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.

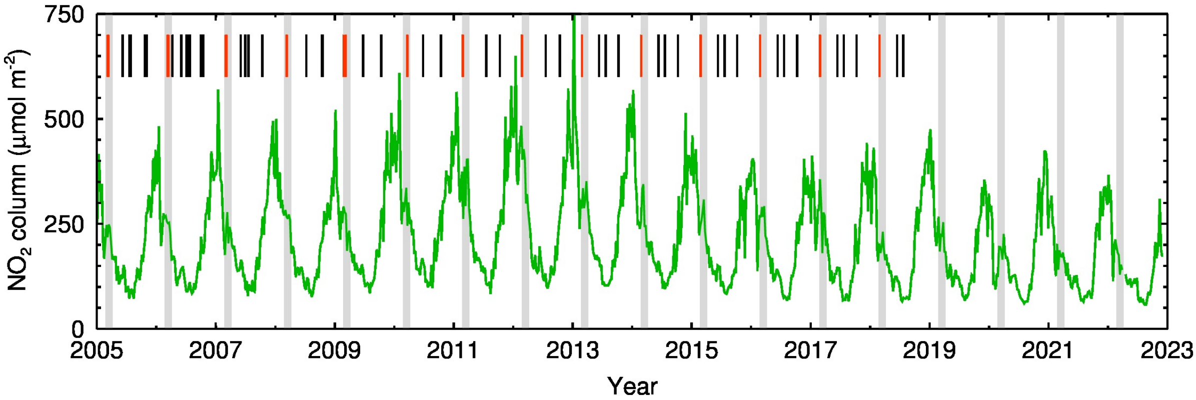

Figure R1. Long-term variation of seven-day mean tropospheric NO_2 column observed by OMI during the past two decades (2005-2022) over croplands of the NCP only. Intersections of the gray bars and the green lines denote a sub-peak of NO_2 column occurred in each March, and the short bars represent the 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.

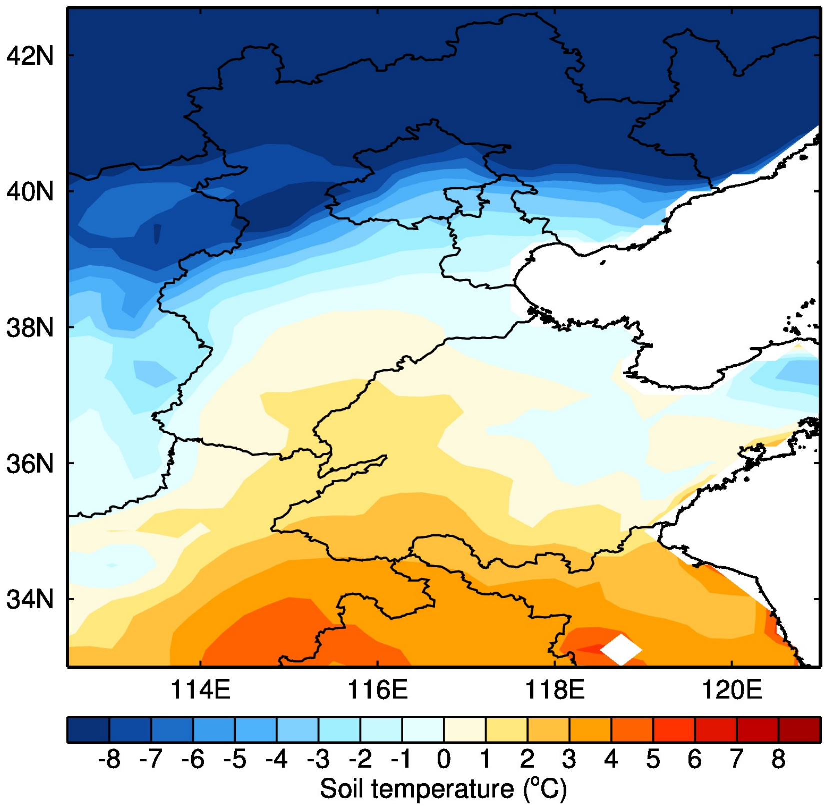

Figure S4. Spatial distribution of the minimum daily soil temperature of the top layer over the NCP during the period from 20 February to 31 March, 2020. Data are from the ERA5 reanalysis. The white areas show waters.

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.

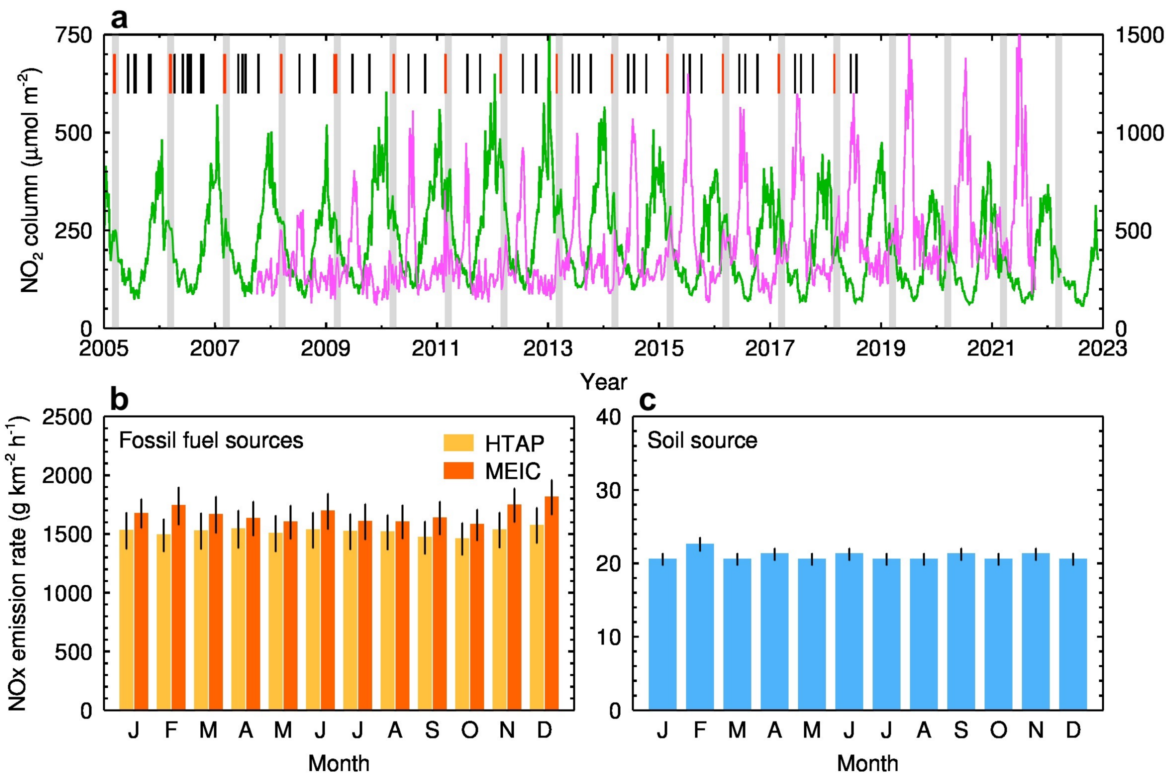

Figure R1. NO_2 and NH_3 column pulses in March and NO_x emissions from fossil fuel and soil sources over the NCP. (a) Long-term variations of seven-day mean tropospheric NO_2 column observed by OMI (green) and NH_3 column by IASI (pink) during the past two decades (2005-2022). Intersections of the gray 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 $\pm 1\boldsymbol{\sigma}$ 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:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

$$NO_2 + h\nu\ (+O_2) \rightarrow NO + O_3 \quad (2)$$

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.

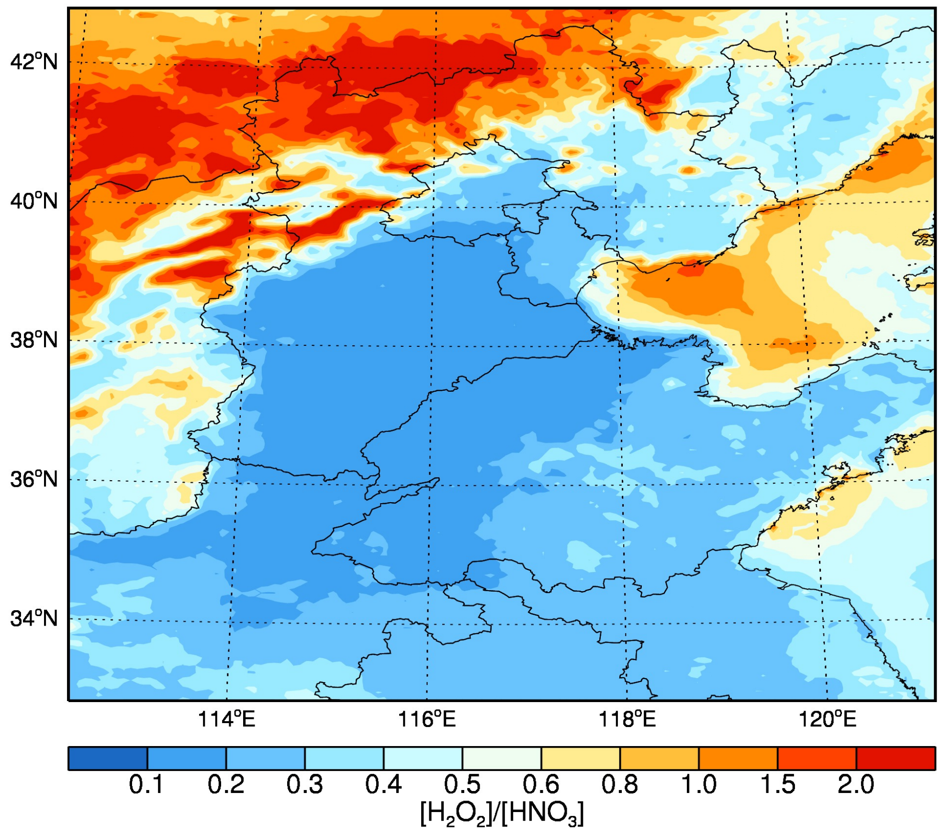

Figure S6. Spatial distribution of O_3 formation sensitivity to precursors indicated by the $[H_2O_2]/[HNO_3]$ ratio. A ratio less than 0.3, great than 0.5, and between 0.3 and 0.5 indicates the O_3 formation under VOC-sensitive, NO_x-sensitive and transition regimes, respectively.

42. Line 397: two other papers showing increased O_3 in response to fertilizer NO_x: 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).*"

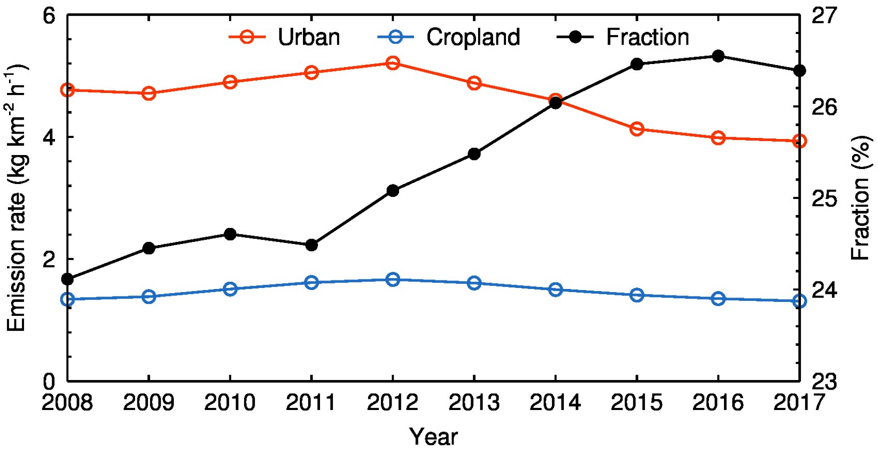

Figure S7. Temporal variations of annual anthropogenic NOx emission rate averaged over urban areas (red) and croplands (blue), respectively, in the NCP and the fraction of the *emission over croplands in the total (black) during 2008-2017. The data are derived from the MEIC v1.3 emission inventory.*

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.