Response to Referee #2

Title: Uncertainties in fertilizer-induced emissions of soil nitrogen oxide and the associated impacts on ground-level ozone and methane

MS number: egusphere-2025-1416

Authors: Cheng Gong, Yan Wang, Hanqin Tian, Sian Kou-Giesbrecht, Nicolas Vuichard, and Sönke Zaehle

Comments:

The manuscript titled "Uncertainties in fertilizer-induced emissions of soil nitrogen oxide and the associated impacts on ground-level ozone and methane," written by Gong et al., quantifies the uncertainties in soil NOx emissions induced by N fertilizer application (SNOx-Fer) using different estimation approaches and investigates the associated impacts on the simulation of global O3 and CH4 concentrations. Overall, this manuscript is well-structured, and the conclusion is important. However, I would like to raise two major concerns and several minor suggestions for improvement.

Response:

We appreciate reviewer's acknowledgment on the importance of our work and the constructive comments to help further improve this work. The manuscript has been revised accordingly. Please see our point-to-point response below.

Major concerns:

I can tell by Figures 2, 3, 4, and Section 4.2 that, in general, regions with higher SNOx-Fer have higher O3 enhancement. Is this an approximately linear relationship? Does this relationship vary across different sensitivity experiments and different regions? Providing a more detailed analysis of the response of the O3 simulation to NOx estimations would further highlight the importance of this work. The same concern also applies to the OH/CH4 simulation.

Response:

Thank you for this valuable point. The responses of O_3 to NO_x changes could vary a lot depending on the local NOx/VOC ratios, the magnitude of NOx perturbation and metrological variations. Therefore, it is not a simply linear relationship. We agree that the analysis you suggested could help us better understand O_3 in which region is more sensitive to the SNOx-Fer changes, at least in the GEOS-Chem model. Here we further examined the monthly MDA8 O_3 changes in response to SNOx-Fer across all simulated grids in four representative hotspot regions (Fig. R1). Our results show the sensitivities of O_3 to SNOx-Fer changes are all positive, i.e. O_3 increase with enhanced SNOx-Fer, which might because of the relatively coarse resolution, but vary a lot among different regions and different SNOx-Fer estimating approaches. The Eastern U.S. in general has the strongest sensitivity, while sensitivities in the rest three regions are similar. Nevertheless, the R^2 of the linear regressions are not very high (0.04-0.68), indicating the strong non-linearity behind the O3-NOx-VOCs chemistry.

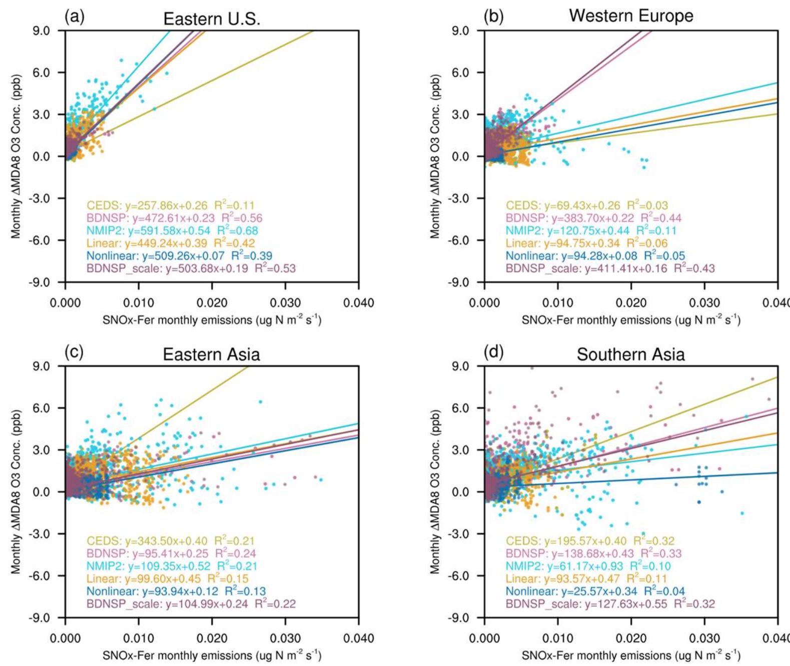

Figure R1. The sensitivity of changes in monthly MDA8 O_3 concentrations (ppbv) to the SNOx-Fer changes (μg N m^{-2} s^{-1}) among different approaches in four agricultural hotspot regions. Each dot indicates the monthly SNOx-Fer emissions and associated monthly MDA8 O_3 changes induced by SNO_x-Fer on a simulated grid. The different SNOx-Fer estimating approaches are indicated by lines with different colors.

Similar patterns are also found in the response of OH to SNOx-Fer changes (Fig. R2). Furthermore, because CH_4 has much longer lifetime and thus the atmospheric transport could smooth the local CH_4 changes induced by varied OH, the regional CH_4 changes are more determined by the global signals rather than local SNOx-Fer perturbation. Nevertheless, we could still find discrepancies in the responses of ground-level CH_4 to SNOx-Fer among different regions and different SNOx-Fer estimates (Fig. R3), indicating the strong non-linearity in CH_4-OH-NOx chemistry.

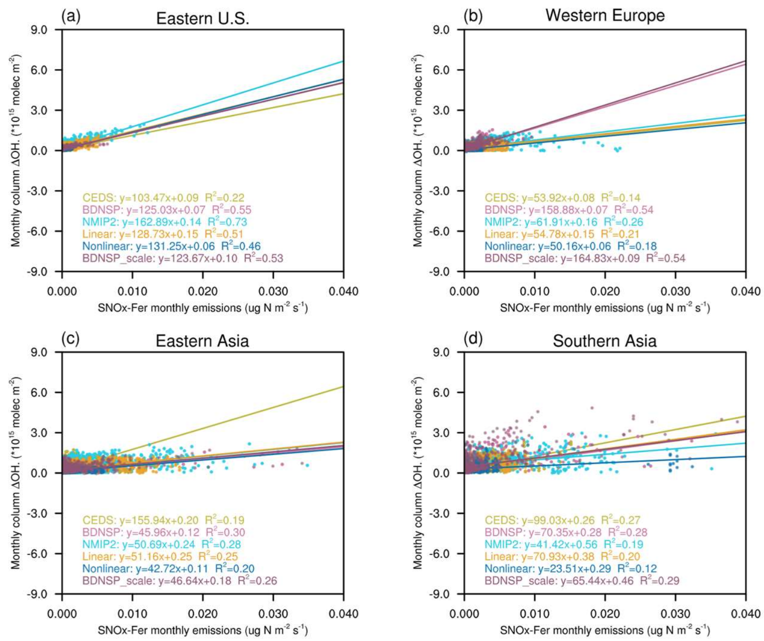

Figure R2. The sensitivity of changes in monthly column OH concentrations ($*10^{15}$ molec m^{-2}) to the SNOx-Fer changes (μg N m^{-2} s^{-1}) among different approaches in four agricultural hotspot regions. Each dot indicates the monthly SNOx-Fer emissions and associated monthly OH changes induced by SNO_x-Fer on a simulated grid. The different SNOx-Fer estimating approaches are indicated by lines with different colors.

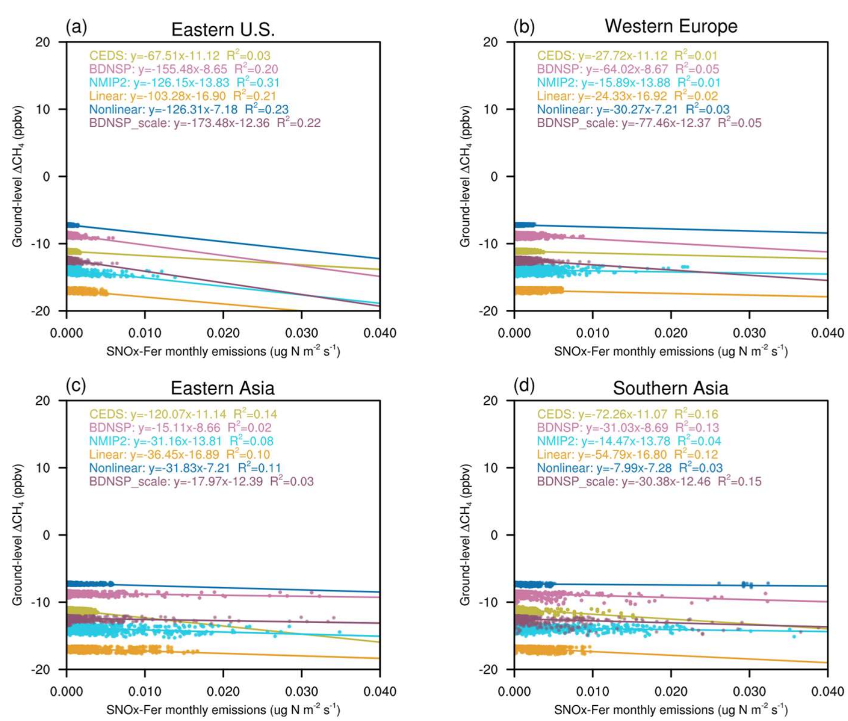

Figure R3. The sensitivity of changes in monthly ground-level CH_4 concentrations (ppbv) to the SNOx-Fer changes (μg N m^{-2} s^{-1}) among different approaches in four agricultural hotspot regions.

Each dot indicates the monthly SNOx-Fer emissions and associated monthly CH_4 changes induced by SNO_x-Fer on a simulated grid. The different SNOx-Fer estimating approaches are indicated by lines with different colors.

We have added discussions about this:

'This range of responses leads to an enhancement in summertime surface MDA8 O_3 concentrations of 0.3 1 ppbv to 3.3 ppbv (0.2%-7.0%) in agricultural hotspot regions. The O_3 enhancement is highest in eastern U.S., while it is not only determined by the SNOx-Fer emissions, but also the diverging sensitivities of O_3 to NO_x depending on different chemical regime in GEOS-Chem (Fig. S6). The varied SNOx-Fer estimates also lead to a reduction in global CH_4 concentrations of 6.7 ppbv (0.4%) to 16.6 ppbv (0.9%) …'

In Lines 125–129, the growing season is defined using monthly-mean 2-meter temperature and leaf area index instead of using some crop calendar datasets. While this approach is straightforward and climate-driven, it may oversimplify the actual crop phenology in diverse agricultural systems. Given that the rates of N inputs are set to zero during the non-growing season, this definition directly controls the temporal pattern of fertilizer application and thus significantly affects the estimates of fertilizer-induced NOx emissions. If crop-specific growing seasons are not distinguishable in this study, the authors should at least discuss the potential implications of this assumption in the discussion section.

Response:

We acknowledge that reviewer raised an important issue when applying the EF method to assess SNOx-Fer, while the rest SNOx-Fer estimating approaches in this study are not dependent on this growing season definition. However, we are afraid that the more detailed crop calendar dataset (e.g. Minoli et al., 2019; Minoli et al., 2022) may still not be sufficient. It is not only because the consistent calendar datasets of pasture and rangeland are not available, but more importantly, the fertilizer management (e.g. how was the annual total fertilizer application distributed across months) should be the key factor that influence the seasonal cycles of SNOx-Fer. However, to our knowledge, the dataset that records the seasonal fertilizer distribution is not available yet.

The definition of growing season used in this study is not only depending on the climate, but also relies on the realistic plant greenness index (e.g. LAI). Such method is also widely used to identify the phenology of agricultural land cover (e.g. used by the Food and Agriculture Organization of the United Nations https://agriculture.africageoportal.com/datasets/d9944082e3c6421098464b1016fbae58/about). As this study only focus on the annual and monthly (not day-to-day) variations of SNOx-Fer, we believe that such simplified definition is sufficient to capture the dominant pattern.

We have explicitly addressed the seasonality analysis among different SNOx-Fer approaches in the revised manuscript (Sect. 4.2 and Figs. 4-5. See the response to Reviewer #1). We discuss the uncertainties induced by the definition of growing season in the revised manuscript as below:

'In the EF approaches, the growing season is determined only by temperature and greenness in this study, which could result in a mismatch with the real crop or pasture calendar, especially ignoring the multiple-harvest crops per year. A refined calendar could further improve the prediction of SNOx-Fer seasonality.'

Minor points:

Are there any top-down methods for estimating NOx emissions? If so, it would be beneficial for the authors also to describe it in the introduction, allowing for a more comprehensive review of the estimation approaches.

Response:

Top-down method could more precisely assess the total NO_x emissions from all sources. However, distinguishing different sources is always challenging. Although there are some studies are able to isolate soil NO_x emissions by assuming the fossil-fuel emissions inventory is accurate or only applying the retrieval in pixels without significant industrial activities (e.g. Bertram et al., 2005; Lin et al., 2024), it is still very difficult to further isolate the background and fertilizer-induced soil NOx emissions.

We have added it as a discussion point in the revised manuscript:

'…. Last but not least, the top-down retrievals of NO_x emissions based on satellite NO_2 products could also have the potential to better constrain SNOx-Fer, while gaps remained in how to precisely isolate the soil NO_x emissions (Bertram et al., 2005; Lin et al., 2024) and even the fertilizer contributions from the total NO_x sources. Synergizing the top-down NO_x retrievals with ultra-high resolutions, where it can be assumed that the atmospheric NO_x is dominantly affected by the soil sources in agricultural regions, with spatiotemporally detailed fertilizer management dataset could be one possible solution. However, more work is definitely needed to integrate such a big data in the future.'

Section 2.2: Consider also adding one or two sentences to describe why this specific inventory is chosen.

Response:

We have added the reason as:

'We use the CEDS (Hoesly et al., 2018) for assessing the fertilizer-induced soil NO_x emissions in the emission inventories. CEDS is one of the most state-of-art emission inventories that comprehensively assess the sources of dominant air pollutants from pre-industrial period to present days, which has been used as the standard emission inventory to drive CMIP6 models.'

Figure 1: Consider merging (a) and (b) into a single figure using a secondary Y-axis for fertilizer input, which would help the reader better interpret the relationship between nitrogen inputs and SNOx-Fer across approaches.

Response:

We have revised the Fig. 1 following both of your and the other reviewer's comment as:

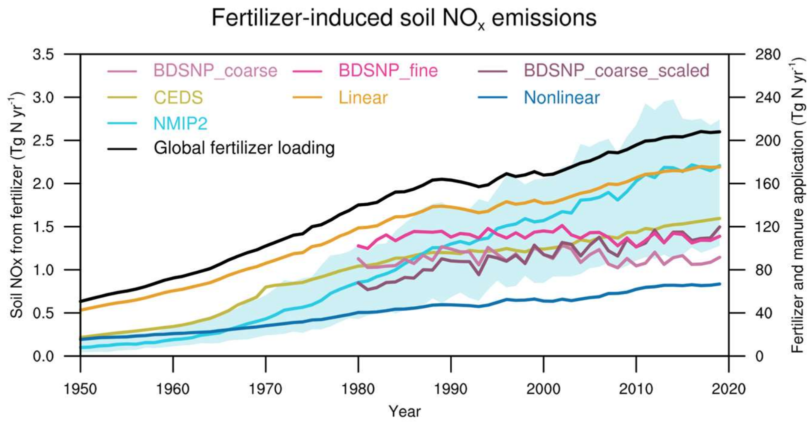

Figure 1. Global estimates of N fertilizer-induced soil NO_x emissions by different approaches. The black line (right Y axis) indicates global annual-mean N synthetic fertilizer and manure inputs over 1950-2019 assessed from the HaNi dataset. The rest lines (left Y axis) indicate the N fertilizer-induced soil NO_x emissions over 1950-2019 estimated by different approaches, including emission inventory (CEDS), linear and non-linear EF, the widely-used CTM parameterization with coarse resolution (2°×2.5°, BDSNP_corase), fine resolution (0.5°×0.625°,BDSNP_fine) and interannually varied N availability (BNDSP_corase_scaled), and the TBM ensembles (NMIP2). The light cyan shadows indicate the spread across three different TBMs in NMIP2.

Section 4.2 and 4.3: When reporting changes in O3 and CH4 concentrations, consider also providing percentage changes rather than only providing the ppbv changes.

Response:

The percentage changes relative to the simulated concentrations have been added accordingly.

The HaNi dataset provided N inputs for cropland, pasture, and rangeland. Consider also providing the NOx emissions from cropland, pasture, and rangeland in the Supplementary Information.

Response:

Added.

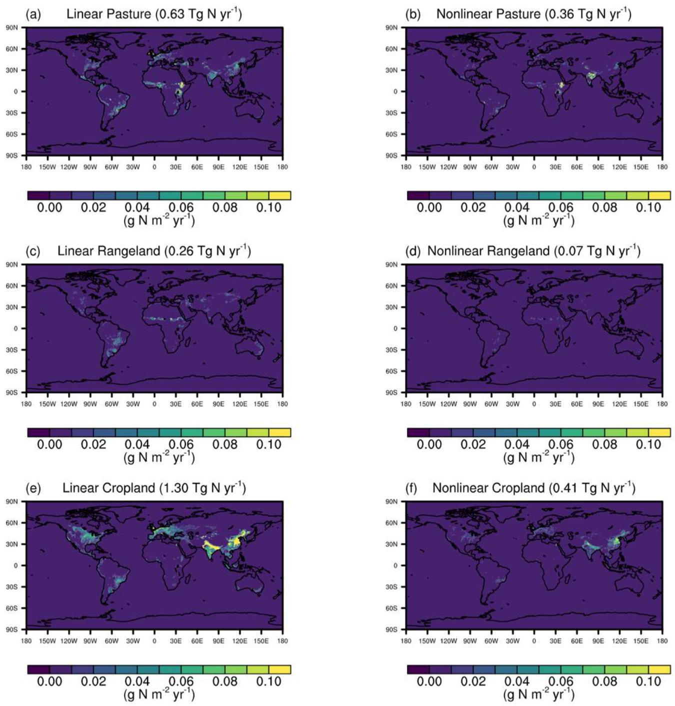

Figure S2. The spatial patterns of SNOx-Fer in pasture, rangeland and crops estimated by linear EF and non-linear EF approaches in 2019. The global total budget of each estimate is given in the sub-titles.

Given the large differences in simulated surface O3 concentrations across the different SNOx-Fer estimation methods (e.g., Fig. 3 and 4), it would be valuable to include a brief comparison with surface O3 observations. While a full validation is beyond the scope of this study, even a qualitative comparison could help indicate which NOx emission estimation method may better reproduce observed O3 levels in key agricultural regions.

Response:

We compared our simulated summertime monthly MDA8 O_3 concentrations against the ground-level observations in Eastern U.S. (https://www.epa.gov/aqs), Western Europe (https://ebas-data.nilu.no/Default.aspx) and China (https://www.cnemc.cn/en/) (Figure S7). The site-level observational O_3 concentrations are averaged on each simulated grid. Note that the differences in SNOx-Fer estimates are not sufficient to explain the model systematic bias, but they are likely induced by uncertainties in other processes such as non-linear chemistry, transport and deposition.

We think it is an open question about how to properly evaluate which SNO_x-Fer approaches are accurate. As we also mentioned above, the high-resolution top-down NOx retrievals could be another possible solution but there are also uncertainties in how to precisely isolate the SNO_x-Fer from the total NO_x emissions. We are glad to add discussions in the end to point out this question:

'Beyond the uncertainties remaining in different SNO_x-Fer estimating approaches, an important but also difficult question is how to better evaluate the performances of each methods, especially in the regional and global scales. The first-hand meta-data collected from the field experiments is actually not an independent source, as it has been used to establish both of the linear and nonlinear EF methods. More importantly, most of the field experiments are manipulation experiments with artificial fertilizer gradients, which may not fully represent the real-world spatiotemporally varied SNO_x-Fer. Furthermore, we use O_3 data from the national or continental air quality observational networks to evaluate simulated

O_3 concentrations as a potential consistency check of the SNO_x-Fer (Fig. S7). However, the uncertainties in SNO_x-Fer are expected to be far less important relative to the uncertainties in the nonlinearity of atmospheric chemistry, emissions of BVOCs or the deposition processes, which together determined the biases between observational and simulated O_3 concentrations. As a result, it is inappropriate to determine the best SNO_x-Fer estimate as the one with the best statistic metrics in O_3 simulation. Moreover, most of the sites that monitor air pollutants are located in the urban regions, where the industrial impacts are far more important than the agricultural sources. A real-time O_3 observational network in the cropland or pasture would be crucial to advance the understandings in SNO_x-Fer and the associated impacts on air quality. Last but not least, the top-down retrievals of NO_x emissions based on satellite NO_2 products could also have the potential to better constrain SNO_x-Fer, while gaps remained in how to precisely isolate the soil NO_x emissions (Bertram et al., 2005; Lin et al., 2024) and even the fertilizer contributions from the total NO_x sources. Synergizing spatiotemporally detailed fertilizer management dataset with the top-down NO_x retrievals with ultra-high resolutions, where the atmospheric NO_x can be assumed to be dominantly affected by the soil sources in agricultural regions, could be one possible solution. However, more work is needed to integrate such a big data in the future.'

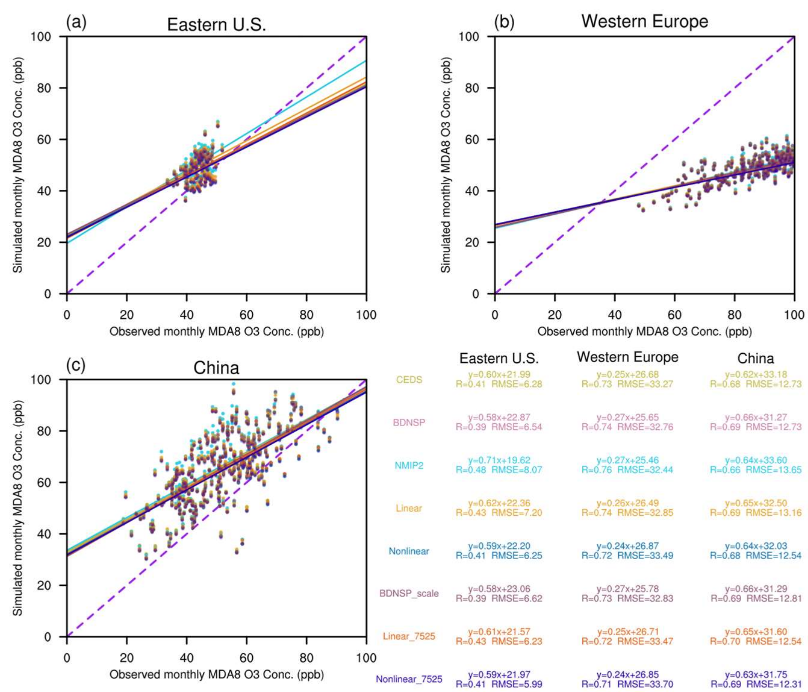

Figure S7. The comparison of monthly-averaged O_3 MDA8 concentrations between site-level observations and the GEOS-Chem simulations. The observational dataset in Eastern U.S., Western Europe and China are assessed via the Air Quality System (AQS, https://www.epa.gov/aqs), European Monitoring and Evaluation Programme (EMEP, https://ebas-data.nilu.no/Default.aspx) and China National Environmental Monitoring Centre (CNEMC, https://www.cnemc.cn/en/), respectively. Each dot indicates one simulated grid, where the observed O_3 concentrations are calculated by averaging all observational sites. The GEOS-Chem sensitivity experiments with different SNOx-Fer estimating approaches are indicated by different colors.

Reference

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