.6 ppb) at the urban site. At the urban site, the average diurnal variations in the NH$_3$ and H$_2$O mixing ratios exhibited opposite trends. The H$_2$O mixing ratio had high values in the night and low values in the day. At the suburban site, the variation characteristics of NH$_3$ and H$_2$O were very similar; however, the peak NH$_3$ concentration occurred 5 hours earlier than the peak H$_2$O concentration. In the spring, in contrast to the NH$_3$ mixing ratio, the H$_2$O mixing ratio at the urban site was 1279 ppm higher than that at the suburban site.
The diurnal variations in the NH$_3$ mixing ratio at the suburban site in the summer were similar with those in the spring. This phenomenon was also observed in the rural areas of Shanghai by Chang et al. (2019). The diurnal variations were considerably affected by the temperature and the contribution from volatile NH$_3$ sources. However, at the urban site, the diurnal variations in the NH$_3$ mixing ratio were different. In the summer, the NH$_3$ mixing ratio increased gradually from 21:00, decreased after reaching its peak value at 7:00, and then reached its lowest value at 14:00. The diurnal variability pattern (with a peak value in the morning) has been observed in other areas, such as rural (Ellis et al., 2011), urban (Gong et al., 2011), and steppe areas located far away from human activity (Wentworth et al., 2016). Kuang et al. (2020) believed that the diurnal variability pattern was caused by the evaporation of dew in the morning, which results in the release of NH$_3$ that was originally stored in the droplets. A lag was observed between the changes in the NH$_3$ with H$_2$O concentrations in the early morning, which supported the hypothesis of Kuang et al (2020). In addition, the increase in the NH$_3$ concentration in the morning might have been caused by the breakup of the boundary layer formed at night. The downward mixing of air with a high NH$_3$ concentration in the residual layer led to an increase in the NH$_3$ concentration on the ground in the morning (Bash et al., 2010). The NH$_3$ and H$_2$O concentrations at the urban and suburban sites exhibited opposite diurnal variations patterns in the spring. In the summer, the NH$_3$ concentrations at the suburban site were significantly higher than those at the urban site during the daytime and first half of the night. However, the NH$_3$ concentrations at the urban site were significantly higher than those at the suburban site during the second half of the night. The average fluctuation in the NH$_3$ concentration was 7.5 and 37 ppb at the urban and suburban site, respectively. Similar with the situation in the spring, the H$_2$O concentrations at the urban site were significantly higher than those at the suburban site in the summer.

In the autumn, the NH$_3$ concentration at the urban site had low values during the day and high values during the night. The peak NH$_3$ concentration occurred at midnight, and the lowest NH$_3$ concentration occurred at 17:00. There was essentially no diurnal variation in the NH$_3$ concentration at the suburban site, but obvious at the urban site with a fluctuation of 2.0 ppb. The concentration of NH$_3$ at the urban site was 1.2 ppb higher than that at the suburban site. The H$_2$O concentration was marginally lower (250 ppm) at the urban site than at the suburban site. The correlation between the diurnal variations in the NH$_3$ and H$_2$O concentrations was strong; however, the lowest value of NH$_3$ occurred later than the lowest value of H$_2$O at the urban site. The correlation between the diurnal variations in the NH$_3$ and H$_2$O concentrations was poor at the suburban site.

In the winter, the NH$_3$ mixing ratios at the urban and suburban sites exhibited similar diurnal variation patterns. The mixing ratios exhibited high values in the night and low values in the day. However, the NH$_3$ mixing ratio at the urban site was higher than that at the suburban site. This result was related to the decrease in the boundary layer height and temperature as well as the slow conversion and easy accumulation of pollutants in the night. In the daytime, increases in the temperature and boundary layer height enhanced the diffusion of pollutants, and the NH$_3$ mixing ratio decreased. The H$_2$O mixing ratio at the suburban site was close to that at the urban site, but higher in the morning. In the winter, the average diurnal variation in the NH$_3$ concentration was well correlated with that in the H$_2$O concentration at the urban site ($R = 0.89$). The correlation was close to that ($R = 0.93$) obtained by Teng et al. (2017) between the NH$_3$ and H$_2$O concentrations in the winter. However, at the suburban site, the mean diurnal variation in the NH$_3$ mixing ratios had a poor correlation with that in the H$_2$O mixing ratios.
The results indicated that although the two sites were under the influence of similar weather systems, the diurnal variations in the NH₃ mixing ratios at the two sites were different in different seasons. This finding suggested that different NH₃ sources and possibly sinks had different contributions to the NH₃ concentrations at the urban and suburban sites. Additional studies should be conducted on the behaviors of NH₃.

### 3.4. Effect of meteorological factors on the NH₃ levels

Table 3 presents the correlations between the daily mean NH₃ mixing ratios and the diurnal mean values of the temperature, relative humidity, and wind speed at the two sites. Annually, the correlations were highly significant as the NH₃ mixing ratios at both sites were significantly and positively correlated with the temperature and relative humidity and negatively correlated with the wind speed. However, in the summer and autumn, no significant correlations were noted between the NH₃ and temperature at the two sites. The relative humidity had the stronger influence on the NH₃ concentration at the two sites than temperature, which phenomenon also can be found in Fig 2. The fluctuations between NH₃ and relative humidity were much more consistent.

| Site     | Time Period | Temperature | Relative humidity | Wind speed |
|----------|-------------|-------------|-------------------|------------|
| Urban    | Annual      | 0.680**     | 0.706**           | -0.370**   |
|          | Spring      | 0.450**     | 0.645**           | -0.540**   |
|          | Summer      | 0.043       | 0.488**           | -0.106**   |
|          | Autumn      | 0.101       | 0.759**           | -0.413**   |
|          | Winter      | 0.596**     | 0.690**           | -0.449**   |
| Suburban | Annual      | 0.745**     | 0.730**           | -0.325**   |
|          | Spring      | 0.256*      | 0.518**           | -0.391**   |
|          | Summer      | 0.126       | 0.576**           | -0.061**   |
|          | Autumn      | 0.135       | 0.792**           | -0.618**   |
|          | Winter      | 0.676**     | 0.663**           | -0.545**   |

*: at the 0.05 significant level; **: at the 0.01 significant level.

Figure 5 display the seasonal mean diurnal variations in the NH₃ mixing ratio, temperature, and relative humidity with their correlation coefficients (also see in Fig. S3) in different seasons at the urban and suburban sites. At urban site, the diurnal variations in the NH₃ mixing ratio at the urban site were positively (negatively) correlated with the temperature (relative humidity) in spring, while in contrast, the diurnal variation of NH₃ mixing ratio were negatively (positively) correlated with temperature (relative humidity) in summer and autumn, and less correlated in winter. At suburban site, the diurnal variations in the NH₃ mixing ratio were positively (negatively) correlated with the temperature (relative humidity) in the spring and
summer, but less correlated in the fall and winter. Similar behaviors were found in spring, but different in other seasons. In general, the annual diurnal behaviors of NH$_3$ with temperature and relative humidity were different at the urban and suburban sites (see Figure S1). Fig. 6 displays the contour maps of the NH$_3$ mixing ratio, temperature, and relative humidity in different seasons at the urban and suburban sites. As displayed in Fig. 6 and Fig. S2, the NH$_3$ mixing ratios at both sites increased with the relative humidity at the same temperature and increased with the temperature at the same relative humidity. In winter, when the temperature was low (< 0 °C), the NH$_3$ mixing ratios at both sites often had low values except in high humidity (>60%). An increase in the temperature increased the NH$_3$ mixing ratios; however, the NH$_3$ concentration at the suburban site was more significantly affected by the temperature than that at the urban site (Table 3), indicating that volatile NH$_3$ sources might have a higher contribution to the NH$_3$ concentration at the suburban site than at the urban site. A higher amount of NH$_3$ removal through chemical transformation was expected during the day at the urban site than at the suburban site because the urban site had a higher relative humidity and higher amounts of primary particulate matter, NO$_x$, and SO$_2$ acid gas emissions than the suburban site did. In 2018, the concentrations of PM$_2.5$, SO$_2$ and NO$_2$ were 50μg/m$^3$, 5μg/m$^3$, 43μg/m$^3$ in Haidian, and 46μg/m$^3$, 6μg/m$^3$, 35μg/m$^3$ in Changping, respectively, which were reported by Beijing Ecology and Environment Statement, 2018.

**Figure 5.** Diurnal variations in and correlation coefficients between the NH$_3$ mixing ratios and temperature (a), relative humidity (b) in different seasons at the urban and suburban sites in Beijing.
To explore the influence of wind on the NH$_3$ mixing ratios, rose charts were drawn for the hourly mean concentration of NH$_3$, wind direction frequency, and wind speed during the observation period (Fig. 7). The large-scale wind circulation in the North China Plain is often influenced by the mountain-plain topography; therefore, the dominant winds in this area originate from the south (often in the day) and north (often at night). As displayed in Fig. 6, some differences existed in the distributions of the surface wind between the urban and suburban sites. The dominant surface winds originated from the northeast and southwest at the urban site and from the northwest and east at the suburban site. At the urban site, the NH$_3$ mixing ratios were relatively high when the winds originated from the southern sectors and relatively low when the winds originated from the northwest sectors. Therefore, under the action of the southwest wind, a polluted air mass from the south of Beijing can be easily transported to the urban site. Meng et al. (2017) examined the effect of long-range air transport on the urban NH$_3$ levels in Beijing during the summer through trajectory analysis. The authors concluded that the air mass from the southeast has a cumulative effect on the NH$_3$ concentration. Although the dominant wind direction at the suburban site was different from that at the urban site, the NH$_3$ mixing ratios were relatively high in the south sectors for both sites. Thus, winds from the southeast, south, and southwest had a cumulative effect on the NH$_3$ mixing ratios at both the urban and suburban sites. The NH$_3$ mixing ratios were relatively low when the wind originated from the northwest sector at urban site and from the west sector at the suburban site, in which the wind speed was strong, which indicated that the northwest/west wind could promote NH$_3$ dilution and diffusion.
Heavy rainfall occurred on a few days in Beijing in 2018. Heavy precipitation occurred for a long duration on August 18, 2018 (Fig. 8). Before the rainfall, the NH₃ concentration at the urban site was higher than the average level in August. After the rainfall occurred, the NH₃ concentration decreased rapidly, and it was significantly lower than the mean value in August. However, the diurnal variation of NH₃ on the rain day did not differ considerably from the average diurnal variation in August.

On August 18, 2018, the NH₃ mixing ratio at the suburban site remained at a low level during the rainfall period and was considerably lower than the mean NH₃ concentration in August. However, the NH₃ mixing ratio increased rapidly after the precipitation and reached the mean level at 17:00. The rainfall might have an obvious clearing effect on NH₃ but needed more cases to support.
4. Conclusion

In this study, the atmospheric NH$_3$ concentrations at an urban site and a suburban site in Beijing were continuously and simultaneously observed from January 2018 to January 2019. The mean NH$_3$ mixing ratios were 21 ± 14 and 22 ± 15 ppb at the urban and suburban sites, respectively. The annual average NH$_3$ mixing ratio at the suburban site was higher than that at the urban site. Moreover, the variation range of the NH$_3$ mixing ratio was larger at the suburban site than at the urban site. In the summer and spring, the NH$_3$ mixing ratio at the suburban site was higher than that at the urban site. In the summer and winter, the NH$_3$ mixing ratio at the suburban site was lower than that at the urban site. The highest NH$_3$ mixing ratios at the urban and suburban sites were observed in July. The lowest NH$_3$ mixing ratio at the urban site occurred in February, and the lowest NH$_3$ mixing ratio at the suburban site occurred in January. In the past decade, the concentration of NH$_3$ in Beijing did not change considerably, and the NH$_3$ levels in Beijing were higher than those in other large cities. The hourly mean NH$_3$ mixing ratios at the urban site were highly correlated ($R = 0.849$, $P < 0.01$) with those at the suburban site. However, the mean diurnal variations in the NH$_3$ mixing ratios at the urban and suburban sites were different. At the urban site, low NH$_3$ mixing ratios were observed in the day and high NH$_3$ mixing ratios were observed in the night. The opposite trend was observed at the suburban site. Although both sites were under the influence of similar weather systems, the seasonal diurnal variations in the NH$_3$ mixing ratio were different at the urban and suburban sites. This result indicated that NH$_3$ sources had different contributions to the NH$_3$ levels at the urban and suburban sites.

The influence of meteorological factors on the NH$_3$ mixing ratio was complex. At the same temperature, the NH$_3$ mixing ratios increased with the relative humidity at the urban and suburban sites. At the same relative humidity, the NH$_3$ mixing ratios increased with the temperature at both sites. The relative humidity had the strongest influence on the NH$_3$ mixing ratio in different seasons at the two sites. No strong correlation was observed between the NH$_3$ concentration and the temperature in the summer and autumn at the two sites. A high wind speed promoted a decrease in the NH$_3$ concentration. The NH$_3$ mixing ratios were higher when the winds originated from the south than when the winds originated from the north and northwest. Rainfall had a certain scavenging effect on NH$_3$; however, it had little effect on the diurnal variations in the NH$_3$ concentration.

Data availability. The data of stationary measurements are available upon request to the contact author Weili Lin (linwl@muc.edu.cn).

Author contributions. ZL and WL developed the idea for this paper, formulated the research goals, and carried out the measurement at urban site. WP and ZM carried out the NH$_3$ field observations at the suburban site.

Competing interests. The authors declare that they have no conflict of interest.
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