

Response to Referee #1

General comments (overall quality):

The paper addresses an important issue relating to atmospheric pollution with ammonia, namely the interaction with SO₂ emissions. The material is highly relevant to the subject matter covered by the journal and the results represent a useful contribution to knowledge concerning the interaction between tropospheric ammonia and SO₂ emissions. The level of English in the manuscript is fulfilling and the length of the submission seems appropriate. The recommendation is for publication of the paper.

Response: We would like to thank the referee for the encouragements and providing the insightful suggestions, which indeed help us to improve the manuscript.

Specific comments (individual scientific questions/issues):

The manuscript states that intensive farming results in lower volatilization rates of NH₃. This may be true, but I associate intensive farming with an increased number of livestock, which has the opposite effect, i.e. more livestock increases ammonia emissions. Already in the abstract it would be interesting to get an indication of how the number of livestock has changed over time, as this is an important factor when it comes to emissions of ammonia. It would be interesting to get an indication of the increase (in percentage) on page 5, row 5, that states: The number of some livestock increased slightly.

Response: Accepted. There are an increased number of livestock animals during 2008–2016. We have shown the detailed information in Table S1. As suggested by the referee, we added the quantitative data in the revised manuscript.

The intensive systems are characterized by lower NH₃ emission factors than the free-range (traditional animal rearing system in rural area) (Huang et al., 2012; Kang et al., 2016; EEA). The increased number of animals will produce more manure in farms, but applying intensive farming in livestock industry lowers the volatilization rates of NH₃ per animal. In this work, we find that the transition from the free-range to the intensive farming in the Chinese livestock industry offset the effect of increased animals on the NH₃ emissions. The resulting livestock NH₃ emissions in northern China do not show a significant trend during this period.

Revision: (Page 5, Line 23-30) "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 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). 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 in livestock animal rearing offset the effect of increased animals on the NH_3 emissions, thereby resulting in the annual livestock emissions in the North China Plain almost constant (around 1.2 Tg yr^{-1}). Overall, the decreasing NH_3 emissions cannot track the upward trend of tropospheric NH_3 concentrations."

In the background or discussion, it would be interesting to read more about other similar studies (outside of China), relating to the result in this study, e.g. Aneja et al (2003), Agricultural ammonia emissions and ammonium concentrations associated with aerosols and precipitation in the southeast United States, or Ferm & Hellsten (2012), Trends in atmospheric ammonia and particulate ammonium concentrations in Sweden and its causes.

Response: Accepted. We cited those related papers in the background and discussions parts in the revised manuscript.

Revision: (Page 3, Line 1-3) "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 region scales (Warner et al., 2017; Yu et al., 2018; Saylor et al., 2014)."

(Page 10, Line 12-23) "Interestingly, increasing trends of gas-phase NH_3 in the atmosphere have also been observed in the last twenty 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 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 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 SO_2 contributed to 2/3 and NO_x to 1/3 of the change in NH_3 over the United States from 2001 to 2016. In this work, we demonstrate that the rapid reduction in 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."

The authors state that “the increase in ammonia concentrations was highest in summer”. However I lack some reasoning regarding seasonal variations in ammonia emissions (e.g. more fertilization of the fields, and higher temperatures in

summertime). It would be useful also to mention this in the discussion and its implications on the result.

Response: The NH₃ emissions in the North China Plain are concentrated in spring and summertime due to frequent fertilization activities and higher temperature, which facilitates the volatilization rates of NH₃. We added the description about the seasonal distribution of NH₃ emissions in the North China Plain in the Methods of the revised manuscript.

However, the main finding of our study is that the rapid reduction in SO₂ emissions in China strongly reduced the concentrations of ammonium sulfate aerosols and transfers NH₃ from particle to gas phases. Therefore, the seasonal feature of the increase in gaseous NH₃ concentrations was mainly determined by that of sulfate concentrations rather than the NH₃ emissions. Both observations and simulation indicate that the concentrations of particulate sulfate demonstrated highest decreases in summer, thereby causing high increase in NH₃.

Revision: (Page 4, Line 28-30; Page 5, Line 1-3) "It shows distinct seasonal feature in NH₃ emissions over the North China Plain. There are 75% of annual NH₃ emissions released in spring and summer months (March-September), during which intensive agricultural fertilization and elevated ambient temperature facilitate the volatilization rates of NH₃. In this study, to integrate our NH₃ inventory into WRF-Chem simulations, we adopted a diurnal profile with 80% of the NH₃ emissions in the daytime, following previous studies (Zhu et al., 2015; Paulot et al., 2016; Asman, 2001)."

(Page 9, Line 1-4) "The seasonal variations in SO₄²⁻ decreases and NH₃ increases were consistent (Fig. 6). We can see that the reduction of sulfate column concentrations between the Run_08 and Run_16 reached 1.3×10^{15} molecules/cm² in summer (JJA), which was about three times larger than in other seasons. The corresponding percent reductions ranged from 15% in DJF to 36% in JJA. As aforementioned, the long-term observations of PM_{2.5} in Beijing also confirmed the highest decrease of sulfate in summer."

Technical corrections

Page Row 1 24 Remove "s" in "increases"

Response: Accepted. We remove it.

Revisions: (Page 1, Line 27) "we demonstrate that this large SO₂ emission reduction is responsible for the NH₃ increase"

2 14 Consider changing "NH3 emission has" to "NH3 emissions have"

Response: Accepted. We change it.

Revisions: (Page 2, Line 17-18) "Until now, NH₃ emissions have not been regulated by the Chinese government, although they serve as an important contributor to haze pollution in China."

3 2 Change "2000" to either "year 2000" or only "2000"

Response: Accepted. We change it.

Revisions: (Page 3, Line 3-4) "Through the widespread use of the flue gas desulfurization in power plants since 2006 in China, SO₂ emissions have gradually decreased."

4 13 Change "were" to "was"

Response: Accepted. We change it.

Revisions: (Page 4, Line 20) "A high-resolution NH₃ emission inventory (1km×1km, month) was developed based on the bottom-up method."

5 5 Remove "animals" 5 6 Change "system" to "systems" 5 7 Change "The increased livestock animals raised but more effective..." to "Despite increased livestock numbers, more effective..."

Response: Accepted. We reword these statements.

Revisions: (Page 5, Line 23-30) "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 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). The intensive systems are characterized with more effective livestock manure management in favor of lower volatilization rates of NH₃ (Kang et al., 2016). The transition from the free-range to the intensive in livestock animal rearing offset the effect of increased animals on the NH₃ emissions, consequently resulting in the annual livestock emissions in the North China Plain being almost constant (around 1.2 Tg per year)."

6 17 Change "hotpot" till "hotspot", and change "had" to "have" 6 18 Consider changing "over" to "in" and "into the atmosphere". We noted..."

Response: Accepted. We reword the statement.

Revisions: (Page 6, Line 21-23) "Spatially, the hotspot of NH₃ was mainly concentrated in Hebei, Shandong and Henan provinces, which have the most intensive agricultural productions in China and thus emit considerable gas-phase NH₃ into the atmosphere."

6 20 Consider adding "s" to emission, i.e. "emissions"

Response: Accepted. We reword it.

Revisions: (Page 6, Line 25) "Recently, NH₃ emissions from the residential coal and biomass combustion for heating are considered to be a potentially important source of NH₃ in suburban and rural areas during wintertime"

6 21 Consider changing to "it has not been fully included...."

Response: Accepted. We change it.

Revisions: (Page 6, Line 27) "it has not been fully included in our bottom-up inventory."

7 16 Change "disappeared"

Response: Accepted. We reword the statement.

Revisions: (Page 7, Line 18-19) "It was noticeable that under these conditions, the increasing trend of NH₃ column concentrations was not observed."

Figures Not consistent when it comes to the units, sometimes writing "μg/m³" and sometimes "g m⁻³", please consistently use the latter.

Response: Accepted. We use the unit of μg m⁻³ in the whole manuscript.

Revisions:

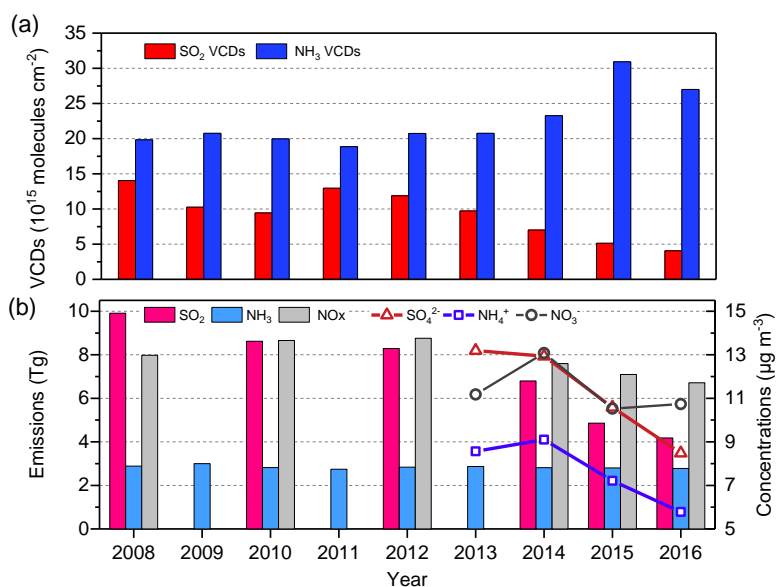


Figure 1. (a) Inter-annual trends of SO₂ and NH₃ VCDs averaged over North China Plain from 2008 to 2016. (b) Inter-annual trends of emissions of SO₂, NH₃, and NO_x in the North China Plain from 2008 to 2016, and annual mean concentrations of PM_{2.5} sulfate, ammonium, and nitrate derived from measurements at an urban station (Beijing, 39.99 °N,

116.3 °E) in North China Plain from 2013 to 2016.

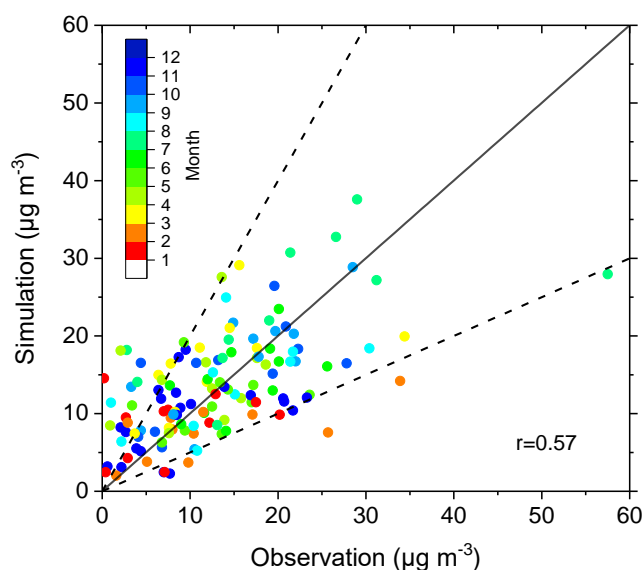


Figure 2. Comparison of modelled gaseous NH₃ concentrations with corresponding monthly measurements of NH₃ from September 2015 to August 2016. The 1:2 and 2:1 dashed lines are shown for reference and the Pearson correlation coefficient (r) is shown inset

References

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- Kang, Y., Liu, M., Song, Y., Huang, X., Yao, H., Cai, X., Zhang, H., Kang, L., Liu, X., Yan, X., He, H., Zhang, Q., Shao, M., and Zhu, T.: High-resolution ammonia emissions inventories in China from 1980 to 2012, *Atmos. Chem. Phys.*, 16, 2043-2058, [10.5194/acp-16-2043-2016](https://doi.org/10.5194/acp-16-2043-2016), 2016.
- Paulot, F., Ginoux, P., Cooke, W. F., Donner, L. J., Fan, S., Lin, M. Y., Mao, J., Naik, V., and Horowitz, L. W.: Sensitivity of nitrate aerosols to ammonia emissions and to nitrate chemistry: implications for present and future nitrate optical depth, *Atmos. Chem. Phys.*, 16, 1459-1477, [10.5194/acp-16-1459-2016](https://doi.org/10.5194/acp-16-1459-2016), 2016.
- Saylor, R., Myles, L., Sibble, D., Caldwell, J., and Xing, J.: Recent trends in

- gas-phase ammonia and PM_{2.5} ammonium in the Southeast United States, *J Air Waste Manag Assoc*, 65, 347-357, 10.1080/10962247.2014.992554, 2015.
- Yu, F., Nair, A. A., and Luo, G.: Long-term trend of gaseous ammonia over the United States: Modeling and comparison with observations, *J. Geophys. Res. Atmos.*, 123, 8315-8325, doi:10.1029/2018JD028412, 2018.
- Zhu, L., Henze, D., Bash, J., Jeong, G. R., Cady-Pereira, K., Shephard, M., Luo, M., Paulot, F., and Capps, S.: Global evaluation of ammonia bidirectional exchange and livestock diurnal variation schemes, *Atmos. Chem. Phys.*, 15, 12823-12843, 10.5194/acp-15-12823-2015, 2015.

Response to Referee #2

This manuscript addresses an important topic that is ultimately related to the air quality issues in China. The methodology is sound, as similarly done for the US regions by Yu et al. (2018). I believe it should be published after addressing the following major and minor issues.

Response: We would like to thank the referee for the insightful comments. We accepted all the comments and suggestions, and improved the manuscript thoroughly.

My major issue is how authors “claim” their results. Their sensitivity studies of (quote) “the SO₂ emission reduction of 50% from 2012 to 2016 could results in a 55% increase in the NH₃ columns, compared to that of 30% recorded by IASI observations.” : : : “the increasing trend of NH₃ can be entirely attributable to the SO₂ emission reductions.” (page 8, line 6-12). I do not believe such a conclusion can be drawn, unless the authors have performed and show quantitatively that all other mechanisms (NO_x, NH₃ emissions, temperatures, precipitations, etc.) do not contribute to the NH₃ increase (see more below). The estimated increase of 55% being larger than the observations of 30% only indicates uncertainties.

Response: Accepted. In addition to the evidences for the effect of SO₂ reduction on the NH₃ increase, we provided quantitative results of other mechanisms in the revised manuscript, as following.

- ◆ NH₃ emissions. Our inventory has demonstrated that NH₃ emissions in northern China experienced an overall decrease of 7% from 2008 to 2016. This decrease is caused by the changes in fertilizer use and livestock rearing practices in farms. The NH₃ emissions would decrease its concentrations in this period.
- ◆ NO_x emissions. The anthropogenic NO_x emissions in the North China Plain first increased from 2008 to 2012 by 10%, and then decreased by 23% afterwards. The overall trend of NO_x emissions is a decrease of 17% during 2008–2016. However, our simulations indicated an increase of 28% in the mean particulate nitrate concentrations in the region from 2008–2016. It can be explained by the significantly increased NH₃ that facilitates the formation of ammonium nitrate as well as enhanced atmospheric oxidizing capacity. We re-run the simulation of 2016 by replacing the NO_x emissions with those in 2008. The results indicate that the change in NO_x emissions between 2008 and 2016 gives rise to a slight decrease in the NH₃ column concentrations of about 3%. So it cannot be responsible for the significant increase of NH₃.

- ♦ Meteorological conditions. We did a sensitive simulation with meteorological fields in 2016 and anthropogenic emissions in 2012 (the period of 2012–2016 showing a rapid increase in NH₃). The change in meteorological fields between the Run_2012 and Run_12_M16 led to a decrease in NH₃ concentrations of ~3% over the North China Plain.

The above mechanisms totally decreased the NH₃ column concentrations by about 13%. So we conclude that the SO₂ emission reductions is responsible for the increasing trend of NH₃. More details for other mechanisms (especially NO_x emissions and meteorology) are shown in the following responses.

Revisions: (Page 5, Line 16-19) "the annual NH₃ 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 during 2011–2016 over the North China Plain (Fig. 1b). The overall trend of NH₃ emissions demonstrated a decrease of about 7%."

(Page 9, Line 21-31) "To quantitatively understand the effect of NO_x emission on the trend of NH₃, we performed a sensitive 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 (17% from 2008 to 2016) decreased the gaseous NH₃ concentrations by about 3% (Fig. S5). Specifically, because the reduced NO_x in this period led to the transition of ozone (O₃) photochemistry from VOC-limited to transitional regime with high O₃ production efficiency (Jin and Holloway, 2015), the simulated annual mean O₃ 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 NO₂ to NO₃⁻ and therefore derive more NH₃ partitioning from gas to particle phases via aerosol thermodynamic equilibrium."

(Page 10, Line5-10) "In this work, we tested the effects of meteorological conditions on NH₃ variations by a simulation with meteorological fields in 2016 and anthropogenic emissions in 2012 (Run_12_M16). We selected these two years because NH₃ concentrations experienced a rapid increase during the period. This change in meteorological fields for the Run_12_M16 resulted in a decrease of 3% in annual mean NH₃ concentrations relative to the Run_12 (Fig. S6)."

(Page 10, Line 20-23) "In this work, we demonstrate that the rapid reduction in SO₂ emissions was responsible for the increase in NH₃ over the North China Plain during 2008–2016, while other potential pathways (NH₃ emissions, NO_x emissions, and meteorological conditions) decreased its concentrations by approximately 13% for this period."

(Page 10, Line 27-30) "First, the long-term NH₃ emission inventory presents a decreasing tendency of -7% in the emission, and therefore it cannot explain the NH₃ increase. The meteorological variations and the change in NO_x emissions in the studying period decreased the NH₃ column concentrations both by about 3%."

The last paragraph before Conclusion (page 9, line 14-22) is ambiguous and handwaving. These "other" mechanisms that are very likely to have also caused the gaseous NH₃ to increase, but were dismissed without sufficient quantitative data or figures to back it up. (quote) " : : particulate nitrate: : : concentrations appear to increase in the North China Plain between 2008 and 2016 despite a 23% reduction in NO_x emission (Fig. S4). The in situ measurements in Beijing indicated that the NO₃-concentrations fluctuated during 2013-2016. It implied that the NO_x emission reduction could not be responsible for the increase in NH₃." Should not "imply" a mechanism that "could not be" responsible: : : The same process for the SO₂ should be repeated for the NO_x, if any conclusions were to be drawn about how NO_x reduction affects the gaseous NH₃ concentration change. The in situ measurement in Beijing was used to make an argument, but no evidence was shown in the manuscript, additionally, the where about of the data is not included, which does not follow the ACP data policy.

Response: Accepted. As suggested by the referee, we performed another sensitive simulation for 2016 by using NO_x emissions in 2008. The resulting NH₃ column concentrations were 2% higher than those in the baseline simulation for 2016. When compared to the 2008 simulation, the reduction in NO_x emissions during 2008–2016 decreased the NH₃ concentrations on average by 3%. We provide quantitative results in the revised manuscript and also show the effect of NO_x emissions in Fig. S6.

The measurements of PM_{2.5} chemical components (including sulfate, nitrate, and ammonium) were conducted in Peking University, Beijing since 2013 (please see Section 2.1). We show the inter-annual trend of PM_{2.5} nitrate concentrations in Fig. 1 in the revised manuscript. The annual mean concentrations of nitrate fluctuated during 2013–2016 without a significant trend.

Based on these evidences from the sensitive simulation and the observations, the change in NO_x emission has a negligible contribution on the NH₃ increase during 2008–2016.

Revisions: (Page 9, Line 16-32) "Since the chemical formation of particulate ammonium nitrate also affects the gas-particle partitioning of NH₃, 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 17% reduction in NO_x emissions (Fig.

S4). This trend can be partially explained by the increased 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 NH_3 , we performed a sensitive 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 (17% from 2008 to 2016)) decreased the gaseous NH_3 concentrations by about 3% (Fig. S5). Specifically, because the reduced NO_x in this period led to the transition of ozone (O_3) photochemistry from VOC-limited to transitional regime with high O_3 production efficiency (Jin and Holloway, 2015), the simulated annual mean 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 gas to particle 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 remain high over the North China Plain during recent years."

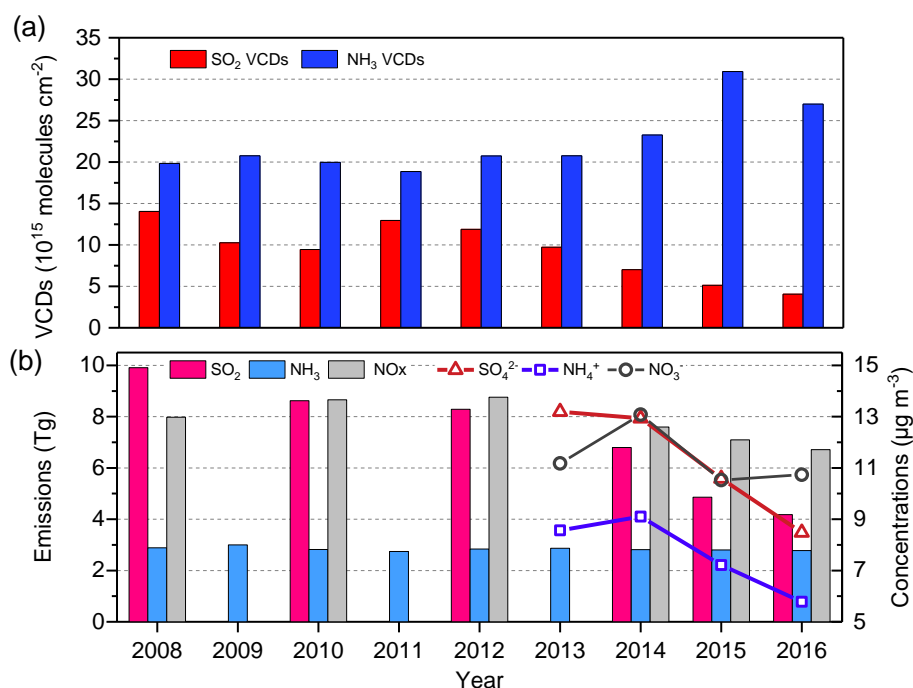


Figure 1. (a) Inter-annual trends of SO_2 and NH_3 VCDs averaged over North China Plain from 2008 to 2016. (b) Inter-annual trends of emissions of SO_2 , NH_3 , and NO_x in the North China Plain from 2008 to 2016, and annual mean concentrations of $\text{PM}_{2.5}$ sulfate, ammonium, and nitrate

derived from measurements at an urban station (Beijing, 39.99 °N, 116.3 °E) in North China Plain from 2013 to 2016.

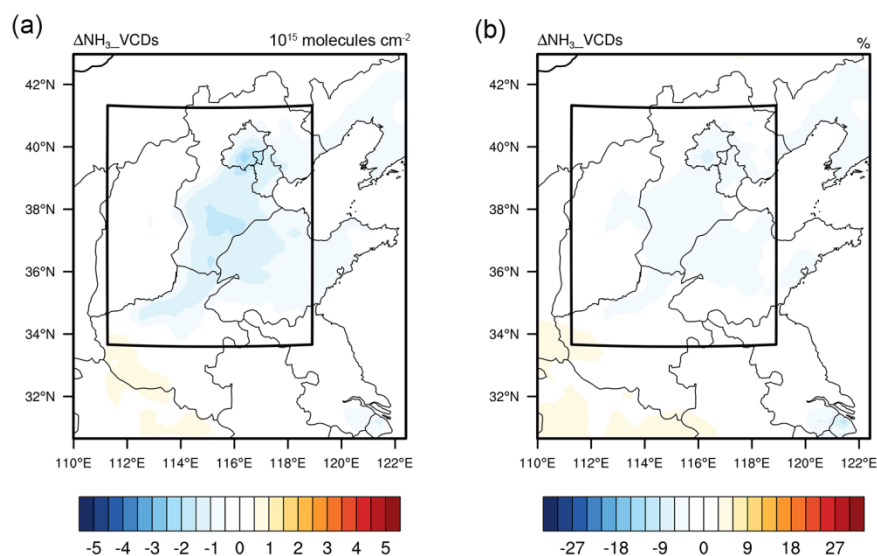


Figure S5. Absolute (a) and percent (b) changes in the simulated column concentrations of NH₃ between the Run_16 and Run_16_N08 (NO_x emissions in 2008). Negative values denote decreases in NH₃ VCDs due to the change in NO_x emissions during 2008–2016. The black box represents the major area of interest in this study.

Similarly, for meteorological effects, quote “We also tested the effects of meteorological conditions on NH₃ variations by a simulation with meteorological fields in 2016 and anthropogenic emissions in 2012 (Run_16_E12). Compared to the Run_12 case, we found the change in meteorological fields (2012 vs. 2016) had a negligible influence on NH₃ concentrations in most of North China Plain.” None of these were shown quantitatively! Can’t make statements like these without any evidence. The following statement “Although temperature increase was reported to partly contribute to the positive trend of NH₃ (Warner et al., 2017; Fu et al., 2017), our simulations indicated that the overall meteorological factors could not explain the observed significant increase tropospheric NH₃ concentrations over North China Plain.” This sentence is misleading, as if the quoted studies were trying to explain the observed significant increase in tropospheric NH₃ concentrations by meteorological factors. In fact, Warner et al. (2017) emphasized the leading cause of the NH₃ increase was the reduction of SO₂ in China, I quote “Over China, a combination of expanded agricultural activities, nascent SO₂ control measures, and increasing temperatures cause the observed increases in ammonia.”

Response: Accepted. The meteorological effects were examined in this study by the simulation for 2016 with anthropogenic emissions in 2012 (there was a pronounced increase in NH₃ columns in the period of 2012–2016). The resulting column concentration of NH₃ on average over the northern China was 3% lower than that in the baseline simulation of 2012. In the area of interest, this influence on the NH₃ column concentrations was

minor (marked with the black box in Fig. S6). We show these quantitative results in the revised manuscript.

We agree with the referee that Warner et al. emphasized the important role of the reduction of SO₂ in China in the trend of NH₃. We cite the finding of Warner et al. (2017) to support our results.

Revisions: (Page 10, Line 3-11) "Besides, meteorological conditions are known to have an influence on NH₃ concentrations. Both Warner et al. (2017) and Fu et al. (2017) have found that elevated annual surface temperature partially contributed to the increase in NH₃ in East China over the past decade. In this work, we tested the effects of meteorological conditions on NH₃ variations by a simulation with meteorological fields in 2016 and anthropogenic emissions in 2012 (Run_12_M16). We selected these two years because NH₃ 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 NH₃ concentrations relative to the Run_12 (Fig. S6). Therefore, the inter-annual variability in meteorological conditions cannot explain the observed significant increase over the North China Plain."

(Page 10, Line 12-17) "Interestingly, increasing trends of gas-phase NH₃ in the atmosphere have also been observed in the last twenty years in the Midwest of the United States and Western Europe by satellite retrievals and ground measurements (Warner et al., 2017; Saylor et al., 2015; Fern and Hellstern, 2012). The marked decreases in SO₂ 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 SO₂ emission reduction in China may be a leading cause of the increased NH₃."

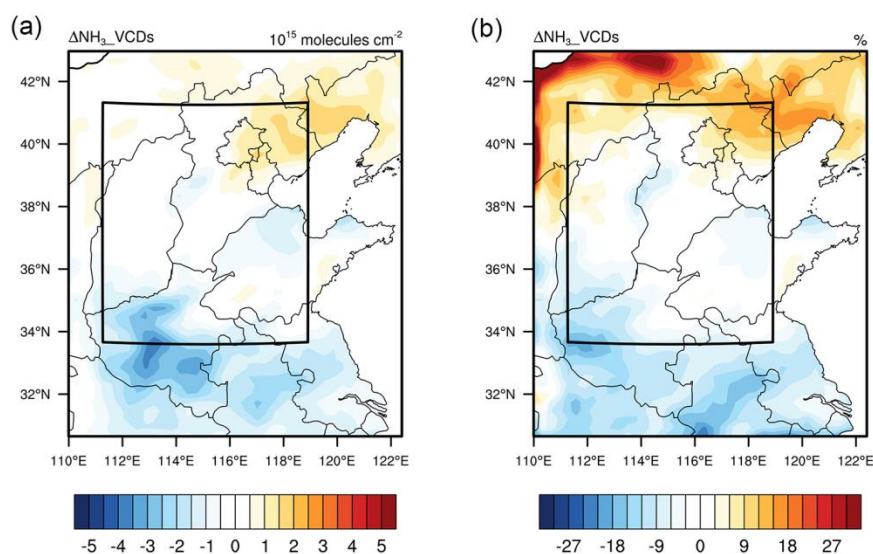


Figure S6. Absolute (a) and percent (b) changes in the simulated column concentrations of NH₃ between the Run_12 and Run_12_16M. Negative values denote decreases due to the change in meteorological fields in the Run_12_16M. The black box represents the major area of interest in this study.

My minor issues are mainly related to language and choice of words. I believe this manuscript needs to go through English editor at ACP. Also, many word choices are not appropriate for concise scientific publications, and somewhat wishy-washy, e.g., “appear to”, “could not be”, “may be a potential”, “could be responsible”, “would bias”, “: : : concentrations disappeared”, “: : : is practically zero: : :”, “could result”, “were almost consistent”, “could make”, implied”, “for almost the entire: : :”, “not well-regulated”, “can increase: : :”, “may alter”: : .

Response: Accepted. We reworded most of these statements to make them clearer and appropriate for scientific publications. Please see the following revisions:

Revision: **Before (abbreviated as B hereafter):** we noted that the simulated particulate nitrate (NO₃⁻) concentrations appear to increase.

Revision (abbreviated as R hereafter): (Page 9, Line 17) 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 17% reduction in NO_x emissions.

B: It implied that the NO_x emission reduction could not be responsible for the increase in NH₃.

R: (Page 10, Line 1) Overall, the limited reduction in NO_x emissions cannot be responsible for the increased NH₃ and even had a negative contribution, because the concentrations of particulate nitrate remain high over the North China Plain during recent years.

B: although it may be a potentially important contributor to haze pollution in China.

R: (Page 2, Line 17) although they serve as an important contributor to haze pollution in China.

B: which could be responsible for such deviation between the model and observations.

R: (Page 6, Line 27) which was partially responsible for such deviation between the model and observations.

B: the relative error weighting mean method would bias a high result.

R: (Page 7, Line 11) the relative error weighting mean method always biased a high result.

B: the increasing trend of NH₃ column concentrations disappeared

R: (Page 7, Line 19) the increasing trend of NH₃ column concentrations

was not observed

B: we found that the rapid SO₂ emission reduction of 50% from 2012 to 2016 could result in a 55% increase in the NH₃ columns

R: (Page 8, Line 13) we found that the rapid SO₂ emission reduction of 50% from 2012 to 2016 resulted in a 55% increase in the NH₃ columns

B: The seasonal variations in SO₄²⁻ decreases and NH₃ increases were almost consistent

R: (Page 8, Line 32) The seasonal variations in SO₄²⁻ decreases and NH₃ increases were consistent

B: which could make the response of SO₄²⁻ concentrations to SO₂ emission reductions more sensitive

R: (Page 9, Line 10) which makes the response of SO₄²⁻ concentrations to SO₂ emission reductions more sensitive

B: It implied that the NO_x emission reduction could not be responsible for the increase in NH₃

R: (Page 10, Line 1-2) the limited reduction in NO_x emissions cannot be responsible for the increased NH₃ and even had a negative contribution, because the concentrations of particulate nitrate remain high over the North China Plain during recent years

B: Our work strongly indicates that the rapid SO₂ emission reductions (60%) from 2008 to 2016 were responsible for almost the entire NH₃ increases

R: (Page 10, Line 30) Our work strongly indicates that the rapid SO₂ emission reductions (60%) from 2008 to 2016 were responsible for the NH₃ increase

B: a continued increase in NH₃ concentrations is anticipated if NH₃ emissions are not well-regulated

R: (Page 11, Line 12) a continued increase in NH₃ concentrations is anticipated if NH₃ emissions are not regulated

Page 2 line 11: "As a major agricultural country, China is the world's largest emitter of NH₃: : : " what about India?

Response: Accepted. The REAS2 inventory estimated the NH₃ emissions in India of 9.87 Tg, which is almost the same as those in China (Li et al., 2017; Kurokawa et al., 2013). We reword this sentence.

Revisions: (Page 2, Line 13) "As a major agricultural country, China is one of the world's largest emitters of NH₃."

Page 2 line 15: ": : : may be potentially important contributor to haze: : : " It's a known fact!

Response: Accepted. We rewrite this sentence.

Revisions: (Page 2, Line 17-18) "Until now, NH₃ emissions have not been regulated by the Chinese government, although they serve as an important contributor to haze pollution in China."

Page 2 line 17-19: "Interestingly, satellite observations over the past decade have shown an increase in tropospheric columns of gaseous NH₃ in this area (Warner et al., 2017). But no quantitative studies have been performed to explain it." Warner et al. (2017) was a quantitative study using observations. Should be "But no sensitivity studies: : :"

Response: Accepted. We reworded the sentence.

Revisions: (Page 2, Line 22-23) "But no sensitive studies have been performed to explain it, especially from a modelling perspective."

Page 2 line 19-20: "Along-term bottom-up inventory indicated that NH₃ emissions in China have displayed a slightly decreasing tendency." Needs references!

Response: Accepted. The corresponding reference is added here.

Revisions: (Page 2, Line 23-25) "A long-term bottom-up inventory indicated that NH₃ emissions in China have displayed a slightly decreasing tendency (Kang et al., 2016)."

Page 3 line 10: "Here, we hypothesize that the rapid SO₂ emission reduction is the reason for the increase in tropospheric NH₃: : : " Several studies have published the fact that the SO₂ emission reduction is the reason: : ;, not a hypothesis anymore. Should reference others' publications here, for global studies or in other regions, than in the North China.

Response: Accepted. We provide those references in the revised manuscript.

Revisions: (Page 3, Line 1-3) "Several studies have proposed that reduction in SO₂ emissions or NO_x emissions is an important factor in determining the increase in atmospheric NH₃ concentrations on the global and region scales (Warner et al., 2017; Yu et al., 2018; Saylor et al., 2014)."

(Page 3, Line 13-14) "Here, we hypothesize that the rapid SO₂ emission reduction is the main cause of the increase in tropospheric NH₃ concentrations over the North China Plain."

Page 4 line 9: Please pay attention to the order when acronyms are introduced and used throughout the paper.

Response: Accepted. We check the use of acronyms throughout the manuscript, including WRF-Chem, IASI, MEIC, etc.

Page 4 line 15: MEIC should be defined on Page 3 line 7.

Response: Accepted. We add a related reference for MEIC.

Revisions: (Page 3, Line 9) "the Multi-resolution Emission Inventory for China (MEIC) (Zheng et al., 2018)."

Page 4 line 15: "were cut" use reduced.

Response: Accepted. We reword it.

Revisions: (Page 4, Line 16-17) "the annual SO₂ emissions in North China Plain were reduced by about 60% "

Page 4 line 19: remove "by our research group"

Response: Accepted. We remove it.

Revisions: (Page 4, Line 20-21) "A high-resolution NH₃ emission inventory (1km×1km, month) was developed based on the bottom-up method."

Page 4 line 21: "in our previous studies: : : " should be "studies by: : : "

Response: Accepted. We reword the sentence.

Revisions: (Page 4, Line 22-23) "The full details can be found in studies by"

Page 5 line 5-7: "Meanwhile: : : " needs references.

Response: Accepted. The data about agricultural activities were shown in Table S1. The references for the source of data were shown in the supplementary file.

Revisions: (Page 5, Line 23-26) "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 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)."

Page 5 line 11: use IASI.

Response: Accepted. We reword the sentence.

Revisions: (Page 5, Line 6) "According to the measurements by IASI, the North China Plain showed the highest VCDs of NH₃ in China"

Page 6 line 22: "which could be responsible", add partially responsible: : :

Response: Accepted. We reword the sentence in the revised paper.

Revisions: (Page 6, Line 26-28) "but it has not been fully included in our bottom-up inventory, which was partially responsible for such deviation between the model and observations"

Page 6 line 23-24: bad sentence, rewrite.

Response: Accepted. We rewrite it.

Revisions: (Page 6, Line 29-31) "We calculated the NH₃ VCDs from the simulations by integrating NH₃ molecular concentrations from the surface level to top troposphere. The results agreed well with the observed NH₃ columns of 2016 on the magnitude and spatial-temporal patterns (Fig. S2)."

Page 7 line 3: "Moreover, we also: : :", remove also.

Response: Accepted. We remove it.

Revisions: (Page 7, Line 2) "Moreover, we evaluated the modelled SNA concentrations using the filter-based PM_{2.5} samples at an urban atmospheric monitoring station in North China Plain during 2014–2016."

Page 7 line 18-19: "These tests support: : :" Too absolute! No other mechanisms?

Response: Accepted. We rewrite this statement.

Revisions: (Page 7, Line 25-27) "Therefore, we deduce that the rapid SO₂ emission reductions are responsible for the increased NH₃ levels during 2008–2016, while other mechanisms may be negative contributors. More details on these effects are shown in the following."

Fig. 2: use whole words for Sim., Obs., Sep., and Aug.

Response: Accepted. We modify the words and the figure.

Revisions:

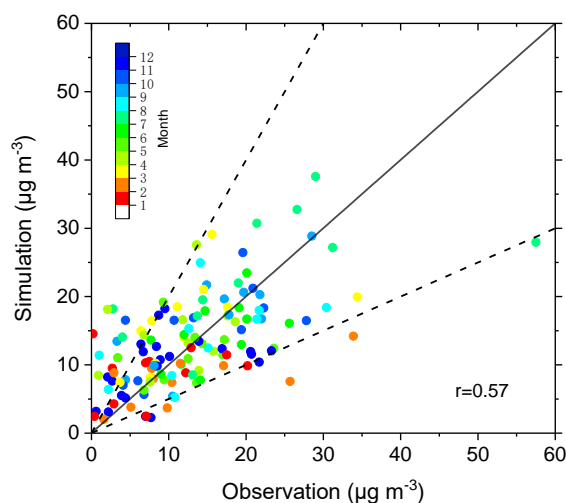


Figure 2. Comparison of modelled gaseous NH_3 concentrations with corresponding monthly measurements of NH_3 from September 2015 to August 2016. The 1:2 and 2:1 dashed lines are shown for reference and the Pearson correlation coefficient is shown inset.

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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
20 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
25 rapidly declined by about 60% over recent few years. By integrating local measurement datasets,
long-term anthropogenic emission inventories, and chemical transport model simulations, we
demonstrate 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
30 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
35 in other seasons. Besides, the changes in NO_x emissions and meteorological conditions both decreased**

the NH_3 column concentrations by about 3% in the studying period. Our simulations suggest that the moderate reduction in NO_x emissions (16%) favors the formation of nitrate by elevating ozone concentrations in the lower troposphere.

1 Introduction

5 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 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 (SNA), which constitute a significant fraction of atmospheric fine particles ($\text{PM}_{2.5}$) associated with potential human health impacts
10 (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 ($\sim 10 \text{ Tg yr}^{-1}$) exceeds the sum of those in Europe ($\sim 4.0 \text{ Tg yr}^{-1}$) and North America ($\sim 4.0 \text{ Tg yr}^{-1}$)
15 (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) is a hotspot of NH_3
20 loadings, as revealed by satellite detection and in situ 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 sensitive studies have been performed to explain it, especially from a modelling perspective. A long-term bottom-up inventory indicated that NH_3 emissions in China have displayed a slightly decreasing tendency (Kang et al., 2016).**
25 During 2006–2016, ammonium bicarbonate for crop fertilization was replaced by urea fertilizer (its fraction of application increasing from 60 to 90% of all nitrogen fertilizers). In the meantime, the traditional free-range livestock system was gradually replaced by 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). These changes in agricultural practices have lowered the
30 volatilization rates of NH_3 (Kang et al., 2016).

Several studies have proposed that reduction in SO₂ emissions or NO_x emissions is an important factor in determining the increase in atmospheric NH₃ concentrations on the global and region 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, SO₂ 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 SO₂ 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 SO₂ emission reduction is the main cause of the increase in tropospheric NH₃ 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 NH₃ and SO₂ concentrations. A comprehensive long-term NH₃ emission inventory, developed by our recent studies based on bottom-up methods, was also used to demonstrate the inter-annual variations of NH₃ emissions in this region. Then, we performed multi-year simulations with a chemical transport model to examine the impact of changes in SO₂ emissions on tropospheric NH₃ concentrations in terms of the magnitude and seasonal variation. Besides, other potential mechanism (NO_x emission and meteorology) were discussed.

2 Methods

2.1 Observations datasets

Observations from space and ground stations were used in this study. Tropospheric vertical column densities (VCDs) of NH₃ were derived from the measurements of Infrared Atmospheric Sounding Interferometer (IASI) onboard MetOp-A (Van Damme et al., 2015; Clarisse et al., 2009; Van Damme et al., 2017). We determined the annual averages of NH₃ 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 NH₃ concentrations were measured using passive NH₃ diffusive samplers (Analysts, CNR-Institute of Atmospheric Pollution, Roma, Italy) from September 2015 to

August 2016 at 11 sites over Northern China (Pan et al., 2018). The SO₂ VCDs were provided by the ozone monitoring instrument (OMI) measurements to test the trend of SO₂ concentrations. They were derived from the daily level 3 data set OMSO₂e, released by the NASA Goddard Earth Sciences Data and Information Services Center. Besides, daily PM_{2.5} were 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 water-soluble inorganic compounds (e.g., NH₄⁺, NO₃⁻, and SO₄²⁻) were analyzed by ion-chromatography.

2.2 WRF-Chem simulations

In this study, the simulations with Weather Research and Forecast Model coupled Chemistry (Grell et al., 2005) version 3.6.1 (WRF-Chem) were conducted for the domain of 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 × 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 configuration 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 SO₂ emissions in 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, then decreased to 6.7 Tg in 2016.**

2.3 NH₃ emission inventory

A high-resolution NH₃ emission inventory (1km×1km, 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 etc. The full details can be found in studies by Kang et al. (2016), Huang et al. (2012), and Huo et al. (2015). The inventory had 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 the inter-annual variability in activity levels and agricultural practices. It shows distinct seasonal feature in NH₃ emissions over the North China Plain. There are 75% of annual NH₃ emissions released in spring and summer months (March-September), during which intensive agricultural fertilization and elevated

ambient temperature facilitate the volatilization rates of NH₃. Moreover, to integrate this inventory into WRF-Chem simulations, we adopted a diurnal profile with 80% of NH₃ emissions in the daytime, following previous studies (Zhu et al., 2015; Asman, 2001; Paulot et al., 2016).

3 Results and Discussions

5 3.1 Trends in emissions and concentrations of NH₃ vs. SO₂

According to the measurements by IASI, the North China Plain showed the highest VCDs of NH₃ in China, which mostly ranged from 15 to 30 × 10¹⁵ molecules cm⁻² during 2008–2014, and increased to above 30 × 10¹⁵ molecules cm⁻² in 2015 and 2016 (Fig. S1). We found the annual NH₃ column concentrations increased significantly (*p* value < 0.05) over the North China Plain between 2008 and 10 2016 (Fig. 1a). The average tropospheric NH₃ columns first fluctuated between 2008 and 2013, and then rapidly increased from 21 × 10¹⁵ molecules cm⁻² in 2013 to 27 × 10¹⁵ molecules cm⁻² in 2016. It showed an overall increase of 30%, or an average annual increase of 0.9 × 10¹⁵ molecules cm⁻² yr⁻¹. Seasonally, the increase in NH₃ columns was more pronounced in summertime (June–August, JJA), with an annual increase rate of 1.8 × 10¹⁵ molecules cm⁻² yr⁻¹ between 2008 and 2016, which was much 15 higher than in other seasons (< 1 × 10¹⁵ molecules cm⁻² yr⁻¹).

In contrast to the trends in tropospheric NH₃ concentrations, the annual NH₃ 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 NH₃ emissions demonstrated a decrease of about 7%. It is because the changes in 20 mineral fertilizer use and livestock rearing practices have lowered NH₃ emission rates. The increasing use of urea fertilizer (from 4.7 and 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 NH₃ emissions from fertilizer application during 2008–2016 (Table S1). On the other hand, the number of some major 25 livestock increased (Beef -20%, Dairy +39%, Goat -23%, sheep +55%, Pig +18%, and Poultry +19%; see Table S1 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). The intensive systems are characterized with more effective livestock manure management in favor of lower volatilization rates of NH₃ (Kang et al., 2016). The transition from the free-range to the intensive in livestock animal rearing offset the effect of increased animals on the NH₃ emissions, thereby resulting in the annual livestock 30 emissions in the North China Plain almost constant (around 1.2 Tg yr⁻¹). Overall, the decreasing NH₃

emissions cannot track the upward trend of tropospheric NH₃ concentrations.

During 2008–2016, SO₂ column concentrations were subject to a dramatic decline ($p < 0.01$) due to a 60% decrease in SO₂ emissions. The annual mean SO₂ VCDs 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 SO₂ 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 SO₄²⁻ concentration in PM_{2.5} decreased by 35% (2013–2016) along with rapid SO₂ reductions, which was accompanied by a 33% decrease of particulate NH₄⁺ (Fig. 1b). Seasonally, the decrease in SO₄²⁻ during summertime (JJA) reached 60%, which was much higher than in other seasons.

3.2 Simulations of increasing trend in NH₃ columns

We performed numerical simulations with WRF-Chem to interpret the cause of the NH₃ increase. We first evaluated model results against measurements of surface NH₃ concentrations available in North China Plain as well as the satellite-retrieved NH₃ columns. The simulated monthly averaged surface NH₃ concentrations at 11 stations (mean + standard deviation: $13.5 \pm 6.8 \mu\text{g m}^{-3}$) generally agreed with corresponding observations ($13.4 \pm 9.7 \mu\text{g m}^{-3}$) with a correlation coefficient of 0.57. More than 70% of the comparisons differed within a factor of two (Fig. 2). Both simulations and observations show high NH₃ concentrations of about $30 \mu\text{g m}^{-3}$ in warm seasons (March–October) due to enhanced NH₃ volatilization and frequent fertilization activities, and lower values (mostly $< 15 \mu\text{g m}^{-3}$) in other months (Fig. 3). Spatially, the hotspot of NH₃ was mainly concentrated in Hebei, Shandong and Henan provinces, which have the most intensive agricultural productions in China and thus emit considerable gas-phase NH₃ into the atmosphere. We note that the simulated NH₃ concentrations were underestimated by about a factor of two in wintertime (January, February, and December). Recently, NH₃ emissions from the residential coal and biomass combustion for heating are considered to be a potentially important source of NH₃ 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.

We calculated the NH₃ VCDs from the simulations by integrating NH₃ molecular concentrations from the surface level to top troposphere. The results agreed well with the observed NH₃ columns of 2016 on the magnitude and spatial-temporal patterns (Fig. S2). 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 also evaluated the modelled SNA concentrations using the filter-based $\text{PM}_{2.5}$ samples at an urban atmospheric monitoring station in North China Plain during 2014–2016 (Fig. S3). The model generally reproduced the observed SNA concentrations, with small annual mean bias for sulfate (–2%) and ammonium (–13%) and a relatively large bias for nitrate (–24%). Overall, the model performed well in modelling 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 during 2008–2016 (Fig. 4). **The modelled NH_3 columns were systemically 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 increase of 0.8×10^{15} molecules $\text{cm}^{-2} \text{yr}^{-1}$ 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 sensitive simulations were about 40% ($8\text{--}10 \times 10^{15}$ 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_4^{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 much effective SO₂ emission reductions. Given that the vapor pressure of H₂SO₄(g) is practically zero over atmospheric particles, atmospheric SO₄²⁻ is predominately in the particle phase and can combine with NH₃ available in air, forming sulfate salts (mostly ammonium sulfate/bisulfate) (Seinfeld and Pandis, 2006). Since North
5 China Plain is typically under rich NH₃ regimes, SO₄²⁻ is mainly in the form of ammonium sulfate (Meng et al., 2011; Huang et al., 2017); and the aforementioned SO₄²⁻ reductions would therefore increase atmospheric NH₃ concentrations by driving the phase state of NH₃ from particulate to gaseous.

By assuming that a 1 mol decrease in simulated SO₄²⁻ would lead to a 2 mol increase in ambient gaseous NH₃ in this region, the average annual increase in the tropospheric NH₃ columns due to the
10 reductions of SO₄²⁻ was estimated to be approximately 1.5×10^{15} molecules cm⁻² yr⁻¹ over 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 (0.9×10^{15} molecules cm⁻² yr⁻¹). By neglecting the deposition processes, we found that the rapid SO₂ emission reduction of 50% from 2012 to 2016 resulted in a 55% increase in the NH₃ columns, compared to that of 30% recorded by IASI observations. Overall, the
15 estimation results confirmed that the increasing trend of NH₃ was mainly determined by the SO₂ emission reductions.

We compared the spatial patterns of decreased SO₄²⁻ and increased NH₃ between 2008 and 2016 (Run_08 – Run_16). Large reductions of $6\text{--}10 \times 10^{15}$ molecules cm⁻² in annual averages of sulfate
20 columns were concentrated in Hebei, Shandong and Henan provinces, the area subject to high SO₂ loadings and stringent emission controls (Fig. 5a). Meanwhile, the simulated increases in NH₃ columns reached more than 8×10^{15} molecules cm⁻² in most parts of the North China Plain (Fig. 5b), and were comparable with those observed by the IASI ($8\text{--}16 \times 10^{15}$ molecules cm⁻²). In addition, we found that NH₄⁺ concentrations have decreased with a similar magnitude of the increases in gas-phase NH₃ levels
25 between Run_08 and Run_16. The proportion of NH₃ in the total (NH₃ + NH₄⁺) increased on average from 26% in 2008 to 37% in 2016 over North China Plain. Figure 5c, d illustrated that without the large SO₂ emission reductions between 2008 and 2016 (i.e., replacing SO₂ emissions in 2016 by those in 2008, Run_08 – Run_16_S08), the sulfate columns partly increased. Correspondingly, the NH₃ columns remained constant or decreased by about 5×10^{15} molecules cm⁻² (–13% relative to the 2008 level) in
30 parts of the North China Plain. Thus, the increase in the tropospheric NH₃ columns was the result of a transition in NH₃ phase partitioning, which was strongly associated with the decreased formation of ammonium sulfate due to SO₂ emission reductions.

The seasonal variations in SO₄²⁻ decreases and NH₃ increases were consistent (Fig. 6). We can see

that the reduction of sulfate column concentrations between the Run_08 and Run_16 reached 1.3×10^{15} molecules cm^{-2} in summer (JJA), which was about three times larger than in other seasons. The corresponding percent reductions ranged from 15% in DJF to 36% in JJA. As aforementioned, the observations of $\text{PM}_{2.5}$ in Beijing also confirmed the highest decrease of sulfate in summer. Considering that the SO_2 emission reductions were uniform throughout the year, this seasonal pattern was likely attributed to the conversion efficiency of SO_2 to H_2SO_4 . Our simulations showed that a 1 mol decrease in SO_2 corresponded to an approximately 0.7 mol decrease in particulate sulfate in summer over North China Plain, but the values dropped to below 0.4 in other seasons. It is known that the photochemical oxidation of SO_2 by OH radical is most active in summertime due to high atmospheric oxidizing capacity, and it dominates the formation of SO_4^{2-} , which makes the response of SO_4^{2-} concentrations to SO_2 emission reductions more sensitive (Paulot et al., 2017; Huang et al., 2014). The comparison of modelled NH_3 columns also showed a markedly higher increase in summer months than during other seasons, driven by the variations in SO_4^{2-} . Furthermore, by comparing the model results between the Run_16 and Run_16_S08 cases, we found that without considering the SO_2 emission reductions, the seasonal increases in NH_3 columns and decreases in SO_4^{2-} concentrations were not observed.

Since the chemical formation of particulate ammonium nitrate also affects the gas-particle partitioning of NH_3 , the role of NO_x emissions should be discussed. We noted that unlike the trend of particulate sulfate in $\text{PM}_{2.5}$, the simulated concentrations of particulate nitrate in $\text{PM}_{2.5}$ increased on average by 28% over the North China Plain between 2008 and 2016, despite a 16% reduction in NO_x emissions (Fig. S4). This trend can be partially explained by the increased 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 NH_3 , we performed a sensitive 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 NH_3 concentrations by about 3% (Fig. S5). Specifically, because the reduced NO_x in this period led to the transition of ozone (O_3) photochemistry from VOC-limited to transitional regime with high O_3 production efficiency (Jin and Holloway, 2015), the simulated annual mean 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 gas to particle 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 remain 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) have found that elevated annual surface temperature partially contributed to the increase in NH_3 in East 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 two 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). Therefore, the inter-annual 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 twenty 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 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 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 SO_2 contributed to 2/3 and NO_x to 1/3 of the change in NH_3 over the United States from 2001 to 2016. In this work, we demonstrate that the rapid reduction in 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 has been 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 meteorological variations and the change in NO_x emissions in the studying 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 emissions reduction decreased the regional mean SO_4^{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 sensitive 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 summertime than in other seasons.

Given the on-going 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 $\text{PM}_{2.5}$ control. That is supported by the fact that NO_3^- concentrations remain high in Northern China and have become increasingly important in contributing to $\text{PM}_{2.5}$ 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/NH3/>. The SO_2 vertical column density retrieved from the Ozone Monitoring Instrument is available from Level-3 Aura/OMI Global OMSO2e Data Products released by NASA Goddard Earth Science Data and Information Service Center (<https://disc.sci.gsfc.nasa.gov/>). Anthropogenic emissions in industry, power plants, transportation, and residential sectors are obtained from Multi-resolution Emission Inventory for China (MEIC, <http://www.meicmodel.org/>). The PKU- NH_3 emission inventory is freely available from the corresponding author Y.S. (songyu@pku.edu.cn) upon reason request.

Author contributions. Y.S., M.H., and T.Z. designed the study. Z.W. and M.H. conducted in situ measurements of aerosol chemical compositions. Y.P. conducted in situ measurements of gas-phase ammonia concentrations. Q.Z. developed the MEIC emission database. M.L. and X.H. contributed to the development of ammonia emission inventory. M.L., X.H., Y.S., S.W., L.Z and T.Z. analyzed data.
5 M.L. led the writing with input from all co-authors.

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

Acknowledgments. This study was funded by National Key R&D Program of China (2016YFC0201505) and National Natural Science Foundation of China (NSFC) (91644212 and 41675142).

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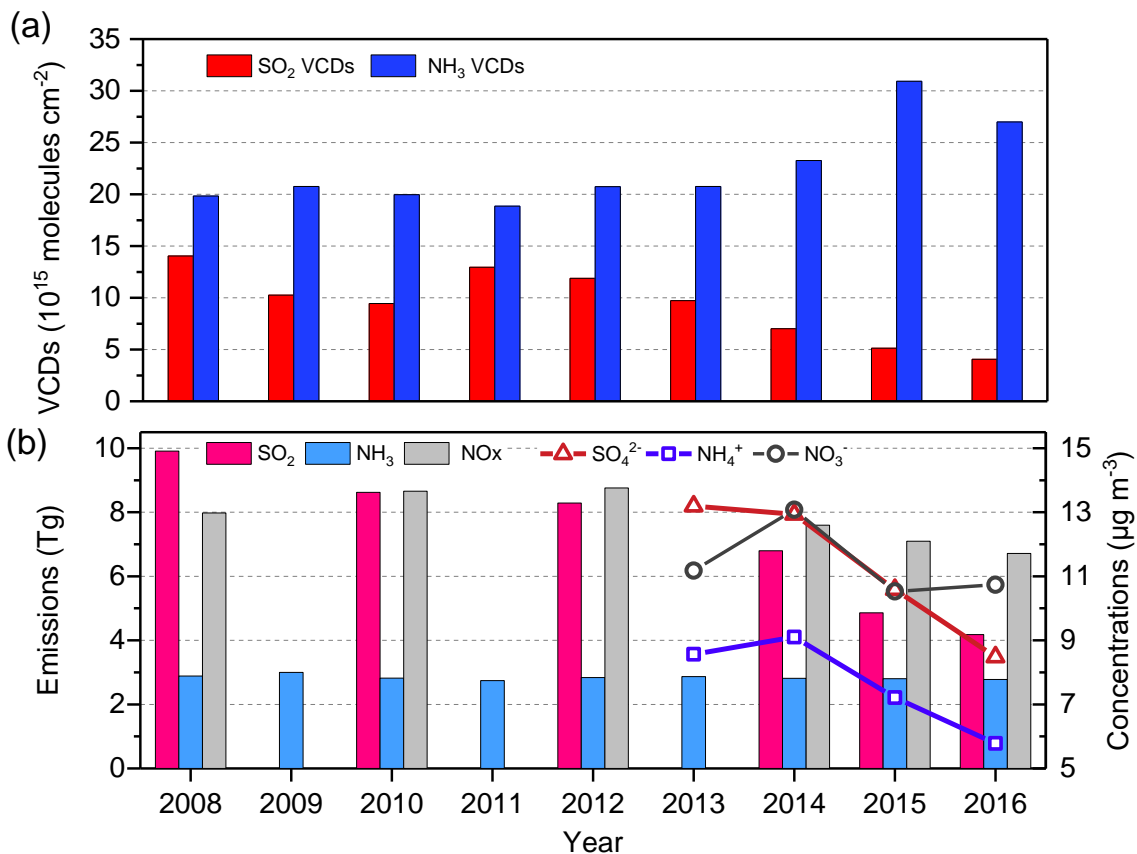


Figure 1. (a) Inter-annual trends of SO_2 and NH_3 VCDs averaged over North China Plain from 2008 to 2016. (b) Inter-annual trends of emissions of SO_2 , NH_3 , and NO_x in the North China Plain from 2008 to 2016, and annual mean concentrations of $\text{PM}_{2.5}$ sulfate, ammonium, and nitrate derived from measurements at an urban station (Beijing, 39.99°N , 116.3°E) in North China Plain from 2013 to 2016.

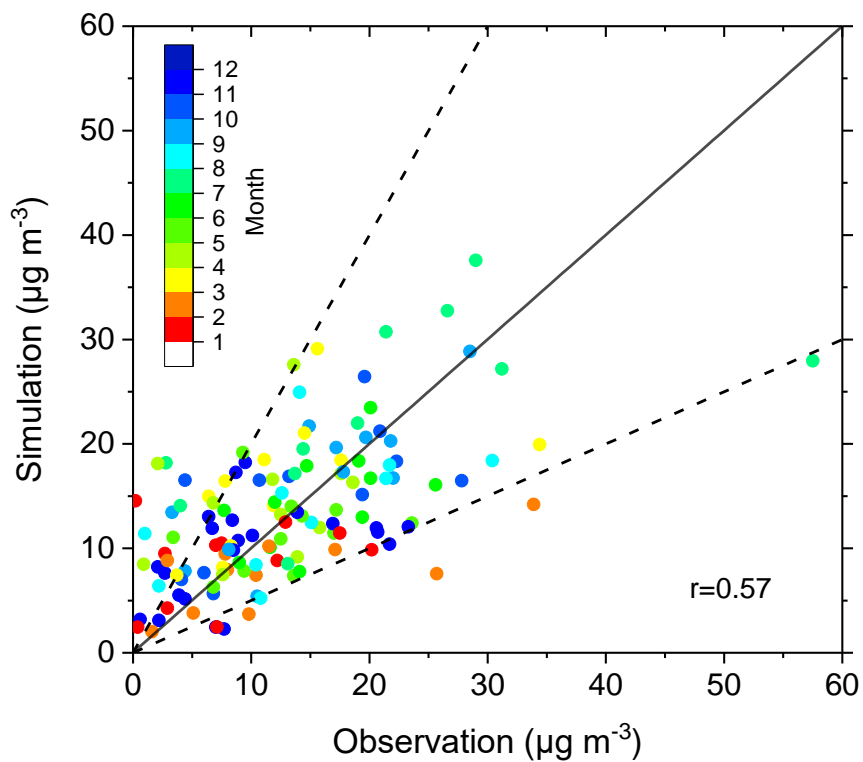


Figure 2. Comparison of modelled gaseous NH₃ concentrations with corresponding monthly measurements of NH₃ from September 2015 to August 2016. The 1:2 and 2:1 dashed lines are shown for reference and the Pearson correlation coefficient (r) is shown inset.

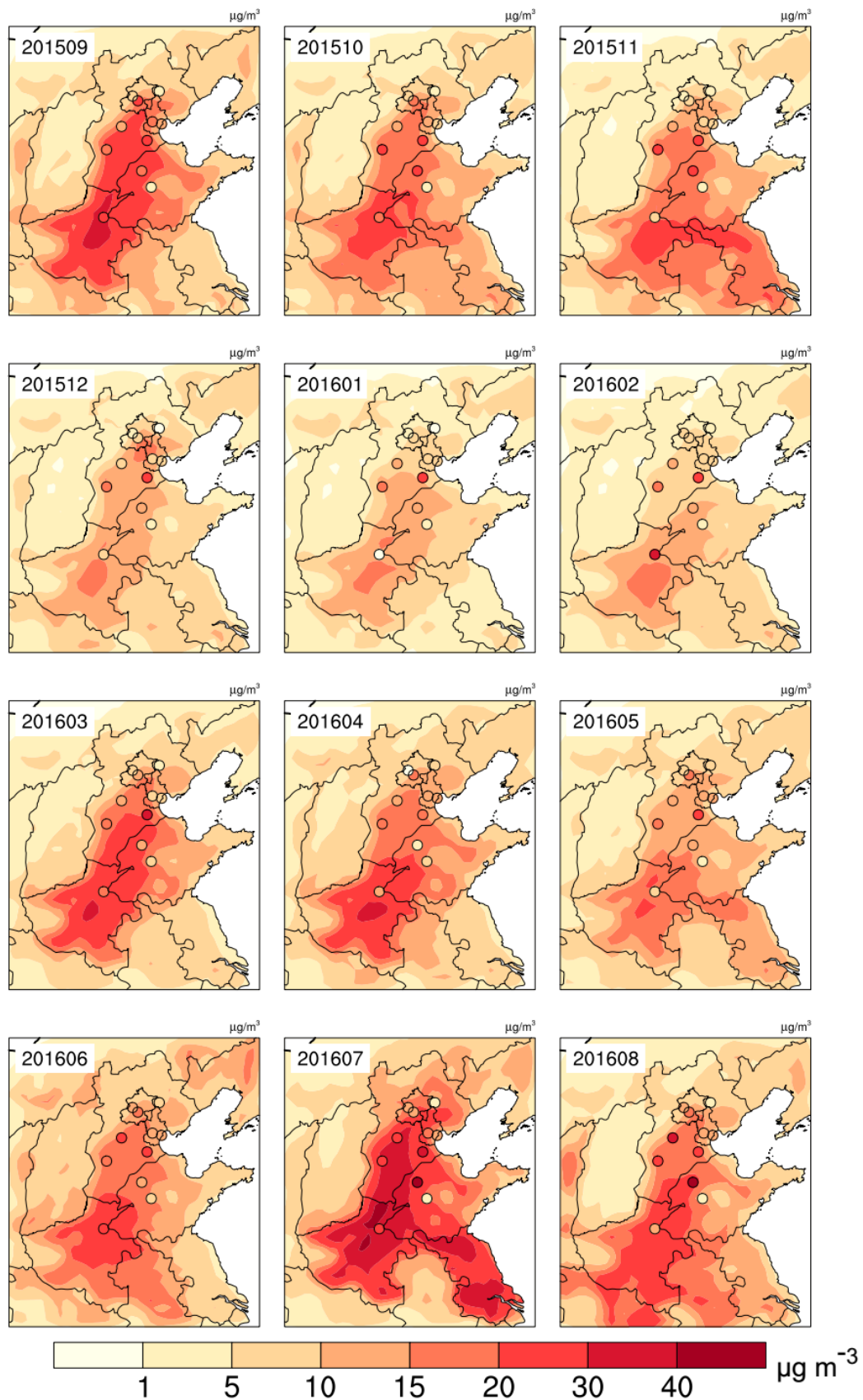


Figure 3. Spatial distribution of modelled ground NH_3 concentrations ($\mu\text{g m}^{-3}$) and monthly measurements over North China Plain from September, 2015 (201509) to August, 2016 (201608).

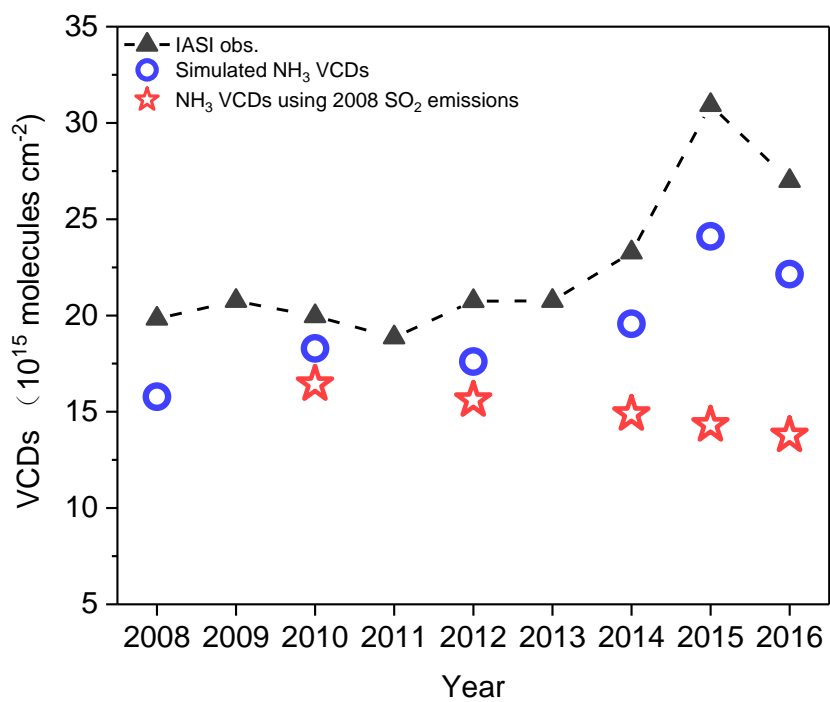


Figure 4. Trends in the annual averages of observed and simulated NH₃ columns over the North China Plain. The red stars denote the simulated NH₃ columns under the 2008 SO₂ emissions levels (i.e., Run_10_S08 to Run_16_S08).

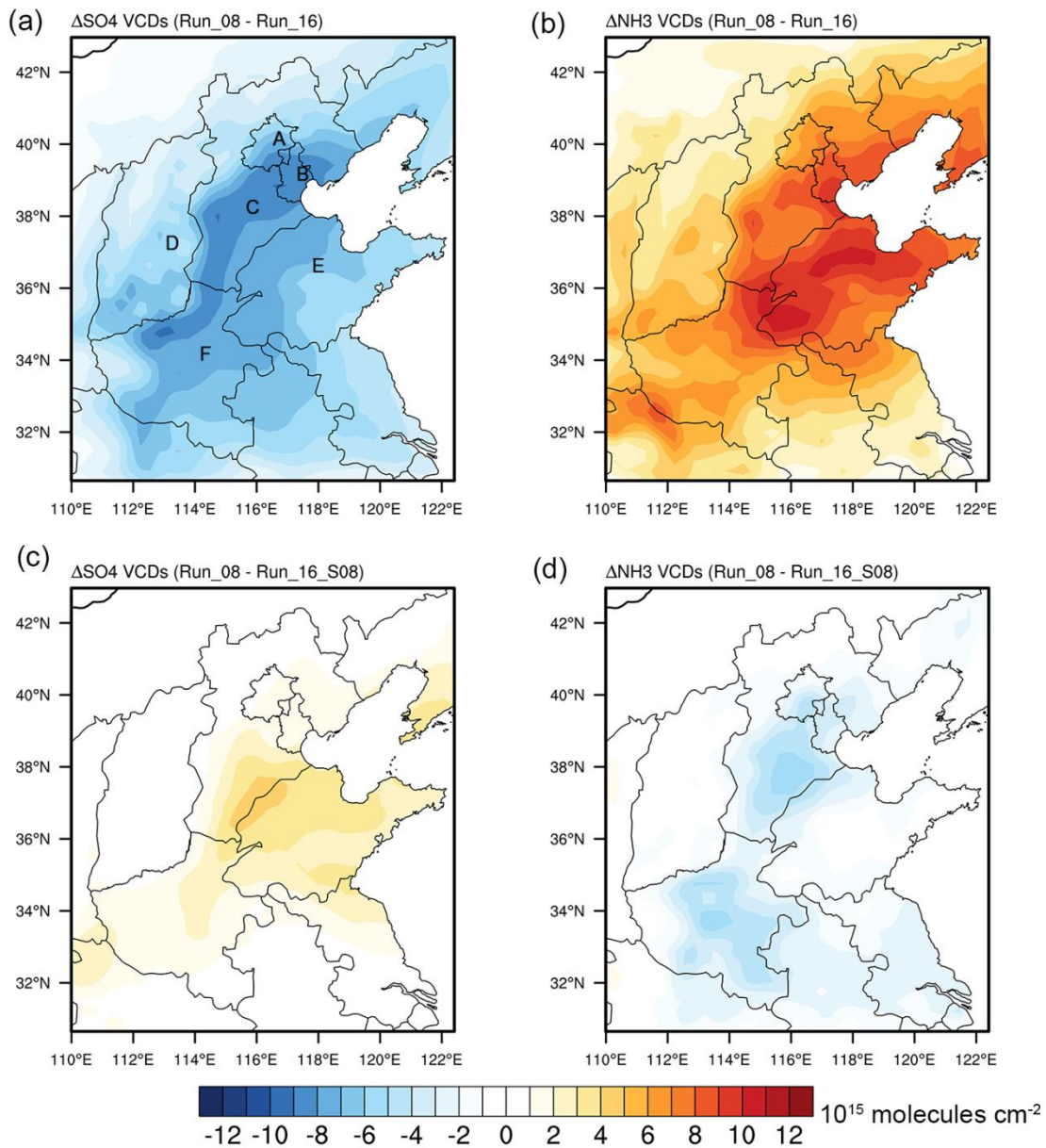


Figure 5. The differences between Run_08 and Run_16 (a, b), and between Run_08 and Run_16_S08 (c, d). A-F in Figure. 3a denote Beijing, Tianjin, Hebei, Shanxi, Shandong, and Henan Provinces, respectively.

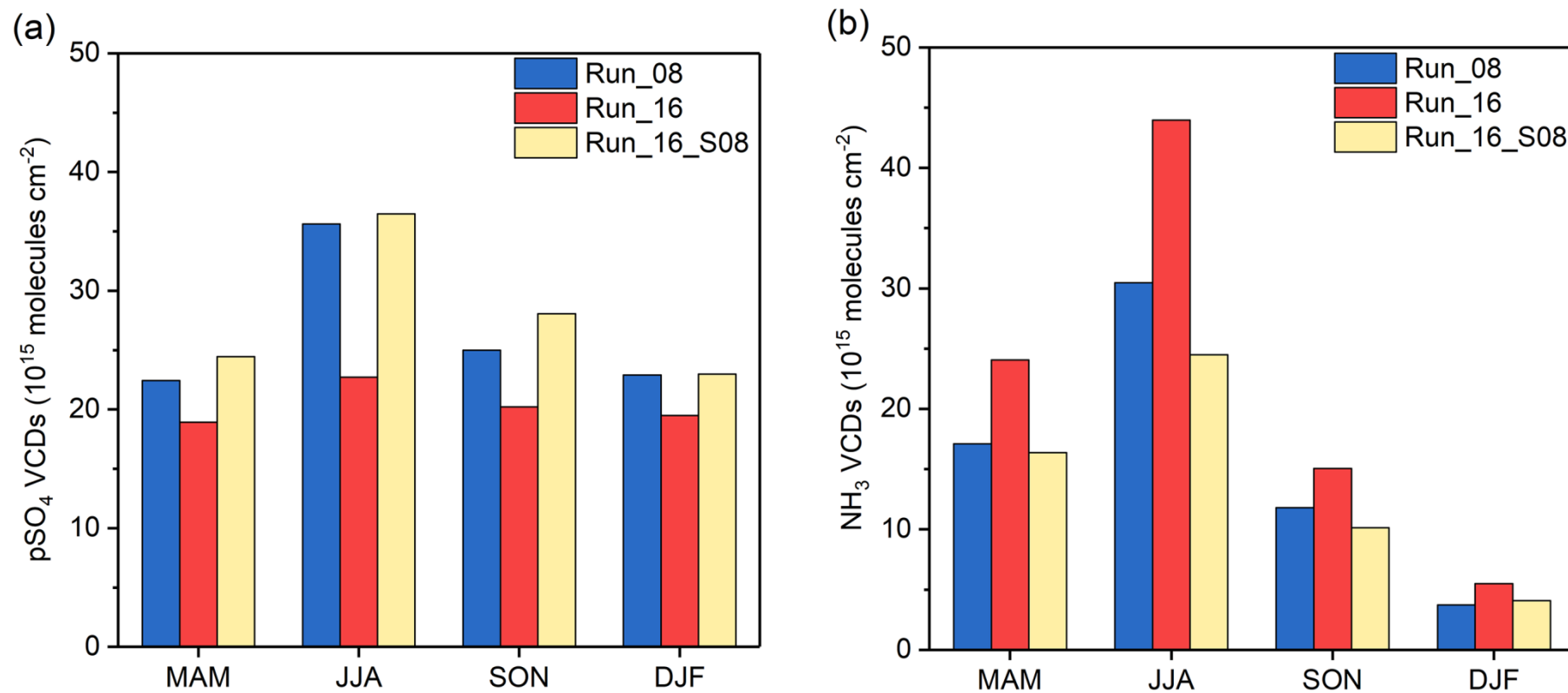


Figure 6. Seasonal patterns of simulated SO_4^{2-} (a) and NH_3 (b) columns for Run_08, Run_16, and Run_16_S08 (the simulation for 2016 with SO_2 emissions in 2008) cases. MAM, JJA, SON and DJF represent spring (March, April and May), summer (June, July and August), autumn (September, October and November) and winter (December, January and February) months.