April 23, 2025

Dear Editor,

We have received the comments from the reviewers of the manuscript. We greatly appreciate your consideration and the reviewers' comments. Below are our responses and the revisions that we have made in the manuscript.

Thank you for your efforts on this manuscript. We look forward to hearing from you.

Best regards,

Guohui Li, PhD

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 NH₃ 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 NO₂ 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 NH₃ 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 NO₂ and NH₃ 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 NO₂, O₃, and PM₂.₅ mass concentrations at 141 sites in the NCP are from the China National Environmental Monitoring Centre (CNEMC, Figure S1).*"
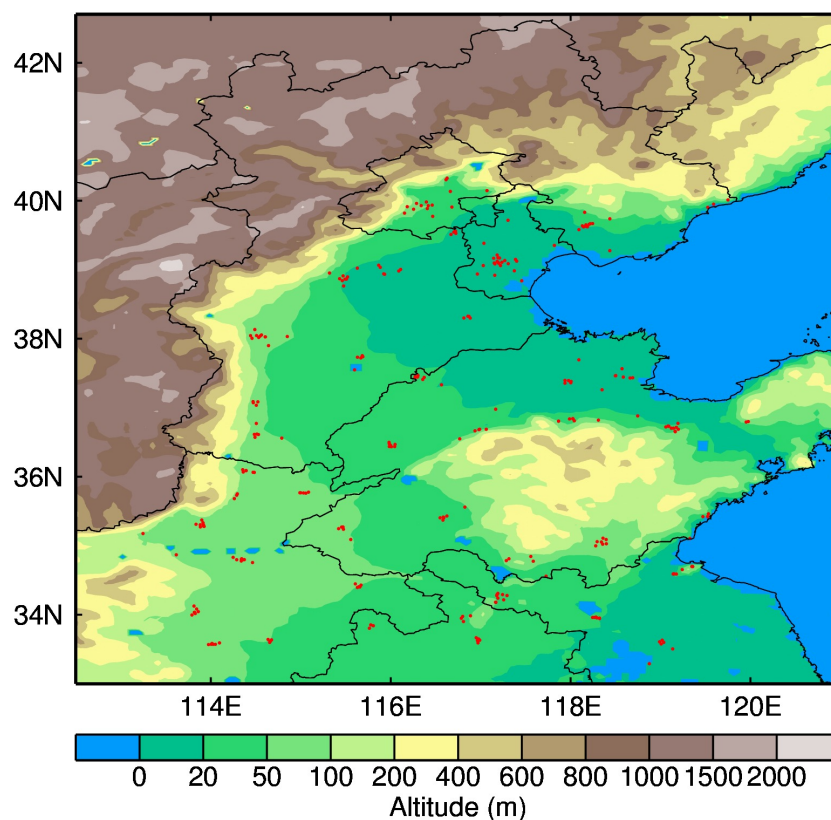
Figure S1. Map showing the locations of the 141 monitoring stations for air quality (red dots) over the North China Plain. Data are from the CNEMC. The color shading represents the topography of this region, with water areas depicted in blue.

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 NO₂ and NH₃ 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 NO₂ 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.
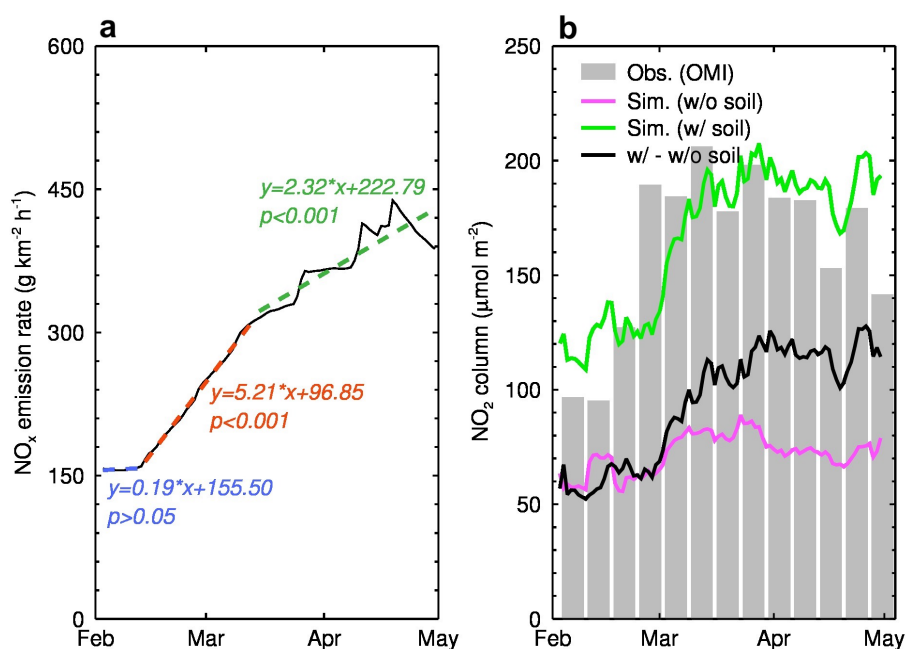
Figure 3. NO$_x$ emissions from agricultural fertilization and resultant NO$_2$ column. (a) Calculated NO$_x$ emission rate from croplands with N-fertilizer application in the model. The black curve represents daily variation in NO$_x$ emission rate around the fertilization, and the blue, red, and green 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.*

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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 ΔO₃ instead of the ΔNO₂.

Response: We have corrected this figure to present the diurnal change of O_3 concentration rather than NO_2 in Line 447.
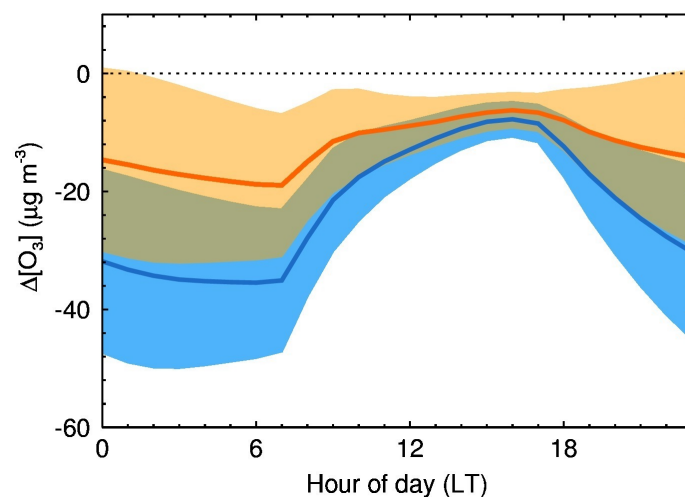
Figure 9. Secondary impact of soil NOₓ emissions from agricultural fertilization on surface O₃. Diurnal cycles of changes in surface O₃ concentrations due to fertilization-related soil emissions over croplands and urban areas in the NCP. The blue and orange shadings show ±1σ of the data.

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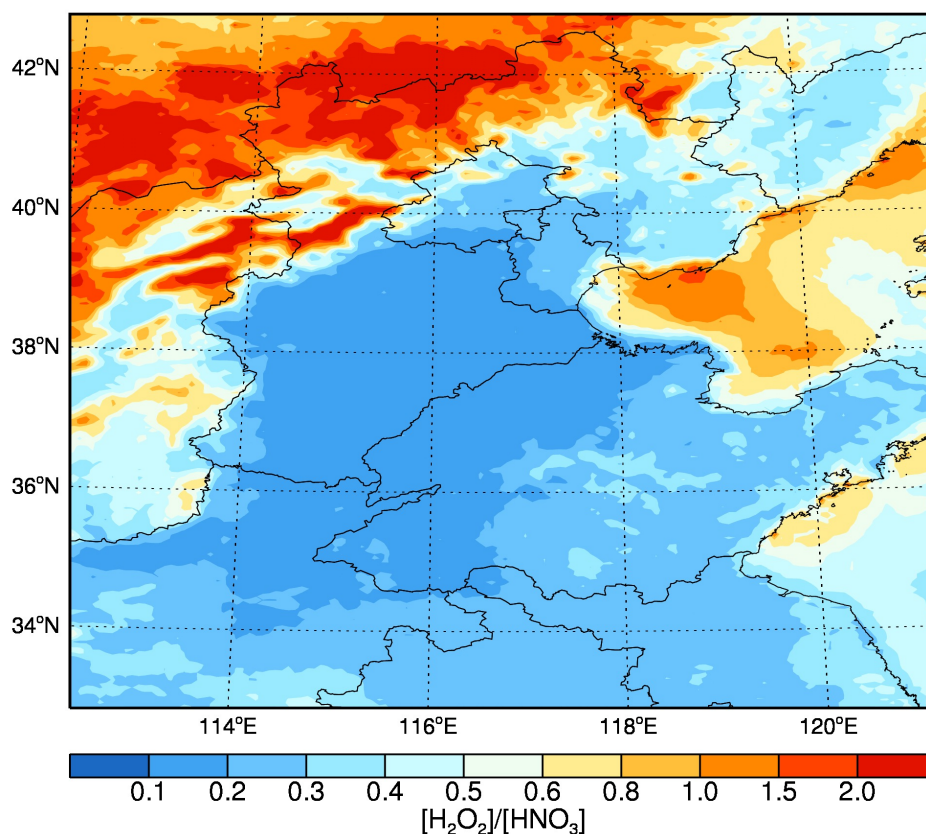
Figure S6. Spatial distribution of O_3 formation sensitivity to precursors indicated by the $[H_2O_2]/[HNO_3]$ ratio. A ratio less than 0.3, great than 0.5, and between 0.3 and 0.5 indicates the O_3 formation under VOC-sensitive, NO_x-sensitive and transition regimes, respectively.

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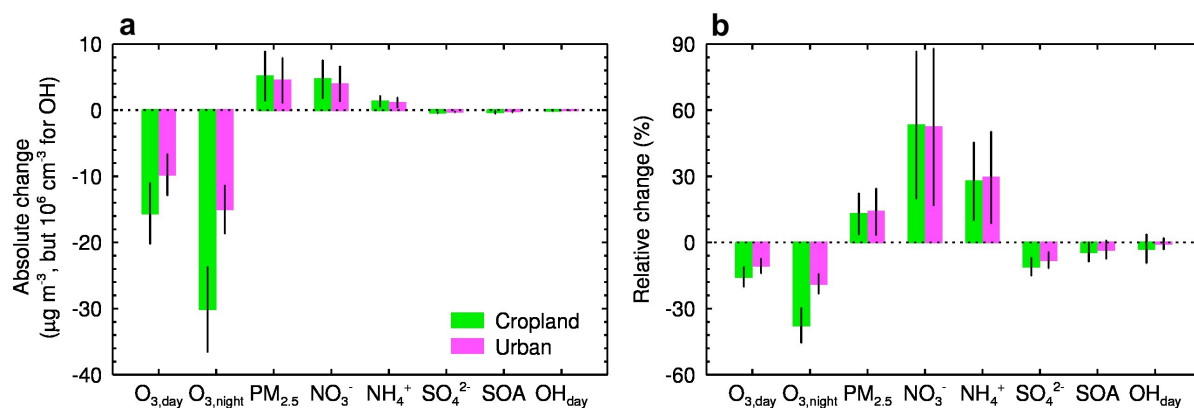
Figure 8. Complex impacts of agricultural fertilization on O_3, $PM_{2.5}$, and OH. (a) Changes in mass concentrations of O_3, $PM_{2.5}$, aerosol constituents, i.e., nitrate, ammonium, sulfate and secondary organics, and OH radical due to soil NO_x emission from agricultural fertilization in agricultural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

Response to Referee #2:

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.

The authors use a chemical transport model, satellite retrievals of NO_2 and NH_3, and surface station observations to evaluate fertilizer-induced NO emissions and their impacts on atmospheric composition in a region of China. An analysis of OMI tropospheric NO_2 columns reveals a putative peak around March each year, roughly corresponding to the timing of a fertilizer application at a single agricultural research station in the region, and to peaks of total column NH_3 from IASI. They implement the BDSNP soil NO_x emission scheme into WRF-Chem, and conduct simulations for spring 2020, finding that the inclusion of soil emissions produces a better match to both satellite and station observations of NO_2. The simulations exhibit an increase in ozone concentrations when soil emissions are included, which the authors attribute to NO_x titration during nighttime and to consumption of OH during daytime. The simulations also exhibit an increase in nitrate and ammonium aerosols, but a decrease in sulfate aerosols, which they attribute to reduced SO_4 production resulting from the consumption of OH.

Assessment:

I like what the authors are trying to do here, and I think they have laid the groundwork for a compelling paper highlighting the role of agricultural emissions in determining atmospheric composition in North China during spring. I do think the manuscript requires substantial revision prior to publication.

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.

General comments:

1. When using OMI data across the entire measurement period, the OMI row anomaly needs to be acknowledged—it needs to be mentioned in the text and either the decision not to remove pixels affected by the row anomaly needs to be justified, or the approach used to compensate for the row anomaly needs to be described. If seasonality is the only temporal variability being analyzed, it might be fine to use all the data from the retrieval. But once a multi-year time series is used, it may be more appropriate to exclude any pixels affected by the row anomaly from all years of retrievals. (Also, in particular because of the reduced coverage provided by OMI in 2020 as a result of the row anomaly, TROPOMI would probably provide an improved benchmark for comparisons to WRF-Chem. I don't know that it's necessary for publication, though.)

Response: In this study, we use the Level-3 product of the daily NO_2 column from OMI. The OMI row anomaly issue does affect the data quality derived from it. For the Level-3 product, only pixel level data of good quality are used to generate global daily dataset at a resolution of 0.25°×0.25°. We have included more details about the OMI dataset in Lines 185-189: "*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).*" Actually, the Level-3 product of OMI provides high-quality daily NO_2 columns globally, which has been

widely used in researches. To make it consistent throughout the study, we use the OMI dataset to validate the model performance instead of TROPOMI.

2. Additional analysis incorporating land use masks (e.g., using MODIS) would strengthen the attribution of the changes in OMI NO_2 (and IASI NH_3) columns to agriculture.

Response: During the analysis, we also incorporated land use masks to examine the satellite data, and found that the results over agricultural areas of the NCP only (Figure R1) are almost the same as that over the NCP (Figures 2a and 1b) with very little differences, which is probably related with the large fraction of agricultural areas in the NCP. Therefore, we use the results over the NCP in the present study.
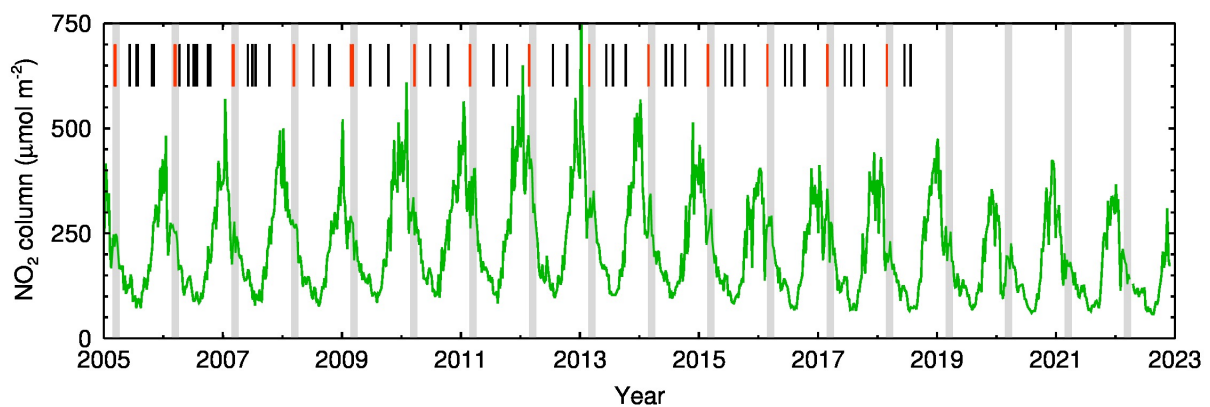

Figure R1. Long-term variation of seven-day mean tropospheric NO_2 column observed by OMI during the past two decades (2005-2022) over croplands of the NCP only. Intersections of the gray bars and the green lines denote a sub-peak of NO_2 column occurred in each March, and the short bars represent the timing record for agricultural fertilization at Fengqiu station in the NCP, of which the red ones indicate the fertilization period in early spring.

3. I fully expect the March sub-peaks to be related to fertilizer, but it seems necessary to exclude the possibility that these could be pulses related to soil thaw. Soil freeze/thaw transitions are sources of huge pulses of N_2O in higher latitude agricultural ecosystems.

There's at best mixed evidence as to whether there are also substantial NO pulses, but there's some suggestion (presented at the most recent American Geophysical Union meeting) that the N_2O pulses may result from nitrification rather than denitrification, which could suggest a role for NO.

I think all that needs to be established is that soils in the region thaw well in advance of the initiation of the March pulse. This could be done with SMAP, which has a global freeze/thaw flag – it is an official product for latitudes above 50N, but it is available for all pixels. Reanalysis soil temperature could also be used, but note that soil temperature freezing points may vary and are not 0C. (But if temperatures are consistently above 0C in February, that seems like it reasonably eliminates the possibility).

Response: To exclude the possibility of the impacts of soil thaw, we have analyzed the soil temperature of the top layer (since the lower layers are generally warmer) in February and March, 2020 using the ERA5 reanalysis. We found that the daily soil temperature was consistently higher than 0 over the NCP during the period from February 20 to March 31. We think that this can reasonably eliminate the possibility of soil thaw. We have included this analysis in Lines 252-254: "*Additionally, it is seen that the daily soil temperature was consistently higher than 0°C during March 2020 and the ten days before. Therefore, the sub-peak of NO_2 column is not expected to be originated from soil thaw either.*" We have also included a new figure (Figure S4 in the latest version) in the Supplement.
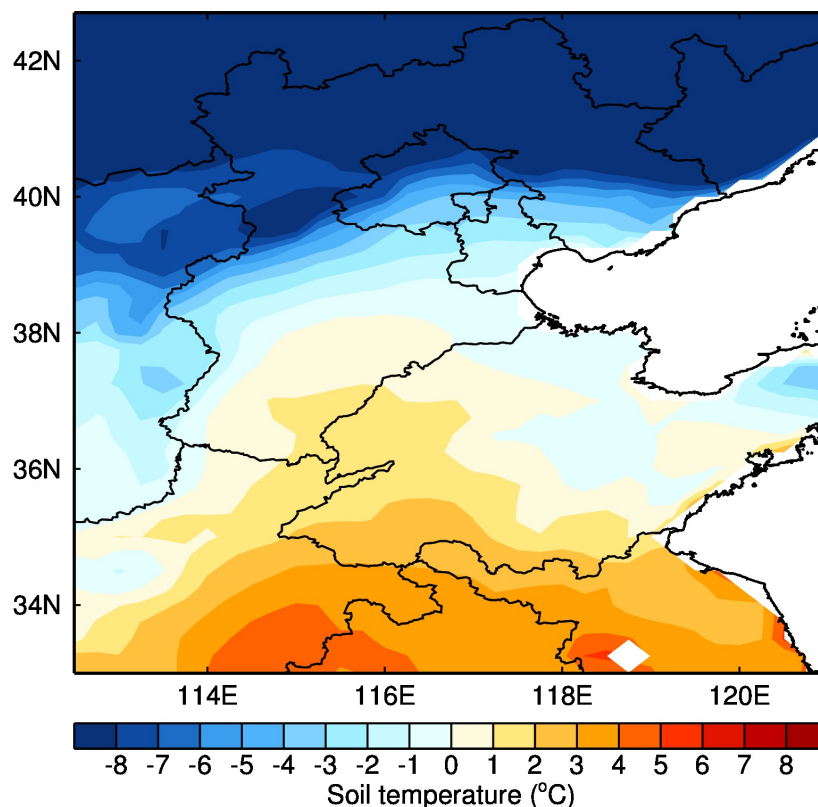
Figure S4. Spatial distribution of the minimum daily soil temperature of the top layer over the NCP during the period from 20 February to 31 March, 2020. Data are from the ERA5 reanalysis. The white areas show waters.

4. It appears that there is an NH_3 module added to WRF-Chem that is not described.

Response: We have included a description of the NH_3 emission in Lines 118-120: "*Specifically, monthly ammonia (NH_3) emissions are incorporated from a high-resolution NH_3 emission inventory developed by Huang et al., (2012), which includes emissions from fertilizer application, livestock, and other sources.*" We have also revised Table 1 and included a row to introduce the NH_3 emission. The References section has been updated accordingly.

5. I think it's very important to frame the WRF-Chem simulations as a case study: there are only 3 months of simulation as the basis for all of the insights into emissions, atmospheric chemistry, and atmospheric composition. The limited duration of the simulation is a big

limitation on the generalizability of the model results, and the presentation of results needs to reflect this limitation.

Response: We have included a statement of the limitation of this work as a case study in Lines 559-563: "*Nevertheless, one should be aware of the limitation in the present case study that there are only three months of simulation as the basis for all of the insights into the soil NO$_x$ emission and its influences on atmospheric chemistry and composition. More studies in terms of soil NO$_x$ emissions, particularly during springtime, are in need to validate and generalize our model results.*"

6. Due to an error in formatting references, it is not possible to determine what fertilizer and manure datasets were used (and I believe the reference for these datasets are not included in the reference list). The manuscript does need more information on how fertilizer was handled in WRF-Chem. If the fertilizer and manure datasets are the ones used by Hudman et al. 2012, they are datasets for the year 2000, with fertilizer application timing determined by MODIS EVI for 2001-2004. So the fertilization application rates and timing may be quite different from practices in 2020, the year simulated in this study.

In addition, it is not clear how fertilization dates and application amounts in the simulation were determined. If using the fertilizer files from Hudman et al. 2012, they include an assumption that 75% of fertilizer is added at the green-up day as determined by MODIS EVI, with the remaining 25% applied constantly throughout the rest of the season, which was probably an error (the reverse is a common assumption in crop models). It is also likely quite a different temporal distribution of fertilizer applications from the fertilization practices at the Fengqiu station, and so should be discussed. In addition, we need information on how fertilizer emissions were scaled in WRF-Chem (in the original BDSNP, fertilizer NO emissions were scaled to Stehfest & Bouwman 2006's estimate of 1.8 Tg N

yr-1; DOI:10.1007/s10705-006-9000-7, but there are quite a range of estimates). Understanding and discussing the fertilizer datasets used—especially the fertilization rates--is absolutely necessary to understand the atmospheric composition implications—it will make a big difference if these are 100 kg N ha^{-1} rates vs. 600 kg N ha^{-1} rates.

More generally, the manuscript would benefit from more information on agricultural and fertilizer management in the region—there is almost nothing presented. North China has been notorious for having high fertilization rates (https://doi.org/10.1126/science.1170261), which may be central to understanding the magnitude of the emissions impact and its effects on chemistry. When comparing to other studies (e.g., Oikawa 2015, Almaraz 2018), it is also important to understand what the cropping systems are. But the manuscript provides no information on fertilization rates or practices in the region or used in the simulations.

Response: We have included more discussion on the uncertainties originated from the setting of fertilizer application in the model in Lines 332-341: "*We still cannot ignore the discrepancies between the model results and observations. These biases may largely originate from the soil NO$_x$ emission mechanism. The fertilization dates in the BDSNP mechanism are determined by the beginning and end of the growing season that is derived from the MODIS Land Cover Dynamics product (MCD12Q2) averaged over the years from 2001 to 2004 (Hudman et al., 2012). This may be quite different from practices in 2020, the year we simulated in this study. We use the default assumption in the mechanism that 75% of fertilizer is added at the green-up day with the remaining 25% applied constantly throughout the rest of the season (Hudman et al., 2012). Though the 75/25 treatment is the most typical global farming practice (Matson et al., 1998), it may probably introduce extra biases in a specific region.*"

To clarify the fertilization in the model, we have included additional description of the fertilizer application in the adopted BDSNP mechanism in Lines 157-165: "*Fertilizer applications data are interpolated from the global gridded chemical fertilizer and manure application inventory at 0.5°× 0.5° (Potter et al., 2010; Yan et al., 2005). The chemical and manure fertilizers are obtained from the International Fertilizer Association (IFA) and the Food and Agriculture Organization of the United Nations (FAO). The Chinese chemical fertilizer application (straight N application) from IFA is about 19.6 Tg N a^{-1} for 2000, quite close to the amount of 19.9 Tg N a^{-1} for 2020 from the China Statistical Yearbook (https://www.stats.gov.cn/sj/ndsj/2021/indexch.htm). More details of the scheme are found in related studies elsewhere (Hudman et al., 2012; Lu et al., 2021).*"*

To give more information on agricultural and fertilizer management in the study region, we have included more introduction in Lines 79-89: "*The North China Plain (NCP) is one of the major grain-producing regions in China. Winter wheat-maize double cropping is a typical rotation system mainly practiced in this region (Liu et al., 2003; Zhu et al., 1994). China has been the world's largest consumer of N-fertilizer since 2000 (Liu et al., 2013), with annual usage peaking at approximately 31.2 Tg N in 2014 (Yu et al., 2022). About half of this fertilizer is lost to the environment (Liu et al., 2013), indicating a significant potential source for NO_x emissions from China's croplands. The agricultural management in the NCP has been known for incorporating high fertilization rates according to the solar terms with excessive N fertilization (Sun et al., 2022; Vitousek et al., 2009; Zhao et al., 2006). Thus, this region is primarily responsible for agricultural N-fertilizer consumption (Yu et al., 2022) and has shown substantial soil NO_x emissions (Liu et al., 2010; Tang et al., 2020; Zhang et al., 2011).*" and in Lines 265-275: "*The wheat-maize double-cropping system is predominate in the NCP, where the agricultural activities are strongly dependent on the lunar calendar. For winter wheat, the planting date ranges from early to mid-October (after maize harvest). Fertilization is generally*

divided into three stages: 1) Pre-planting during late September – early October; 2) Jointing stage during mid-March – early April; 3) Grain filling during late April for high-yield fields. The planting date of summer maize ranges from early to mid-June (after wheat harvest), and the stages of fertilization include: 1) At planting during early June; 2) V6-V8 stage during early July; 3) Tasseling stage during late July for high-yield fields. The agricultural fertilization is closely associated with three solar terms, i.e., Waking of Insects in March (the 3rd solar term), Grain in Beard in June (the 9th solar term) and Cold Dew in October (the 17th solar term)."

All the newly added references have been included in the References section.

Minor comments:

7. The reference list is incomplete, and includes a number of references not cited in the manuscript, and which do not seem related to the manuscript (e.g., multiple references from Li, G. et al on organic aerosols, HONO, and garbage burning)

Response: We have checked and updated the references carefully in the latest version to make it complete. We cite the references from Li, G. et al on organic aerosols, HONO, and garbage burning because the modified version of the WRF-Chem model was developed by Li, G. et al and the model improvements were reported in these papers from different aspects.

8. All figures need to include information on the time period (I think always Feb-April 2020?) and the domain represented (I think almost always the domain described in Figure 1a + Table 1).

Response: We have specified the time period and domain represented in all the figures including those in the Supplement. The time period in Figures 3 and 4 is February-April 2020 and that in Figures 5-11 is March 2020. The domain is the NCP shown in Figure 1b for all the figures.

9. It could be very interesting to compare the diurnal WRF-Chem analyses to GEMS NO$_2$ and ozone.

Response: We have accessed the GEMS NO$_2$ and ozone datasets and tried to find available data for a comparison with the model results (2020). However, the data are available since 2023.

10. In general, the discussion does little to contextualize the findings within what is already known. This is also true of the introduction: there is very limited background on the rather large literature on NO emissions from agriculture, including in China.

Response: We have included more discussion on the findings about soil NOx emissions in recent papers 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." and in Lines 435-439: "*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. Since the emission rate of HONO is only half that of NOx from soils in the NCP (Tan et al., 2023), we speculate that soil HONO emission would further weaken the AOC slightly in spring.*"

We have included introduction of soil NO_x emission, particularly from agricultural areas, in the Introduction section in Lines 57-94: "*… Model- and satellite-based studies estimate that global annual soil NO_x emissions, with the largest contributor of cultivated croplands, range from 9 to 27 Tg N (Hudman et al., 2012; Steinkamp and Lawrence, 2011; Vinken et al., 2014; Yan et al., 2005), accounting for about 15% of total NO_x emissions (Hudman et al., 2012). This wide range is due to the complex response of soil NO_x emissions to driving factors like fertilization, temperature, and soil moisture (Huber et al., 2020; Oikawa et al., 2015) ….*

The emission rates from fertilized croplands are 1 to 2 orders of magnitude higher than nearby grasslands and forest soils (Almaraz et al., 2018; Anderson and Levine, 1987; Guo et al., 2020; Yienger and Levy, 1995). Recent studies show significant NO_x emissions from croplands post-fertilization, exceeding pre-fertilization rates by an order of magnitude (Almaraz et al., 2018; Hickman et al., 2017; Laville et al., 2011; Liu et al., 2005; Oikawa et al., 2015; Zhao et al., 2015). Despite these robust evidences of strong NO_x emissions from agricultural fertilization, the lack of extensive in-situ measurements hinders accurate estimation of these emissions and their environmental impacts. Additionally, the effect of agricultural fertilization on air quality has not received sufficient global attention, although some pioneering studies have pointed the implications for air quality since the 1990s (Davidson et al., 1998; Hall et al., 1996). In recent

years, studies have reported that agricultural soil emissions significantly increase atmospheric NO_x levels (Almaraz et al., 2018; Hickman et al., 2017; Huang et al., 2018; Oikawa et al., 2015) and enhance O_3 formation in summer in California (Oikawa et al., 2015) or during the growing season of crops in sub-Saharan Africa (Hickman et al., 2017; Huang et al., 2018). The North China Plain (NCP) is one of the major grain-producing regions in China. Winter wheat-maize double cropping is a typical rotation system mainly practiced in this region (Liu et al., 2003; Zhu et al., 1994). China has been the world's largest consumer of N-fertilizer since 2000 (Liu et al., 2013), with annual usage peaking at approximately 31.2 Tg N in 2014 (Yu et al., 2022). About half of this fertilizer is lost to the environment (Liu et al., 2013), indicating a significant potential source for NO_x emissions from China's croplands. The agricultural management in the NCP has been known for incorporating high fertilization rates according to the solar terms with excessive N fertilization (Sun et al., 2022; Vitousek et al., 2009; Zhao et al., 2006). Thus, this region is primarily responsible for agricultural N-fertilizer consumption (Yu et al., 2022) and has shown substantial soil NO_x emissions (Liu et al., 2010; Tang et al., 2020; Zhang et al., 2011). 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). These concerns typically focus on the warm season when higher temperatures favor NO_x emissions from soils. However, frequent agricultural activities and N-fertilizer use also occur during transitional seasons, and how periodic agricultural fertilization affects soil NO_x emission and regional air quality remains unclear."

Line comments:

11. Line 24: use 'nitrogen dioxide (NO_2)' at first occurrence in abstract

Response: We have changed "*NO_2*" to "*nitrogen dioxide (NO_2)*" in Line 24.

12. Line 44: need to define NO and NO$_2$ as nitric oxide and nitrogen oxide

Response: We have changed "*Nitrogen oxide (NO$_x$ = NO+NO$_2$)*" to "*Nitrogen oxide (NO$_x$ = nitric oxide (NO) + nitrogen dioxide (NO$_2$))*" in Line 45.

13. Line 49: Huber is not an appropriate reference here. I did not check the other references.

Response: We have replaced the reference of Huber et al, (2020) with Janssens-Maenhout et al., (2015) that reports the NO$_x$ emission are mainly from fossil fuel combustion in the HTAP v2.2 emission inventory to support the statement there. We have also checked other references in the manuscript to make them proper.

14. Line 53: To be more specific, it is particularly after the rewetting of dry soils.

Response: To make it more specific, we have changed "*particularly after rainfall*" to "*particularly after the rewetting of dry soils*" in Line 54.

15. Line 55-58: the references here are not appropriate, and do not support the global budget. The Oikawa, Huber, and Almarez references are all regional studies within the US. The Tang reference is a technical paper with 10 days of measurements from a single site.

Response: We have remove the unproper references and revised the sentence as: "*Model- and satellite-based studies estimate that global annual soil NO$_x$ emissions, with the largest contributor of cultivated croplands, range from 9 to 27 Tg N (Hudman et al., 2012; Steinkamp and Lawrence, 2011; Vinken et al., 2014; Yan et al., 2005), accounting for about 15% of total NO$_x$ emissions (Hudman et al., 2012).*" in Lines 57-60.

16. Line 62: again, the Almarez reference is only applicable to southern California and cannot support this statement. Much better references: DOI: 10.1111/gcb.16864, DOI: 10.1111/gcb.16193, DOI: 10.1007/s10705-006-9000-7, doi:10.1029/2001GB001811, etc.

Response: We have revised this sentence and updated the references in Lines 57-66: "*Model- and satellite-based studies estimate that global annual soil NO_x emissions, with the largest contributor of cultivated croplands, range from 9 to 27 Tg N (Hudman et al., 2012; Steinkamp and Lawrence, 2011; Vinken et al., 2014; Yan et al., 2005), accounting for about 15% of total NO_x emissions (Hudman et al., 2012). ... The emission rates from fertilized croplands are 1 to 2 orders of magnitude higher than nearby grasslands and forest soils (Almaraz et al., 2018; Anderson and Levine, 1987; Guo et al., 2020; Yienger and Levy, 1995).*"

17. And generally soils emit NO, not NO_x.

Response: We have changed "*soil NO_x emissions*" to "*soil NO emissions*" in Lines 57-58.

18. Line 65: Note that both references are for California. For other world regions see doi:10.1016/j.agrformet.2010.10.008, doi: 10.1111/gcb.13644, and DOI: 10.1007/s11104-005-4894-4, http://dx.doi.org/10.1016/j.atmosenv.2014.11.052, among many other studies.

Response: We have included more relevant references in Lines 68-69: "*... (Almaraz et al., 2018; Hickman et al., 2017; Laville et al., 2011; Liu et al., 2005; Oikawa et al., 2015; Zhao et al., 2015)*". The References section has been updated accordingly.

19. Line 68: as noted in my comment on line 65, there is a substantial body of literature reporting in situ measurements of NO fluxes in agricultural systems going back at least to the early 1990s.

Response: We have revised the sentences and included relevant references in Lines 71-78: "*Additionally, the effect of agricultural fertilization on air quality has not received sufficient global attention, although some pioneering studies have pointed the implications for air quality since the 1990s (Davidson et al., 1998; Hall et al., 1996). In recent years, studies have reported that agricultural soil emissions significantly increase atmospheric NO_x levels (Almaraz et al., 2018; Hickman et al., 2017; Huang et al., 2018; Oikawa et al., 2015) and enhance O_3 formation in summer in California (Oikawa et al., 2015) or during the growing season of crops in sub-Saharan Africa (Hickman et al., 2017; Huang et al., 2018).*". The References section has been updated accordingly.

20. Lines 68-73: Please also see additional studies explicitly focused on the effects of fertilizer-induced soil NO emissions on air quality, including one conducted at a continental scale: doi: 10.1111/gcb.13644 and 10.1016/j.atmosenv.2018.02.040

Response: We have revised the sentence and included relevant references in Lines 74-78: "*In recent years, studies have reported that agricultural soil emissions significantly increase atmospheric NO_x levels (Almaraz et al., 2018; Hickman et al., 2017; Huang et al., 2018; Oikawa et al., 2015) and enhance O_3 formation in summer in California (Oikawa et al., 2015) or during the growing season of crops in sub-Saharan Africa (Hickman et al., 2017; Huang et al., 2018).*" The References section has been updated accordingly.

21. Line 84: again, because Oikawa is focused on California's Imperial Valley, it is not an appropriate reference for a discussion of the timing of fertilizer applications in North China. The introduction does need a paragraph on cropping systems and agricultural practices (including fertilizer use) in the region.

Response: We have removed the reference of Oikawa et al., (2015) in the sentence, and included descriptions on the cropping systems and agricultural practices in the region in Lines 79-89: "*The North China Plain (NCP) is one of the major grain-producing regions in China. Winter wheat-maize double cropping is a typical rotation system mainly practiced in this region (Liu et al., 2003; Zhu et al., 1994). China has been the world's largest consumer of N-fertilizer since 2000 (Liu et al., 2013), with annual usage peaking at approximately 31.2 Tg N in 2014 (Yu et al., 2022). About half of this fertilizer is lost to the environment (Liu et al., 2013), indicating a significant potential source for NO_x emissions from China's croplands. The agricultural management in the NCP has been known for incorporating high fertilization rates according to the solar terms with excessive N fertilization (Sun et al., 2022; Vitousek et al., 2009; Zhao et al., 2006). Thus, this region is primarily responsible for agricultural N-fertilizer consumption (Yu et al., 2022) and has shown substantial soil NO_x emissions (Liu et al., 2010; Tang et al., 2020; Zhang et al., 2011). ...*"

22. Line 86: I'm not convinced that a pulse is 'unexpected', but it is interesting and surprising that it is not in the HTAP inventory. I think it's worth looking to see if this is true for other inventories.

Response: This pulse in ambient NO_2 column only exists for days, rather than the whole month. We have checked the MEIC, MIX, and HTAP emission inventories, which are widely used in recent studies focusing on this region, and confirmed that there is not this pulse in them, because all these inventories are monthly that cannot provide messages of the daily variation. We used the word 'unexpected' because there are so many human activities in the North China Plain that we did not speculate that soil NO emission can perturb ambient NO_2 column so heavily. And there are indeed no studies reporting this pulse over this region before.

23. Line 99: BDSNP does not include a parameterization for NH_3 emissions (or, more appropriately, bi-directional NH_3 flux). It exclusively simulates NO emissions. Also, define NH_3 as ammonia at this first occurrence.

Response: We have clarified this issue in Lines 107-109: "… *in which we implement the BDSNP mechanism by Hudman et al. (2012) to calculate soil NO_x emission related to agricultural fertilization and the influences on regional air quality in the NCP.*" and in Lines 118-120: "*Specifically, monthly ammonia (NH_3) emissions are incorporated from a high-resolution NH_3 emission inventory developed by Huang et al., (2012), which includes emissions from fertilizer application, livestock, and other sources.*" The References section has been updated accordingly.

24. Figure 1: I'm afraid I only see lighter orange contours, and then dark orange pixels. Might be useful to indicate how the agriculture and urban locations were defined.

Response: We have included descriptions on how the agriculture and urban locations were defined in the figure caption in Lines 129-131: "*The agricultural areas in orange within the NCP are defined as croplands with altitude less than 100 m, and the urban areas in red are defined as built-up areas within the NCP.*"

25. Table 1: Please include a description in the text of the simulation experiments conducted, in addition to the Table. 3 months of simulation limits generalizability; multiple years would provide more compelling evidence.

Response: We have included a description about the model experiments in Lines 385-387: "*We perform a model experiment that excludes the soil sources in the study domain to examine the impacts of soil emissions on regional air quality. The model results are compared to the benchmark scenario with soil sources involved to examine these impacts.*"

We agree with the reviewer's suggestion that multiple years would provide more compelling evidence and our three months of simulation limits its generalizability. We have included a statement regarding this limitation in Lines 559-563: "*Nevertheless, one should be aware of the limitation in the present case study that there are only three months of simulation as the basis for all of the insights into the soil NO_x emission and its influences on atmospheric chemistry and composition. More studies in terms of soil NO_x emissions, particularly during springtime, are in need to validate and generalize our model results.*"

26. Line 121-156: The reference formatting used in these lines is incorrect (making it impossible to know what papers are being referred to).

Response: We have checked the references throughout the text and updated them according to the journal citation and reference style.

27. Line 126: I don't believe this is accurate: in BDSNP there are dynamic N pools from fertilizer and deposition, but there is not a separate natural N pool. Natural soil emissions are captured partly by the representation of N deposition in N_{avail}, and partly by A'_{biome}, which is a fixed value.

Response: We have revised the sentence to make it more accurate in Lines 138-140: "*The scheme comprehensively considers various factors, including available soil nitrogen content (N_{avail}, ng N m^{-2}) from the fertilizer application and nitrogen deposition ...*"

28. Line 160-168: There is not enough detail here. Were L2 or L3 data used? If L2, how was regridding conducted? Also, it's fairly standard to include more information on the instruments—overpass time, launch date, orbit, etc. And, critically, with OMI, the row anomaly needs to be discussed (see general comments).

Response: We have revised this paragraph to present more details about the satellite datasets 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.*"

29. Line 169: please include the frequency of measurements—are the Picarro measurements conducted at the same frequency as the other species?

Response: We have included the frequency of measurements in Lines 209-212: "*... The sampling time is 1 min for these monitoring devices, which is averaged for hourly data. Agricultural NH_3 concentration is monitored by a Picarro analyzer based on the principle of*

cavity ring-down spectroscopy (CRDS) at the rural Xianghe station (Figure 1), with a sampling

frequency of 1 Hz."

30. Figure 2: please add the IASI NH_3 time series to Figure 2a, perhaps in blue.

Response: We have added the IASI NH_3 time series to Figure R1 to present the satellite data together as shown below. However, Figure 2 mainly illustrates NO_2 data and NO_x emissions, which is our focus and presented in Section 3.1, so we still leave the NH_3 time series in the Supplement.
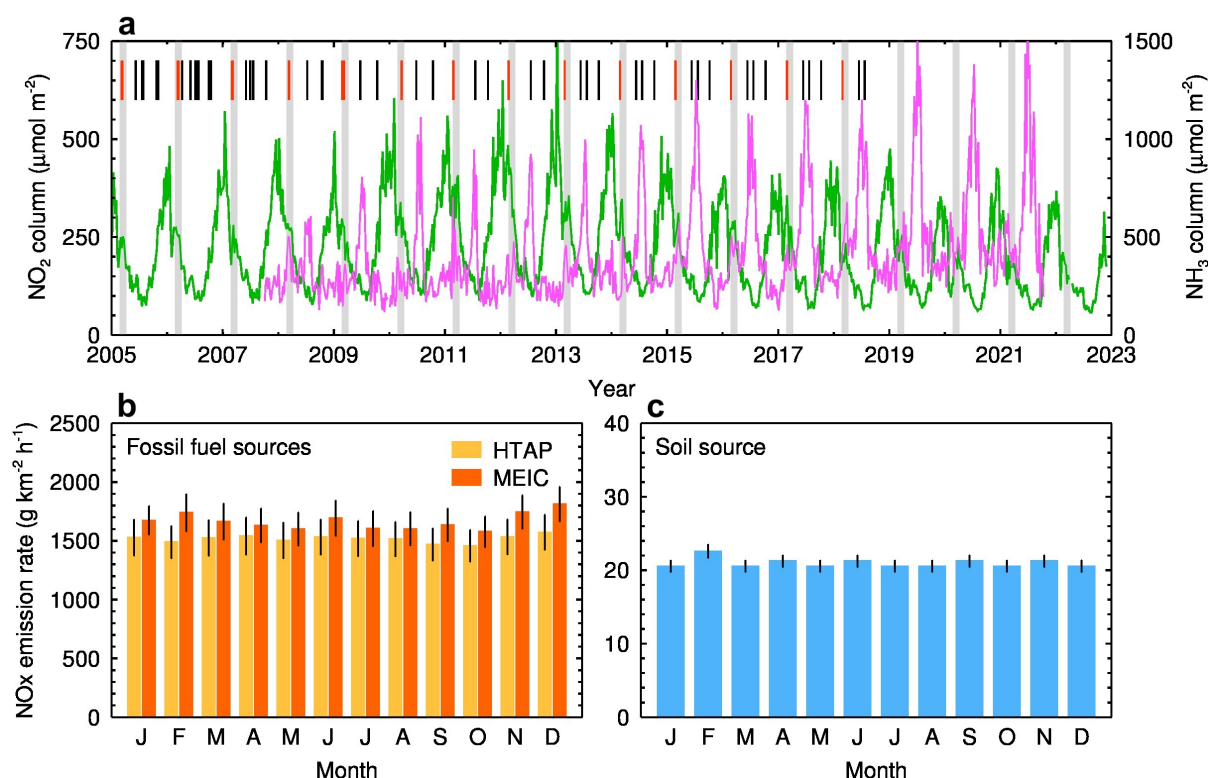
Figure R1. NO_2 and NH_3 column pulses in March and NO_x emissions from fossil fuel and soil sources over the NCP. (a) Long-term variations of seven-day mean tropospheric NO_2 column observed by OMI (green) and NH_3 column by IASI (pink) during the past two decades (2005-2022). Intersections of the gray bars and the green lines denote a sub-peak of NO_2 column occurred in each March, and the short bars represent the timing record for agricultural fertilization at Fengqiu station in the NCP, of which the red ones indicate the fertilization period in early spring. (b) Monthly mean NO_x emission rates with $\pm 1\sigma$ standard deviation (SD) in two

sets of anthropogenic emission inventories, the HTAP v3 (2005-2018, orange) and MEIC v1.3 (2008-2017, red). (c) Same as (b), but for NO_x emission rates from soils in the HTAP v3 inventory (2005-2018).

31. Line 231/232 and line 237/238: Quantitative data on agricultural practices would be very helpful here. With respect to the timing of planting, this can vary interannually, typically responding to temperature or precipitation patterns, and in a season, will vary among farms within a region. It is clear in Figure 2a that the timing of fertilizer applications at Fengqiu station varies considerably from year to year. And in general, research station practices are not always reflective of regional practice: it would strengthen the argument to have additional data on planting or fertilization dates from the region.

Response: We have included planting and fertilization dates in the NCP croplands in Lines 265-275: "*The wheat-maize double-cropping system is predominate in the NCP, where the agricultural activities are strongly dependent on the lunar calendar. For winter wheat, the planting date ranges from early to mid-October (after maize harvest). Fertilization is generally divided into three stages: 1) Pre-planting during late September – early October; 2) Jointing stage during mid-March – early April; 3) Grain filling during late April for high-yield fields. The planting date of summer maize ranges from early to mid-June (after wheat harvest), and the stages of fertilization include: 1) At planting during early June; 2) V6-V8 stage during early July; 3) Tasseling stage during late July for high-yield fields. The agricultural fertilization is closely associated with three solar terms, i.e., Waking of Insects in March (the 3rd solar term), Grain in Beard in June (the 9th solar term) and Cold Dew in October (the 17th solar term).*"

32. Line 241: the reference is not included (probably Tang 2020). In any event, it has been well known for decades that fertilization is a significant source of NO (there are, after all,

national inventories of fertilizer-induced NO$_x$), and there's a large literature that can be cited; citing just this one reference is not an effective way to make this argument.

Response: We have included more relevant references to support the statement in Lines 282-285: "*Field campaigns have measured a high NO emission rate of 266.3 g km^{-2} h^{-1} in croplands after fertilization and irrigation in autumn in eastern China (Tang et al., 2020; Tian et al., 2020) and also other regions (Hickman et al., 2017; Huang et al., 2018; Huber et al., 2020) ...*". The References section has been updated accordingly.

33. Line 247: the NH$_3$ module (presumably one that can accommodate bi-directional fluxes) has not been described.

Response: We have revised the sentence in Lines 291-292: "*... we introduce a flexible soil NO$_x$ emission module and NH$_3$ emission into the WRF-Chem model ...*" and we have included descriptions on the NH$_3$ emission in Lines 118-120: "*Specifically, monthly ammonia (NH$_3$) emissions are incorporated from a high-resolution NH$_3$ emission inventory developed by Huang et al., (2012), which includes emissions from fertilizer application, livestock, and other sources.*".

34. Line 249: I do not understand what this sentence is intending to express: "Soil NO$_x$ emission rate calculated by the model gradually increases while adding the soil NO$_x$ emission mechanism related to agricultural fertilization."

Response: We have removed that sentence in Line 293.

35. Line 254-259: the manuscript relies very heavily on Oikawa 2015, Tang 2020, and a few other papers—expanding the use of the literature would improve the manuscript. Here, Hudman 2010 (https://acp.copernicus.org/articles/10/9943/2010/) may be particularly

relevant—it presents work with OMI and GEOS-Chem looking at fertilizer NO emissions over the US, among other topics.

Response: Here, we compare the model predicted soil NO emission rates with the limited available measurements to validate the model performance in simulating soil emissions. However, there is no *in-situ* measurements during the simulation period in the study domain, so we compare with some relevant measurements in China and the US.

36. Figure 3: How are the fertilization periods determined in Figure 3a? With respect to 3b, the match between WRF-Chem and OMI is remarkable, given that BDSNP emission rates are scaled globally.

Response: The fertilization periods are embedded in the available soil nitrogen content (N_{avail}) in soils, which is a gridded dataset and used as an input data for the model. With the consideration of soil emissions, the model does perform well in replicating the observed NO_2 variation by OMI.

37. Line 281-290 and Figure 4: Be specific about what this comparison is –is this one surface site and one grid cell being compared?

Response: These observations are averaged over the sites from CNEMC as we described 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).*". We have revised and specified the comparison in Lines 324-326: "*We also validate the modified model performance on temporal variations of routine surface pollutant measurements (NO$_2$, O$_3$ and PM$_{2.5}$) associated with NO$_x$ emissions at the CNEMC sites throughout the simulation period (Figure 4).*"

38. Line 286, 287: spell out IOA and MB

Response: We have spell out IOA and MB in Line 360: "*mean bias (MB, Text S2)*" and in Line 361: "*index of agreement (IOA, Text S2)*".

39. Line 338: Please provide more detail on the difference between NH_3 and NO_2 in Figure 7. If these are fertilizer emissions, and they are being produced in WRF-Chem (with, presumably, soil N being the primary driver of emission rate), why and how would the "spatial distribution of NH_3 emission rates" explain the difference?

Response: The NH_3 is from the soil emission inventory by Huang et al. (2012), which is a separate monthly emission inventory. This inventory is totally different from the process-based estimate of NO emission by the BDSNP scheme, and there are nonnegligible discrepancies in the derived emission rates between these two approaches, which still deserves more in-depth studies. We have included more details on the difference between NH_3 and NO_2 in Figure 7 in Lines 397-402: "*Spatial distribution of the increased NH_3 concentration is highly similar to that of the increased NO_2 concentration, but some differences exist in the southeast of the NCP. It should be noted that the NH_3 emission in the model is from Huang et al. (2012), a separate monthly emission inventory. The emission rates of NH_3 in the southeast of the NCP is lower than that of NO from the BDSNP scheme. This indicates nonnegligible discrepancies in the derived emissions between these two approaches, which deserves more in-depth studies.*"

40. Line 343: Minor comment, but I don't understand why different units are used for NO_2 and NH_3 here

Response: In Figure 6, the unit for the measured surface NH_3 concentration is 'ppb', so to make it consistent with the measurements, we use 'ppb' as the unit for surface NH_3 concentration throughout the manuscript including Figure 7.

41. Line 353: the decrease in ozone concentrations in agricultural areas is interesting and unexpected—one thinks of ozone being NO_x limited in rural areas. Repeating a concern from a major comment, are the fertilizer rates used in WRF-Chem very high (e.g., 300 kg N ha^{-1}), and may that contribute to the differences with other world regions? Can you include ozone isopleths? Since soils emit NO_x in the form of NO, perhaps the equilibrium reactions for $NO + NO_2$ contributes to the reduction in ozone:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

$$NO_2 + h\nu\ (+O_2) \rightarrow NO + O_3 \tag{2}$$

Response: The fertilizer rates are high in the study domain as reported by relevant studies (Sun et al., 2022; Vitousek et al., 2009; Zhao et al., 2006), which contributes to ambient NO_x largely. But we do not think this results in the difference with other regions in the world. Actually, even in the North China Plain, the soil NO emission enhances ozone formation in summer, which has been usually reported in recent studies. However, the situation in spring is different in the present study. It is not easy to show ozone isopleths due to the demand for a large number of model simulations. Alternatively, we present the ozone formation sensitivity in Figure S6 by the indicator of $[H_2O_2]/[HNO_3]$ ratio, which has been widely used in researches regarding atmospheric chemistry (Sillman, 1995). We have included discussion on ozone formation in the NCP compared to relevant studies 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." The new figure (Figure S6) is added in the Supplement and the References section is updated accordingly.
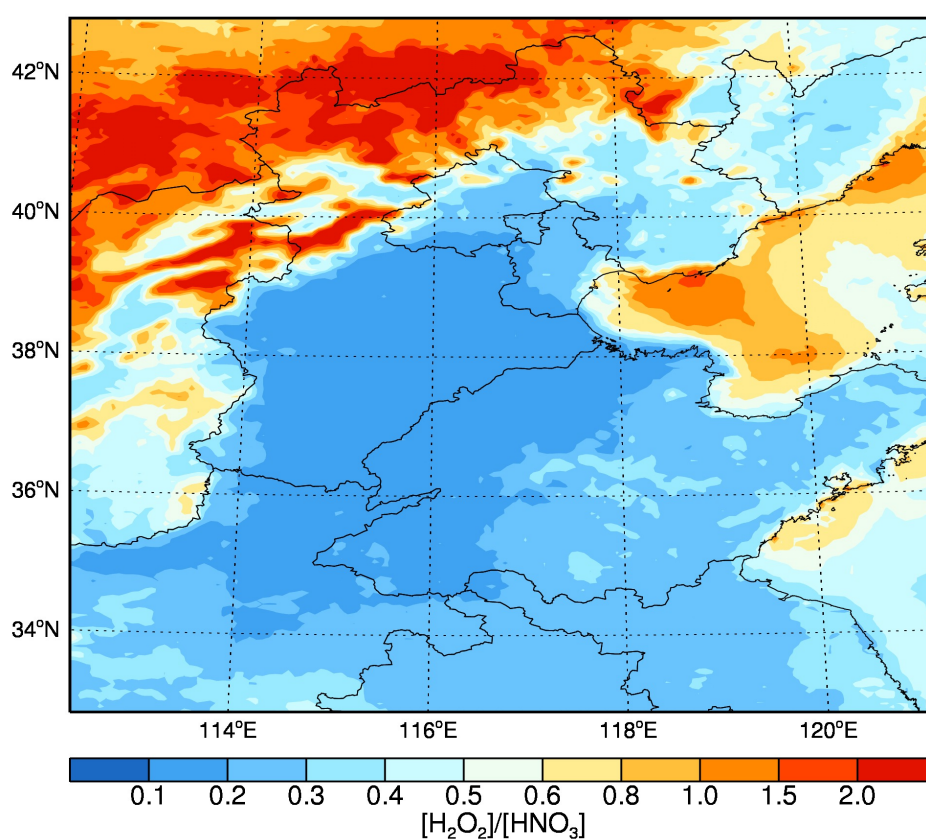
Figure S6. Spatial distribution of O₃ formation sensitivity to precursors indicated by the [H₂O₂]/[HNO₃] ratio. A ratio less than 0.3, great than 0.5, and between 0.3 and 0.5 indicates the O₃ formation under VOC-sensitive, NOₓ-sensitive and transition regimes, respectively.

42. Line 397: two other papers showing increased O₃ in response to fertilizer NOₓ: 10.1111/gcb.13644, 10.1016/j.atmosenv.2018.02.040

Response: We have included these papers as references in Lines 466-467: "*Similar scenarios are also reported during the growing season of crops in sub-Saharan Africa (Hickman et al., 2017; Huang et al., 2018).*" The References section has been updated accordingly.

43. Line 432-435: this argument could be strengthened if it quantified the emissions from the urban areas and compared them to the agricultural emissions.

Response: We have included an additional figure (Figure S7) to strengthen the statement in Lines 506-508: "*Additionally, the ongoing stringent control measures on emission sources significantly reduce anthropogenic emissions in urban areas, thus the impact of agricultural fertilization on urban air quality is becoming more pronounced (Figure S7).*"
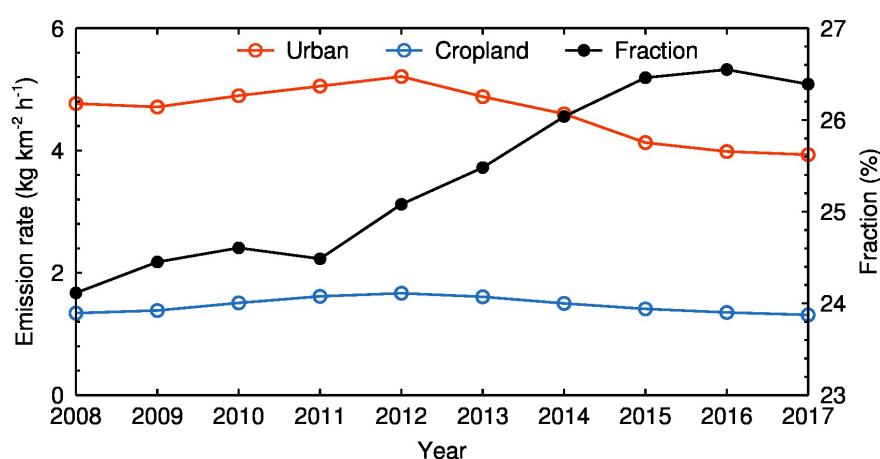

Figure S7. Temporal variations of annual anthropogenic NOx emission rate averaged over urban areas (red) and croplands (blue), respectively, in the NCP and the fraction of the

emission over croplands in the total (black) during 2008-2017. The data are derived from the

MEIC v1.3 emission inventory.

44. Line 435: the connection to global warming/climate change is not clear. I would remove it. maybe spend time on the unexpected response of ozone instead.

Response: In this section, we focus on the impacts of soil NO emission on aerosol formation, particularly nitrate and $PM_{2.5}$. The impacts on ozone formation have been discussed before that. As suggested by the other reviewer here, we have revised the sentence 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).*"

45. Lines 450-453: I'm not sure the authors are fully representing what we know about agricultural NO emissions. I'd like to see the literature much better represented here, and in the discussion in general.

Response: We have included more references in the Conclusion section in Lines 525-529: "*Impact of soil NO_x emissions from agricultural fertilization on the atmospheric environment remains unclear worldwide (Guo et al., 2020; Huang et al., 2018; Sha et al., 2021; Shen et al., 2023). In particular, this issue has not yet received enough attention in China, where substantial N-fertilizers are year by year consumed due to extensive agricultural cultivation areas (Sun et al., 2022; Vitousek et al., 2009; Zhao et al., 2006).*" And we have also included additional references in the discussion such as in Lines 435-439: "*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. Since the emission rate of*

HONO is only half that of NOx from soils in the NCP (Tan et al., 2023), we speculate that soil HONO emission would further weaken the AOC slightly in spring." and in Lines 462-475: "*... 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).*"

46. Line 455: I'd change "long-term fertilization record" to a "2-decade record of fertilization events at a research station." (I'd really love to see additional information on fertilizer management in the region: research stations are not necessarily representative of local or regional practices). In addition, the model simulations are decidedly not long-term.

Response: We have changed "*long-term fertilization record*" to "*two-decade record of fertilization events at a research station*" in Line 531. Additional information on fertilizer management in the region is provided in Lines 79-89: "*The North China Plain (NCP) is one of the major grain-producing regions in China. Winter wheat-maize double cropping is a typical*

rotation system mainly practiced in this region (Liu et al., 2003; Zhu et al., 1994). China has been the world's largest consumer of N-fertilizer since 2000 (Liu et al., 2013), with annual usage peaking at approximately 31.2 Tg N in 2014 (Yu et al., 2022). About half of this fertilizer is lost to the environment (Liu et al., 2013), indicating a significant potential source for NO_x emissions from China's croplands. The agricultural management in the NCP has been known for incorporating high fertilization rates according to the solar terms with excessive N fertilization (Sun et al., 2022; Vitousek et al., 2009; Zhao et al., 2006). Thus, this region is primarily responsible for agricultural N-fertilizer consumption (Yu et al., 2022) and has shown substantial soil NO_x emissions (Liu et al., 2010; Tang et al., 2020; Zhang et al., 2011)." and in Lines 265-275: "*The wheat-maize double-cropping system is predominate in the NCP, where the agricultural activities are strongly dependent on the lunar calendar. For winter wheat, the planting date ranges from early to mid-October (after maize harvest). Fertilization is generally divided into three stages: 1) Pre-planting during late September – early October; 2) Jointing stage during mid-March – early April; 3) Grain filling during late April for high-yield fields. The planting date of summer maize ranges from early to mid-June (after wheat harvest), and the stages of fertilization include: 1) At planting during early June; 2) V6-V8 stage during early July; 3) Tasseling stage during late July for high-yield fields. The agricultural fertilization is closely associated with three solar terms, i.e., Waking of Insects in March (the 3rd solar term), Grain in Beard in June (the 9th solar term) and Cold Dew in October (the 17th solar term).*"

47. Line 456: change "provide sufficient evidence to illustrate their" to "provide evidence consistent with a"

Response: We have changed "*provide sufficient evidence to illustrate their*" to "*provide evidence consistent with a*" in Line 532.

48. Line 461 change "leads" to "lead"

Response: We have changed "*leads*" to "*lead*" in Line 537.

49. Line 461-470: These results are really quite limited: they are for a single 3-month period in 2020. I think in this conclusion section in particular, it really needs to be emphasized that these quantitative estimates are from a limited case study; we have no idea if the responses are similar in other years with different meteorology.

Response: We have emphasized that these quantitively estimates are from a limited case study in Lines 559-563: "*Nevertheless, one should be aware of the limitation in the present case study that there are only three months of simulation as the basis for all of the insights into the soil NO$_x$ emission and its influences on atmospheric chemistry and composition. More studies in terms of soil NO$_x$ emissions, particularly during springtime, are in need to validate and generalize our model results.*"

50. Line 469: specify that this increase occurs when? March 2020?

Response: We have specified the time in Line 545: "*... in March 2020*".

51. Line 469-471: There is an enormous literature on efforts to reduce N losses from fertilizer—this statement doesn't really reflect that effort, or the fact that historically, fertilizer has been over-applied in North China and could be used much more efficiently. Additional discussion on how the results may depend on the fertilizer inputs used would be valuable.

Response: We have included discussion on this issue in Lines 550-557: "*In China, the excessive use of N-fertilizer still remains severe (Sun et al., 2022; Vitousek et al., 2009; Zhao et al., 2006), though a lot of efforts have taken to increase the N-fertilizer efficiency and to*

reduce N losses from fertilizer (Li et al., 2018; Qiao et al., 2022; YAN et al., 2008). Fortunately, the consumption of N-fertilizer reached its peak in 2014 in China and has been decreasing since then (Yu et al., 2022). Policymakers should manage to further reduce emissions from N-fertilizers application, for example, improving N-fertilizers efficiency and developing alternative fertilizers friendly to the environment are highly necessary." The References section has been updated accordingly.

52. Line 473-475: Temperature response has not been a topic in this manuscript, and there's no sense of how much changes in temperature will affect emissions in this manuscript. I would remove this.

Response: We have removed this in Line 557.