Response to Referee #1:

We thank the reviewer for the careful reading of our manuscript and helpful comments. We have revised the manuscript following the suggestion, as described below.

General comments:

This study investigates fertilizer-induced soil NO_x emissions and their contributions to atmospheric NO_2, as well as quantifies the impacts on regional air quality during March over North China. Unlike previous studies that focused on summertime, this work examines the early spring fertilizer application season, providing new insights into the significance of soil NO_x on regional particulate matter (PM) and ozone concentrations. These insights are particularly important as fossil fuel combustion-related NO_x emissions decline, making other sources, such as soil emissions, increasingly important.

The authors first analyze two decades of satellite-retrieved atmospheric NO_2 data over North China and identify recurring sub-peaks in March. They link these sub-peaks to fertilizer application activities and validate this hypothesis through air quality model simulations using the BDSNP mechanism for NO emission estimations. The study further assesses the impacts of fertilizer-induced NO_x emissions on PM and ozone levels, highlighting the importance of this often-overlooked source in the context of air quality management.

Overall, this paper provides evidence to support its conclusions and presents a relatively comprehensive analysis of the influence of soil NO_x emissions on air quality. The manuscript is well-organized and clear. However, there are some concerns regarding the uncertainties associated with BDSNP mechanisms in the WRF-Chem model, which may introduce some biases into the analysis. These uncertainties are not sufficiently discussed. Additionally, some details are missing in the method part, and certain discussions are insufficient, along with several technical issues that need to be addressed.

I recommend accepting this paper once these concerns have been addressed.

Response: We thank the reviewer for the constructive suggestions on our manuscript. We have carefully read the comments, addressed the comments point by point, and revised the manuscript accordingly. Specifically, we have included more discussion on the uncertainties associated with the BDSNP mechanism in the WRF-Chem model.

Specific comments:

1. Line 77: I recommend defining the study area as “North China Plain (NCP)” rather than “North China” for accuracy and consistency with the geographical locations shown in Figure 1 and other similar studies.

Response: We have changed “*North China*” to “*the North China Plain*” in the title and throughout the manuscript for accuracy and consistency with the geographical locations in Figure 1 and similar studies.

2. Please cite recent key studies on soil NO_x emissions and their air quality impacts in the NCP or China in the Introduction, such as
   - Lu, Xiao, et al. “The underappreciated role of agricultural soil nitrogen oxide emissions in ozone pollution regulation in North China.” *Nature Communications* 12.1 (2021): 5021.
   - Huang, Ling, et al. “Insights into soil NO emissions and the contribution to surface ozone formation in China.” *Atmospheric Chemistry and Physics* 23 (2023): 14919-14932.

Response: We have included the recent key studies in the Introduction in Lines 89-90: “*The emissions significantly increase ambient NO_x levels and enhance O_3 formation in summer*

(Huang et al., 2023; Lu et al., 2021; Wang et al., 2022)." and the References have been updated accordingly.

3. Line 130: Please specify the unit for the variables in the formula.

Response: We have specified the units for the variables in the BDSNP scheme in Lines 138-141: "*The scheme comprehensively considers various factors, including available soil nitrogen content (N_{avail}, ng N m^{-2}) from the fertilizer application and nitrogen deposition, in which the soil NO_x emission (E_{soil}, ng N m^{-2} s^{-1}) is a function of N_{avail}, climate, and edaphic conditions ...*", in Lines 143-146: "*where N_{avail} is available soil nitrogen mass, and A'_{biome} (ng N m^{-2} s^{-1}) represents the biome-dependent emission factor. $f(T)$ (dimensionless) and $g(\theta)$ (dimensionless) are parameters regulated by soil temperature and moisture, respectively. $P(l_{dry})$ (dimensionless) denotes the pulsed soil emission from wetting of dry soils.*", in Lines 149-150: "*where T ($0 \leq T \leq 30°C$) is soil temperature and θ ($0 \leq \theta \leq 1$, dimensionless) is water-filled pore space ...*", and in Lines 156-157: "*where l_{dry} (hours) represents the length of the antecedent dry period, and c ($c = 0.068\ h^{-1}$) is a constant rate denoting the rise/fall time of the pulse.*"

4. Line 159-164: Please add details of the OMI-NO_2 and IASI-NH_3 products, such as the hosting satellites, product versions, orbit types, and local overpass times.

Response: We have added details of the OMI-NO_2 and IASI-NH_3 products in Lines 184-201: "*Satellite-derived tropospheric NO_2 columns are from OMI hosted by the Aura satellite that is launched by the National Aeronautics and Space Administration (NASA). The Level-3 product, where pixel level data of good quality are binned and "averaged" into 0.25°×0.25° grids, was retrieved and analyzed in the present study. The dataset is for all atmospheric conditions, and for sky conditions with cloud fraction less than 30% (https://cmr.earthdata.nasa.gov/search/concepts/C1266136111-GES_DISC.html). The Level-*

2 product of NH_3 columns is employed, which is from the Space Administration and the Infrared Atmospheric Sounding Interferometer (IASI) hosted on the MetOp series of satellites. Both of the satellites operate in a sun-synchronous polar orbit and have a local overpass time of around 13:45 (local time, LT) (once a day) and 9:30 am / 9:30 pm (twice a day), respectively, in North China. The tropospheric column of NO_2 screened for cloud fraction less than 30% global daily composite, has a spatial resolution of 13 km × 24 km, with a temporal coverage of 2005-2022 (Lamsal et al., 2021), and the trajectory NH_3 from IASI is integrated into each 0.125° × 0.125° grid cell with the average during 2007-2021 (Clarisse et al., 2023). Low-quality satellite data are filtered out due to the interference of clouds. To cover all the domain (Figure 1), the data used in this study are merged into seven-day mean datasets of NO_2 and NH_3 columns with a non-overlapping 7-day window. The data are interpolated into the model grids using bilinear interpolation."

5. Line 164: Please clarify the interpolation method to map the IASI and OMI data to your study region and resolutions. For example, is it area-weighted or error-weighted?

Response: We have clarified the method in Lines 200-201: "*The data are interpolated into the model grids using bilinear interpolation.*"

6. Line 169: Please include a map showing the spatial distribution of the 141 observation sites.

Response: We have included a map showing the spatial distribution of the 141 observational sites in Figure S1 in the revised manuscript. This figure is cited in the text in Lines 202-203: "*Ambient surface NO_2, O_3, and $PM_{2.5}$ mass concentrations at 141 sites in the NCP are from the China National Environmental Monitoring Centre (CNEMC, Figure S1).*"

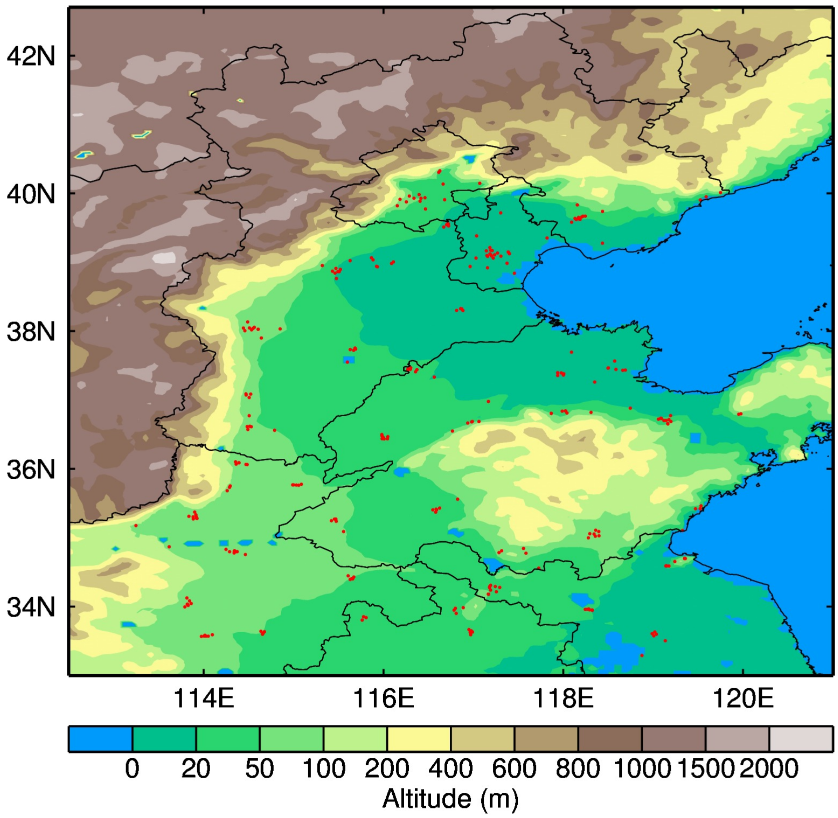

Figure S1. Map showing the locations of the 141 monitoring stations for air quality (red dots) over the North China Plain. Data are from the CNEMC. The color shading represents the topography of this region, with water areas depicted in blue.

7. Please clarify how you calculate the seven-day means. Is it a moving averaging?

Response: The seven-day average of the data, rather than moving average, is calculated in this study and we have clarified this issue in Lines 199-200: "*... the data used in this study are merged into seven-day mean datasets of NO_2 and NH_3 columns with a non-overlapping 7-day window.*"

8. I recommend adding a figure (possibly in the Supplement) to show the full annual cycle of NO_2 columns, to better illustrate the seasonal variation and highlight the sub-peak in March compared to other months, rather than showing only March in the main text and June and October in the Supplement.

Response: Actually, Figure 2a shows the full annual cycle of NO_2 columns from 2005 to 2022. We have highlighted the sub-peaks in March of each year with a gray bar. Because we focus on the spring sub-peaks in the present study, we only highlight the ones in March and leave those in June and October in the Supplement. We have also analyzed the monthly variation of NO_2 columns during the years, but the sub-peaks in March is overwhelmed by the signals in the non-sub-peak days in March. Therefore, we use the seven-day average of the NO_2 columns to present the annual cycle.

9. Please clarify whether the NO_2 column density refers to the total column density or near-surface levels.

Response: The NO_2 column density is tropospheric only according to the OMI product. We have specified this issue in Line 184: "*Satellite-derived tropospheric NO_2 columns are from OMI ...*"

10. Please revise the title of Figure 2 to better reflect its content, which includes NO_2 columns in March and annual emission inventories.

Response: We have revised the title of Figure 2 to better reflect its content in Lines 231-232: "*Figure 2. NO_2 column pulses in March and NO_x emissions from fossil fuel and soil sources over the NCP. ...*"

11. Line 207: Please clarify how HTAP calculates the soil NO_x emissions and how this differs from the BDSNP mechanism.

Response: We have clarified the HTAP soil NO_x emissions and how it differs from the BDSNP mechanism in Lines 174-177: "*Agricultural emissions are involved in the latest HTAP v3 inventory, which includes soil NO_x emissions (Crippa et al., 2023). Nevertheless, the soil* *emissions in this inventory are calculated using traditional "bottom-up" method (Kurokawa and Ohara, 2020), rather than estimated by a process-based emission module.*" The References section has been updated accordingly.

12. Figure S3 & S4: Please spell out "VCD".

Response: We have revised the y-axis titles in Figures S4 and S5 (Figures S3 and S4 in the original version) as "*NH_3 column (μg m^{-3})*" to make it in line with Figures 2, S2, and S3 in the latest version.

13. Line 241: Missing citations?

Response: We have corrected this citation as "*(Tang et al., 2020)*" in Line 299.

14. Line 261: I recommend adding a line on Figure 3b to show the differences between the simulations with and without soil NO_x emissions to emphasize their impact on the sub-peaks of atmospheric NO_2.

Response: We have revised the figure and added a line to show the difference between the simulations with and without soil NO_x emissions. The figure caption has been updated as: "… *The gray histogram represents NO_2 column observed by satellite (OMI). The green and pink lines represent simulated NO_2 column with and without soil NO_x emissions, and the black line shows the difference between them. ...*" in Lines 308-311.

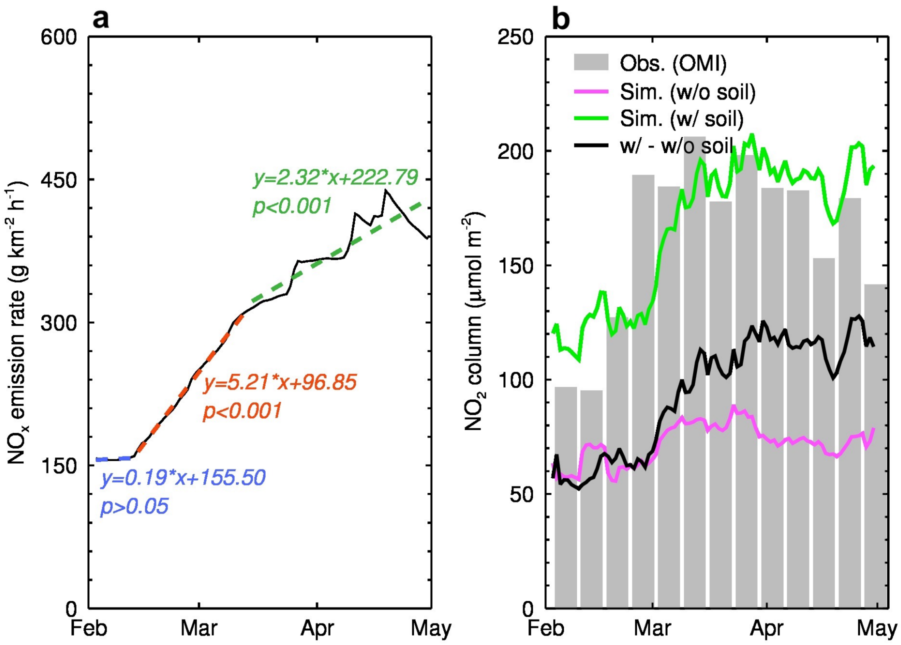

Figure 3. NO_x emissions from agricultural fertilization and resultant NO_2 column. (a) Calculated NO_x emission rate from croplands with N-fertilizer application in the model. The black curve represents daily variation in NO_x emission rate around the fertilization, and the blue, red, and green dash lines correspond to the trends of NO_x emission rates in croplands during the pre-fertilization, fertilization and post-fertilization periods, respectively. (b) Observed and simulated NO_2 column. The gray histogram represents NO_2 column observed by satellite (OMI). The green and pink lines represent simulated NO_2 column with and without soil NO_x emissions, and the black line shows the difference between them. The model well replicates the rapid increase in observed NO_2 column by considering soil NO_x emissions from agricultural fertilization.

15. Line 292: Please show the locations of these observation sites. Are they near agricultural areas?

Response: The locations of the observational sites include 141 sites over the NCP as shown in Figure S1, and these sites are almost deployed in urban areas for the air quality monitoring purpose. We have revised the figure caption in Line 345-346: "*Figure 4. Simulated vs.*

measured surface pollutants averaged over the monitoring sites of the NCP (Figure S1) during February-April in 2020. ...".

16. Although the authors attempt to evaluate the model performance in predicting soil NO_x emissions, the lack of direct comparisons against flux measurements remains a limitation. Please discuss the uncertainties that may be introduced with the BDSNP scheme.

Response: We have included discussion on the uncertainties in Lines 364-368: "*It is important to acknowledge the limitation posed by the absence of direct comparisons with flux measurements of NO_x emissions from soils, due to the unavailability of such data. The simulated NO_x emission flux from the BDSNP scheme cannot be well examined, which may introduce uncertainties to the predicted emission rates and mixing ratios in the atmosphere.*"

17. Line 322. The referenced information does not appear in Figure S1. Please correct the citation or clarify.

Response: We have corrected the citation as "*Figure 1*" in Lines 380-381.

18. Regarding the O_3 diurnal cycle, please clarify whether the BDSNP mechanism in your WRF-Chem simulates diurnal variation in soil NO_x emissions or first performs monthly predictions with fixed scaling factors to determine the diurnal changes. If not, discuss how this may affect the interpretation of diurnal O_3 patterns.

Response: The BDSNP mechanism in the model simulates diurnal variation of soil NO_x emissions. We implement the mechanism in the model to calculate soil NO_x emission at each model time step.

19. Line 348: The italicization of "via" is unnecessary.

Response: We have corrected the italicization of "via" in Line 411.

20. Line 381: Please verify whether the y-axis label should be ΔO_3 instead of the ΔNO_2.

Response: We have corrected this figure to present the diurnal change of O_3 concentration rather than NO_2 in Line 447.

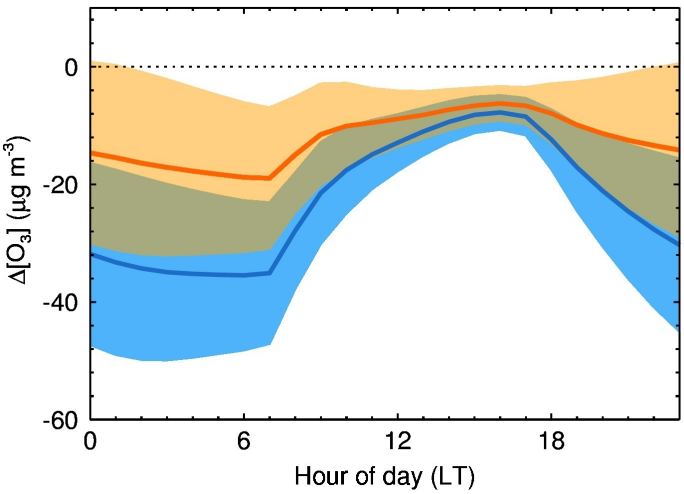

Figure 9. Secondary impact of soil NO_x emissions from agricultural fertilization on surface O_3. Diurnal cycles of changes in surface O_3 concentrations due to fertilization-related soil emissions over croplands and urban areas in the NCP. The blue and orange shadings show ±1 ***σ*** *of the data.*

21. Line 359: The difference between r = 0.997 and r = 0.994 is minimal and likely not significant. Consider tempering this statement.

Response: We have revised the statement as "*... $r < -0.99$ and $p < 0.001$ for both the agricultural and the urban areas ...*" in Line 423.

22. Line 371: Soil is also an important HONO source, a precursor of OH radicals. Does your model include soil HONO emissions? If not, please discuss how this omission might affect your conclusions on OH and atmospheric oxidation capacity.

Response: We did not include soil HONO emission in the model. We have discussed the effect of soil HONO emission on OH and atmospheric oxidation capacity in Lines 435-440: "*We note that soil nitrous acid (HONO) emission can also perturb atmospheric chemistry and the AOC (Feng et al., 2022; Tan et al., 2023) via providing NO and OH through photolysis. The emission rate of HONO from soil is much less than that of NO_x in the NCP (Tan et al., 2023), which increases daytime O_3 and OH concentrations slightly during summer (Feng et al., 2022; Tan et al., 2023). However, the influence in springtime still remains to be elucidated.*"

23. Line 394-405: In this paragraph, the authors compare their findings with other studies to highlight the different impacts of soil NO_x on ozone formation, showing suppression in springtime in this study versus enhancement in summertime in other studies. However, the comparison is incomplete. Several recent studies focusing on soil NO_x and ozone formation in North China are not mentioned, while studies from California are cited instead, despite potentially different background conditions and atmospheric environments. I recommend including more regionally relevant studies to support the comparison, considering the nonlinear responses of ozone to its precursors.
    - Lu, Xiao, et al. "The underappreciated role of agricultural soil nitrogen oxide emissions in ozone pollution regulation in North China." *Nature Communications* 12.1 (2021): 5021.
    - Huang, Ling, et al. "Insights into soil NO emissions and the contribution to surface ozone formation in China." *Atmospheric Chemistry and Physics*23 (2023): 14919-14932.
    - Shen, Y., Xiao, Z., Wang, Y., Xiao, W., Yao, L., & Zhou, C. (2023). Impacts of agricultural soil NOx emissions on O_3 over Mainland China. *Journal of Geophysical Research: Atmospheres*, *128*(4), e2022JD037986.

- Tan, W., Wang, H., Su, J., Sun, R., He, C., Lu, X., ... & Fan, S. (2023). Soil emissions of reactive nitrogen accelerate summertime surface ozone increases in the North China Plain. Environmental Science & Technology, 57(34), 12782-12793.

Additionally, the authors attribute the seasonal differences in ozone responses to sunlight intensity driving ozone formation regime shifts. However, this explanation is not robust, as no ozone sensitivity indicators (such as empirical metrics or modeled VOC-/NO_x-limited regimes) are provided to support this claim. Please consider expanding this section with additional localized studies and include more concrete evidence to justify your conclusions.

Response: We have revised this paragraph to include more relevant recent studies on the impacts of soil NO_x emission on ozone formation and to provide more robust evidence of ozone sensitivity indicators to support our results in Lines 462-478: "*Interestingly, these findings regarding the impacts of soil NO_x emission on O_3 formation in spring are different from previous studies revealing that agricultural NO_x emissions enhance the O_3 formation in summer over the NCP (Huang et al., 2023; Lu et al., 2021; Tan et al., 2023; Wang et al., 2022) and northeast China (Shen et al., 2023) and in the Imperial Valley, California (Oikawa et al., 2015). Similar scenarios are also reported during the growing season of crops in sub-Saharan Africa (Hickman et al., 2017; Huang et al., 2018). This is largely attributed to the sensitivity of O_3 to its precursors under different conditions of solar radiation. During early spring, the insolation is relatively weak, unfavorable for the O_3 photochemical production in the NCP. As a result, a large amount of agricultural NO_x (mainly NO) emission even causes a NO titration effect during daytime, decreasing O_3 concentrations, when the O_3 chemistry is under the VOC-sensitive or the transitional regimes (Figure S6) (Sillman, 1995). In contrast, the intensified solar radiation in summer significantly facilitates the O_3 photochemical production, shifting the O_3 chemistry from VOCs-sensitive to NO_x-sensitive (Sha et al., 2021; Wang et al., 2022).*

In this scenario, the O_3 *production is primarily controlled by* NO_x *emissions, meaning that the* O_3 *concentration increases with rising* NO_x *levels. This seasonal difference in* O_3 *sensitivity to its precursors highlights a seasonally dependent response of* O_3 *production to agricultural fertilization.*" A new figure (Figure S6) is added in the Supplement and the References section is updated accordingly.

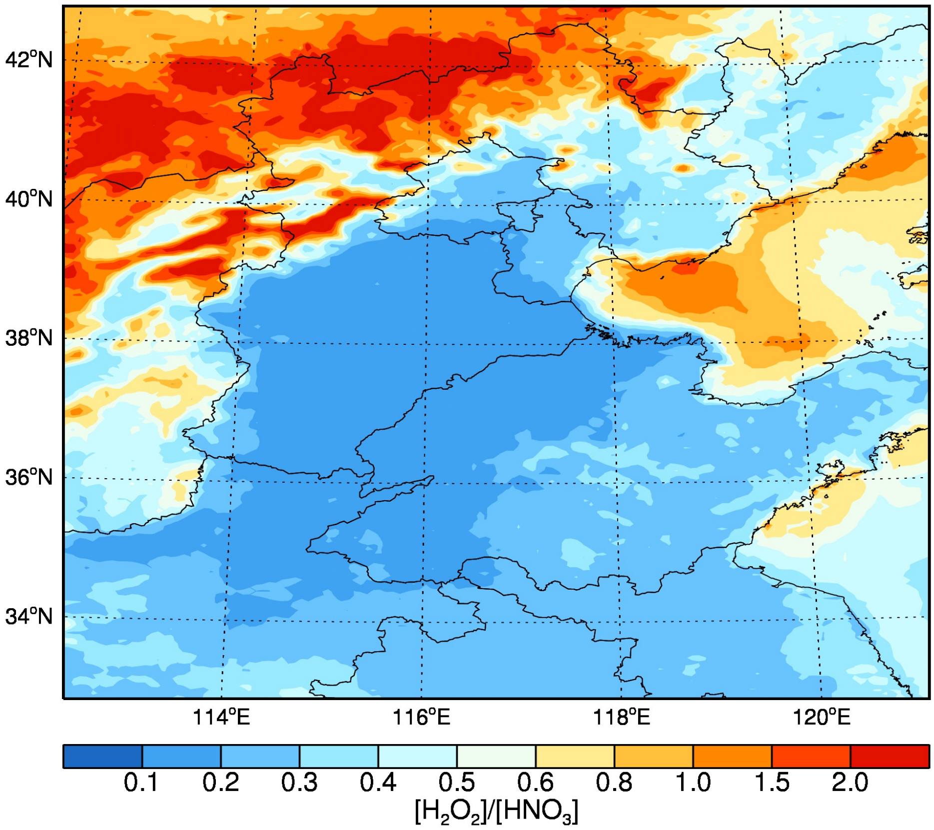

Figure S6. Spatial distribution of O_3 *formation sensitivity to precursors indicated by the* $[H_2O_2]/[HNO_3]$ *ratio. A ratio less than 0.3, great than 0.5, and between 0.3 and 0.5 indicates the* O_3 *formation under VOC-sensitive,* NO_x*-sensitive and transition regimes, respectively.*

24. Line 416 Please consider adding OH changes to Figure 8 as you describe the changes in OH when mentioning the atmospheric oxidizing capacity.

Response: We have included OH changes in Figure 8, and the figure caption has been updated accordingly.

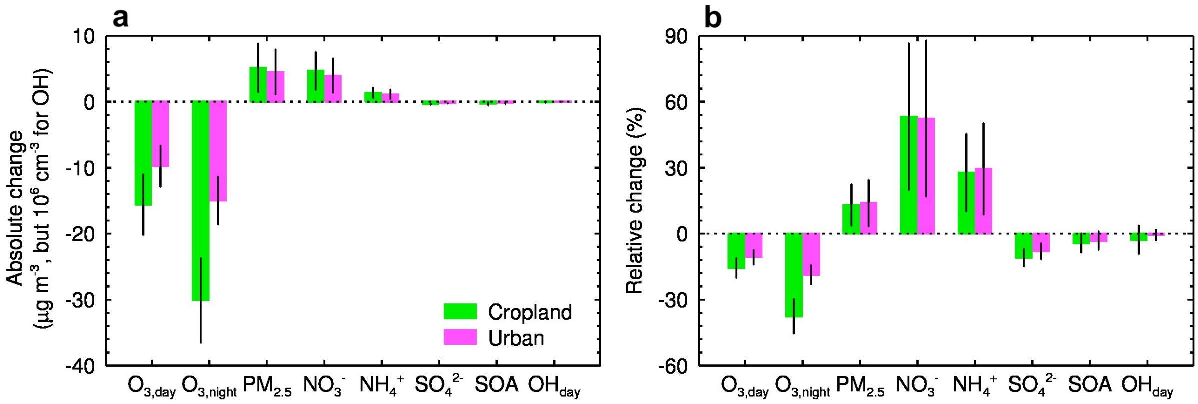

Figure 8. Complex impacts of agricultural fertilization on O_3, $PM_{2.5}$, and OH. (a) Changes in mass concentrations of O_3, $PM_{2.5}$, aerosol constituents, i.e., nitrate, ammonium, sulfate and secondary organics, and OH radical due to soil NO_x emission from agricultural fertilization in agricultural (green) and urban (pink) areas. The error bar denotes ±1σ. (b) Same as (a), but for percentage changes.

25. Line 425: Please clarify whether this statement about PM and NO_2 sensitivity refers specifically to NO_2 from soil sources.

Response: The statement about PM and NO_2 sensitivity is induced by the NO_x emission from soil sources. We have clarified this issue in Line 494: "... *due to the NO_x emission from agricultural fertilization* ...".

26. Line 433 to 438: Please add supporting references, such as FAO reports on fertilizer trends and studies linking global warming with soil NO emissions.

Response: We have included references to link global warming with soil NO emissions in Lines 508-512: "*Since soil NO_x emission is sensitive to soil temperature, as global warming is ongoing, routine events like agricultural fertilization will continue to have amplified impacts on air quality with the joint help of atmospheric dispersion/transport and chemical* *transformation processes (Bennetzen et al., 2016; Ma et al., 2022; Tubiello et al., 2013).*" The References section has been updated accordingly.

27. Please check the accessibility of the real-time air pollution data website http://beijingair.sinaapp.com in the Code/Data availability part.

Response: The website has been updated by the owners, and we have revised the website in Line 571: "*... can be accessed on the website https://quotsoft.net/air/*".

Technical corrections:

28. The subscript formatting of NO_x is inconsistent throughout the manuscript, for example, between Line 47 and Line 99. Please ensure the notation of NO_x is consistent across the text, figures, and tables.

Response: We have checked that throughout the manuscript to make it consistent, and the revisions have been highlight in the text.

29. Citation formatting is inconsistent. In some sections, numbered citations are used, while in others, author–year formats appear. Please standardize the citation style according to the journal's guidelines and ensure consistency throughout the manuscript.

Response: We have checked the citation formatting throughout the manuscript and revised all the references and citations according to the journal's guidelines.