Effects of reactive nitrogen gases on the aerosol formation in Beijing from late autumn to early spring

Zhang Wen, Wen Xu, Xingyi Pan, Mengjuan Han, Chen Wang, Katie Benedict, Aohan Tang, Jeffrey Lee Collett Jr and Xuejun Liu

1 Beijing Key Laboratory of Farmland Soil Pollution Prevention and Remediation, College of Resources and Environmental Sciences, China Agricultural University, Beijing 100193, People’s Republic of China
2 National Academy of Agriculture Green Development, China Agricultural University, Beijing 100193, People’s Republic of China
3 Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, United States of America

E-mail: aohantang@cau.edu.cn and liu310@cau.edu.cn

Keywords: NH$_3$, precursors, aerosol formation, gas-particle partitioning, RH, Beijing

Supplementary material for this article is available online

Abstract
To investigate the formation and evolution mechanism of haze pollution in Beijing cold days, we measured reactive nitrogen gases (e.g. NH$_3$ and HNO$_3$), SO$_2$ and major water-soluble inorganic ions of PM$_{2.5}$ simultaneously in a two-year (from November to April) study. We found that NH$_3$ and NO$_3^-$ have the highest concentrations among the gaseous precursors and inorganic components of PM$_{2.5}$, respectively. The total NH$_x$ (gaseous NH$_3$ and particle NH$_4^+$) was mostly in excess the need to neutralize acid compounds. During the whole study period, the aerosol pH with an average value of 4.05. From normal period into haze episodes, the aerosol pH tends to decrease and the concentration of all species (gases and particles) increases. Meanwhile, declined gas fractions exhibited that enhanced partitioning from HNO$_3$, NH$_3$ and SO$_2$ to their corresponding particle phases. Under the heavy haze period, most HNO$_3$ (79%) has entered into NO$_3^-$, about 41% NH$_3$ remaining as free NH$_3$, while only about 51% of SO$_2$ has been oxidized to SO$_4^{2-}$, implying the severe Nr pollution in atmosphere of Beijing in winter. Further analysis shows relative humidity (RH) plays an important driving role on the SNA (sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$) formation and particulate NO$_3^-$ formed at a relatively low RH (20%–60%) and SO$_4^{2-}$ at a high RH (40%–80%). Thus, synchronized abatement of multi-pollutants emissions especially for NH$_3$ emission reduction at a regional scale is necessary for mitigating megacities ambient PM$_{2.5}$ pollution and achieving the UN sustainable development goal through improving N use efficiency in agriculture.

1. Introduction
With the appearance of United Nations Sustainable Development Goal for 2030, food security and breathing clean air are both important issues worldwide, while managing nitrogen (N) in a sustainable way is crucial to realize both targets (Liu et al 2020b). In recent years, high levels of PM$_{2.5}$ have become one of the most serious environmental problems across China and have captured the common attention of the public, governments, and scientists. Studies have shown that secondary inorganic aerosols contribute about 40%–65% of PM$_{2.5}$ mass concentration, that are mainly composed of sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), and ammonium (NH$_4^+$) (briefly, SNA) (Yang et al 2011, Huang et al 2014, Sun et al 2015). In addition to direct emissions, most SNA are derived from oxidation and neutralization of associated gaseous pollutants, including reactive nitrogen gases (NO$_x$, NH$_3$) and SO$_2$ (Baek et al 2004, Behera and Sharma 2010, Luo et al 2014). Part of the SO$_2$ emitted into the atmosphere is oxidized into sulfates and NO$_x$ is transformed into nitric acid (HNO$_3$) (Stockwell and Calvert 1983, Seinfeld and Pandis 2016). Then, NH$_3$ neutralizes acid components (SO$_2$ and HNO$_3$) and reactants dynamically partition into the aerosol phase (Walker et al 2004). Considering PM$_{2.5}$ has broad adverse impacts on air quality, climate forcing and human health (Tegen et al 2000, Wu et al 2005, Gurjar et al 2010, Li et al 2018), a better
understanding of the precursors emission and aerosol formation is critical for effective mitigation of PM$_{2.5}$ pollution.

China’s government has made great efforts on the SO$_2$ and NO$_x$ emissions control since 2005 and resulting in the reduction of 59% and 21% for SO$_2$ and NO$_x$ from 2013 to 2017 (Zheng 2018). Variations in PM$_{2.5}$ concentrations are mainly driven by the emission of their precursors (SO$_2$ and NO$_x$). The decreased in SO$_2^{2−}$ corresponded to the changes in SO$_2$ emissions, whereas the relative increase in NO$_3^{−}$ was not catchable with NO$_x$ emissions reduction (Geng et al 2017, Li et al 2019). During this time period, little attention has been paid to NH$_3$ emission control. It has been reported that atmospheric NH$_3$ experienced an increasing trend or remains stable. Zhang et al (2017) reported total NH$_3$ emissions substantially increased at an annual rate of 1.9%, from 12.1 Tg N yr$^{-1}$ in 2000 to 15.6 Tg N yr$^{-1}$ in 2015 across China. Agricultural activities are the main source of NH$_3$, including livestock manure and synthetic fertilizer application, accounting for 80%–90% to total emissions. (Bouwman et al 1997, Xu et al 2019). Whereas there are also other a variety of significant sources, such as fossil fuel consumption, biomass burning and vehicles emission, etc (Behera et al 2013, Meng et al 2017, Chang et al 2019). As a key alkaline species for neutralizing acid pollutants in the atmosphere, several studies revealed the importance of NH$_3$ to the formation of secondary inorganic and organic aerosols (Babar et al 2017, Meng et al 2018). Taken together, based on the reduction of atmospheric SO$_2$ emissions in recent years in Beijing, knowledge of the contributions in every precursor especially N$_r$ (NH$_3$ and NO$_x$) to PM$_{2.5}$ components can be better identifying the air quality issue of Beijing.

Many haze-related aspects of Beijing have been investigated, including PM$_{2.5}$ chemical composition (Liu et al 2016, Zhang et al 2018), aerosol formation mechanisms (Chen et al 2019, Duan et al 2019), pollutants regional transport (Li et al 2015, Yang et al 2017) and effects of meteorology (Dang and Liao 2019, Zhao et al 2019). Despite a large number of aforementioned studies, the evolutionary mechanisms responsible for the gas–particle partitioning during haze events remain poorly characterized, may be due to there were few simultaneous high time-resolution measurements of major precursors and inorganic compositions in PM$_{2.5}$. For example, Geng et al (2017) reported the changes of SO$_4^{2−}$ and NO$_3^{−}$ concentrations in PM$_{2.5}$ were in line with the increase in NO$_x$ emission and the decrease of SO$_2$ emission while on a national-year scale. Thus, it is worthwhile to study the formation mechanisms for heavy haze via simultaneous measurement of gas precursors and particulate matter, especially in the stage of frequent air pollution.

In this study, 2 year daily sampling of HNO$_3$, SO$_2$, NH$_3$ and PM$_{2.5}$ were conducted at the ground site from November to April in Beijing to fill the gaps in simultaneous measurement. Aerosol acidity and water content were calculated by the thermodynamic equilibrium model (ISORROPIA-II) in order to analyze atmosphere characteristics. Based on the in situ measurements and simulated datasets, we investigated the gas–particle partitioning under different pollution levels and the meteorology effect on SNA formation.

2. Methods

2.1. Field measurement site

A Beijing winter field measurement was conducted from November 2017 to April 2018 (first study period, except 2–27 February) and November 2018 to April 2019 (second study period, except 16 January–23 February) at China Agricultural University (CAU, 40°01′29″ N, 116°17′07″ E), which is located outside the north fifth ring road in Beijing. The CAU is a suburban site with mainly influences from local traffic and resident sources. Daily sampling starts at 8:00 am each day and the sampler is replaced at 8:00 am of the next day.

2.2. Instrumentation and measure methods

In this study, a University Research Glassware (URG) Corporation annular denuder/filter-pack sampler (URG-3000C, URG Corporation, USA) was deployed to capture both gases and aerosol. First, the URG system draws ambient air through a Teflon-coated PM$_{2.5}$ cyclone to remove particles with aerodynamic diameters greater than 2.5 μm. Then, a 10% Na$_2$CO$_3$ solution (water:methanol = 9:1) coated glass denuder captures HNO$_3$ and SO$_2$ and a 10% phosphorous acid (water:methanol = 1:9)-coated denuder captures NH$_3$. Next, a filter pack with a 37 mm diameter nylon filter captures PM$_{2.5}$. Finally, a supplementary phosphoric acid-coated denuder was placed after the filter to lock any volatilized NH$_3$ that from particle captured on the filters. Briefly, the URG system actively collects ambient air under the action of the pump at a nominal flow rate of 10 L min$^{-1}$. Meanwhile, the sample air volume was recorded by a dry gas meter (Evanoski-Cole et al 2017). After finish sampling, denuder and filter samples were extracted with deionized water (18.2 MΩ) and analyzed by ion chromatography (ICS-600, Dionex, USA). Blank samplers, including field blank and laboratory blank, were analyzed simultaneously.

2.3. Data collection

Meteorological data (wind speed, wind direction, temperature, relative humidity (RH)) were collected from the China Meteorological Administration (www.cma.gov.cn/) and weather underground website (www.wunderground.com/). AQI (Air Quality Index) and PM$_{2.5}$ data came from
China National Environmental Monitoring Centre (www.cnemc.cn/).

The aerosol acidity (pH) and aerosol liquid water content (ALWC) were predicted by the ISORROPIA II model. The model in our case was run in the forward mode and could obtain the equilibrium partitioning concentrations based on measurements of total gaseous NH₃ and particulate NH₄⁺ (TNH, NH₃ + pNH₄⁺), total gaseous HNO₃ and particulate NO₃⁻ (THNO, HNO₃ + pNO₃⁻), and particulate SO₄²⁻ (pSO₄²⁻), other water-soluble inorganic components, averaged daily temperature and RH under the Na⁺–K⁺–Ca²⁺–Mg²⁺–NH₄⁺–SO₄²⁻–NO₃⁻–Cl⁻–H₂O aerosol system. Besides, the model was assumed as metastable conditions. Measured and predicted concentrations display a strong correlation (figure S1 (available online at stacks.iop.org/ERL/16/025005/mmedia)) in NH₃ ($R^2 = 0.81$), pNO₃⁻ ($R^2 = 0.88$), pNH₄⁺ ($R^2 = 0.77$), pSO₄²⁻ ($R^2 = 0.86$), except for HNO₃, which has a bias in the simulation may be due to the effects of significant variation in RH and temperature over 24 h period on gas–particle phase partitioning (Guo et al 2017b).

The 24 h backward trajectories were calculated using the Meteoninfo model (www.meteothink.org/). The trajectories terminated at the height of 100 m above the ground. The trajectory calculations were performed at 24 times (00:00, 01:00, 02:00, 03:00, …, 20:00, 21:00, 22:00 and 23:00) per day. Then daily concentrations of THNO, TNH, TSO (SO₂ + pSO₄²⁻) were loaded into model and ordered from high to low, then top 10% air masses were selected for cluster analysis.

2.4. Identification of NH₃-poor and NH₃-rich

Total NH₃ concentrations (gas plus particle phases) and required NH₃ concentrations for overall charge balance were calculated, and excess NH₃ concentrations to distinguished NH₃-rich and NH₃-poor conditions:

$$\text{Total NH}_3 = [\text{NH}_3] + [\text{NH}_4^+] (p)$$

$$\text{Required NH}_3 = \sum C_{\text{cations}} + \text{HNO}_3(g) + \text{HCl}(g) - \sum C_{\text{anions}}$$

$$\text{Excess NH}_3 = \text{total NH}_3 - \text{required NH}_3$$

where, $\sum C_{\text{cations}}$ represent the measured non-volatile cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) needed to be equivalent with all anions ($\sum C_{\text{anions}}$, including SO₄²⁻, NO₃⁻, Cl⁻) and HNO₃, HCl in equivalent concentration of hydrogen ion (e.g. for 1 μmol l⁻¹ Ca²⁺ = 2 μeq l⁻¹ H⁺).

2.5. Characteristics of particles formation

Three gas fractions were used to determine the degree of gaseous precursors converted into SNA and indicate secondary transformation processes (Stratton et al 2019):

$$\text{FHNO}_3 = \frac{[\text{HNO}_3(g)]}{[\text{HNO}_3(g)] + [\text{NO}_3^-(p)]}$$

$$\text{FNH}_3 = \frac{[\text{NH}_3(g)]}{[\text{NH}_3(g)] + [\text{NH}_4^+(p)]}$$

$$\text{FSO}_4 = \frac{[\text{SO}_4(g)]}{[\text{SO}_2(g)] + [\text{SO}_4^2-(p)]}.$$

Similarly, the concentration of all gases and particles are molar concentrations.

2.6. Sensitivity of aerosol pH to SO₄²⁻, THNO, TNH, RH and T

To explore the major influencing factors on aerosol pH, sensitivity tests were performed (Ding et al 2019). In the sensitivity analysis, SO₄²⁻, THNO, TNH, RH and T were selected as the variables since SO₄²⁻, NO₃⁻ and NH₄⁺ are major ions in aerosols. To assess how a variable affects PM₂.₅ pH, these variables are divided into six levels between measured maximum and minimum, respectively, and then input into ISORROPIA II together with the average of the other species (Na⁺, Mg²⁺, K⁺, Ca²⁺, Cl⁻). The magnitude of the relative standard deviation (RSD) of the calculated aerosol pH can reflect the impact of variable sensitivity on aerosol acidity. The higher the RSD is, the greater the impact, and vice versa. The average value and variation range for each variable are listed in table S1. The sensitivity analysis in this work only reflected the characteristics during the observation periods, and further work is needed to determine whether the sensitivity analysis is valid in other environmental conditions.

3. Results and discussion

3.1. Daily variation of gaseous precursors and particles species

Time series for observed gaseous precursors of HNO₃, NH₃, SO₂ and major inorganic aerosol species (pNO₃⁻, pNH₄⁺, pSO₄²⁻) concentrations were observed in Beijing during November 2017 to April 2018 (except February) and November 2018 to April 2019 (except February) (figure 1). Average active nitrogen and sulfur concentrations were over 1.5 folds greater for the entire second study period compared to the first study period except pSO₄²⁻. In general, the average NH₃ concentration was highest (11.7 ± 0.48 μg m⁻³) compared with HNO₃ (6.68 ± 0.29 μg m⁻³) and SO₂ (7.47 ± 0.36 μg m⁻³) and shown monthly temporal variability with higher concentration appeared
in early spring, March and April (figure S1). While
the concentrations of HNO$_3$ and SO$_2$ exhibited an
opposite temporal trend that increased in January
indicated serious acid gas pollution in Beijing winter.
The pNO$_3^-$ concentration in PM$_{2.5}$ remained high
value with an average of 16.3 ± 1.17 µg m$^{-3}$ and
the ratio of SNA was almost greater than 50%,
indicating the need for NO$_x$ reductions. In com-
parison, the pSO$_4^{2-}$ presented a relatively lower
level and averaged 4.39 ± 0.30 µg m$^{-3}$ during
the whole study period. The pNH$_4^+$ concentration
peaked in March, while there was no significant dif-
ference with other months, and averaged 10.7 ± 0.64
µg m$^{-3}$. The six active nitrogen and sulfur species showed
significant correlations (table S2), and higher $R^2$
value between HNO$_3$/NO$_2$ and SO$_2$
($R^2 = 0.76$, 0.52, $p < 0.01$) suggesting that they may
have similar sources or the results of boundary layer
movement. The daily average PM$_{2.5}$ concentrations of
two study periods were 53.5 and 56.0 µg m$^{-3}$, both
exceeded 35 µg m$^{-3}$, the threshold for the Stage I
of Chinese National Ambient Air Quality Standard
(figure S2), meaning there is still room for air quality
improvement. There was good correlation between
PM$_{2.5}$ and pNO$_3^-$, pSO$_4^{2-}$, pNH$_4^+$ ($p < 0.01$),
respectively. The contribution of SNA to PM$_{2.5}$ mass
concentration was averaged around 62%, revealing
important component of PM$_{2.5}$ to be dominated
by SNA.

3.2. Characteristics of Beijing atmosphere
Excess NH$_3$ was calculated to identify NH$_3$-poor and
NH$_3$-rich conditions. The relationship of total NH$_x$
and required NH$_x$ are shown in figure 2(a). Total
NH$_x$ was much more than required NH$_x$, indicat-
ing that Beijing was characterized by sufficiently free
NH$_3$. In summary, the amount of total NH$_x$ was rich
enough to neutralize available acid compounds in gas
and particle phases in Beijing from autumn to spring.
With the gradual decrease in agricultural activities
in Beijing, the agricultural sources of NH$_3$ emis-
sions are gradually decreasing, especially in winter.
In colder days, non-agricultural sources may be the
main source of NH$_3$. In our previous study, signific-
ant high concentrations of NH$_3$ in air as well as NH$_4^+$
in PM$_{2.5}$ at traffic in situ monitoring sites indicate that
vehicular source played a vital role in local emission
(Xu et al 2017). Isotope technique also reveals persist-
ent non-agricultural and periodic agricultural emis-
sions drive atmospheric NH$_3$ concentration in urban
Beijing (Zhang et al 2020). On the other hand, the
large reduction in SO$_2$ and NO$_x$ emissions are limit-
ing particulate matter formation and NH$_3$ is in large
excess (Lachatre et al 2019), especially in North China
Plain (Fu et al 2017, Liu et al 2018). Therefore, as SO$_2$
and NO$_x$ emissions continue to decline in the future,
there is inevitably going to be more NH$_3$ free in the
atmosphere.

Daily aerosol pH and ALWC calculated by ISOR-
ROPIA II and displayed in figure 2(b). The pH value
varies in the range of 0.37–7.95 with an average of 4.05 ± 0.09 for the whole period, indicating a medium acidic condition for fine particles. Higher aerosol pH was caused by higher mass fractions of K⁺, Mg²⁺, Ca²⁺ (figure S3). Overall, aerosol pH during the study periods was comparable to the result (4.2) found by Liu et al (2017a) and that (4.5) found by Guo et al (2017a). The average ALWC was 28.7 ± 4.48 µg m⁻³ and higher ALWC corresponds to higher PM_{2.5} mass concentration (p < 0.01), suggesting an important role in the increase of air pollution. The aerosol hygroscopic growth processes speed up, and the particle surface increases, which enhances the aerosol extinction ability and accelerates the atmospheric chemical reaction rates, favoring the gas to particle heterogeneous reactions (Faust et al 2017). In turn, it was also reported that ALWC exceeded 200 µg m⁻³ in winter in Beijing, with nitrate and sulfate playing dominant roles in determining the abundant ALWC (Wu et al 2018) (figure S4). Generally, pH depends on both the presence of ions and the amount of particle liquid water. There was no correlation between ALWC and pH in this study. This is different from Guo et al (2015): pH pattern was mainly driven by the dilution of aerosol water. Part of (NH₄)₂SO₄ and NH₄NO₃ will hydrolyze under the high ALWC condition and produce more H⁺ so that a positive correlation between ALWC and pH. Noted that extremely high concentrations of NH₃ during our study period and produces more portion of NH₄⁺, which prevent the dissociation of H⁺ and then hence disturbing the particles acidity (Ge et al 2019).

In our work, the effects of SO₄²⁻, THNO, TNH, temperature and RH on aerosol pH were determined through RSD analysis. The most important factor was THNO (91%), followed by TNH (67%), SO₄²⁻ (60%), RH (47%), temperature (20%) (table 1). In general, acid compounds are crucial to the decreased pH. In recent years, NO₃⁻ mass fraction in PM_{2.5} in Beijing has increased significantly and dominates the inorganic ions with the strict control measures for SO₂ emission in recent years (Cheng et al 2019, Li et al 2019), which leads to the maximal changes in aerosol acidity with elevated THNO. There was a relative limit sensitive to pH for TNH. The thermodynamic equilibrium between NH₄⁺ and NH₃ makes aerosol remain acidic (Webber et al 2016), an increase with a factor of 10 in NH₃ concentrations corresponds to a changing pH by 1 unit (Guo et al 2017a), which may explain the reason that pH is still at low level though there are a lot of NH₃ in Beijing atmosphere.

3.3. Formation of SNA under different pollution levels

Figures 3(a) and (f) show the gases and particle concentrations at different levels. The AQI is divided into five levels: AQI < 50 (excellent day), AQI > 50 and ≤100 (acceptable day), AQI > 100 and ≤150 (light pollution day), AQI > 150 and ≤200 (medium pollution day), AQI > 200 (heavy pollution day). ‘Acceptable days’ was the main air quality level during the study period, indicating a requirement for air quality improvement during autumn to spring. Gas and particle concentrations dramatically increased from clean days to polluted periods, except SO₂ under heavy pollution conditions. On average, the sum of SNA contributed to almost 56% of PM_{2.5} during haze episodes (AQI > 100), with NO₃⁻, NH₄⁺ and SO₄²⁻, accounting for 30%, 18%, and 8%, respectively. These contributions suggest that NO₃⁻ plays an important role in the aggravate of pollution level. Meanwhile, the aerosol pH under excellent and good conditions spanned 0–8, while that under polluted conditions was mostly concentrated from 2 to 5. NO₃⁻ and SO₄²⁻ mainly concentrated in the fine mode and

---

**Table 1. Sensitivity of aerosol pH to SO₄²⁻, THNO, TNH, RSD.**

| Impact factor | SO₄²⁻ | THNO | TNH | Temp | RH |
|--------------|-------|------|-----|------|----|
| RSD          | 59.8% | 91.2%| 67.3%| 20.4%| 47.1%|

| a | THNO: gas HNO₃ + particle NO₃⁻. |
| b | TNO: gas NH₃ + particle NH₄⁺. |
| c | RSD: relative standard deviation. |

---

![Figure 2. Relationship between total NH₃ and required NH₃ concentrations (a) and time series of simulated aerosol pH and aerosol liquid water content (ALWC) by ISORROPIA II (b).](image-url)
increased significantly on heavily polluted periods resulted in the growth of acid generation capacity (Pye et al. 2020), which may be the main reason for the decrease in aerosol pH consistent with the worsening of air quality level.

Additionally, the relationship of gas fractions (FHNO$_x$, FNH$_x$, FSO$_x$) together with total concentrations of gas and particle (THNO, TNH, TSO) under different pollution levels were illustrated in figures 3(g) and (i). From clean entered into polluted days, THNO, TNH, TSO increased be accompanied by FHNO$_x$, FNH$_x$, FSO$_x$ decreased. In other words, less gaseous HNO$_3$, NH$_3$, SO$_2$ were related to more portion of NO$_3^-$, NH$_4^+$, SO$_4^{2-}$ in particles with haze aggravated. In the case of heavy pollution, TNH was the highest, up to 4 µmol m$^{-3}$, followed by THNO and TSO. Under heavily polluted conditions, about 41% of NH$_3$ existed in the gas phase. FHNO$_x$ and FSO$_x$ decreased from 0.53 to 0.21, and 0.77 to 0.49, meaning almost HNO$_3$ were converted into particle phase, while on the contrary, the oxidation reaction from SO$_2$ to SO$_4^{2-}$ was not complete. Similarly, FNO$_x$ quantifies the degree of NO$_2$ and is defined as the mole ratio of NO$_2$ to total nitrogen (TNO, NO$_2$ + pNO$_3^-$), was shown in figure S5. The TNO increased and FNO$_x$ decreased with the aggravation of pollution that has a close agreement with the observed correlation between THNO and FHNO$_x$, which means the transformation degree increases. However, the value of FNO$_x$ is higher than that of FSO$_x$, especially when AQI is greater than 100, indicating that the more SO$_2$ oxidation occurred in the case of serious heavy pollution. This is consistent with the finding by Zhang et al. (2018), who also reported the average values of FNO$_x$ and FSO$_x$ were 0.83 and 0.73 in Beijing winter, respectively. The ratio of total cation to anion was 1.2 on average under serious pollution conditions, meanwhile average ratio between

\[ \frac{\text{total cation}}{\text{total anion}} = 1.2 \]

Figure 3. HNO$_3$, NH$_3$, SO$_2$, pNO$_3^-$, pNH$_4^+$, pSO$_4^{2-}$ concentrations (a)–(f) and the relationship of gas fractions (FHNO$_x$, FNH$_x$, FSO$_x$) and total concentrations of gas and particle (THNO, TNH, TNH) (g); FHNO$_x$ and THNO (HNO$_3$ + pNO$_3^-$), (h): FNH$_x$ and TNH (NH$_3$ + pNH$_4^+$), and (i): FSO$_x$ and TSO (SO$_2$ + pSO$_4^{2-}$) under different pollution levels.
Figure 4. 24 h back trajectories of the air masses with the highest 10% of THNO (HNO$_3$ + pNO$_3^-$), TNH (NH$_3$ + pNH$_4^+$), TSO (SO$_2$ + pSO$_4^{2-}$) concentrations for two study periods (a)–(b) and corresponding meteorological conditions (c)–(d): different wind directions, RH and concentrations of gas and particle. 0: north; 45: northeast; 90: east; 135: southeast; 180: south; 225: southwest; 270: west; 315: northwest. Different colored lines in (a) and (b) mean that the air masses are originating from different directions.

NO$_3^-$ + 2SO$_4^{2-}$ and NH$_4^+$ increased to 0.75, indicating that the rapid increase of NO$_3^-$ and SO$_4^{2-}$ neutralized partly NH$_4^+$ and/or other non-volatile cations (figures S6(a) and (b)). During the study period, the concentrations of Cl$^-$ ranged from 0 to 0.1 µmol l$^{-1}$, donating partly neutralizing effect to cations. In addition, organic acid salts may contribute to charge balance which is not measured in this study. In view of a large amount of NO$_x$ in the atmosphere, the neutralization potential of NH$_3$ (text S1) was calculated in figure S6, and it was found that there was still a strong neutralization room for HNO$_3$ even under the serious haze.

3.4. Influence of meteorology

A similar time of two samplings in this study avoided a bias from seasonal differences. The temperature varied slightly between the two study periods ($p > 0.05$), with the first period being −9.71 °C to 21.6 °C which is colder on average than another study period (table S3). Higher temperatures will facilitate the volatility of NH$_3$ ($p < 0.05$) and result in higher NH$_3$ concentrations in early spring than in winter (Burch and Fox 1989), suggests a higher risk of NH$_3$ emissions from volatility-driven sources in warm days. Different from NH$_3$, there were negative correlations between HNO$_3$, SO$_2$ concentrations and temperature during the observation period. Wintertime home heating in Beijing and surrounding provinces (November–March) is fully covered in this study. At present, natural gas/electric heating contributes almost 97% in Beijing and gradually spread in the surrounding provinces, while coal-fired heating still remains dominant in north China (http://tjj.beijing.gov.cn/). Natural gas consumption could account for 23.4% of total NO$_x$ emissions in the heating season in Beijing (Xue et al 2017). At the same time, the lower mixed layer height in winter could lead to pollutant accumulation and adverse to dispersion.

Previous studies have shown a strong correlation between regional transport patterns and local air quality in Beijing, with wind speed and direction playing an important role (Chen et al 2019, Duan et al 2019). However, the concentrations of gas precursors and corresponding PM$_{2.5}$ ion components were higher in the second study period compared to the first one, but the winds in the second period were more frequent and stronger from the north, which was thought to deliver more clean air masses (figures S7 and S8). Figures 4(a) and (b) shows the 24 h back trajectories of the air masses with the highest 10% of THNO (HNO$_3$ + pNO$_3^-$), TNH (NH$_3$ + pNH$_4^+$), TSO (SO$_2$ + pSO$_4^{2-}$) concentrations in Beijing. Back trajectories clearly showed that the highest concentrations associated with transport mainly from the south, and the significant contribution from Hebei.
Province for the second period about 45.8%. Non-centralized coal heating, un-fully controlled sources in heavy industries, intensive agriculture and dominated highway transportation have caused serious pollutant emissions in Hebei province, which in turn has aggravated Beijing air quality through regional transport (Wang et al 2017). Figures 4(c) and (d) present gas and particle concentrations at different RH and wind directions, which coincides with simulation of backward trajectory and further explains the difference between our study and normal cognition. Overall concentrations were closely related to RH. Air masses from the south (Hebei province) during the second period were wetter and may carry more anthropogenic gas and particulate matter, or gas precursors underwent rapid oxidation in the humid atmosphere environment of Beijing, which had led to a higher sensitivity of aerosols regional transport to Beijing even under the relatively lower frequency of prevailing south winds.

As shown in figure S9, higher RH were generally associated with polluted days than clean days, with RH higher than 57% in pollution days that AQI > 100 and averaged 36% during clean days (AQI = <100). There were positive correlations between RH and FHNOx, FNHx, FSOx, indicating the contribution of aqueous-phase processing to the SNA formation. Apart from providing the available heterogeneous reacting medium via enhancing aerosol surface areas and volumes, liquid water also can liquify the aerosol particles, increase the ALWC and uptake due to solubility, and reduce the kinetic limitation of mass transfer for gaseous precursors (Engelhart et al 2011, Xie et al 2017). As clearly shown in figure 5, the more complete conversion of HNO3 to pNO3− at the lower RH, which displays formation of NH4NO3 occur at RH from 20% to 60% under NH3-rich atmosphere in our case, consistent with the previous study (Quan et al 2015). NO3− is formed from NOx through the gas-phase reaction between OH and NO2 during the daytime and the heterogeneous uptake of N2O5 during the nighttime (Baas-andorj et al 2017, Yun et al 2018). The hygroscopic growth of particles facilitated the condensational loss of N2O5 and HNO3 to particles contributing pNO3−. In this study, day and night samples of gas and particulate matter from a pollution event were collected. The ambient RH increased from 53% (daytime) up to 78% (nighttime) during 22 April 2019 and 38% (daytime) up to 73% (nighttime) during 25 April 2019 when pNO3− concentrations increased by about twice (figure S10), suggesting nocturnal pNO3− formation maybe stronger than that of daytime during the haze period. Different from HNO3, rapid formation of SO42− occurs at RH between the range of 40% and 80%, as estimated by about 80% by Kreidenweis and Asaawuku (2014). Generally, SO2 is oxidized to pSO42− via reaction with OH or aqueous reactions driven by O3 and H2O2 or transition metal ions. SO3 oxidation by NO2 has recently been proposed as an important oxidant in urban areas (Cheng et al 2016, Wang et al 2016, Au Yang et al 2018). Neglecting the NO2 oxidation pathway leads to overestimate SO2 oxidation by transition metal ions and OH. In fact, SO2 oxidation rate is very sensitive to both pH and oxidant concentration. According to Guo et al (2017), major SO42− oxidation through a NO3−-mediated pathway is not likely in China where the aerosol is consistently more acidic. Actually, NO2 acted as the initiator of radical formation and the synergy of NO2 and O3 resulted in much fast SO42− formation (Yu et al 2018). The heterogeneous reactions of atmospheric oxidants with liquid core of aerosols can be also influenced by ionic strength, which in turn can impact important atmospheric processes. For example, high solute strength of the aerosol particles significantly enhances the SO42− formation rate for the H2O2 oxidation pathway (Liu et al 2020a, Mekic and Gligorovski 2021). Furthermore, recent studies have shown aqueous-phase SO2
oxidation and $\text{SO}_4^{2-}$ formation by $\text{NO}_2$ and $\text{OH}$ produced from photolysis of $\text{pNNO}_3^-$ with high RH and $\text{NH}_3$ neutralization or under cloud conditions (Wang et al 2016; Gen et al 2019). It is worth noting that the above-mentioned oxidation pathways were under abundant liquid water conditions. Thus, an effective $\text{SO}_2$ oxidation mechanism requires higher RH. Gas fractions decreased with increasing RH likely due to these aqueous reactions. Most importantly, once polluted gases are emitted or transported, combined with moist air masses, the positive feedback ‘RH–ALWC–heterogeneous reactions’ would be triggered: ALWC rises as RH increases, and provides the medium for heterogeneous reactions that will result in the secondary aerosol formation, which in turn will increase ALWC by the contribution of hygroscopic accumulation mode particles (Tan et al 2017, Liu et al 2017b).

4. Conclusions

In this paper, we simultaneously measured daily precursor gases ($\text{HNO}_3$, $\text{NH}_3$, $\text{SO}_2$) and PM$_{2.5}$ during November 2017 to April 2018 and November 2018 to April 2019 (excluding February in both periods) in Beijing to investigate the temporal variation, atmospheric characteristics, gas–particle partitioning and meteorological influencing factors.

These results clearly indicated total $\text{NH}_3$ was mostly in excess of the $\text{SO}_4^{2-}–\text{NO}_3^-–\text{NH}_4^+$–water equilibrium system and it is necessary to identify the complex urban $\text{NH}_3$ sources and joint control with acid pollutants. Surprisingly, aerosols in Beijing (winter) are still medium acidic. Compared with the clean days, the polluted episodes were characterized as having more gas and particles, lower pH value and higher ALWC. Under heavy polluted condition, almost HNO$_3$ were entering into particle phase, while the oxidation reaction of $\text{SO}_2$ was not complete. Further analysis revealed that RH is an important driving factor in haze evolution. Results found that the formation of $\text{NH}_4\text{NO}_3$ occurred under RH $<60\%$, while $\text{SO}_4^{2-}$ increased sharply in the state of RH around 40%–80%. Although our finding has been conducted by analyzing observations in Beijing, it may be also applicable to other mega cities with similar emissions and meteorological conditions. Meanwhile, it is necessary to further explore the differences of gas–particle partitioning in urban and rural areas. During the hazy periods of Beijing in winter, about 40% of $\text{NH}_3$ still remains in atmosphere as the gas. Considering the significant effect of aerosol acidity on secondary aerosol formation and the solution of metals by acid dissociation, as well as gradually mitigated $\text{SO}_2$ pollution, the emissions of Nr need more attention, especially for $\text{NH}_3$ since $\text{NO}_x$ concentrations have recently been decreasing with years (Wen et al 2020). In addition, in view of the role of transportation, regional joint control and prevention are essential. For example, Hebei is a province with intensive agricultural activities close to Beijing that produces large amounts of $\text{NH}_3$ and contributes to the formation of aerosols, but these aerosols and some precursors may be transported to Beijing, causing local haze pollution. Therefore, an important work of the next stage in China is to achieve the UN sustainable development goal through four improved nitrogen management strategies: improved farm management practices with nitrogen use reductions, machine deep placement of fertilizer, enhanced-efficiency fertilizer use, and improved manure management (Guo et al 2020).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Acknowledgments

This work was supported by the State Key Research and Development Programme (2016YFC0207906, 2017YFC0210100, DQGG0208), the National Natural Science Foundation of China (41425007), the GEF/UNEP project towards the International Nitrogen Management System (‘Towards INMS’), the High-level Innovative Talent Project of China Agricultural University and Major projects of Inner Mongolia Natural Science Foundation (2019ZD02).

ORCID iD

Katie Benedict https://orcid.org/0000-0002-0530-8835

References

Au Yang D, Bardoux G, Assayag N, Laskar C, Widory D and Cartigny P 2018 Atmospheric $\text{SO}_2$ oxidation by $\text{NO}_x$ plays no role in the mass independent sulfur isotope fractionation of urban aerosols Atmos. Environ. 193 109–17

Baasandorj M et al 2017 Coupling between chemical and meteorological processes under persistent cold-air pool conditions: evolution of wintertime PM$_{2.5}$ pollution events and $\text{N}_2\text{O}_5$ observations in Utah’s Salt Lake Valley Environ. Sci. Technol. 51 5941–50

Babar Z, Park J H and Lim H J 2017 Influence of $\text{NH}_3$ on secondary organic aerosols from the ozonolysis and photooxidation of $\alpha$–pinene in a flow reactor Atmos. Environ. 164 71–84

Baek B H, Aneja V P and Tong Q 2004 Chemical coupling between ammonia, acid gases, and fine particles Environ. Pollut. 129 89–98

Behera S N and Sharma M 2010 Investigating the potential role of ammonia in ion chemistry of fine particulate matter formation for an urban environment Sci. Total Environ. 408 3569–75

Behera S N, Sharma M, Aneja V P and Balasubramanian R 2013 Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies Environ. Sci. Pollut. Res. 20 8092–131

Bouwman A, Lee D, Asman W, Dentener F, van der Hoek K and Olivier J 1997 A global high-resolution emission inventory for ammonia Glob. Biogeochem. Cycles 11 561–87
Guo Y X and Fox R H 1989 The effect of temperature and initial soil moisture content on the volatilization of ammonia from surface-applied urea Soil Sci. 147 311–8

Chang Y, Zou Z, Zhang Y, Deng C, Hu J, Shi Z, Dore A J and Collett J I Jr 2019 Assessing contributions of agricultural and nonagricultural emissions to atmospheric ammonia in a Chinese megacity Environ. Sci. Technol. 53 1823–33

Chen L, Zhu J, Liao H, Gao Y, Qiu Y, Zhang M, Liu Z, Li N and Wang Y 2019 Assessing the formation and evolution mechanisms of severe haze pollution in the Beijing–Tianjin–Hebei region using process analysis Atmos. Chem. Phys. 19 10845–64

Cheng J et al 2019 Dominant role of emission reduction in PM_{2.5} air quality improvement in Beijing during 2013–2017: a model-based decomposition analysis Atmos. Chem. Phys. 19 6123–46

Cheng Y et al 2016 Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China Sci. Adv. 2 e1601530

Dang R and Liao H 2019 Severe winter haze days in the Beijing–Tianjin–Hebei region from 1985 to 2017 and the roles of anthropogenic emissions and meteorology Atmos. Chem. Phys. 19 10801–16

Ding J, Zhao P S, Su J, Dong Q, Du X and Zhang Y F 2019 Aerosol pH and its driving factors in Beijing Atmos. Chem. Phys. 19 7939–54

Duan J et al 2019 Distinctions in source regions and formation mechanisms of secondary aerosol in Beijing from summer to winter Atmos. Chem. Phys. 19 10319–34

Engelhart G, Hildebrandt L, Kostenuik E, Mihalopoulos N, Donahue N and Pandis S N 2011 Water content of aged aerosol Atmos. Chem. Phys. 11 911–20

Evansoki-Cole A et al 2017 Composition and sources of winter haze in the Balken oil and gas extraction region Atmos. Environ. 156 77–87

Faust A J, Wang J P S, Lee A K Y and Abbatt J P D 2017 Role of aerosol liquid water in secondary organic aerosol formation from volatile organic compounds Environ. Sci. Technol. 51 1405–13

Fu X, Wang S, Xing J, Zhang X, Wang T and Hao J 2017 Increasing ammonia concentrations reduce the effectiveness of particle pollution control achieved via SO_2 and NO_x emissions reduction in East China Environ. Sci. Technol. Lett. 4 221–7

Ge B et al 2019 Role of ammonia on the feedback between AWC and inorganic aerosol formation during heavy pollution in the North China Plain Earth Sci. 6 1675–93

Gen M, Zhang K, Huang D D, Li Y and Chan C K 2019 Heterogeneous SO_2 oxidation in sulfate formation by photolysis of particulate nitrate Environ. Sci. Technol. Lett. 6 86–91

Geng G, Zhang Q, Tong D, Li M, Zheng Y, Wang S and He K 2017 Chemical composition of ambient PM_{2.5} over China and relationship to precursor emissions during 2005–2012 Atmos. Chem. Phys. 17 9187–203

Guo H Y, Liu J M, Froyd K D, Roberts J M, Veres P R, Hayes P L, Jimenez J L, Nenes A and Weber J R 2017b Fine particle pH and gas–particle phase partitioning of inorganic species in Pasadena, California, during the 2010 CalNex campaign Atmos. Chem. Phys. 17 5703–19

Guo H Y, Weber R J and Nenes A 2017 High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production Sci. Rep. 7 12109

Guo H et al 2015 Fine-particle water and pH in the southeastern United States Atmos. Chem. Phys. 15 5211–28

Guo H, Weber R J and Nenes A 2017a High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production Sci. Rep. 7 1–7

Guo Y X et al 2020 Air quality, nitrogen use efficiency and food security in China are improved by cost-effective agricultural nitrogen management Nat. Food 1 648–58

Gurjar B, Jain A, Sharma A, Agarwal A, Gupta P and Nagpure A S and Lelieveld J 2010 Human health risks in megacities due to air pollution Atmos. Environ. 44 4606–13

Huang R J et al 2014 High secondary aerosol contribution to particulate pollution during haze events in China Nature 514 218–22

Kreidenweis S M and Asaasuwuki A 2014 Aerosol hygroscopicity: particle water content and its role in atmospheric processes Treatise on Geochemistry vol 5 2nd edn pp 331–61

Lachat M, Fortems-Chiney A, Foret G, Siotur G, Dufour G, Clarisse I, Clerbaux C, Coheur P-F, van Damme M and Beekmann M 2019 The unintended consequence of SO_2 and NO_x regulations over China: increase of ammonia levels and impact on PM_{2.5} concentrations Atmos. Chem. Phys. 19 6701–16

Li H, Cheng J, Zhang Q, Zheng B, Zhang Y, Zheng G and He K 2019 Rapid transition in winter aerosol composition in Beijing from 2014 to 2017: response to clean air actions Atmos. Chem. Phys. 19 11485–99

Li P, Yan R, Yu S, Wang S, Liu W and Bao H 2015 Reinvest regional transport of PM_{2.5} as a major cause of severe haze in Beijing Proc. Natl Acad. Sci. USA 112 E2739–40

Li T et al 2018 All-cause mortality risk associated with long-term exposure to ambient PM_{2.5} in China: a cohort study Lancet 3 470–71

Liu M et al 2018 Rapid SO_2 emission reductions significantly increase tropospheric ammonia concentrations over the North China Plain Atmos. Chem. Phys. 18 17933–43

Liu M, Song Y, Zhou T, Xu Z, Yan C, Zheng M, Wu Z, Hu M, Wu Y and Zhu T 2017a Fine particle pH during severe haze episodes in northern China Geophys. Res. Lett. 44 5213–21

Liu T Y, Clegg S L and Abbatt J P D 2020a Fast oxidation of sulfur dioxide by hydrogen peroxide in deliquesced aerosol particles Proc. Natl Acad. Sci. USA 117 1354–9

Liu X et al 2020b Environmental impacts of nitrogen emissions in China and the roles in policies in emission reduction Phil. Trans. R. Soc. A 378 20190324

Liu Y et al 2017b Submicrometer particles are in the liquid state during heavy haze episodes in the urban atmosphere of Beijing, China Environ. Sci. Technol. Lett. 4 427–22

Liu Z, Hu B, Zhang J, Yu Y and Wang Y 2016 Characteristics of aerosol size distributions and chemical compositions during wintrytime pollution episodes in Beijing Atmos. Res. 168 1–12

Luo X, Tang A H, Shi K, Wu L H, Li W Q, Shi W Q, Shi X K, Erisman J W, Zhang F S and Liu X J 2014 Chinese coastal wintertime pollution episodes in Beijing, China Atmos. Chem. Phys. 14 32145–57

Meng Z et al 2018 All-cause mortality risk associated with long-term exposure to ambient PM_{2.5} in China: a cohort study Lancet 3 470–71

Mekic M and Gligorovski S 2021 Ionic strength effects on heterogeneous and multiphase chemistry: clouds versus aerosol particles Atmos. Environ. 244 117911

Meng W et al 2017 Improvement of a global high-resolution ammonia emission inventory for combustion and industrial sources with new data from the residential and transportation sectors Environ. Sci. Technol. 51 2821–9

Meng Z et al 2018 Role of ambient ammonia in particulate ammonium formation at a rural site in the North China Plain Atmos. Chem. Phys. 18 167–84

Pye H O T et al 2020 The acidity of atmospheric particles and clouds Atmos. Chem. Phys. 20 4809–88

Quan J, Liu Q, Li X, Gao Y, Jia X, Sheng J and Liu Y 2015 Effect of heterogeneous aqueous reactions on the secondary formation of inorganic aerosols during haze events Atmos. Environ. 122 306–13

Seinfeld J H and Pandis S N 2016 Atmospheric Chemistry and Physics: From Air Pollution to Climate Change (New York: Wiley)

Stockwell W R and Calvert J G 1983 The mechanism of the HO–SO_2 reaction Atmos. Environ. 17 2231–5

Stratton J, Ham J, Collett J L Jr, Benedict K and Borch T 2019 Assessing the efficacy of nitrogen isotopes to distinguish
Colorado Front Range ammonia sources affecting Rocky Mountain National Park Atmos. Environ. 215 116881
Sun Y, Wang Z F, Du W, Zhang Q, Wang G Q, Fu P Q, Pan X L, Li J, Jayne J and Worsnop D R 2015 Long-term real-time measurements of aerosol particle composition in Beijing, China: seasonal variations, meteorological effects, and source analysis Atmos. Chem. Phys. 15 10149–65
Tan H, Cai M, Fan Q, Liu L, Li F, Chan P W, Deng X and Wu D 2017 An analysis of aerosol liquid water content and related impact factors in Pearl River Delta Sci. Total Environ. 579 1822–30
Tegen I, Koch D, Lacis A A and Sato M 2000 Trends in tropospheric aerosol loads and corresponding impact on direct radiative forcing between 1950 and 1990: a model study J. Geophys. Res. Atmos. 105 26971–89
Walker J, Whitall D R, Robarge W and Paerl H W 2004 Ambient ammonia and ammonium aerosol across a region of variable ammonia emission density Atmos. Environ. 38 1233–46
Wang G et al 2016 Persistent sulfate formation from London Fog to Chinese haze Proc. Natl Acad. Sci. USA 113 13630–5
Wang Y, Liu H, Mao G, Zuo J and Ma J 2017 Inter-regional and sectoral linkage analysis of air pollution in Beijing–Tianjin–Hebei (Jing–Jin–Ji) urban agglomeration of China J. Clean. Prod. 155 1436–44
Weber R J, Guo H, Russell A G and Nenes A 2004 Ambient acidity despite declining atmospheric sulfate concentrations over the past 15 years Nat. Geosci. 9 282
Wen Z et al 2020 Changes of nitrogen deposition in China from 1980 to 2018 Environ. Int. 144 106022
Wu D, Tie X, Li C, Ying Z, Lai A K H, Huang J, Deng X and Bi X 2005 An extremely low visibility event over the Guangzhou region: a case study Atmos. Environ. 39 6566–77
Wu Z J et al 2018 Aerosol liquid water driven by anthropogenic inorganic salts: implying its key role in the haze formation over North China Plain Environ. Sci. Technol. Lett. 5 160–6
Xie Y, Ye X, Ma Z, Tao Y, Wang R, Zhang C, Yang X, Chen J and Chen H 2017 Insight into winter haze formation mechanisms based on aerosol hygroscopicity and effective density measurements Atmos. Chem. Phys. 17 7277
Xu R, Tian H, Pan S, Prior S A, Feng Y, Batchelor W D, Chen J and Yang J 2019 Global ammonia emissions from synthetic nitrogen fertilizer applications in agricultural systems: empirical and process-based estimates and uncertainty Glob. Change Biol. 25 314–26
Xu W et al 2017 Air quality improvement in a megacity: implications from 2015 Beijing Parade Blue pollution control actions Atmos. Chem. Phys. 17 31–46
Xue Y, Nie L, Zhou Z, Tian H, Yan J, Wu X and Cheng L 2017 Historical and future emission of hazardous air pollutants (HAPs) from gas-fired combustion in Beijing, China Environ. Sci. Pollut. Res. 24 16946–57
Yang F, Tan J, Zhao Q, Du Z, He K, Ma Y, Duan F and Chen G 2011 Characteristics of PM2.5 speciation in representative megacities and across China Atmos. Chem. Phys. 11 5207–19
Yang W, Wang G and Bi C 2017 Analysis of longrange transport effects on PM2.5 during a short severe haze in Beijing, China Aerosol Air Qual. Res. 17 1610–22
Yu T, Zhao D F, Song X J and Zhu T 2018 NO2-initiated multiphase oxidation of SO2 by O3 on CaCO3 particles Atmos. Chem. Phys. 18 6679–89
Yun H, Wang W, Wang T, Xia M, Yu C, Wang Z, Poon S C, Yue D and Zhou Y 2018 Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China Atmos. Chem. Phys. 18 17515–27
Zhang R, Sun X, Shi A, Huang Y, Yan J, Nie T, Yan X and Li X 2018 Secondary inorganic aerosols formation during haze episodes at an urban site in Beijing, China Atmos. Environ. 177 275–82
Zhang X M et al 2017 Ammonia emissions may be substantially underestimated in China Environ. Sci. Technol. 51 12089–96
Zhang Y, Benedict K B, Tang A, Sun Y, Fang Y and Liu X 2020 Persistent nonagricultural and periodic agricultural emissions dominate sources of ammonia in urban Beijing: evidence from 15N stable isotope in vertical profiles Environ. Sci. Technol. 54 102–9
Zhao D, Xin J, Gong C, Quan J, Liu G, Zhao W, Wang Y, Liu Z and Song T 2019 The formation mechanism of air pollution episodes in Beijing city: insights into the measured feedback between aerosol radiative forcing and the atmospheric boundary layer stability Sci. Total Environ. 692 371–81
Zheng B 2018 Trends in China’s anthropogenic emissions since 2010 as the consequence of clean air actions Atmos. Chem. Phys. 18 4095–111