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 (NOx, 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 SO_2 reduction on the NH_3 increase, we provided quantitative results of other mechanisms in the revised manuscript, as following.

- NH_3 emissions. Our inventory has demonstrated that NH_3 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 NH_3 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 NH_3 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 NH_3 column concentrations of about 3%. So it cannot be responsible for the significant increase of NH_3.

- 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 NH_3). The change in meteorological fields between the Run_2012 and Run_12_M16 led to a decrease in NH_3 concentrations of ~3% over the North China Plain.

The above mechanisms totally decreased the NH_3 column concentrations by about 13%. So we conclude that the SO_2 emission reductions is responsible for the increasing trend of NH_3. 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 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 during 2011−2016 over the North China Plain (Fig. 1b). The overall trend of NH_3 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 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."

(Page 10, Line5-10) "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 3% in annual mean NH_3 concentrations relative to the Run_12 (Fig. S6)."

(Page 10, Line 20-23) "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."

(Page 10, Line 27-30) "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%."

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 NOx emission (Fig. S4). The in situ measurements in Beijing indicated that the NO3- concentrations fluctuated during 2013-2016. It implied that the NOx 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 NOx, if any conclusions were to be drawn about how NOx 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 NH_3 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 NH_3 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 NH_3 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 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 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."

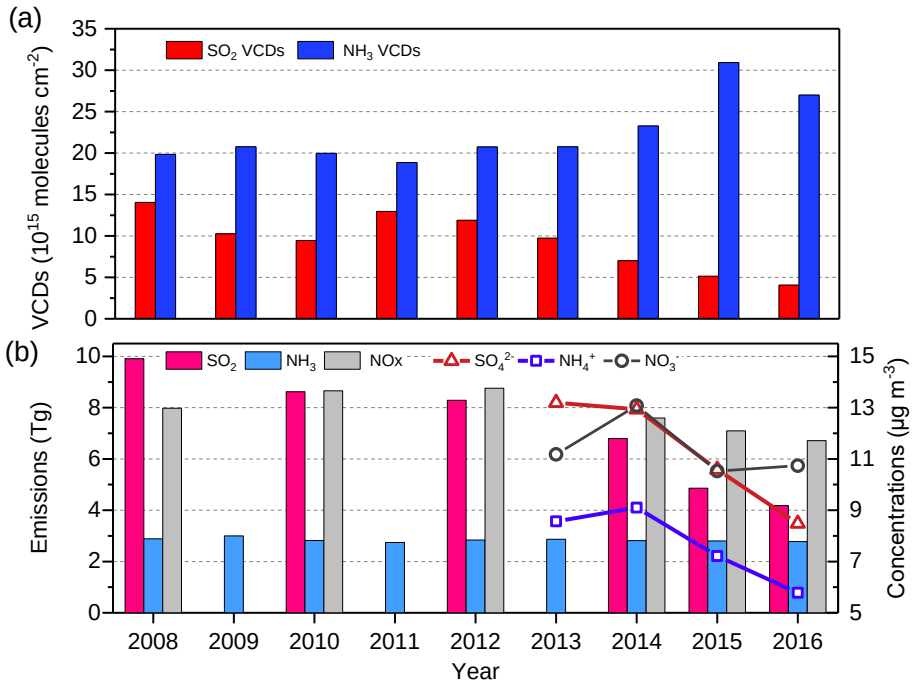

Figure 1. (a) Inter-annual trends of SO_2 and NH_3 VCDs averaged over North China Plain from 2008 to 2016. (b) Inter-annual trends of emissions of SO_2 NH_3, and NO_x in the North China Plain from 2008 to 2016, and annual mean concentrations of $PM_{2.5}$ sulfate, ammonium, and nitrate

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

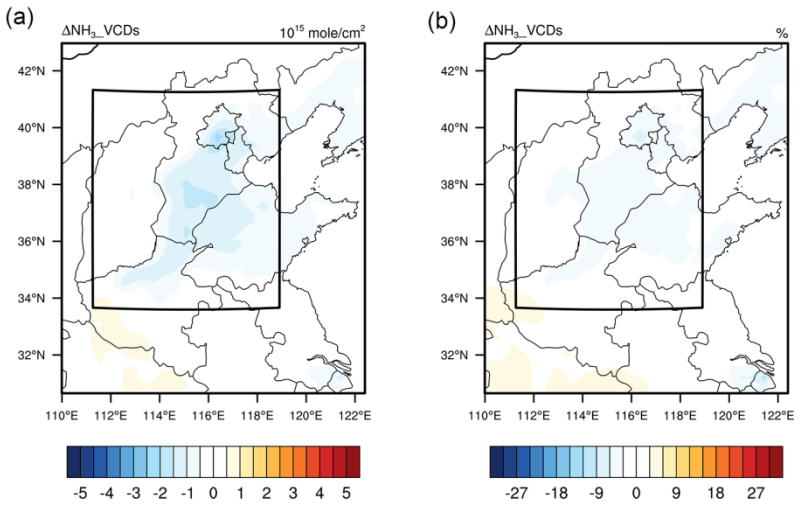

Figure S5. Absolute (a) and percent (b) changes in the simulated column concentrations of NH_3 between the Run_16 and Run_16_N08 (NO_x emissions in 2008). Negative values denote decreases due to the change in NO_x emissions in the Run_16_N08. The black box represents the major area of interest in this 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 20 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 NH_3 columns in the period of 2012−2016). The resulting column concentration of NH_3 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 NH_3 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 SO_2 in China in the trend of NH_3. 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 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."

(Page 10, Line 12-17) "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 (Warner et al., 2017; Saylor et al., 2015; Ferm and Hellstern, 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."

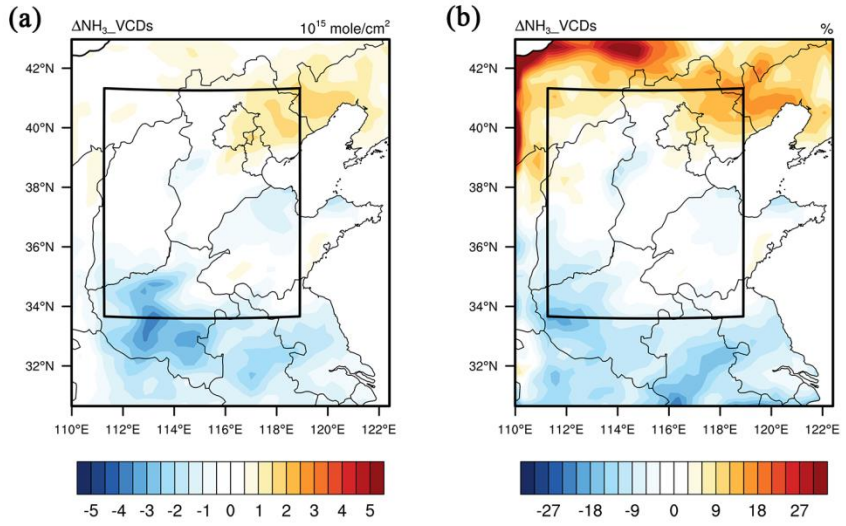

Figure S6. Absolute (a) and percent (b) changes in the simulated column concentrations of NH_3 between the Run_12 and Run_12_16M. Negative values denote decreases due to the change in meteorological fields in the Run_12_16M. The black box represents the major area of interest in this study.

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 (NO_3^-) 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 NH_3.
R: (Page 10, Line 1) Overall, the limited reduction in NO_x emissions cannot be responsible for the increased NH_3 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 NH_3 column concentrations disappeared
R: (Page 7, Line 19) the increasing trend of NH_3 column concentrations

was not observed

B: we found that the rapid SO_2 emission reduction of 50% from 2012 to 2016 could result in a 55% increase in the NH_3 columns
R: (Page 8, Line 13) 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

B: The seasonal variations in SO_4^{2-} decreases and NH_3 increases were almost consistent
R: (Page 8, Line 32) The seasonal variations in SO_4^{2-} decreases and NH_3 increases were consistent

B: which could make the response of SO_4^{2-} concentrations to SO_2 emission reductions more sensitive
R: (Page 9, Line 10) which makes the response of SO_4^{2-} concentrations to SO_2 emission reductions more sensitive

B: It implied that the NO_x emission reduction could not be responsible for the increase in NH_3
R: (Page 10, Line 1-2) the limited reduction in NO_x emissions cannot be responsible for the increased NH_3 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 SO_2 emission reductions (60%) from 2008 to 2016 were responsible for almost the entire NH_3 increases
R: (Page 10, Line 30) Our work strongly indicates that the rapid SO_2 emission reductions (60%) from 2008 to 2016 were responsible for the NH_3 increase

B: a continued increase in NH_3 concentrations is anticipated if NH_3 emissions are not well-regulated
R: (Page 11, Line 12) a continued increase in NH_3 concentrations is anticipated if NH_3 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 NH_3 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 NH_3."

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, NH_3 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 NH3in 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 NH_3 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 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 3, Line 13-14) "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."

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 SO_2 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 NH_3 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 NH_3 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 NH_3 VCDs from the simulations by integrating NH_3 molecular concentrations from the surface level to top troposphere. The results agreed well with the observed NH_3 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 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."

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

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

Revisions:

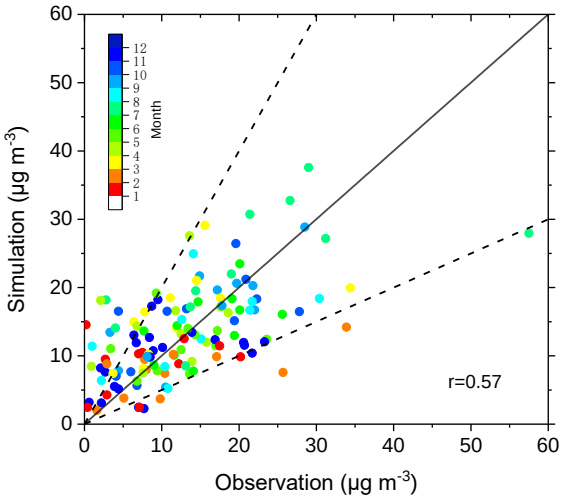

Figure 2. Comparison of modelled gaseous NH_3 concentrations with corresponding monthly measurements of NH_3 from September 2015 to August 2016. The 1:2 and 2:1 dashed lines are shown for reference and the Pearson correlation coefficient is shown inset.

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