Rapid SO₂ emission reductions significantly increase tropospheric ammonia concentrations over the North China Plain

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Abstract. The North China Plain has been identified as a significant hotspot of ammonia (NH₃) due to extensive agricultural activities. Satellite observations suggest a significant increase of about 30% in tropospheric gas-phase NH₃ concentrations in this area during 2008–2016. However, the estimated NH₃ emissions decreased slightly by 7% because of changes in Chinese agricultural practices, i.e., the transition in fertilizer types from ammonium carbonate fertilizer to urea, and in the livestock rearing system from free-range to intensive farming. We note that the emissions of sulfur dioxide (SO₂) have rapidly declined by about 60% over the recent few years. By integrating measurements from ground and satellite, a long-term anthropogenic NH₃ emission inventory, and chemical transport model simulations, we find that this large SO₂ emission reduction is responsible for the NH₃ increase over the North China Plain. The simulations for the period 2008–2016 demonstrate that the annual average sulfate concentrations decreased by about 50%, which significantly weakens the formation of ammonium sulfate and increases the average proportions of gas-phase NH₃ within the total NH₃ column concentrations from 26% (2008) to 37% (2016). By fixing SO₂ emissions of 2008 in those multi-year simulations, the increasing trend of the tropospheric NH₃ concentrations is not observed. Both the decreases in sulfate and increases in NH₃ concentrations show highest values in summer, possibly because the formation of sulfate aerosols is more sensitive to SO₂ emission reductions in summer than in other seasons. Besides, the changes in NOₓ emissions and meteorological conditions both decreased the NH₃ column concentrations by about 3% in the study period. Our simulations suggest that the moderate reduction in NOₓ emissions (16%) favors the formation of particulate nitrate by elevating ozone concentrations in the lower troposphere.


1 Introduction

Ammonia (NH$_3$) is considered the most important alkaline gas in the atmosphere. On both a global and regional scale, NH$_3$ is mostly emitted from agricultural activities, mainly including the fertilization and livestock industry (Bouwman et al., 1997). Gas-phase NH$_3$ can react with ambient sulfuric and nitric acids to form ammonium sulfate/bisulfate and ammonium nitrate aerosols (SNAs), which constitute a significant fraction of atmospheric fine particles (PM$_{2.5}$) associated with potential human health impacts (Pope et al., 2009; Seinfeld and Pandis, 2006). Ammonia and ammonium (NH$_4^+$) is ultimately deposited back to the earth surface, contributing to acid deposition and eutrophication (Asman, 1998; Behera et al., 2013; Pozzer et al., 2017).

As a major agricultural country, China is one of the world’s largest emitters of NH$_3$, the amount of which (~10 Tg yr$^{-1}$) exceeds the sum of those in Europe (~4.0 Tg yr$^{-1}$) and North America (~4.0 Tg yr$^{-1}$) (Huang et al., 2012; Bouwman et al., 1997; Paulot et al., 2014). Fertilizer application and livestock manure management contribute to nearly 90% of China’s NH$_3$ emissions (Huang et al., 2012; Zhang et al., 2018). Until now, NH$_3$ emissions have not been regulated by the Chinese government, although they serve as an important contributor to haze pollution in China.

The North China Plain (the spatial definition of this area is illustrated in Fig. S1 in the Supplement) is a hotspot of NH$_3$ loadings, as revealed by satellite detection and ground measurements (Clarisse et al., 2009; Pan et al., 2018). Interestingly, satellite observations over the past decade have shown an increase in tropospheric columns of gaseous NH$_3$ in this area (Warner et al., 2017). But no sensitivity studies have been performed to explain it, especially from a modeling perspective. A long-term bottom-up inventory indicates that NH$_3$ emissions in China have displayed a slightly decreasing tendency (Kang et al., 2016). During 2006–2016, ammonium bicarbonate for crop fertilization was replaced by urea fertilizer (its fraction of application increasing from 60% to 90% of all mineral nitrogen fertilizers). In the meantime, the traditional free-range livestock system was gradually replaced by the intensive animal rearing system (i.e., raising livestock in confinement at a high stocking density) in the livestock industry (increasing from 21% in 2006 to 48% in 2016; shown in Table S1 in the Supplement). These changes in agricultural practices have lowered the volatilization rates of NH$_3$ (Kang et al., 2016).

Several studies have proposed that reduction in SO$_2$ emissions or NO$_x$ emissions is an important factor in determining the increase in atmospheric NH$_3$ concentrations on the global and regional scales (Warner et al., 2017; Yu et al., 2018; Saylor et al., 2015). Through the widespread use of the flue gas desulfurization in power plants since 2006 in China, SO$_2$ emissions have gradually decreased (Lu et al., 2011; Li et al., 2010). Li et al. (2017) found it was reduced by 70% from the peak year (around 2006) to 2016 based on satellite observations and bottom-up methods. Specifically, the initiation of the Action Plan for Air Pollution Prevention and Control (referred to as the national Ten Measures for Air) since 2013 resulted in a rapid reduction of about 50% over recent few years, from ~30 Tg in 2012 to ~14 Tg in 2016 according to the Multi-resolution Emission Inventory for China (MEIC) (Zheng et al., 2018). To our knowledge, such a strong decrease in SO$_2$ emissions is only found in China. In contrast, emissions of nitrogen oxides (NO$_x$) in MEIC peaked around 2012 with only a moderate decrease of ~20% from 2012 to 2016 (Liu et al., 2016).

Here, we hypothesize that the rapid SO$_2$ emission reduction is the main cause of the increase in tropospheric NH$_3$ concentrations over the North China Plain. To verify this, we first used observation datasets from the ground and space to infer the relationship between the trends in NH$_3$ and SO$_2$ concentrations. A comprehensive long-term NH$_3$ emission inventory, developed by our recent studies based on bottom-up methods, was also used to demonstrate the inter-annual variations of NH$_3$ emissions in this region. Then, we performed multi-year simulations with a chemical transport model to examine the impact of changes in SO$_2$ emissions on tropospheric NH$_3$ concentrations in terms of the magnitude and seasonal variation. Besides, other potential mechanisms (NO$_x$ emission and meteorology) were discussed.

2 Methods

2.1 Observation datasets

Observations from space and ground stations were used in this study. Tropospheric vertical column densities (VCDs) of NH$_3$ were derived from the measurements of Infrared Atmospheric Sounding Interferometer (IASI) on board MetOp-A (Van Damme et al., 2015, 2017; Clarisse et al., 2009). We determined the annual averages of NH$_3$ column concentrations over the North China Plain on a 0.25° × 0.25° grid during 2008–2016, based on the relative error weighting mean method (Van Damme et al., 2014). The monthly NH$_3$ concentrations were measured using passive NH$_3$ diffusive samplers (Analyst, CNR Institute of Atmospheric Pollution, Rome, Italy), from September 2015 to August 2016 at 11 sites over northern China (Pan et al., 2018). The SO$_2$ VCDs were provided by the Ozone Monitoring Instrument (OMI) measurements to test the trend of SO$_2$ concentrations. They were derived from the Level-3 Aura/OMI Global SO$_2$ Data Products (OMSO2e), released by the NASA Goddard Earth Sciences Data and Information Services Center (Krotkov et al., 2015). Besides, daily PM$_{2.5}$ was sampled by quartz-fiber filters at an urban atmosphere environment monitoring station in Peking University (39.99°N, 116.3°E) of Beijing, China, since 2013. The major watersoluble inorganic compounds (e.g., NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$) were analyzed by ion chromatography.
2.2 WRF-Chem simulations

In this study, the simulations with the Weather Research and Forecasting Model coupled with Chemistry (Grell et al., 2005) version 3.6.1 (WRF-Chem) were conducted for the domain of the North China Plain for the years 2008, 2010, 2012, 2014, 2015, and 2016 (referred to as Run_08–16). We ran the model with a horizontal resolution of $30 \times 30$ km and 24 vertical layers, extending from the surface to 50 hPa. The initial and boundary meteorological condition was derived from 6 h National Centers for Environmental Prediction reanalysis data. The detailed model configurations were described in our previous study (Huang et al., 2014). The anthropogenic emissions from power plant, industrial, residential, and vehicle sectors were taken from the MEIC database. The MEIC data show that the annual SO$_2$ emissions in the North China Plain were reduced by about 60%, from 9.9 Tg in 2008 to 4.2 Tg in 2016, while NO$_x$ emissions first increased from 8.0 to 8.8 Tg during 2008–2012, and then decreased to 6.7 Tg in 2016.

2.3 NH$_3$ emission inventory

A high-resolution NH$_3$ emission inventory ($1 \text{ km} \times 1 \text{ km}$, month) was developed based on the bottom-up method. The emission factors were parameterized with regional farming practices, ambient temperature, soil pH, and wind speeds. The full details can be found in studies by Kang et al. (2016), Huang et al. (2012), and Huo et al. (2015). The inventory has similar spatial features with recent satellite observations (Van Damme et al., 2014), and its amount is close to the emission estimated by the inversion model using ammonium wet deposition data (Paulot et al., 2014). Recent modeling results also showed its good performance by comparing with ammonium observations in China (Huang et al., 2015). The inventory has covered the period from 1980 to 2016 and considered its good performance by comparing with ammonium wet deposition data (Paulot et al., 2014). Recent modeling results also showed its good performance by comparing with ammonium observations in China (Huang et al., 2015). The inventory has covered the period from 1980 to 2016 and considered the inter-annual variability in activity levels and agricultural practices. It shows a distinct seasonal feature in NH$_3$ emissions over the North China Plain. A total of 75% of annual NH$_3$ emissions are released in the spring and summer months (March–September), during which intensive agricultural fertilization and elevated ambient temperature facilitate the volatilization rates of NH$_3$. Moreover, to integrate this inventory into WRF-Chem simulations, we adopted a diurnal profile with 80% of NH$_3$ emissions in the daytime, following previous studies (Zhu et al., 2015; Asman, 2001; Paulot et al., 2016).

3 Results and discussions

3.1 Trends in emissions and concentrations of NH$_3$ vs. SO$_2$

According to the measurements by IASI, the North China Plain showed the highest VCDs of NH$_3$ in China, which mostly ranged from 15 to $30 \times 10^{15}$ molecules cm$^{-2}$ during 2008–2014 and increased to above $30 \times 10^{15}$ molecules cm$^{-2}$ in 2015 and 2016 (Fig. 1a). The average tropospheric NH$_3$ columns first fluctuated between 2008 and 2013, and then rapidly increased from $21 \times 10^{15}$ molecules cm$^{-2}$ in 2013 to $27 \times 10^{15}$ molecules cm$^{-2}$ in 2016. It showed an overall increase of 30%, or an average annual increase of $0.9 \times 10^{15}$ molecules cm$^{-2}$ yr$^{-1}$. Seasonally, the increase in NH$_3$ columns was more pronounced in summertime (June–August, JJA), with an annual increase rate of $1.8 \times 10^{15}$ molecules cm$^{-2}$ yr$^{-1}$ between 2008 and 2016, which was much higher than in other seasons ($< 1 \times 10^{15}$ molecules cm$^{-2}$ yr$^{-1}$).

In contrast to the trends in tropospheric NH$_3$ concentrations, the annual NH$_3$ emissions first experienced a decreasing tendency from 2008 to 2011 (3.0 Tg in 2009 to 2.8 Tg in 2011) and then remained constant at around 2.8 Tg yr$^{-1}$ during 2011–2016 over the North China Plain (Fig. 1b). The overall trend of NH$_3$ emissions demonstrated a decrease of about 7%. It is because the changes in mineral fertilizer use and livestock rearing practices have lowered NH$_3$ emission rates. The increasing use of urea fertilizer (from 4.7 to 5.2 Tg yr$^{-1}$) and compound fertilizers (from 1.2 to 1.7 Tg yr$^{-1}$) but decreased ammonium bicarbonate (from 1.5 to 0.4 Tg yr$^{-1}$) led to a 20% reduction in NH$_3$ emissions from fertilizer application during 2008–2016 (Table S1 in the
Supplement). On the other hand, the number of some major livestock increased (beef −20 %, dairy +39 %, goat −23 %, sheep +55 %, pig +18 %, and poultry +19 %; see Table S1 in the Supplement for details), while the proportion of intensive animal rearing systems rises to nearly half of the livestock industry in 2016, compared to only 28 % in 2008 (Table S1 in the Supplement). The intensive systems are characterized with more effective livestock manure management in favor of lower volatilization rates of NH$_3$ (Kang et al., 2016). The transition from the free-range to the intensive system in livestock animal rearing offsets the effect of increased animals on the NH$_3$ emissions, thereby resulting in the annual livestock emissions in the North China Plain being almost constant (around 1.2 Tg yr$^{-1}$). Overall, the decreasing NH$_3$ emissions cannot track the upward trend of tropospheric NH$_3$ concentrations.

During 2008–2016, SO$_2$ column concentrations were subject to a dramatic decline ($p<0.01$) due to a 60 % decrease in SO$_2$ emissions. The annual mean SO$_2$ VCDs were reduced from 14 × 10$^{15}$ molecules cm$^{-2}$ (2008) to 4 × 10$^{15}$ molecules cm$^{-2}$ (2016), showing a percent reduction of nearly 70 %. Especially during 2012–2016, the decreases in SO$_2$ emissions and VCDs accelerated owing to the implementation of the Action Plan for Air Pollution Prevention and Control by the Chinese government (Zheng et al., 2018). The ground measurements in a typical urban station in the North China Plain indicated that the annual average SO$_2^-$ concentration in PM$_{2.5}$ decreased by 35 % (2013–2016) along with rapid SO$_2$ reductions, which was accompanied by a 33 % decrease in particulate NH$_3^-$ (Fig. 1b). Seasonally, the decrease in ground-level SO$_2^-$ reached 60 % during summertime (JJA), which was much higher than in other seasons.

### 3.2 Simulations of increasing trend in NH$_3$ columns

We performed numerical simulations with WRF-Chem to interpret the cause of the NH$_3$ increase. We first evaluated model results against measurements of surface NH$_3$ concentrations available in the North China Plain as well as the satellite-retrieved NH$_3$ columns. The simulated monthly averaged surface NH$_3$ concentrations at 11 stations (mean ± standard deviation: 13.5 ± 6.8 µg m$^{-3}$) generally agreed with corresponding observations (13.4 ± 9.7 µg m$^{-3}$) with a correlation coefficient of 0.57. More than 70 % of the comparisons differed within a factor of 2 (Fig. 2). Both simulations and observations show high NH$_3$ concentrations of about 30 µg m$^{-3}$ in warm seasons (March–October) due to enhanced NH$_3$ volatilization and frequent fertilization activities, as well as lower values (mostly < 15 µg m$^{-3}$) in other months (Fig. 3). Spatially, the hotspot of NH$_3$ was mainly concentrated in Hebei, Shandong, and Henan provinces, which have the most intensive agricultural production in China and thus emit considerable gas-phase NH$_3$ into the atmosphere. We note that the simulated monthly NH$_3$ concentrations were underestimated by 25 %–70 % in several stations in wintertime (January, February, and December). Recently, NH$_3$ emissions from the residential coal and biomass combustion for heating are considered to be a potentially important source of NH$_3$ in suburban and rural areas during wintertime (Li et al., 2016), but it has not been fully included in our bottom-up inventory, which was partially responsible for such deviation between the model and observations.

The model generally reproduced the observed SNA concentrations using the filter-based PM$_{2.5}$ samples at an urban atmospheric monitoring station in the North China Plain during 2014–2016 (Fig. S3 in the Supplement). Both IASI measurements and the WRF-Chem simulation showed high annual mean NH$_3$ column concentrations in Hebei, Shandong, and Henan provinces, reaching above 30 × 10$^{15}$ molecules cm$^{-2}$. Moreover, we evaluated the modeled SNA concentrations using the filter-based PM$_{2.5}$ samples in the urban atmospheric monitoring station in the North China Plain during 2014–2016 (Fig. S3 in the Supplement). The model generally reproduced the observed SNA concentrations, with a small annual mean bias for sulfate (−2 %) and ammonium (−13 %) and a relatively large bias for nitrate (−24 %). Overall, the model performed well in modeling the concentrations in tropospheric NH$_3$ as well as secondary inorganic aerosols, which provides high confidence for the following interpretation of the NH$_3$ increases.

The model successfully reproduced the observed increasing trend in NH$_3$ columns over the North China Plain dur-
Figure 3. Spatial distribution of modeled ground NH$_3$ concentrations (µg m$^{-3}$) and monthly measurements over the North China Plain from September 2015 (201509) to August 2016 (201608).

The modeled NH$_3$ columns were systematically lower than the measurements because the relative error weighting mean method always biased a high result due to the smaller relative error in a larger column (Van Damme et al., 2014; Whitburn et al., 2016). An overall increase of 39% in NH$_3$ columns with an average annual in-
crease of $0.8 \times 10^{15}$ molecules cm$^{-2}$ yr$^{-1}$ was found in the simulations between 2008 and 2016, and meanwhile the SO$_2$ columns averaged over the North China Plain decreased by approximately 50% in this period. These results were close to the measurements.

To verify our hypothesis, we replaced SO$_2$ emissions during 2010–2016 by those in 2008 and repeated the simulations (referred to as Run_10_S08 to Run_16_S08). It was noticeable that, under these conditions, the increasing trend of NH$_3$ column concentrations was not observed, and even a decrease of 13% took place (Fig. 4). The largest differences were found in 2015 and 2016, when the annual NH$_3$ columns in these sensitivity simulations were about 40% ($8–10 \times 10^{15}$ molecules cm$^{-2}$) lower than those in the baseline cases, corresponding to the 60% reduction in SO$_2$ emissions between 2008 and 2016. By comparing the results among Run_08, Run_16, and Run_16_S08, we found that the reduction in SO$_2$ emissions increased the NH$_3$ column concentrations by 52% during 2008–2016, which was even higher than the overall increase (39%) in the baseline cases. Therefore, we deduce that the rapid SO$_2$ emission reductions are responsible for the increased NH$_3$ levels during 2008–2016, while other mechanisms may be negative contributors. More details on these effects are shown in the following.

3.3 Influence of SO$_2$ emission reductions on tropospheric NH$_3$ concentrations

As we indicated above, SO$_2^{2−}$ was observed to be decreasing over recent years in response to the reductions of SO$_2$ emissions. This was also reproduced by our simulations, which showed that the annual average sulfate concentrations decreased by almost 50% in the lower troposphere. This decreasing trend was especially pronounced after 2013 owing to the very effective SO$_2$ emission reductions. Given that the vapor pressure of H$_2$SO$_4$(g) is practically zero over atmospheric particles, atmospheric SO$_2^{2−}$ is predominately in the particle phase and can combine with NH$_3$ available in air, forming sulfate salts (mostly ammonium sulfate/bisulfate) (Seinfeld and Pandis, 2006). Since the North China Plain is typically under rich NH$_3$ regimes, SO$_2^{2−}$ is mainly in the form of ammonium sulfate (Meng et al., 2011; Huang et al., 2017); and the aforementioned SO$_2^{2−}$ reductions would therefore increase atmospheric NH$_3$ concentrations by driving the phase state of NH$_3$ from particulate to gaseous.

By assuming that a 1 mol decrease in simulated SO$_2^{2−}$ would lead to a 2 mol increase in ambient gaseous NH$_3$ in this region, the average annual increase in the tropospheric NH$_3$ columns due to the reductions of SO$_2^{2−}$ was estimated to be approximately $1.5 \times 10^{15}$ molecules cm$^{-2}$ yr$^{-1}$ over the North China Plain during 2008–2016. This is comparable with or higher than the simulated results from Run_08 to Run_16, as well as the IASI observations ($0.9 \times 10^{15}$ molecules cm$^{-2}$ yr$^{-1}$). By neglecting the deposition processes, we found that the rapid SO$_2$ emission reduction of 50% from 2012 to 2016 resulted in a 55% increase in the NH$_3$ columns, compared to that of 30% recorded by IASI observations. Overall, the estimation results confirmed that the increasing trend of NH$_3$ was mainly determined by the SO$_2$ emission reductions.

We compared the spatial patterns of decreased SO$_2^{2−}$ and increased NH$_3$ between 2008 and 2016 (Run_08 vs. Run_16). Large reductions of $6–10 \times 10^{15}$ molecules cm$^{-2}$ in annual averages of sulfate columns were concentrated in Hebei, Shandong, and Henan provinces, the area subject to high SO$_2$ loadings and stringent emission controls (Fig. 5a). Meanwhile, the simulated increases in NH$_3$ columns reached more than $8 \times 10^{15}$ molecules cm$^{-2}$ in most parts of the North China Plain (Fig. 5b) and were comparable with those observed by the IASI ($8–16 \times 10^{15}$ molecules cm$^{-2}$). In addition, we found that NH$_3^+$ concentrations have decreased with a similar magnitude to the increases in gas-phase NH$_3$ levels between Run_08 and Run_16. The proportion of NH$_3$ in the total (NH$_3$ + NH$_3^+$) increased on average from 26% in 2008 to 37% in 2016 over the North China Plain. Figure 5c and d illustrate that, without the large SO$_2$ emission reductions between 2008 and 2016 (i.e., replacing SO$_2$ emissions in 2016 by those in 2008, Run_08 vs. Run_16_S08), the sulfate columns partly increased. Correspondingly, the NH$_3$ columns remained constant or decreased by about $5 \times 10^{15}$ molecules cm$^{-2}$ (−13% relative to the 2008 level) in parts of the North China Plain. Thus, the increase in the tropospheric NH$_3$ columns was the result of a transition in NH$_3$ phase partitioning, which was strongly associated with the decreased formation of ammonium sulfate due to SO$_2$ emission reductions.
Figure 5. The differences between Run_08 and Run_16 (a, b), and between Run_08 and Run_16_S08 (c, d). A–F in (a) denote the Beijing, Tianjin, Hebei, Shanxi, Shandong, and Henan Provinces, respectively.

Figure 6. Seasonal patterns of simulated SO$_2^-$ (a) and NH$_3$ (b) columns for Run_08, Run_16, and Run_16_S08 (the simulation for 2016 with SO$_2$ emissions in 2008) cases. MAM, JJA, SON, and DJF represent spring (March, April, and May), summer (June, July, and August), autumn (September, October, and November), and winter (December, January, and February) months.
The seasonal variations in $\text{SO}_4^{2-}$ decreases and $\text{NH}_3$ increases were consistent (Fig. 6). We can see that the reduction of sulfate column concentrations between the Run_08 and Run_16 reached $1.3 \times 10^{15}$ molecules $\text{cm}^{-2}$ in summer (JJA), which was about 3 times larger than in other seasons. The corresponding percent reductions ranged from 15% in DJF to 36% in JJA. As aforementioned, the observations of PM$_{2.5}$ in Beijing also showed the highest decrease in sulfate in summer. Considering that the $\text{SO}_2$ emission reductions were uniform throughout the year, this seasonal pattern was likely attributed to the conversion efficiency of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$. Our simulations showed that a 1 mol decrease in $\text{SO}_2$ corresponded to an approximately 0.7 mol decrease in particulate sulfate in summer over the North China Plain, but the values dropped to below 0.4 in other seasons. It is known that the photochemical oxidation of $\text{SO}_2$ by OH radical is most active in summertime due to high atmospheric oxidizing capacity, and it dominates the formation of $\text{SO}_4^{2-}$, which makes the response of $\text{SO}_4^{2-}$ concentrations to $\text{SO}_2$ emission reductions more sensitive (Paulot et al., 2017; Huang et al., 2014). The comparison of modeled $\text{NH}_3$ columns also showed a markedly higher increase in summer months than during other seasons, driven by the variations in $\text{SO}_4^{2-}$.

Furthermore, by comparing the model results between the Run_16 and Run_16_S08 cases, we found that, without considering the $\text{SO}_2$ emission reductions, the seasonal increases in $\text{NH}_3$ columns and decreases in $\text{SO}_4^{2-}$ concentrations were not observed.

Since the chemical formation of particulate ammonium nitrate also affects the gas–particle partitioning of $\text{NH}_3$, the role of NO$_x$ emissions should be discussed. We noted that, unlike the trend of particulate sulfate in PM$_{2.5}$, the simulated concentrations of particulate nitrate in PM$_{2.5}$ increased on average by 28% over the North China Plain between 2008 and 2016, despite a 16% reduction in NO$_x$ emissions (Fig. S4 in the Supplement). This trend can be partially explained by the increased $\text{NH}_3$ in the atmosphere that would facilitate the formation of ammonium nitrate. To quantitatively understand the effect of NO$_x$ emission on the trend of $\text{NH}_3$, we performed a sensitivity experiment by repeating the simulation of 2016 with the NO$_x$ emissions in 2008 (Run_16_08N). By comparing the results among Run_16, Run_16_08N, and Run_08, we found that the reduction in NO$_x$ emissions (16% from 2008 to 2016) decreased the gaseous $\text{NH}_3$ concentrations by about 3% (Fig. S5 in the Supplement). Specifically, because the reduced NO$_x$ in this period promoted the transition of ozone ($\text{O}_3$) photochemistry from a volatile organic compound (VOC)-limited to a transitional regime with high $\text{O}_3$ production efficiency (Jin and Holloway, 2015), the simulated annual mean $\text{O}_3$ concentrations were elevated by 3.7 ppb over the North China Plain between the Run_16_08N and Run_16 cases. The resultant enhancement in atmospheric oxidizing capacity would favor the conversion of NO$_2$ to NO$_3^-$ and therefore derive more NH$_3$ partitioning from gaseous to particulate phases via aerosol thermodynamic equilibrium. Moreover, the measurements at an urban station of Beijing indicated a fluctuating trend of the annual mean NO$_3^-$ concentrations during 2013–2016 (Fig. 1). Overall, the limited reduction in NO$_x$ emissions cannot be responsible for the increased NH$_3$, because the concentrations of particulate nitrate has remained high over the North China Plain during recent years.

Besides, meteorological conditions are known to have an influence on NH$_3$ concentrations. Both Warner et al. (2017) and Fu et al. (2017) found that elevated annual surface temperature has partially contributed to the increase in NH$_3$ in eastern China over the past decade. In this work, we tested the effects of meteorological conditions on NH$_3$ variations by a simulation with meteorological fields in 2016 and anthropogenic emissions in 2012 (Run_12_M16). We selected these 2 years because NH$_3$ concentrations experienced a rapid increase during the period. This change in meteorological fields for the Run_12_M16 resulted in a decrease of about 3% in annual mean NH$_3$ concentrations relative to the Run_12 (Fig. S6 in the Supplement). Therefore, the interannual variability in meteorological conditions cannot explain the observed significant increase over the North China Plain.

Interestingly, increasing trends of gas-phase NH$_3$ in the atmosphere have also been observed in the last 20 years in the Midwest of the United States and Western Europe by satellite retrievals and ground measurements (Saylor et al., 2015; Warner et al., 2017; Ferm and Hellsten, 2012). The marked decreases in $\text{SO}_2$ and NO$_x$ emissions were largely responsible for these increases, as confirmed by the corresponding trends of particulate sulfate and nitrate concentrations. Warner et al. (2017) infer that $\text{SO}_2$ emission reduction in China may be a leading cause of the increased NH$_3$. More recently, Yu et al. (2018) quantified the contributions of the acid gases on the trends of NH$_3$ and found that emissions of $\text{SO}_2$ contributed to two-thirds and NO$_x$ to one-third of the change in NH$_3$ over the United States from 2001 to 2016. In this work, we demonstrate that the rapid reduction in $\text{SO}_2$ emissions was responsible for the increase in NH$_3$ over the North China Plain during 2008–2016, while other potential pathways (NH$_3$ emissions, NO$_x$ emissions, and meteorological conditions) decreased its concentrations by approximately 13% for this period.

4 Conclusion

By integrating chemical model simulations and ground and satellite observations, this study investigates an increase (∼30%) in tropospheric NH$_3$ column concentrations that was observed from the space over the North China Plain during 2008–2016. First, the long-term NH$_3$ emission inventory presents a decreasing tendency of −7% in the emission, and therefore it cannot explain the NH$_3$ increase. The meteo-
logical variations and the change in NO$_3$ emissions in the study period decreased the NH$_3$ column concentrations both by about 3%. Our work strongly indicates that the rapid SO$_2$ emission reductions (60%) from 2008 to 2016 were responsible for the NH$_3$ increase. The multi-year WRF-Chem simulations capture the increasing trend of NH$_3$ and decreasing trend of particulate sulfate well. Simulation results demonstrate that the SO$_2$ emission reductions decreased the regional mean SO$_2$ concentrations by about 50% in the lower troposphere, which reduced the formation of ammonium sulfate particles and consequently increased the average proportions of gas-phase NH$_3$ from 26% (2008) to 37% (2016) within the total NH$_3$ column concentrations. The sensitivity simulations by fixing SO$_2$ emissions of 2008 show that, without the reductions in SO$_2$ emissions, the increase in NH$_3$ is not observed during 2008–2016, and even a decrease of 13 % takes place, which is associated with the effects of other mechanisms (NH$_3$ emissions, NO$_x$ emission, and meteorology). Seasonally, both simulation and observations show the highest decrease in sulfate concentrations, making the increasing trend of NH$_3$ more pronounced in this season. This is likely due to a more sensitive response of sulfate concentrations to SO$_2$ emission reductions in summer than in other seasons.

Given the ongoing stringent controls on SO$_2$ emissions in China, a continued increase in NH$_3$ concentrations is anticipated if NH$_3$ emissions are not regulated. The increased tropospheric NH$_3$ levels may have a significant impact on air pollution and nitrogen deposition in China. For instance, the elevated NH$_3$ would facilitate ammonium nitrate formation based on the aerosol thermodynamic equilibrium and negatively impact PM$_{2.5}$ control. That is supported by the fact that NO$_x$ concentrations remain high in northern China and have become increasingly important in contributing to PM$_{2.5}$ pollution (Wen et al., 2018; Li et al., 2018), despite a moderate NO$_x$ emission reduction. The increased proportion of gas-phase NH$_3$ within the total can increase ammonium–nitrogen deposition since gas-phase ammonia deposits more rapidly than particle ammonium. This may alter the spatial pattern of regional nitrogen deposition with higher levels of NH$_3$ deposited near emission sources. These effects are important for human and ecosystem health and need to be investigated in future studies.

Data availability. NH$_3$ vertical column density data are freely available through the AERIS database: http://iasi.aeris-data.fr/NH$_3$ (last access: 13 September 2017) (Whitburn et al., 2017). The SO$_2$ vertical column density retrieved from the Ozone Monitoring Instrument is available from the Level-3 Aura/OMI Global SO$_2$ Data Products (OMSO2e) released by the NASA Goddard Earth Sciences Data and Information Service Center (https://disc.sci.gsfc.nasa.gov) (last access: 1 March 2018) (Krotkov et al., 2015). Anthropogenic emissions in industry, power plants, transportation, and residential sectors are obtained from the Multi-resolution Emission Inventory for China (MEIC, http://www.meicmodel.org/, last access: 15 May 2018) (Zheng et al., 2018). The PKU-NH$_3$ emission inventory is freely available from the corresponding author Yu Song (songyu@pku.edu.cn) upon reasonable request.

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Author contributions. YS, MH, and TZ designed the study. ZW and MH conducted measurements of aerosol chemical compositions. YP conducted measurements of gas-phase ammonia concentrations. QZ developed the MEIC emission database. ML, XH, and XL contributed to the development of the ammonia emission inventory. ML, XH, YS, TX, SW, LZ, and TZ analyzed the data. ML led the writing with input from all co-authors.

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

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