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Temporal characteristics and vertical distribution of atmospheric ammonia and ammonium in winter in Beijing

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ABSTRACT

To understand the temporal characteristics and vertical distributions of ammonia (NH₃) and ammonium (NH₄) in urban Beijing, we conducted ground-based and tower-based measurements of gaseous NH₃ and submicron aerosol composition. The average mixing ratio of NH₃ was 16.5 ± 7.4 ppb, ranging from 3.8 to 36.9 ppb. Gas-to-particle partitioning of NHₓ (≡ NH₃ + NH₄) played a significant role on NH₃ concentration as the molar ratio of NH₃ to NHₓ decreased as a function of NH₄ concentration. The NH₃ concentrations increased as a function of PM₁ at lower levels (< 125 µg m⁻³), but remained relatively constant at higher PM and NH₄ levels, indicating an enhanced gas-to-particle conversion of NH₃ during highly polluted conditions. The potential sources of NHₓ were found to include fossil fuel combustion and biomass burning. Regional transport could also play an important role on NH₃ concentration during the formation stage of haze episodes due to particle-to-gas conversion. Four distinctive types of vertical profiles (87% of the time) of both NH₃ and fine particle light extinction coefficient (bₑₓₜ) were observed and they were associated with well-mixed atmosphere, fast accumulation of local emissions, regional transport aloft, and the formation of low urban boundary layer, respectively. However, the vertical profiles of NH₃ typically (96% of the time) showed a more homogeneous characteristic than those of bₑₓₜ below 260 m, except periods with both strong temperature inversion and large aerosol gradient, the formation of urban boundary layer shall cause a significant transition in the vertical distribution of NH₃ below 260 m. During highly polluted situations (PM₁ > 125 µg m⁻³), the strong effect of gas-to-particle partitioning of NHₓ sometimes (7% of the time) caused opposite trends in vertical profiles of NH₃ and bₑₓₜ.

Key words: Ammonia, NHₓ, Vertical distribution, Extinction coefficient, Beijing
1. Introduction

NH$_3$ plays an important role in urban air pollution processes, such as the formation of secondary inorganic aerosol species of SNA (sulfate + nitrate + ammonium) (Wang et al., 2011). Other fine particle chemical species, e.g., organics, chloride, nitrate, sulfate and black carbon are relatively well understood during severe haze episodes in China (Sun et al., 2013; Wang et al., 2015; Zhang et al., 2015), the evolution mechanisms for ammonium remain poorly characterized. In addition, NH$_x$ (= NH$_3$ + NH$_4$) control has been found playing an effective role on reduction of PM$_{2.5}$ pollution (Giannadaki et al., 2018; Guo et al., 2018; Pozzer et al., 2017). NH$_3$ is mainly released from agricultural activities and breeding industry on a global scale (Van Damme et al., 2018), however, the sources for the high level of NH$_3$ observed in urban areas remain a controversial topic (Zhang et al., 2017) as there are little local contributions from the two sources mentioned above. Traffic emission has been reported as an important source for NH$_3$ in urban areas (Elser et al., 2018). Coal combustion and biomass burning, which are major contributors to severe haze pollution in Beijing, have been found to emit significant amount of NH$_3$ (Li et al., 2016). Some point sources, e.g., wastewater treatment plants, can also emit NH$_3$ (Van Damme et al., 2018). The sources for NH$_3$ were studied via N isotopic ratios in nitrate and simulated NH$_3$ in Pan et al. (2016; 2018), and via direct measurement of NH$_3$ in Chang et al. (2015), however, the relationship between ammonium and NH$_3$ was not further discussed. NH$_3$ concentration was usually found depending exponentially on temperature (Chang et al., 2015), especially during winter time (Teng et al., 2017), indicating a significant effect of gas-particle partitioning on the concentration of NH$_3$. The uncertainties of ammonia emissions, together with the huge variations in the relationship between emissions and ambient concentrations of NH$_3$, are causing difficulties in abating NH$_4$ levels. Thus, it is worthwhile to study the sources and
evolution mechanisms for NH$_x$ via simultaneous measurement of both gaseous NH$_3$ and particulate ammonium, especially in severely polluted megacities that suffer high level of NH$_x$ (Wang et al., 2015).

The complex vertical evolution of air pollutants is attracting attention due to its strong influence on the accurate prediction of air quality models (Wang et al., 2014). Regional transport usually affected air pollution in urban areas initially above the urban canopy, which could be observed based on the vertical distribution of air pollutants (Sun et al., 2015; Wang et al., 2018). The weekly vertical distribution of ammonia (NH$_3$) measured at 16 different heights on the Beijing 325 m meteorological tower (BMT) showed that NH$_3$ was rich during all seasons below 320 m (Zhang et al., 2018). High time resolution method for vertically resolved studies shows that NH$_3$ concentration at higher altitudes appears to be driven by transport while that at lower altitudes is strongly influenced by surface emissions and boundary layer height (Tevlin et al., 2017). To date, the vertical profiles of NH$_x$ at urban area in highly polluted megacities in China have rarely been studied.

In this study, highly time-resolved measurements of gaseous NH$_3$ were conducted at ground site, and the vertically resolved measurements of NH$_3$ and fine particle extinction coefficient ($b_{ext}$) were performed from ground level to 260 m on the BMT in November and December 2016. In addition, simultaneous real-time measurements of ammonium in PM$_1$ particles were conducted at the ground level and 260 m from the tower, along with measurements of the other PM$_1$ species (i.e., organics, sulfate, nitrate, chloride, and BC) and trace gases (i.e., CO, SO$_2$, O$_3$ and nitrogen oxides). Our goals are to elucidate the vertical evolution mechanisms of NH$_x$ and the potential sources for NH$_3$ within urban boundary layer (UBL) during wintertime in Beijing.
2. Experimental methods

2.1. Sampling site

All measurements were conducted at an urban site between the 3rd and 4th ring road in Beijing located at the Tower Branch of Institute of Atmospheric Physics (TBIAP, 39°58′N, 116°22′E; elevation: 49 m ASL), Chinese Academy of Sciences from November 16 to December 10, 2016. The site is surrounded by roads, expressways, gas stations, residential areas, park, commercial buildings, and restaurants (Fig. 1).

2.2. Ground measurements

NH$_3$ at ground level was measured using an online LGR ammonia analyzer (DTL-100, Los Gatos Research, California) (Baer et al., 2002) at a time resolution of about 50 s (Location B; Fig. 1). Meng et al. (2018) reported that there was a lag in the results of the LGR ammonia analyzer, and hourly average could reduce this influence. NH$_3$ measured by the LGR ammonia analyzer tracked well with the measurement at 102 m on the BMT from an open path quantum cascade-laser (QCL)-based NH$_3$ sensor (Aerodyne Research Inc., USA) using a 3 m fast-response counter-flow impactor inlet, with $R^2 = 0.70$, slope = 0.89 (Fig. S1). Note that a slight time lag of a few seconds was observed between the two measurements. However, the water vapor measured at 50 s resolution by the LGR ammonia analyzer compared extremely well with that measured at 2 s resolution from a ground meteorological station ($R^2 = 0.99$, slope = 1.19; Fig. S1), and the water vapor and NH$_3$ measured by the LGR ammonia analyzer were also highly consistent, indicating that the time lag between the LGR ammonia analyzer and the QCL-based NH$_3$ sensor can be ignored.

Gas analyzers (Thermo Scientific) were deployed from a nearby container (Location C; Fig. 1)
to measure NO/NO₂ (Model 42i), CO (Model 48i), O₃ (Model 49i), and SO₂ (Model 43i) simultaneously. CO₂ at 8 m above the ground were measured from the tower using a LI-7500 CO₂/H₂O infrared gas analyzers (LI-COR, Inc., Nebraska, USA) on the BMT (Liu et al., 2015).

At the rooftop of a two-story building (~8 m high) (Location A; Fig. 1), non-refractory submicron aerosol (NR-PM₁) species, including organics (Org), sulfate (SO₄), nitrate (NO₃), ammonium (NH₄) and chloride (Chl) were measured by an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS hereafter); BC was measured by a 7-wavelength aethalometer (AE33, Magee Scientific Corp.); extinction coefficients of dry fine PM₁ at 630 nm by a CAPS particle single-scattering albedo monitor (CAPS PMSSA, Aerodyne Research Inc.). The organic aerosol spectral matrices of the AMS were analyzed by Positive Matrix Factorization (PMF) to resolve 6 organic aerosol (OA) factors (Xu et al., 2018), i.e., a fossil-fuel-related OA (FFOA), a cooking OA (COA), a biomass burning OA (BBOA), an oxidized POA (OPOA), an oxygenated OA (OOA), and an aqueous-phase OOA (aq-OOA). Measurements of NH₃ and PM₁ chemical species at ground level were extended to December 22 2016.

2.3. Measurements at 260 m above the ground

Simultaneous measurements of BC, CO, O₃, and SO₂ were conducted at 260 m on the tower using the same type of instruments as those used for the ground observations except that NR-PM₁ was measured with an Aerodyne Aerosol Chemical Speciation Monitor (ACSM) (Sun et al., 2015). The ACSM had been deployed in parallel with the AMS through the same sampling inlet during December 14 to 16, 2016, and the $R^2$ for the NR-PM₁ species comparisons between the two instruments were 0.97, 0.98, 0.99, 0.99, and 0.98, respectively for Org, SO₄, NO₃, NH₄, and Chl.
High correlation for parallel sampling comparisons of BC and precursor gases with the same model of instruments for measurement at the two heights were also confirmed. $b_{\text{ext}} (\lambda = 630 \text{ nm})$ of PM$_{2.5}$ at 260 m was measured by a CAPS particle extinction monitor (CAPS-PM$_{\text{ext}}$, Aerodyne Research Inc.).

2.4. Vertically resolved measurements

A container suspended from a cable car style lift system installed on the BMT was used for vertically resolved measurements at a constant moving speed of ~ 8 m min$^{-1}$. The ammonia analyzer and a Photo-Acoustic Extintiometer (PAX, Droplet Measurement Technologies, Inc.) were placed inside the container for measurements of NH$_3$ and light extinction coefficient at $\lambda = 870$ nm of PM$_{2.5}$, respectively. All instruments were powered by Uninterrupted Power Supply, and the vertically resolved measurements were performed between the ground level and aloft about every 4 h during daytime (260 m) and every 6 h during nighttime (240 m) for safety; for the remainder of the time the instruments provided ground measurements, which was similar to the arrangements reported in Wang et al. (2018). In total, 50 sets of vertical profiles (VPs) for $b_{\text{ext}}$ (VPs$_{b_{\text{ext}}}$) and NH$_3$ (VPs$_{\text{NH}_3}$) were obtained. Due to the interruption of power supply, 4 VPs$_{\text{NH}_3}$ were incomplete. Wind speed (WS), wind direction (WD), relative humidity (RH), and temperature ($T$) at 15 different heights (8, 15, 32, 47, 63, 80, 100, 120, 140, 160, 180, 200, 240, 280, and 320 m) were measured on the BMT.

3. Results and discussion

3.1. Overview of pollution levels

The average mass concentration of PM$_{1}$ was 83.3 ± 80.3 µg m$^{-3}$ (Table S1) from November 16 to December 10, with organics, nitrate, sulfate, ammonium, chloride, and black carbon accounted for on average 39.8%, 19.6%, 16.3%, 10.0%, 7.3%, and 7.0%, respectively, indicating a high level of
aerosol pollution in urban Beijing. The average NH$_3$ mixing ratio during this study was 16.5 ± 7.4 ppb (12.3 ± 5.5 µg m$^{-3}$), higher than the values previously observed in Shanghai (about 5 ppb in winter and autumn) (Chang et al., 2015) and in winter 2007 in Beijing (5.5 µg m$^{-3}$), lower than the level observed at a rural site (36.2 ppb) and in urban Beijing in summer 2007 (25.4 µg m$^{-3}$) (Shen et al., 2011), and was less than 1/10 of those observed in tunnel studies (Chang et al., 2015; Liu et al., 2014). Compared with the results in the heating season of 2012 (Wang et al., 2015), SO$_2$ was lower by more than 50%. However, CO, NO, NO$_2$ were at comparable levels, suggesting similar intensity of traffic emission but a significant reduction of coal combustion emission. High values of O$_3$ could be observed both at daytime and nighttime with low PM$_1$ mass loadings, indicating that the high background of NO$_x$ and VOCs in Beijing (Fig. 2). High level of O$_3$ and low levels of other pollutants typically appeared when the northwest wind prevailed (Fig. 2). Low values of O$_3$ during high pollution episodes were relevant to the lower solar radiation and weak oxidation of atmospheric condition, and high NO that titrated O$_3$ substantially as the diurnal cycle of O$_3$ was generally in accordance with that of solar radiation (Wang et al., 2015), and was opposite to those of NO$_x$, NO$_2$, and SO$_2$ (Fig. S2). High RH generally coincided with highly polluted episodes, which is a common feature for severe haze in Beijing (Sun et al., 2014b; Sun et al., 2012; Sun et al., 2013). High f$_{NH3}$ (= NH$_3$ / NH$_x$ in molar concentrations) appeared during low pollution situations (Fig. 2f) partly due to low RH which tended to inhibit the transformation of NH$_3$ to ammonium.

The diurnal cycle of NH$_3$ was similar to those of Chl, BC, CO, and NO, suggesting coal combustion and traffic were two important sources for NH$_3$ and NH$_4$. Both NO and CO$_2$ peaked at 8:00, indicating that traffic emission was an important source of CO$_2$ in our study. The diurnal profile of SO$_2$, a gas species dominantly from coal combustion emissions, generally agreed well with that of
NH$_3$ ($R^2 = 0.67$), with low values occurring around 8:00 and 15:00 – 18:00, and high values at nighttime. Previous studies also showed that fossil fuel emissions could contribute 90% of the total NH$_3$ during haze days in urban Beijing (Pan et al., 2016). These results suggest that coal combustion could be an important source of NH$_3$ in urban Beijing. The similar diurnal trends of NH$_3$ and NH$_4$ indicated a regional transport characteristic for NH$_x$ during this study. A great difference between the diurnal cycles of NH$_3$ and NH$_x$ occurred during 8:00 – 16:00 when there was a negative correlation between f$_{NH3}$ and NH$_x$ due to the conversion of particle to gas.

3.2. Gas-particle partitioning of NH$_x$

In Fig. 3, during clean periods (PM$_1 \leq 17$ µg m$^{-3}$) NH$_3$ was about 8 µg m$^{-3}$ (10 ppb). f$_{NH3}$ correlated negatively with PM$_1$, indicating enhanced gas-to-particle conversion of NH$_3$ during high PM pollution situation (Figs. 3 and S3). Line A, Zones B, C and D were marked by dotted lines in Fig. 3. Line A illustrates the average background NH$_3$ concentration that appeared during clean days with strong northeast wind (Fig. 2), when NH$_3$ in Beijing during the winter season was mainly affected by emissions from regional agriculture and breeding industry of north China. NH$_3$ increased fast with the increase of PM$_1$ in Zone B (17 < PM$_1 \leq 125$ µg m$^{-3}$), indicating the linear and positive correlation with the accumulation of PM$_1$. Average NH$_3$ was relatively constant at an average ($\pm 1\sigma$) concentration of 17.0 ± 3.5 µg m$^{-3}$ (or 22.8 ± 4.7 ppb) in Zone C (125 < PM$_1 \leq 272$ µg m$^{-3}$), and especially in zone D (272 < PM$_1 \leq 500$ µg m$^{-3}$). This is an indication that the basic NH$_3$ gas was still in excess relative to acidic gases (e.g., HNO$_3$ and HCl) during severe haze episodes.

There was a good exponential relationship between f$_{NH3}$ and NH$_3$ (Fig. 4), as the $R^2$ and Slope between the measured and the reconstructed values of f$_{NH3}$ were 0.92 and 0.99, respectively (Fig. S4).
Exponential relationships were usually observed between $T$ and concentration of NH$_3$ (Aneja et al., 2000; Chang et al., 2015; Teng et al., 2017) as $T$ is an important factor for gas-particle partitioning. The correlation between NH$_3$ and dew point (DP) was tightest among those of NH$_3$, NH$_x$, or NH$_4$ vs DP, RH, or $T$ (Table S2). There was a border line of $T$ at about 5 °C, as high values of NH$_4$ and NH$_3$ appeared when $T < 5$ °C and $T > 5$ °C, respectively (Fig. 5).

3.3. Potential sources and emission ratio (ER) for NH$_x$.

Considering the strong activity of gas-particle partitioning of NH$_3$, it is reasonable to detect the potential sources for NH$_x$ instead of for NH$_3$ as NH$_x$ approximately had a linear relationship with PM$_1$. The $R^2$ between the time series of tracers of potential sources and NH$_3$ and NH$_x$ are presented in Table S3 for different time resolution (5 min, 6 h, and 1 day), in view of some instantaneous processes that might cause a delay in increase of NH$_3$, e.g., due to conversion to NH$_4$ through secondary aerosol formation. Tracers that had weak correlations with NH$_3$ and NH$_x$ suggested insignificant contributions from the corresponding source, e.g., cooking was not an identified source of NH$_x$. In addition, NH$_3$ from traffic emission can vary not only between different running status of a car (Sun et al., 2014a), but also between different cars (Li et al., 2006). Hence, here we split the time series of NH$_x$ into 35 segments to calculate the $R^2$ and slopes between the tracers and NH$_x$ (Fig. S5).

CO, BC, and Chl correlated well with NH$_x$, with $R^2 = 0.77$, 0.72 and 0.68, respectively, suggesting that traffic and coal combustion were two significant sources of NH$_x$ (Wang et al., 2015). Zhang et al. (2018) reported that local sources such as traffic emissions appeared to be important contributors to NH$_3$ in urban Beijing. CO$_2$ had relatively lower correlation with NH$_x$ than CO did at
measurement time resolution of 5 min. Incomplete combustion of fossil fuels, e.g., cold start or low running speed of the car (Sun et al., 2014a), and charcoal barbecue or scattered coal burning (Li et al., 2016) usually caused spikes in the time series of CO. The $R^2$ between CO$_2$ vs NH$_x$ was also lower than CO vs NH$_x$ for lower time resolution of 6 hours or 1 day, indicating that incomplete combustion of fossil fuels was an important contributor to ER of NH$_x$. In view of the highly polluted surrounding areas (Wang et al., 2014), regional transport of NH$_4$ was likely a strong contributor to NH$_x$ in Beijing. As the N fertilizer used in November and December were as low as ~ 2% of the whole year (Fu et al., 2015), and the NH$_3$ levels were correspondingly low in the two months (Damme et al., 2015) in the North China Plain, thus the agricultural emission from regional transport was unlikely an important source of NH$_3$ in Beijing during our study period.

NH$_x$ correlated better with Aq-OOA (O:C = 0.82) and semi-volatile species such as particulate nitrate ($R^2 = 0.83$, and 0.88, respectively) than with the more oxidized OOA (O:C = 1.09) and SO$_4$ ($R^2 = 0.58$ and 0.81, respectively), appearing that local sources contributed more significantly to NH$_x$ in urban Beijing. High correlation coefficients between O$_3$ and NH$_x$ in our study were all observed during noon time (Fig. S5), e.g., in segments 6, 16, 20, 26, 32, 33, 35, when NH$_x$ were also correlated well with BBOA, or FFOA. O$_3$ could be produced both from photochemical process and nighttime chemistry (Millet et al., 2016), and NH$_3$ was found to promote the generation of secondary organic aerosol (Huang et al., 2012; Na et al., 2006) during ozone-initiated reaction. Further research on the behavior of NH$_x$ during atmospheric chemical reactions is still needed.

NH$_x$ correlated best with CO among all primary tracers, thus CO was the most typical primary species for ER calculation of NH$_x$ here. The high correlations of CO and NO$_x$ ($R^2 = 0.74$) and vs Chl
\(R^2 = 0.84\) suggest that traffic and coal combustion were the major sources of CO in our study. The ER of \([\text{NH}_3]/[\text{CO}]\) (ppbv/ppbv) ranged between 0.001 – 0.03 with a mean value of 0.011 (Table S4). The mean value was significantly lower than the ER of \([\text{NH}_3]/[\text{CO}]\) (ppbv/ppbv) reported previously for traffic emissions (~ 0.03) (Sun et al., 2014a), and the automobiles and dairy facilities emission (~ 0.035) (Nowak et al., 2012). Biomass burning emissions and secondary formation also likely played a significant role for the high level of \(\text{NH}_x\) in Beijing as the ER of \([\text{NH}_x]/[\text{BBOA}]\) (1.99 ppbv/\(\mu\)g m\(^{-3}\)) was higher than that of \([\text{NH}_x]/[\text{FFOA}]\) (1.39 ppbv/\(\mu\)g m\(^{-3}\)), and the ER of \([\text{NH}_x]/[\text{OOA+aq-OOA}]\) (3.86 ppbv/\(\mu\)g m\(^{-3}\)) was higher than that of \([\text{NH}_x]/[\text{FFOA+BBOA}]\) (3.38 ppbv/\(\mu\)g m\(^{-3}\)).

Bivariate plots of \(\text{NH}_x\) (Fig. S6) show high concentration in the center area with low wind speed and also the south region with high wind speed, suggesting that the elevated \(\text{NH}_x\) concentration was mainly associated with local emissions and air masses transported from the south. Regional transport could also affect primary species, e.g., BBOA and Chl. The regional characteristics of \(\text{NH}_3\) was unlikely caused by primary emissions, but rather due to the thermodynamics effect of the transported \(\text{NH}_4\). The bivariate plot of \(f_{\text{NH}_3}\) was similar to that of \(\text{O}_3\), as both peaked when northwest wind prevailed. High \(\text{NH}_3\) was mainly associated with east wind that resulted in high RH. The concentration of \(\text{NH}_x\) was low in the northwest direction due to less emission sources of pollutants, but there was an enhancement of the concentration of \(\text{NH}_3\) in the farthest northwest direction under high wind speeds caused by the transport effect in clean situations. Sources of \(\text{NO}_2\), \(\text{SO}_2\), and OOA were mainly from the southwest, which was different with that of \(\text{NH}_x\), indicating the weak contribution of these sources to \(\text{NH}_x\). However, the distributions of the high concentrations of CO, NO, BC, Chl, FFOA, BBOA, and aq-OOA were generally within that of \(\text{NH}_x\) in Fig. S6, indicating similar source contributions for these species.
3.4. Vertical profiles of NH$_3$

The VPs$_{\text{b}_{\text{ext}}}$ in this study (Fig. S7) were classified into four categories (Table S5) as discussed in detail in Wang et al. (2018), i.e., uniformly distributed (Fig. 6a), higher at lower heights caused by enhanced local emissions (Fig. 6b), higher aloft caused by regional transport (Fig. 6c), and significant transition caused by the formation of UBL (Fig. 6d). Mostly (87% of the time), the VPs$_{\text{NH}_3}$ were consistent with the VPs$_{\text{b}_{\text{ext}}}$. The vertical profiles of temperature in Fig. 6 followed the rules discussed in Wang et al. (2018). For example, there was no evident temperature inversion in Figs. 6a and b as the largest $T$ inversion value was 0.2 °C, but significant $T$ inversion was found in Fig. 6c (3.3 °C at 80 m to 4.8°C at 280 m) and d (3.0 °C at 80 m to 7.8 °C at 280 m). More detailed explanations for the four kinds of distinctive profiles can be found in Wang et al. (2018).

The 20$^{\text{th}}$ VP$_{\text{b}_{\text{ext}}}$ (VP$_{\text{b}_{\text{ext}}}$–20) and VP$_{\text{NH}_3}$ (VP$_{\text{NH}_3}$–20) (Fig. S8 and Fig. 7a) were of a new kind of vertical profile, which decreased from 130 m to 170 m and increased above 170 m. As shown in Fig. S8, PM$_1$ during this vertical observation was increased from 106 µg m$^{-3}$ at 6:05 to 112 µg m$^{-3}$ at 7:05 at ground level with SNA (= sulfate+ nitrate + ammonium) accounting for about 35% of the PM$_1$ mass, and from 128 µg m$^{-3}$ at 6:30 to 132µg m$^{-3}$ at 6:41 at 260 m with SNA accounting for about 43%, indicating larger contribution of SNA and higher aerosol pollution level at 260 m. Small wind (~ 2 m s$^{-1}$) at the height range of 260 – 500 m was from the south during 6:30 – 8:00 (Figs. S8e and f), and $T$ inversion occurred at about 80 m (Table S5), thus the shape of VP$_{\text{b}_{\text{ext}}}$–20 seemed to be a combination of the typical vertical profiles of III and IV in Figs. 6c and d, possibly caused by transport of pollutants from the south and/or the formation of low residual layer in the morning.

Besides, the PM$_1$ at 260 m was rich in nitrate (~ 22% of PM$_1$), not in ammonium (~ 10% of PM$_1$),
thus, although the $b_{ext}$ was increased by $\sim 210$ Mm$^{-1}$ from 200 m to 235 m, the NH$_3$ was just increased by $\sim 1$ ppb, indicating weak particle-to-gas partitioning of NH$_3$ in case of the insufficient particle ammonium.

However, the vertical distribution of NH$_3$ showed a more homogeneous characteristic than those of $b_{ext}$ below 260 m in general (Fig. S7), and occasionally, for 7% of the time, the VPs_NH$_3$ varied oppositely to the VPs$_{b_{ext}}$. VP$_{22\_up}$ ("up" means that the container was moving upward), VP$_{23\_up}$ (Fig. 7b) and VP$_{24}$ (Fig. 7c) were discussed here as the representative examples. The differences of RH and $T$ between VP$_{22\_up}$ and VP$_{22\_down}$ ("down" means that the container was moving downward) were less than 5% and 0.5 °C, respectively. The wind generally varied from east to south, indicating a similar meteorological condition for the two vertical profiles. PM$_1$ at ground level and 260 m was increased by 28 µg m$^{-3}$ and 10 µg m$^{-3}$ (Fig. S9), respectively. The contributions of NH$_4$ and NO$_3$ were generally constant at the two heights, and the increased contribution of SO$_4$ shall not promote the increase of NH$_3$, thus, the difference of NH$_3$ between VP$_{22\_up}$ and VP$_{22\_down}$ was probably due to the faster and direct emission of NH$_3$ from fossil fuel combustion at ground level as CO, CO$_2$ and NO$_x$ in Fig. 2 all increased.

From VP$_{23\_up}$ to VP$_{23\_down}$, PM$_1$ decreased by 32 µg m$^{-3}$ at 260 m while increased by 91 µg m$^{-3}$ at ground level (Fig. S9), indicating a strong accumulation of aerosol at ground level. Enhanced accumulation of NO$_x$, SO$_2$, and NO$_x$ were also observed at ground level (Fig. 2). Thus, the variation of VP_NH$_3$$_{23\_up}$ was mainly caused by the enhanced local NH$_3$ emission, e. g., traffic emission and coal combustion. By contrast, the slower increase of VP_NH$_3$$_{23\_down}$ was generally driven by the enhanced consumption of NH$_3$ due to gas-to-particle partitioning at high level of RH ($\approx$
70%) as the fNH3 was larger (Fig. 2). The UBL was confined to below 200 m during VP_23_down. RH was increased by ~ 10%, T was decreased by ~ 1 °C below 200 m, which would facilitate the formation of NH4, but it played a much weaker role on NH3 than on aerosol as the vertical differences of VP_NH3_23_down and VP_bext_23_down were 8% and 32%, respectively.

For VP_24, T inversion occurred at about 150 m when bext gradually decreased with the height, indicating the formation of low UBL. PM1 at 260 m was decreased by only ~ 2% (from 292 µg m\(^{-3}\) to 286 µg m\(^{-3}\)), and at ground level was by about 8% (from 433 µg m\(^{-3}\) to 467 µg m\(^{-3}\)) (Fig. S9) from VP_24_up to VP_24_down. VP_bext_24 was of the type IV in Fig. 6d, but the trend of VP_NH3 was totally an opposite. One explanation was that, at such high level of PM and RH (~ 95%) below 200 m, NH3 was mainly determined by gas-particle partitioning balance affected by both of the temperature and aerosol chemical composition, as to maintain an ion balance, it still needed NH4 (= SO4/96×2×18 + NO3/62×18 + Chl/35.5×18 - NH4) of about 35 µg m\(^{-3}\) and 20 µg m\(^{-3}\), respectively at ground level and 260 m, thus NH3 was greatly consumed to provide NH4. It is consistent with that particle is acidic during winter haze episodes (Guo et al., 2017; Liu et al., 2017). Later, higher temperature and lower aerosol mass concentration for VP_24_up caused higher values of NH3 than that for VP_24_down.

3.5. The vertical difference between NH3 and particles

In Fig. 8, all the data points measured during the vertically resolved experiments fell in the region defined by measurements from the ground level, indicating similar evolution mechanism of NH3 versus bext below 260 m. The data points measured during each vertically resolved experiment were usually clustered due to the uniform vertical distribution of NH3 concentration. Compared with
the relationship between VP_NO2 vs VP_bext reported in Wang et al. (2018), VP_NH3 increased faster with VP_bext and NH3 had a maximum value of about 35 ppb in the bext range of 0 – 2000 Mm⁻¹. In Fig. 9a, both bext and NH3 were higher during nighttime due to lower UBL, as well as enhanced coal heating and truck emissions. The diurnal variation (= (nighttime- daytime)/whole campaign) of average VP_NH3 and VP_bext in Fig. 9a are 0.13 and 0.93 respectively, indicating much smaller diurnal variation of VP_NH3 below 260 m, which supports the result that NH3 is rich below 260 m. The comparison between diurnal variation of average VP_NH3 and VP_bext were shown in Fig. 9b. Regional transport and the formation of residual layer above 200 m caused higher values above 200 m during nighttime of VP_bext and VP_NH3. Low UBL height at nighttime resulted in the decrease in VP_bext below 200 m, however, the VP_NH3 showed an opposite trend mainly due to the gas-to-particle partitioning of NHx. For instance, more NH3 was needed to form ammonium salt at ground level as 13 µg m⁻³ of NH4 was in shortage to maintain ion balance, higher than that during daytime (6 µg m⁻³) and at 260 m (3 – 8 µg m⁻³). The nocturnal NH3/bext was smaller than the diurnal NH3/bext, it was partly caused by large values of NH3/bext in clean periods (Fig. S7) that usually appeared during daytime, e. g., the NH3/bext of VPs_9 – 12, VP_15, and VP_16 were in the range of 250 – 1600 ppt/Mm⁻¹, and the lower T and higher RH (Fig. S10) during nighttime that facilitated the gas-to-particle partitioning of NHx.

In Fig. S11, most VPs_bext decreased with height, however, about half of VPs_NH3 showed opposite trend. 96% of the vertical variation (the ratios of one standard deviation to mean value (Sdev/Avg), (Max-Min)/(2×Avg)) of NH3 were smaller than that of bext. The average value of Sdev/Avg of VP_bext was about 4 times of that of VP_NH3, proving, once again, the much more homogeneous vertical distribution of NH3 in urban area in Beijing below 260 m.
In Fig. 10, the ratios of PM$_1$ and NH$_4$ at 260 m to ground level were 1.35 and 1.25, respectively, whereas, the ratios for NH$_3$ and f$_{NH3}$ were very close to 1 (0.98 and 0.93, respectively; Fig. 10c and d). Moreover, NH$_3$ concentration correlated better between the two heights ($R^2 = 0.88$; Fig. 10c) than PM$_1$ or NH$_4$ ($R^2 = 0.81$ for both; Fig. 10a and b) also suggested a more homogeneous mixing of NH$_3$. The exponential relationships between NH$_3$ vs. PM$_1$ and f$_{NH3}$ vs. NH$_4$ were very similar between ground level and 260 m (Fig. 11), indicating similar gas-particle partitioning mechanisms below 260 m. The small difference of DP between 8 m and 280 m (approximately 2 °C in this study; Fig. S12a) might be a reason for this similar gas-particle partitioning mechanism.

Besides, SO$_2$ and CO at 260 m correlated well with those at ground level ($R^2 = 0.57$ and 0.63, respectively), indicating similar combustion sources for NH$_x$ within 260 m (Fig. S13a). The average ratios of SO$_2$ and CO at ground level to those at 260 m were 0.7 and 1.1, respectively. It is reasonable that coal combustion for residential heating has been well controlled in urban Beijing, and SO$_2$ emitted from coal combustion was more likely from surrounding areas, especially during night time (Fig. S13b). Comparatively, CO was generally higher at ground level than 260 m due to the influence of traffic emissions in urban Beijing.

4. Conclusions and implications

The average NH$_3$ concentration was 12.3 µg m$^{-3}$ (16.5 ppb) in winter in Beijing, lower than those reported in tunnel studies and in summer in rural Beijing. NH$_3$ remained constant during both clean periods (PM$_1 < 17$ µg m$^{-3}$) and heavily polluted episodes (PM$_1 > 272$ µg m$^{-3}$), with average concentration at about 8 µg m$^{-3}$ and 17 µg m$^{-3}$, respectively. Gas-particle partitioning played less distinctive role in controlling NH$_3$ during periods with PM$_1$ ranging from 17 to 125 µg m$^{-3}$ (NH$_3 = 8 – 16$ µg m$^{-3}$) when NH$_3$ correlated positively and linearly with PM$_1$. NH$_x$ in Beijing came from
complex sources. Primary emissions of biomass burning, coal combustion, and traffic were three significant contributors to NH₃. The regional transport was also a strong contribution to NH₃ as it correlated well with secondary species, e.g., aq-OOA, NO₃, and SO₄. The average wind speed was usually about 5 m s⁻¹ at the height of 280 m, thus the pollutants from surrounding areas within about 400 km, e.g., Hebei (Wang et al., 2014) and Shandong Provinces (Wang et al., 2016), could arrive at Beijing in one day. Once the exact sources for NH₃ had been resolved, the source contributions for NH₃ could be reconstructed according to the good exponential relationship between f_{NH₃} and NH₄.

Vertically resolved measurements also showed four types of vertical profiles for b_{ext}, which were associated with well mixed atmosphere, fast accumulation of local emissions, regional transport aloft, and the formation of low urban boundary layer, consistent with those reported in Wang et al. (2018). The vertical distribution of NH₃ was generally consistent with that of b_{ext}, but was more homogeneous due to the stronger diffusivity of NH₃. The strong gas-particle partitioning effect associated with high contribution of sulfate, nitrate and chloride was an important reason for the different vertical distributions between NH₃ and b_{ext} during high PM pollution situation. The formation of UBL played a much weaker role on NH₃ than on aerosol, just when both the strong temperature inversion and large aerosol gradient occurred, the formation of UBL shall play a significant role on the vertical profiles of NH₃ below 260 m, e. g. VP_25 (Fig. 6d).

Appendix A. Supplementary material

Supplementary Information accompanies this paper (Figs. S1-S12, Tables S1-S5) including detailed description of the data quality, methodology, bivariate polar plots of pollution species, correlations between pollution species, aerosol chemical compositions, and information of vertical
profiles of NH$_3$ and $b_{ext}$.

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Notes

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Fig. 1. Sampling site and its surroundings.

Fig. 2. Time series of (a) WS, WD, RH, and T; (b) O$_3$ and NO$_2$; (c) NH$_3$, NO$_2$, and CO; (d) NO,
SO₂, and CO₂; mass concentrations of (e) NH₄ and PM₁; (f) molar concentration of NHₓ, f_NH₃, and dew point at the ground level of TBIAP (39°58′N, 116°22′E; elevation: 49 m ASL).

Fig. 3. Variations of (a) NH₃, (b) NH₄, (c) NHₓ, and (d) f_NH₃ as a function of PM₁ mass concentration with the boxes showing the mean (blue circles), median, 10th, 25th, 75th and 90th percentiles of the data values.

Fig. 4. Relationships between f_NH₃ and NH₄, and between measured and reconstructed f_NH₃ with NH₄.
Fig. 5. RH and T dependence of (a) molar concentration of NH$_x$, mass concentration of (b) NH$_3$ and (c) NH$_4$, and (d) f$_{NH3}$.

Fig. 6. Examples for four typical types of VP$_{NH3}$ which are consistent with VP$_{b_{ext}}$ according to the results reported in Wang et al. (2018), together with the corresponding vertical profiles of RH, WD, WS, and T. The serial number of the vertically resolved experiments were added in each figure, and the moving directions of the container were marked in red (UP) and black (DOWN) color, respectively.
Fig. 7. The typical types of VP_NH₃ that could not be classified with the method in Wang et al. (2018), together with the corresponding vertical profiles of bₑₓts, RH, and T. The serial number of the vertically resolved experiments were added in each figure, and the moving directions of the container were marked in red (UP) and black (DOWN) color for the vertical profiles, respectively.

Fig. 8. Comparison of NH₃ vs bₑₓts measured at ground level (gray points) and during vertically
resolved measurements (round points colored by heights were measured during each vertically resolved measurement, red circles are the average values for each vertically resolved measurement.

Fig. 9. Average vertical distribution of (a) $b_{ext}$, NH$_3$, and NH$_3$/b$_{ext}$ for all data points, and for data points that during daytime and nighttime, respectively. (b) Comparison of vertical distribution of NH$_3$ vs $b_{ext}$ measured during daytime and nighttime and the corresponding PM chemical composition at 260 m and ground level.

Fig. 10. Comparisons of (a) PM$_1$, (b) NH$_4$, (c) NH$_3$ and (d) f$_{NH3}$ between 260 m and ground level.

Data points were marked by the serial number of the experiments (Fig. S7). Data points
measured for up and down experiments were marked in red and black color, respectively. Data points for down experiment 14, 19, 20, and 25 were not used for calculation of $R^2$ and Slope due to the incomplete measurement of VP_NH$_3$. NH$_3$ measured at 240 m during nighttime was approximately used as the value at 260 m as the moving time from 240 m to 260 m is about 2.5 minutes (=20/8min).

![Graph](image)

**Fig. 11.** (a) Variations of NH$_3$ as a function of PM$_1$ mass concentration, and (b) relationship between $f_{NH3}$ and NH$_4$ concentration at ground level (black circles) and 260 m (red circles) during the vertically resolved experiments.
Graphical abstract
HIGHLIGHTS

Gas-particle partitioning plays a significant role on NH$_3$ concentration.
NH$_3$ remains relatively constant at high PM and NH$_4$ levels.
Gas-to-particle partitioning can cause opposite vertical profiles of NH$_3$ and $b_{ext}$.
Vertical distribution of NH$_3$ is more homogeneous than that of $b_{ext}$.