Response to comments on "Atmospheric NH_3 in urban Beijing: long-term variations and implications for secondary inorganic aerosol control"

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This study presents 11-year NH3 data in an urban environment and explored the long-term trends of NH3, the influence meteorological variables played on NH3, and the role NH3 played on secondary inorganic aerosol formation. While the data presented here are useful, the analysis can be improved. More importantly, the discuss and presenting quality needs significant improvement. More specific comments are provided below.

---- We are very grateful for your critical comments and thoughtful suggestions. Based on your comments, we have made detailed revisions to the manuscript.

Abstract:

Abstract needs a significant revision to better summarize major findings. Too many general statements, but lack of specific results.

----- We have revised the abstract, and the specific modifications are as follows:

Line 13, better replace "The total average" with "The 11-year average".

----- Thank you for your suggestion. We have updated the original sentence to "The 11-year average NH_3 mixing ratio was 26.9 ± 19.3 ppb".

Lines 14-15: Why not show the total percentage increase between 2009-2017 and percentage decrease between 2017-2020? This way can better reflect the two contrasting trends during the 11-year period.

----- We added quantitative descriptions to the sentence. The original statement has been amended to "NH_3 mixing ratios initially increased and peaked in 2017 but subsequently decreased. From 2009 to 2017, NH_3 mixing ratios increased by 50%, while there was a decrease of 49% in 2020 compared to 2017."

Line 17: This sentence does not provide any useful information. Most pollutants would have seasonal and diurnal variations. You need to specify what kind of seasonal and diurnal patterns.

----- We agree that the sentence was somewhat awkward, and have removed it in the revised version.

Liens 18-19: the non-linear relation is well known in literature. You need to show some specific results. Same comment for several other sentences in this section.

----- We have added specific results to the sentences: Thermodynamic modeling revealed the nonlinear response of SIAs to NH_3, with increased sensitivity to NH_3 when its concentration decreases by 60%. Although reducing NH_3 concentrations can improve air quality during winter, controlling acid gas concentrations has a greater effect than controlling NH_3 concentrations on reducing SIA concentrations, until NH_3 and acidic gas concentrations are reduced below 80% of their current levels. Nevertheless, the increase in the proportion of ammonium salts in SIAs during the observation period indicates that future control measures for NH_3 concentrations may need to be prioritized in Beijing.

Introduction

This section also needs some major rewriting. The topic of this research is on urban NH3 and its long-term trends. Thus, the Induction should cover these areas: (i) brief discussion on the important role NH3 played in various research areas (this is covered in the current Introduction, but could be simplified since such materials are rich in literature); (2) brief discussion on the major sources of NH3 in urban environments and major debate on this topic in literature, noting that existing studies have different opinion on the major sources (this is not mentioned at all in the current Introduction and should be added in the revision. Such materials may help explain the trends in Section 3.1); and (3) brief discussion on the studies of NH3 long-term trends, first worldwide (see Yao and Zhang. 2009, ACS Omega, 4, 22133-22142, as an example), then China, then Beijing. Then point out the knowledge gaps based on the summary of the knowledge presented above. Finally present the goals of this study.

----- Thank you for your suggestions. We have simplified the discussion on the environmental impact of NH_3, expanded the discussion on urban NH_3 sources, and re-summarized the studies on long-term NH_3 trends. Below is the revised introduction section:

Excessive input of anthropogenic nitrogen into the environment can directly harm ecosystems and influence climate change. As the most abundant alkaline trace gas in the atmosphere, NH_3 interacts with the oxidized products of atmospheric acidic gases to form secondary aerosols, which considerably affect the radiative balance of the atmosphere and ai. Over the years, China has been committed to controlling air pollution and has effectively managed the emissions of primary pollutants such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x). However, particulate matter 2.5 ($PM_{2.5}$, particulate matter with a diameter less than 2.5 μm in size) pollution is still a severe problem. Research on controlling SO_2 and NO_x emissions indicate that controlling NH_3 emissions is the most economically effective way for reducing $PM_{2.5}$. However, the effectiveness of NH_3 reduction varies by region, and there is still debate regarding the efficacy of NH_3 reduction measures.

Anthropogenic sources are the primary contributors to atmospheric NH_3 emissions. In China, agricultural sources dominate, accounting for approximately 80% of total emissions. However, the contribution of non-agricultural sources in urban areas is considered significant. Studies indicate that over 30% of NH_3 emissions observed in urban areas can be attributed to traffic. Nevertheless, some research suggests that biogenic sources (primarily green spaces) predominate in urban and account for approximately 60% of emissions, while the contribution from traffic sources is negligible. The complexity of urban NH_3 sources results in intricate variability in its atmospheric characteristics.

Long-term observations are important for analyzing the environmental impacts and control strategies of atmospheric NH_3. In Europe, North America and Asia, countries have conducted studies on NH_3 variations over a period of 5 years or more. In most of these regions, NH_3 concentrations have either remained stable or have exhibited an increasing trend. Satellite observations detected rising global atmospheric NH_3 concentrations, influenced by reductions in acidic gas emissions, temperature increases, and the rising use of chemical fertilizers. In China, according to the monitoring results from the Nationwide Nitrogen Deposition Monitoring Network (NNDMN), NH_3 concentrations at 12 urban sites and 43 rural sites increased by approximately 80% from 2011 to 2018. Satellite data analysis by Dong et al. (2023) indicated a significant increase (~32%) in NH_3 vertical column densities in China from 2008 to 2019. In the North China Plain, a hotspot for global NH_3 emissions, Luo et al. (2020) found a rapid increase in urban NH_3 concentrations from 2011 to 2018. Wen et al. (2024) found a 26% decrease in Beijing NH_3 concentrations from August 2005 to August 2020, and a 50% increase from January 2005 to January 2024. Currently, long-term ground-based observations of atmospheric NH_3 at high temporal resolution are relatively rare in China, and the contrasting trends between NH_3 emissions, satellite and in-situ measured concentrations in urban areas have not been fully explored

The present study examined high temporal resolution NH_3 observations at the surface in urban Beijing from 2009 to 2020. Using data from emission inventories, satellite observations, meteorological elements, concentrations of various types of atmospheric pollutants, and particle ion composition, the present study aims to obtain the characteristics of long-term variations, influencing factors, and the contributions of NH_3 to particle formation in the atmosphere of Beijing. Analyzing long-term NH_3 observations can help to understand how changes in NH_3 concentrations have affected atmospheric pollution in the past. This knowledge is crucial for predicting future atmospheric pollution and formulating effective environmental policies. Additionally, it provides a scientific basis and reference for developing future NH_3 control strategies.

Materials and methods

Line 79-80: need to specify the height above the ground of the two measurement sites (after the third floor and 14th floor).

----- We added descriptions of the elevations: The ground-floor elevations of both buildings are 56 m, and the observation heights above the ground are 10 m on the 3rd floor and 56 m on the 14th floor.

Line 90: change “subjected” to “subject”

----- Done.

Line 126: change “2.1 Methods” to “2.2 Data analysis methods”. You already used Methods for Section 2, here you need to use a more specific sub-section title.

----- This has been done as suggested.

Line 134-135: This statement is not accurate. EEMD has also been used in air-quality trend analysis studies in more recent years (for example: Yao and Zhang, 2016. ACP 16, 11465-11475. Wang et al., 2022. Environment International, 159, 107031. Wang and Zhang, 2023, Environmental Pollution, 333, 122079). You need to cite more relevant studies instead of not-so-relevant studies.

----- We have rewritten this sentence according to your suggestion: Currently, EEMD has been used in studies on air-quality trend analysis (Yao and Zhang, 2016; Fu et al., 2020; Wang et al., 2022; Wang and Zhang, 2023).

3 Results and discussion

This section needs a better organization and more in-depth analysis.

A large portion of Section 3.1 is used to compare the NH3 data with literature, and the discussions on the trends and associated causes are limited. While comparing to literature data is needed, it should not be the main focus of the discussion. Besides, from Lines 190-191: if this statement is true, then it means that the uncertainties in the obtained trends (due to changing location and measurement height) are larger than the actual trends, making your discuss on trends meaningless. I would recommend reorganizing Section 3.1 in this order: First present the trends from the monitored data using a quantitative statement, e.g., either using annual decreasing/increasing rate, or percentage decrease/increase during a period. Split the 11-year period into two periods since contrasting trends were observed during the whole measurement period. Use quantitative statements wherever possible and show the significance level of the trends. Then present the trends generated from the satellite data using the same rules as described above. Then discuss the similarities and differences between these two sets of trends, only at this stage you need to cite literature data to support your results and/or provide explanations on the causes of the differences between different data sets.

----- Thank you for your constructive comments and recommendations, we have reorganized Section 3.1: From June 2009 to July 2020, the hourly average mixing ratio of atmospheric NH_3 in Beijing was 26.9 ± 19.3 ppb (median, 23.5 ppb). Table S1 summarizes results from various NH_3 monitoring studies conducted in urban areas. The results of the present study are basically consistent with the annual NH_3 mixing ratio averages that were observed in urban Beijing by other researchers through optical instrument. The primary reasons for this phenomenon are the frequent agricultural activities and the presence of highly alkaline soils in the North China Plain, where Beijing is located. As a densely populated country with intensive agriculture activities, China contains several areas that are major global hotspots for the atmospheric NH_3 concentration. The monitoring results of the present study indicate that the overall NH_3 mixing ratio in Beijing is lower than that in Delhi but considerably higher than those in other developed cities such as New York, Toronto, and Rome. Even within China, the NH_3 mixing ratio in Beijing is higher relative to that in Shanghai, which is also a megacity (i.e., the NH_3 mixing ratio in Shanghai is less than one-third of that in Beijing), and only a few cities in North China have mixing ratios comparable to that in Beijing. The primary reasons for this phenomenon are the frequent agricultural activities and the presence of highly alkaline soils in the North China Plain, where Beijing is located.

Due to significant data gaps from January 2013 to June 2013 and from May 2017 to August 2017, the period from 2009 to 2020 was divided into three segments for linear regression analysis (Figure S7). From June 2009 to January 2013, the observed hourly average atmospheric NH_3 mixing ratio showed a decreasing trend ($R = -0.23$, $p < 0.05$, slope = -0.01); from June 2013 to May 2017, the NH_3 mixing ratio increased ($R = 0.04$, $p < 0.05$, slope = 0.22×10-2); and from September 2017 to July 2020, the NH_3 concentration exhibited a decreasing trend again ($R = -0.03$, $p < 0.05$, slope = -1.42×10^{-3}). Similar to in situ observations, the satellite observations of NH_3 concentration showed a decreasing trend from June 2009 to January 2013 ($R = -0.19$, $p < 0.05$, slope = -3.88×10^{-4}) and an increasing trend from June 2013 to May 2017 ($R = 0.12$, $p < 0.05$, slope = 3.65×10^{-4}), but differed from in situ atmospheric NH_3 trends as it continued to rise from September 2017 to July 2020 ($R = 0.23$, $p < 0.05$, slope = 1.17×10^{-3}).

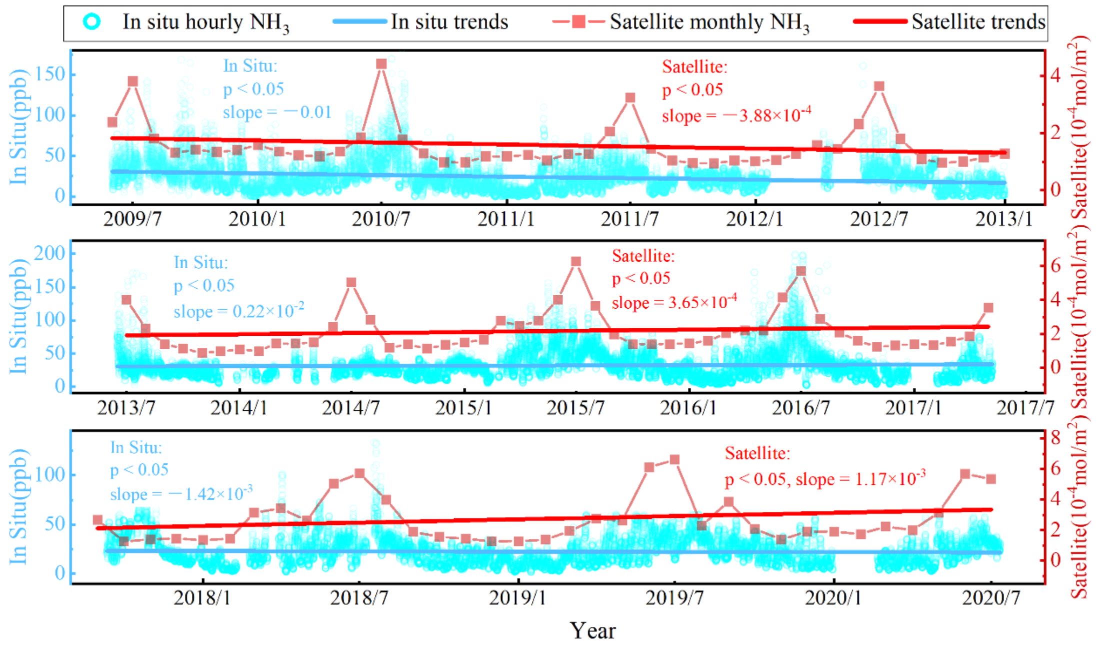

Figure S7. Trends in atmospheric NH_3 concentrations observed in situ and by satellite from June 2009 to January 2013, from June 2013 to May 2017 and from September 2017 to July 2020.

To further analyze the long-term trends of the atmospheric NH_3 concentration, the present study referred to the findings of Vu et al. (2019) and used meteorological factors to construct a random forest model for imputing missing values. The computed time series for the atmospheric NH_3 concentration is presented in Figure S8. The complete dataset obtained through EEMD was used to characterize the changes in atmospheric NH_3 concentrations in Beijing (Figure 1). The NH_3 mixing ratio initially exhibited a slight decrease but started to increase in 2012 and peaked in 2017, subsequently declining. From 2009 to 2017, the NH_3 mixing ratio increased by 50%, but by 2020, the NH_3 mixing ratio had decreased by 49% from its peak in 2017. A comparison of monthly average NH_3 concentrations obtained from satellite observations revealed that prior to 2018, the trend for the surface NH_3 mixing ratio was similar to that observed by satellites, exhibiting a decline followed by an increase in atmospheric NH_3 concentrations. However, starting in 2018, these two trends diverged, with satellite observations indicating a continued increase in NH_3 concentrations, while the surface NH_3 mixing ratio exhibited a decreasing trend.

The monitoring results of this study were compared with NH_3 monthly concentrations observed by NNDMN in Beijing from April 2011 to December 201 and from January 2005 to August 2020 (Figure

S9). From April 2011 to December 2015, both the NH_3 mixing ratio observed in this study ($R = 0.27$, $p < 0.05$) and the satellite-observed concentrations ($R = 0.28$, $p < 0.05$) exhibited increasing trends, while the NNDMN station did not show a significant trend ($R = 0.16$, $p > 0.05$). The NNDMN station observations from January 2009 to August 2020 were significantly correlated with this study's observations ($R_{Aug} = 0.66$, $p < 0.05$; $R_{Jan} = 0.65$, $p < 0.05$), but neither the present study's observations nor the NNDMN observations were significantly correlated with satellite-observed NH_3 concentrations. Satellite observations showed a strong correlation between NH_3 concentrations in the Beijing urban area and the Beijing-Tianjin-Hebei region (Figure S3). However, measurements by Zhang et al. (2020) at five stations in Beijing indicated that four stations had lower NH_3 concentrations in 2017 (winter) than in 2020 (winter + spring), while one station had higher concentrations in 2017 than in 2020, indicating variability in observation results even within the same city. Due to the short atmospheric lifetime, low transport altitude, high dry deposition rate, limited transport distance, and abundance of atmospheric NH_3, its complex temporal and spatial characteristics contribute to the complexity of NH_3 variations. Satellite observations are limited by the observation height and spatial resolution, which may mask variations in local surface NH_3 concentrations. Additionally, differences between the present study's observations and satellite observations may also be due to changes in the monitoring location and observation height in September 2017. However, tower observations conducted by the Institute of Atmospheric Physics, Chinese Academy of Sciences (6.7 km from the present study's site) in the urban area showed only slight variations within a 300 m altitude range. Therefore, the change in observation altitude may have had a limited impact on the change in NH_3 mixing ratio trends after 2017.

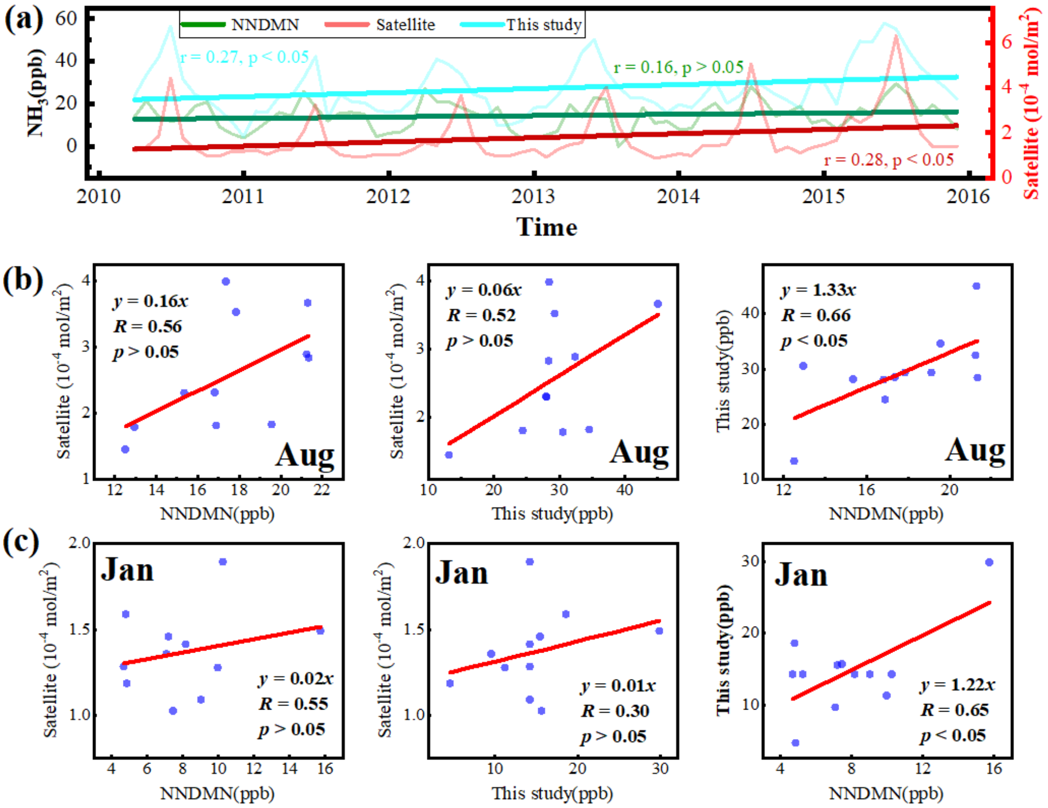

Figure S9. (a) Atmospheric NH_3 monthly average concentrations observed in this study, NNDMN Beijing station, and by satellite in the Beijing urban area and their trends from April 2011 to December 2015. (b) Correlations between NH_3 concentrations observed in this study, NNDMN, and by satellite from January 2009 to January 2020. (c) Correlations between NH_3 concentrations observed in this study, NNDMN, and by satellite from January 2009 to August 2020.

In general, long-term trends are mainly caused by emission changes and to a much less degree by meteorological factors. After discussing the trends in Section 3.1, you can then discuss driving factors of these trends in section 3.2, first focus on emission and then on meteorology. Emission inventory related discussion in Section 3.1 can be moved to section 3.2 to support the discussion. See Lin et al. (2022 ACP, 22, 16073-16090) to get more ideas related to this comment.

----- We have revised the title of section 3.2 to “Influences on variation characteristics of NH_3” and have added a discussion on the impact of emissions at the beginning of this section. The specific additions are as follows:

NH_3 emissions directly affect the variations in atmospheric NH_3 concentrations. The emission inventory data obtained (Figure 1) indicate that from 2009 to 2014, the total NH_3 emissions in Beijing remained stable, peaking in 2012. After 2014, NH_3 emissions in Beijing rapidly decreased, declining by 25% from 2012 to 2017. However, during this period of declining emissions, the NH_3 mixing ratio in Beijing exhibited an increasing trend. Similar phenomena have been reported by studies conducted outside of China. For instance, in Scotland, NH_3 emissions decreased by approximately 15% from 1990 to 2003, whereas atmospheric NH_3 concentrations increased. In Hungary, NH_3 emissions were estimated to have decreased by 50% from 1983 to 1993; however, NH_3 concentrations exhibited a slight upward trend during this monitoring period. A possible reason for these differences between NH_3 emissions and concentrations could be the significant reduction in the concentrations of SO_2 and NO_x, which reduced the amount of atmospheric NH_3 neutralized by acid gases. Over the past 2 decades, Beijing has implemented a series of strict measures to control air pollution and has achieved considerable success. The concentrations of SO_2, NO_2, CO, PM_{10}, and $PM_{2.5}$ in Beijing all exhibited decreasing trends; in particular, the concentration of SO_2 decreased by 88% from 2009 to 2020 (Figure 2).

To discuss the influence of chemical loss on the annual increase in NH_3 concentrations, the present study referred to research by Yao et al. (2019), assuming that NH_4^+ is uniformly distributed in the urban area of Beijing and that changes in NH_4^+ concentrations directly affect atmospheric NH_3 concentrations on a 1:1 basis. By calculating the change in NH_4^+ concentration relative to the baseline year, we adjust the atmospheric NH_3 concentrations. The present study set 2009 as the baseline year, using the annual average NH_4^+ concentration observed by Cheng (2021) in the urban area of Beijing to calculate the adjusted NH_3 concentrations from 2009 to 2017. The calculations show (Figure S10) that overall, the original NH_3 concentration in 2017 was 50% higher than in 2009, and the adjusted NH_3 concentration was 46% higher. Therefore, changes in chemical losses have a limited impact on the increased trend of NH_3 concentrations, and the discrepancy between NH_3 concentrations and emission trends may be due to imperfections in the emission inventory.

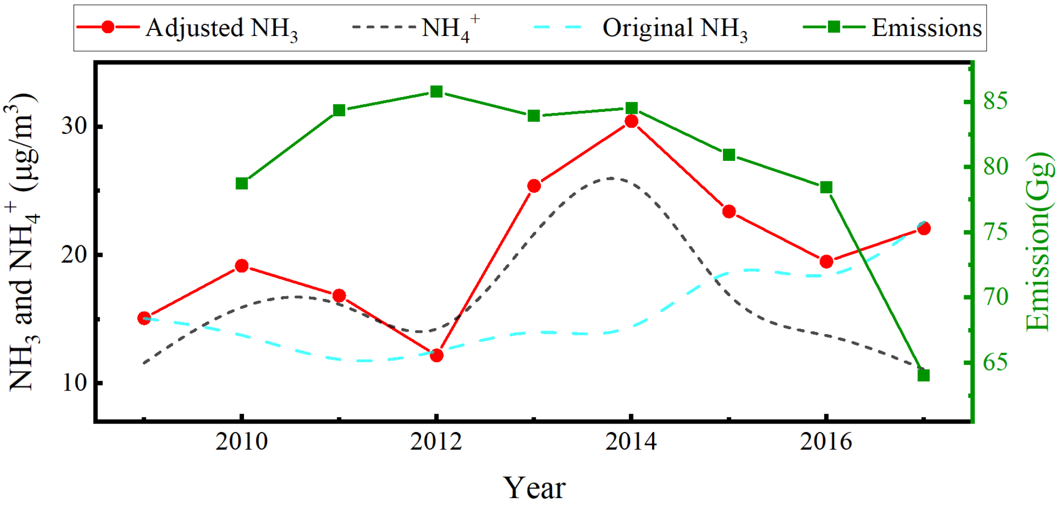

Figure S10. Annual averages of atmospheric NH_3, NH_4^+ in $PM_{2.5}$, and adjusted atmospheric NH_3 and NH_3 emissions in Beijing urban area from 2010 to 2017

Section 3.3 also has too many introductory materials in the first two paragraphs. Follow this rule, in the Results section, present your own results first and use literature data to support your discussion, instead of summarizing literature results separately (which really belong to Introduction section).

----- Thank you for your suggestion. We have revised Section 3.3, removing the introductory material and reorganizing the first paragraph: The present study investigates the role of atmospheric NH_3 in the formation of SIAs in Beijing by analyzing the relationship between NH_3 and SNA concentrations during the observation period. According to the study of Wei et al. (2023) conducted between 2013 and 2020, the SNA concentrations in Beijing exhibited a significant downward trend. However, the proportion of SNA in $PM_{2.5}$ (mass concentration) did not change substantially during this period. Table S2 lists the proportions of various SNA components in $PM_{2.5}$ (mass concentration) recorded in urban areas of Beijing for the years 2009, 2016, 2018, and 2019. In the summer and autumn of 2009, SO_4^{2-} accounted for more than 50% of SNA content, considerably exceeding the concentrations of NO_3^- and NH_4^+. However, by 2016, except for the summer season when SO_4^{2-} was still the predominant component, NO_3^- became the dominant component of the SNA mass concentration. Over time, the proportion of NH_4^+ in the SNA mass concentration increased across multiple seasons. Wen et al. (2024) and Cheng (2021) have also observed this phenomenon in urban Beijing. These findings indicate the necessity of controlling NH_3 and NO_x concentrations to mitigate future $PM_{2.5}$ pollution.

Conclusions

Line 353: “3” should be “4”. Avoid such simple typos.

----- Thanks for your careful checks, we are sorry for our carelessness, the typo has been corrected.

Lines 354-356: Preneet the two different trends (in two periods) using a quantitative statement.

----- We have revised the original text to read: Over these 11 years, the NH_3 concentration in urban Beijing initially increased by 50% in the first 8 years but subsequently decreased by 49% in the following 3 years.

Line 356: have you tried to identify the actual causes of such discrepancies between NH3 concentration and NH3 emission? See possible causes on the same topic in Yao and Zhang (2009, ACS Omega, 4, 22133-22142).

----- Thank you very much for your suggestions. We have added a discussion on potential causes in Section 3.2, the details of which are displayed in the comments above.