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

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Abstract

Natural and agricultural soils are important sources of nitrogen oxides (NO_x), accounting for about 10% - 20% of the global NO_x emissions. The increased application of nitrogen (N) fertilizer in agriculture has strongly enhanced the N availability of soils in the last several decades, leading to higher soil NO_x emissions. However, the magnitude of the N fertilizer-induced soil NO_x emissions remains poorly constrained due to limited field observations, resulting in divergent estimates. Here we integrate the results from meta-analyses of field manipulation experiments, emission inventories, atmospheric chemistry modelling and terrestrial biosphere modelling to investigate these uncertainties and the associated impacts on ground-level ozone and methane. The estimated present-day global soil NO_x emissions induced by N fertilizer application varies substantially (0.84–2.2 Tg N yr^{-1}) among different approaches with different spatial patterns. Simulations with the 3-D global chemical transport model GEOS-Chem demonstrate that N fertilization enhances global surface ozone concentrations during summertime in agricultural hotspots, such as North America, western Europe and eastern and southern Asia by 0.3 to 3.3 ppbv. Our results show that such spreads in soil NO_x emissions also affect atmospheric methane concentrations, reducing the global mean by 7.1 ppbv to 16.6 ppbv as indirect consequence of enhanced N fertilizer application. These results highlight the urgent need to improve the predictive understanding of soil NO_x emission responses to fertilizer N inputs and its representation in atmospheric chemistry modelling.

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1. Introduction

Nitrogen oxides (NO_x=NO + NO_2), as one of the most important reactive atmospheric components, strongly affect the atmospheric oxidation capacity and further influence air quality (Gong et al., 2020; Zhai et al., 2021; Goldberg et al., 2022; Zhao et al., 2023), radiative forcing (Erisman et al., 2011; Pinder et al., 2012; Gong et al., 2024), as well as carbon (C) storage in terrestrial and marine ecosystems (Fowler et al., 2013; Fleischer et al., 2019; Rubin et al., 2023). The major source of present-day atmospheric NO_x is fossil fuel combustion (Martin et al., 2003; Hoesly et al., 2018), but several non-fossil-fuel sources, including emissions from soils, lightning and wildfire (Zhang et al., 2003), contribute to around 30% of the global total NO_x emissions (Delmas et al., 1997; Weng et al., 2020). However, these non-fossil-fuel sources have been widely regarded as 'natural' sources, where the perturbation by anthropogenic activities as well as the associated potentially significant effects on the N cycle are often overlooked. Meanwhile, strict clean-air actions have been applied in many countries in the past decades to sharply reduce the fossil-fuel sources of NO_x (Jiang et al., 2022). As a result, non-fossil sources of NO_x will be increasingly important for future clean air policies.

One of the most important non-fossil-fuel anthropogenic sources of NO_x is through agricultural activities, which have been estimated to enhance soil NO_x emissions by around 5%- 30% (Wang et al., 2022; Gong et al., 2024). To assess the soil NO_x emissions induced by N fertilizer application (hereafter, SNO_x-Fer), the most straightforward and widely-used method is applying the emission factor (EF), which indicates the proportion of N from fertilizer application emitted as NO_x. The Intergovernmental Panel on Climate Change (IPCC) methodology recommended a constant EF value 1.1% with an uncertainty range of 0.06% to 2.18% (Hergoualc'h et al., 2019). Other studies recommend slightly smaller uncertainty ranges (0.47% to 1.61%) based on different meta-analysis datasets (Stehfest and Bouwman, 2006; Liu et al., 2017; Skiba et al., 2021; Wang et al., 2022). This large uncertainty range results from the dependency of the response of soil NO_x emissions on intricate soil biogeochemical processes and varies with crop types, soil texture, fertilizer types and application rate (Wang et al., 2022). To date, limited field experiments are available to constrain this uncertainty range.

Some studies have suggested to use non-linear EF to take account of the observations that the EFs of soil reactive nitrogen gases tend to increase with increasing fertilizer application (Shcherbak et al., 2014; Jiang et al., 2017). Such approach assumes that plants and soil microbes should have priority to access soil available N for their metabolic activities, while the excessive inorganic N can be used by nitrifiers and denitrifiers and loses as the gas form. Such a non-linear EF approach is more ecologically reasonable but there remain large uncertainties in assessing soil NO_x due to the limited available field data. For example, Wang et al. (2024) examined the non-linear EF of soil NO_x based on a global meta-analysis and found a much lower EF (around 0-0.7%) than the IPCC recommended linear EF (1.1%) within the range of normal agricultural crop N fertilizer loading (around 0-600 kg N ha^{-1} yr^{-1}).

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In many of the atmospheric chemical transport model (CTMs), SNO_x-Fer is represented by the agriculture sector of NO_x emission from an anthropogenic emission inventory (e.g. Emissions Database for Global Atmospheric Research (EDGAR) or Community Emissions Data System (CEDS)), which in general apply the method of linear EF to estimate the agricultural NO_x emissions (Hoesly et al., 2018; Janssens-Maenhout et al., 2019; Nicholas Hutchings et al., 2023) with the caveats described above. Furthermore, some advanced CTMs, e.g. the GEOS-Chem model, parametrizes soil NO_x emissions as a function of N availability as well as soil temperature and soil moisture (Steinkamp and Lawrence, 2011; Hudman et al., 2012). The currently widely-used soil NO_x scheme named by the Berkeley-Dalhousie Soil NO_x Parameterization (BDSNP), however, fixes the SNO_x-Fer in the year of 1998 (See the detailed parameterization in Sect. 2). As a result, such parameterization in CTMs do not capture the effect of increasing agricultural N fertilizer application on soil NO_x emissions as well as the associated impacts on atmospheric chemistry.

Recently, another approach to modelling SNO_x-Fer has emerged by the development of global, process-based terrestrial biosphere models (TBMs) with fully-coupled C and N cycles (Zaehle and Friend, 2010; Tian et al., 2019). Driven by data of N inputs (N synthesis fertilizer, N manure application and N deposition), CO_2 concentrations and climate, these TBMs could simulate the coupled-cycles of C and N in the terrestrial biosphere, mimic the competition on the available N between plants and microbes and calculate the rates of nitrification and denitrification (Zaehle and Dalmonech, 2011), which are the two microbial processes that determine the rates of soil NO_x emissions. Even though TBMs provides a more ecologically-mechanistic description of the terrestrial N cycles, large uncertainties remained among different TBMs due to the varying parameterization and modelling schemes on biome N use strategies, mineralization of organic N, nitrification and denitrification processes (Kou-Giesbrecht et al., 2023), which lead to varied responses of soil NO_x to the increased N fertilizer inputs (Gong et al., 2024).

In this study, we attempt to comprehensively quantify the uncertainties in current SNO_x-Fer estimates by integrating results from meta-analyses, emission inventories, as well as CTMs and TBMs. We use this understanding to assess the associated effects of SNO_x-Fer uncertainties on global O_3 and CH_4 concentrations. Section 2 will introduce the N synthetic fertilizer and manure input data and each approach to estimate SNO_x-Fer. Section 3 will introduce the CTM model used in this study and the configuration of sensitive experiments. Section 4 will firstly show the variations of SNO_x-Fer among different approaches, and then analyze the associated uncertainties in global O_3 and CH_4 simulations. Finally, the conclusion and discussions of this study will be given in section 5.

2. Data and Methods

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2.1. Linear and Non-linear EFs and the global fertilizer N dataset

We firstly implement the most traditional method with a constant EF value to estimate the effects of N fertilizer application on soil NO_x emissions, where the value of 1.1% (named as EF_{linear} hereafter) based on the most up-to-date IPCC methodology is adopted (Hergoualc'h et al., 2019). Furthermore, based on the latest meta-analysis dataset developed by Wang et al. (2024), a non-linear EF method ($EF_{non\text{-}linear}$) to describe the variations of soil NO_x emissions with different N fertilizer loadings is also applied:

$$EF_{non-linear} = (0.22 + 0.008 \times Fertilizer_N) \quad (1)$$

where the $EF_{non\text{-}linear}$ (%) is the non-linear EF and $Fertilizer_N$ is the loading of fertilizer N application (kg N ha^{-1}). The detailed derivation of this formula is presented by in Wang et al. (2024), which follows a comparable method as presented by Shcherbak et al. (2014).

We used the dataset of History of anthropogenic Nitrogen inputs (HaNi) (Tian et al., 2022) for the global rate of synthetic fertilizer and manure application, in order to estimate SNOx-Fer with both of the linear and non-linear EF methods. The HaNi dataset includes grid-level annual loadings of (1) NH_4^+-N synthetic fertilizer applied to cropland, (2) NO_3^--N synthetic fertilizer applied to cropland, (3) NH_4^+-N synthetic fertilizer applied to pasture, (4) NO_3^--N synthetic fertilizer applied to pasture, (5) manure NH_4^+-N application on cropland, (6) manure NO_3^--N application on pasture, (7) manure NH_4^+-N deposition on pasture, (8) manure NO_3^--N deposition on rangeland. We use a global map of land use class distributions (Hurtt et al., 2020) (Fig. S1) to convert the unit of N loading in HaNi from g N $grid^{-1}$ to kg N (ha $pasture)^{-1}$, kg N (ha $rangeland)^{-1}$ or kg N (ha $cropland^{-1}$). The annual N synthetic fertilizer and manure from HaNi dataset are evenly applied in the months of growing season, while the rates of N inputs are set as zero during the non-growing season. We define growing season as monthly-mean 2-metre temperature larger than 5 degree Celsius (based on the MERRA2 reanalyzed dataset, see below Sect. 3) and the grid-level monthly-mean leaf area index (LAI) larger than 0.5 (based on MODIS remote sensing dataset postprocessed by Yuan et al. (2011) and updated for the use of GEOS-Chem, http://geoschemdata.wustl.edu/ExtData/HEMCO/Yuan_XLAI/v2021-06/). Finally, the rates of synthetic fertilizer and manure N inputs with the unit of kg N (ha pasture/rangeland/$cropland)^{-1}$ $month^{-1}$ are utilized to estimate global SNO_x-Fer with the both of the linear and non-linear EF approaches.

2.2. The emissions inventory

We use the CEDS (Hoesly et al., 2018) for assessing the fertilizer-induced soil NO_x emissions in the emission inventories. The agricultural NO_x emissions in CEDS is from the EDGAR 4.3.1 (https://edgar.jrc.ec.europa.eu/), where the old IPCC methodology (Eggleston et al., 2006) is used with a constant EF value of 0.7% (Janssens-Maenhout et al., 2019).

2.3. The BDSNP scheme

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The BDSNP scheme in CTMs is firstly developed by Yienger and Levy (1995), and then updated by Hudman et al. (2012). The emission of soil NO_x (S_{nox}) is described as:

$$S_{nox} = \left(A_{w,biome} + N_{avail} \times \bar{E}\right) \times f(T) \times g(\theta) \times P(l_{dry}) \quad (2)$$

Where f(T), g(θ) and P(l_{dry}) indicate the effects of temperature, soil moisture and the rain pulsing. $A_{w,biome}$ is the wet biome-dependent emission (the baseline emission) from Steinkamp and Lawrence (2011). N_{avail} is the soil available N mass in the top 10 cm (ng N m^{-2}), which is calculated by:

$$N_{avail}(t) = N_{avail}(0)e^{-\frac{t}{\tau}} + Fertilizer_N \times \tau \times (1 - e^{-\frac{t}{\tau}}) \quad (3)$$

Where the initial soil available N mass $N_{avail}(0)$ is prescribed. $Fertilizer_N$ is the rate of fertilizer N application, which is set as zero outside the growing season. τ indicates the decay rate and is chosen as 4 months based on the measurement within the top 10 cm soil (Matson et al., 1998; Cheng et al., 2004; Russell et al., 2011). However, it should be noted that magnitude of global SNO_x-Fer (i.e. the $N_{avail} \times \bar{E}$) is scaled by the factor $\bar{E}$ in Eq. (2) to meet 1.8 Tg N yr^{-1}, which is the value obtained in a previous meta-analysis study based on the fertilizer N input dataset in the year of 1998 (Stehfest and Bouwman, 2006). As a result, the BDNSP scheme actually fails to capture the year-to-year variations of soil NO_x emissions with the changing soil N availability. However, as the BDNSP scheme is still widely used by the community of atmospheric chemistry modelling (e.g. Lu et al., 2021; Wang et al., 2022; Huber et al., 2023), here we include it as one optional method to better represent the uncertainties in the soil NO_x emissions induced by N fertilizer application. The soil NO_x emissions are off-line simulated over 1980-2019 within the framework of the Harmonized Emissions Component (HEMCO) in GEOS-Chem, which can be accessed in http://geoschemdata.wustl.edu/ExtData/HEMCO/OFFLINE_SOILNOX/ .

2.4. The TBM ensemble

Simulated soil NO_x emissions were provided by three TBMs (CLASSIC, OCN and ORCHIDEE) with fully-coupled C and N cycles included in the global nitrogen/N_2O model inter-comparison project phase 2 (NMIP2) (Tian et al., 2024). For each TBM model, anthropogenic fertilizer application are estimated by the HaNi dataset (Tian et al., 2022). The SNO_x-Fer can be isolated by summing up the differences between sensitivity experiments SH1 and SH2 (the synthetic fertilizer contribution) and the differences between sensitivity experiments SH1 and SH3 (the manure contribution) (Table S1). It should be noted that the CLASSIC model did not isolate synthetic fertilizer and manure and thus only conducted one sensitivity experiment. The model ensemble mean is utilized to smooth the large discrepancies among different TBMs (Fig. S2) due to the varied terrestrial N-cycle representations, in particular, the varied nitrification and denitrification rates.

3. The GEOS-Chem model and sensitivity experiment configuration

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The GEOS-Chem model is a frequently used state-of-the-art CTMs with fully coupled NOx–Ox–hydrocarbon–aerosol chemistry mechanism (Bey et al., 2001; Park et al., 2004). Here we applied the version 12.0.0 to run the global simulation with a horizontal resolution of 2° latitude × 2.5° longitude. The simulations are driven by the Version two of modern era retrospective-analysis for research and application (MERRA2) reanalyzed meteorological dataset. The photolysis rates were computed by Fast-JX scheme (Park et al., 2004). The atmospheric gas-phase chemistry is solved by the Kinetic Pre-Processor (KPP) (Henze et al., 2007). In particular, the default soil NO_x emissions are simulated by the BDSNP scheme as introduced above.

In order to examine the uncertainties in the SNO_x-Fer and the associated effects on global surface O_3 concentrations, we firstly run a reference simulation in 2019 (named Zero) with zero SNO_x-Fer to exclude the influence of fertilizer application on soil NO_x. Then five different experiments are performed by representing SNO_x-Fer with CEDS agricultural NO_x emissions (named CEDS), the BDSNP (Eq. 2), scheme (named BDSNP), the TBM ensembles (named NMIP2), the linear EF (EF=1.1%) method (named Linear) and the non-linear EF (Eq. 1) method (named Nonlinear), respectively. All of the sensitivity experiments are driven by the meteorological field in the year of 2019 with 6-month spin up, where the anthropogenic emissions of all other tracers also keep at the level of 2019 following the CEDS inventory. Table 1 summarizes the six sensitivity experiments in GEOS-Chem.

Table 1. Summary of the sensitivity experiments in GEOS-Chem.

Experiment name	Emissions of SNOx-Fer
Zero	0
CEDS	CEDS agricultural NO_x sector
BDSNP	BDSNP
NMIP2	TBM ensemble mean
Linear	Linear EF
Nonlinear	Non-linear EF

Because the default GEOS-Chem simulations used above do not account for interactive CH_4 chemistry, we further conducted six more sensitivity experiments with the special 'CH_4 run' in GEOS-Chem (East et al., 2024; Fu et al., 2024) to assess the variations in the atmospheric CH_4 concentrations induced by the uncertain SNO_x-Fer. The special CH_4 run takes CH_4 as the only one atmospheric transport tracer with various prescribed CH_4 sources (summarized in Table S2), while the CH_4 sinks include the tropospheric reactions with hydroxyl radical (OH) and chlorine, stratospheric loss and soil uptake. The

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global monthly mean OH concentrations archived from the six sensitivity experiments (Table 1) are applied in the CH_4 simulation to assess the SNOx-Fer effect on CH_4 lifetime through perturbing atmospheric oxidation capacity. As a result, there will be six more associated sensitivity experiments with the CH_4 run that corresponds to the default GEOS-Chem simulations in Table 1. Each CH_4 simulation runs for 15 years by repeating the meteorological forcings in 2019 to reach a semi-equilibrium with the prescribed emissions and OH concentrations. The last year of the simulation is utilized to analyze the influences of soil NO_x on CH_4 induced by N fertilizer application. The simulated global surface CH_4 concentrations driven by varied OH levels from different sensitivity experiments are shown in Fig. S3.

4. Results

4.1 Varied SNO_x-Fer among different approaches

Figure 1a shows the historical time series of global SNO_x-Fer over 1950-2019 estimated by different approaches, which is mainly driven by the substantial increases in global N fertilizer application (Fig. 1b). Almost all approaches except BDSNP showed enhancements in soil NO_x emissions but with largely varied magnitudes from 0.6 to 2.2 Tg yr^{-1}. The BDNSP scheme, which scales soil NO_x emissions with time-variant temperature and soil moisture, but assumes constant N availability (see Methods), estimates the relatively stable soil NO_x emissions over 1980-2019. The sharpest increase of the soil NO_x emission is simulated by the TBM ensemble, mainly induced by the high estimates of the CLASSIC and ORCHIDEE models (Fig. S2). Soil NO_x estimated by the non-linear EF approach shows substantially weaker response to fertilizer inputs relative to other estimating approaches.

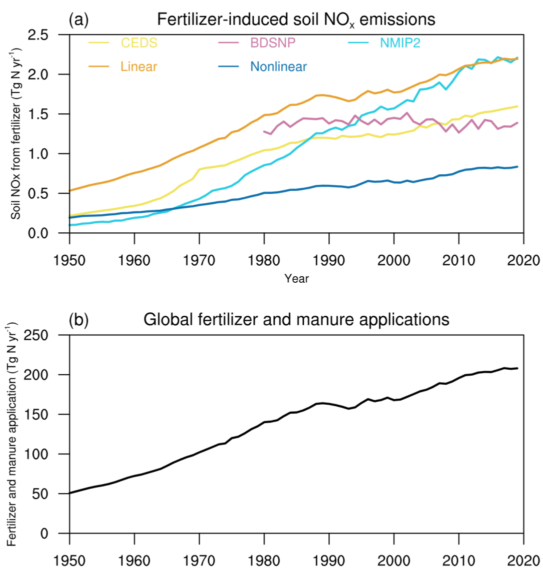

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Figure 1. Global estimates of N fertilizer-induced soil NO_x emissions by different approaches. (a) The global annual-mean N fertilizer-induced soil NO_x emissions over 1950-2019 estimated by emission inventory (CEDS), linear and non-linear EF, the widely-used CTM parameterization (BDSNP) and the TBM ensembles (NMIP2). (b) The global annual-mean N synthetic fertilizer and manure inputs over 1950-2019 assessed from the HaNi dataset.

Figure 2 shows the global spatial patterns of SNO_x-Fer among different approaches. Each approach shows consistent spatial patterns aligned with the distribution of N synthetic fertilizer and manure inputs (Fig. 2a), where eastern U.S., western Europe, eastern and southern Asia are the hotspots with high soil NO_x emissions. Notably, even though the TBM ensemble (NMIP2) and the Linear EF approach estimate similar global total SNO_x-Fer, the spatial distributions of both estimates vary strongly. The SNO_x-Fer estimates by NMIP2 ensemble are higher in agricultural hotspots (Table 3), but lower in regions with less synthetic fertilizer application, e.g. in part of the Africa and South America (Figs. 2d and 2e), relative to the Linear EF approach. This result is likely due to the explicit representation of N dynamics in TBMs, which yields a higher sensitivity of soil NO_x emissions to N fertilizer application in N saturated region, and therefore deviations from the linear EF approach.

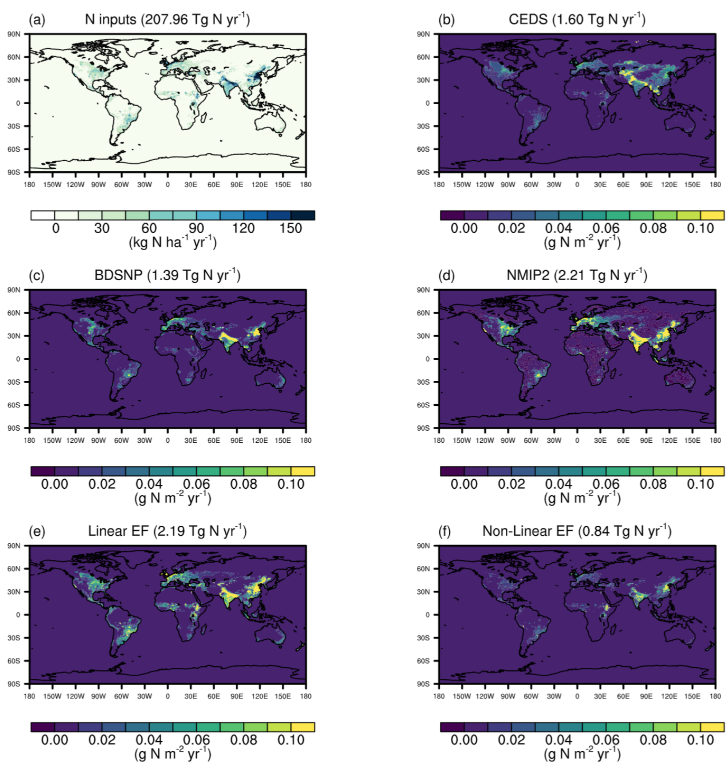

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Figure 2. The global spatial patterns of N synthetic fertilizer and manure application and the N-fertilization induced soil NO_x emissions estimated by different approaches in 2019. (a) The N synthetic fertilizer and manure application in 2019 from the HaNi dataset. (b) - (f) The soil NO_x emissions induced by N fertilizer estimated by the CEDS agricultural sector, the BDNSP scheme in GEOS-Chem, the NMIP2 ensemble, the linear EF and non-linear EF, respectively.

Table 3. The annual soil NO_x emissions (Gg N yr^{-1}) induced by N fertilizer in 2019 in the eastern U.S., western Europe, eastern Asia, southern Asia as well as the global estimates by different approaches. The ranges in NMIP2 indicate the highest and lowest values among three TBMs (CLASSIC, ORCHIDEE and OCN)

	Eastern U.S. (35-45N, 75-90W)	Western Europe (35-60N, 10W-20E)	Eastern Asia (20-50N, 100-125E)	Southern Asia (10-30N, 70-85E)	Globe
CEDS	20.9	99.1	190.0	104.8	1600
BDSNP	15.8	112.1	229.2	185.7	1390
NMIP2	57.0 [15.1, 100.9]	206.3 [67.4, 267.3]	417.5 [261.0, 598.1]	382.4 [78.4, 776.3]	2210 [1280, 2740]
Linear EF	54.3	181.0	376.4	214.7	2190
Non-Linear EF	15.6	60.8	136.5	141.8	840

4.2 Impacts of SNO_x-Fer on surface O_3 concentrations

We next examine how the different SNO_x-Fer estimates influence the surface O_3 concentrations globally. Since soil NO_x emissions typically peak during the summer period, when O_3 pollution tends to be most severe, we focus our analysis on the surface maximum daily 8-h averaged (MDA8) O_3 concentrations averaged over the northern hemisphere summer (June, July and August) based on the sensitivity experiments in Table 1. Figure 3 shows that the N fertilizer application enhanced the globally-averaged surface summertime O_3 MDA8 concentrations by 0.09-0.30 ppbv in 2019. In agricultural regions, the enhancement of O_3 concentrations due to SNOx-Fer reaches 0.3-3.3 ppbv (Fig. 4). Figure 4 also highlights important differences in the spatial effect of NO_x on O_3, consistent with the regional effects on SNOx-Fer (Table 3), that the NMIP2 estimate of SNOx-Fer shows stronger contributions to the O_3 concentrations than the linear EF approach in agricultural regions. The non-linear EF method leads to the lowest O_3 enhancement, although both non-linear EF and TBMs estimates increasing soil NO_x emissions with soil N availability.

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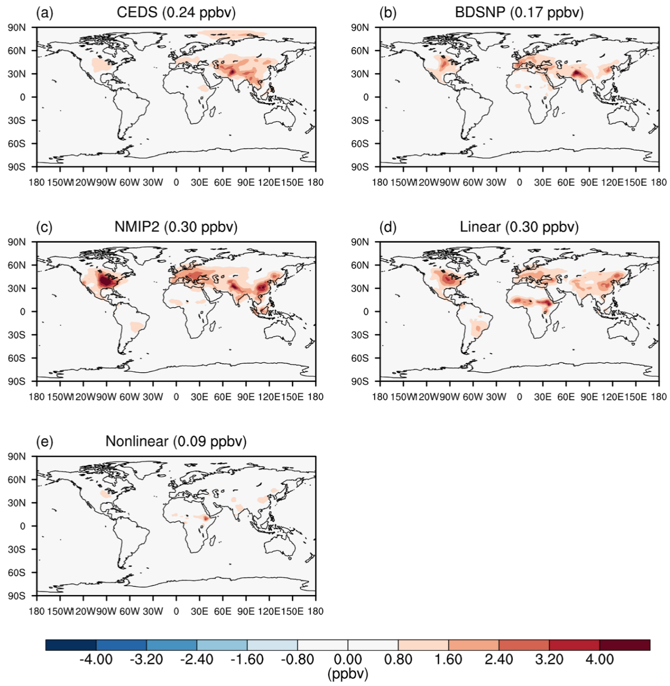

Figure 3. Global simulated changes in surface MDA8 O_3 concentrations induced by different estimating approaches of SNO_x-Fer averaged over June, July and August in 2019. The differences are calculated between corresponding sensitivity experiments in Table 1 and the Zero experiment. The numbers in each sub-title are changes in the global averaged summertime MDA8 O_3 concentrations induced by SNOx-Fer.

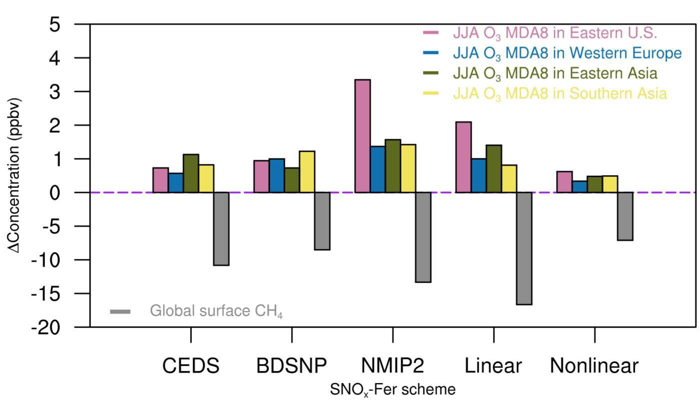

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Figure 4. Changes in summertime averaged surface MDA8 O_3 concentrations (positive Y axis) and global surface CH_4 concentrations (negative Y axis) induced by SNO_x-Fer uncertainties. The regional MDA8 O_3 concentrations are averaged over Eastern U.S. (35-45N, 75-90W), Western Europe (35-60N, 10W-20E), Eastern Asia (20-50N, 100-125E) and Southern Asia (10-30N, 70-85E).

4.3 The impacts of SNO_x-Fer uncertainties on global CH_4 estimates

Figure 4 shows that N fertilizer-induced soil NO_x induced the reduction of global averaged CH_4 concentrations ranging from 7.1 ppbv to 16.6 ppbv in 2019 by affecting atmospheric OH concentrations (Fig. S4). This magnitude of this estimate is consistent with recent estimates of around 17.4 ppbv by Gong et al. (2024), which relies on the same NMIP2 dataset and a simpler CH_4 box model to calculate the impacts of NO_x emissions on the atmospheric lifetime of CH_4. This result highlights an important but indirect role of SNO_x-Fer on atmospheric CH_4 concentrations, which is an often-overlooked aspect for the global CH_4 budget. However, the uncertainty range in our estimates clearly suggests the need to further improve our understanding in soil N biogeochemical processes to better predict global OH reactivity as well as close global CH_4 budget.

5. Discussions

In this study, we integrated knowledge from meta-analyses, the emission inventory, parameterizations in CTMs and the TBM ensembles to better quantify the uncertainties in N fertilizer-induced soil NO_x emissions and the associated impacts on global O_3 and CH_4 concentrations. Our results showed a large variation of the global soil NOx emissions associated with N fertilizer, ranging from 0.84 Tg N yr^{-1} to 2.2 Tg N yr^{-1} in 2019. This range of responses leads to an enhancement in summertime surface MDA8 O_3 concentrations of 0.3 ppbv to 3.3 ppbv in agricultural hotspot regions and a reduction in global CH_4 concentrations of 7.1 ppbv to 16.6 ppbv. These changes highlight a significant role of agricultural N use and soil N biogeochemical processes in affecting regional O_3 concentrations as well as controlling global greenhouse gases. In particular, with the worldwide reduction in fossil-fuel NO_x emissions associated with clean-air actions (Jiang et al., 2022), control of agricultural soil NO_x emissions becomes increasingly important to improve air quality and alleviate the associated public health risks.

However, challenges remain in the accurate assessment of N fertilizer-induced soil NO_x emissions. On the one hand, the overall uncertainties of SNO_x-Fer may still be underestimated. The EF-approach with fixed EF fails to adequately reflect the complexity in soil biogeochemical processes, which is reflected by the large ranges of EFs from 0.06% to 2.18% in a recent meta-analysis (Hergoualc'h et al., 2019). While the non-linear EF method represents an advance over the linear EF approach, as the effects of soil N saturation levels on soil N gas emissions are considered and therefore the approach yields

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relatively good performance in predicting soil N_2O or NH_3 emissions compared to observations (Shcherbak et al., 2014; Jiang et al., 2017), the limited availability of observations to constrain these responses and their limited spatiotemporal representativeness reduce the reliability of this approach. Most of the experimental data in Wang et al. (2024) are collected over China in the past ten years and thus may not be representative of other agricultural regions. Furthermore, 22 out of 55 data points are from vegetable cropping systems and orchard fields, where frequent irrigation may enhance soil moisture and thus inhibit the production of NO_x via nitrification. Last but not least, other factors, such as soil texture, pH, soil organic carbon and fertilizer types, may also affect the response of soil NO_x emissions to the loading of N fertilizer application, which are omitted by either the linear EF or non-linear EF approach. As a result, more representative crop experiments with a gradient series of N addition are necessary to better constrain the soil NO_x response to N fertilizer application.

On the other hand, recent developments of the parameterization of BDNSP in CTMs focused more on the soil NO_x responses to changing temperature or soil moisture (e.g. Wang et al., 2021; Huber et al., 2023), while assuming time invariant soil N availability as shown in Eq. 2. As demonstrated by the comparison of BDNSP with the predictions from both the empirical EF methods and the TBM simulations of NMIP2, this lack of consideration of N availability and soil N legacy will introduce errors when analyzing long-term trends in predictions by CTMs. Meanwhile, terrestrial N availability is a key concept in the development of TBMs, as the process-based TBMs need detailed description of the N cycle to understand nutrient limitation levels and associated C-N coupling. Nevertheless, the soil NO_x emissions have been overlooked by the ecological modelling community because the low emissions may not be important for the terrestrial N cycle, resulting in a limited number of TBMs that include soil NO_x emissions as well as large inter-model variations (Fig. S2). To further reduce the uncertainties in soil NO_x emission estimates, the advantages of TBMs on representing soil N availability can be introduced into CTMs to better examine the effects of agricultural activities on atmospheric chemistry, but at the same time, the terrestrial N cycle needs to be further developed in TBMs to reduce inter-model variations and to better predict soil emissions of reactive N gases (not only NO_x but also N_2O and NH_3).

To summarize, with a comprehensive investigation of different approaches to describe SNO_x-Fer, our results revealed the associated important uncertainties in simulating regional air quality and the global greenhouse gas CH_4. However, the limited number of field experiments impedes accurate assessments of the soil NO_x responses to N fertilizer application as well as improving its representation in both CTMs and TBMs, resulting in large uncertainties in estimates of N fertilizer-induced soil NO_x emissions. We thus highlight the essential necessity to integrate knowledge between agricultural data, atmospheric chemistry modelling and soil biogeochemistry to better represent soil NO_x emissions in models and improve our understanding of the associated effects on air quality and the global CH_4 budget.

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Code and data availability

The GEOS-Chem source code can be assessed in https://github.com/geoschem/geos-chem. The CEDS inventory used in GEOS-Chem can be downloaded at https://ftp.as.harvard.edu/gcgrid/data/ExtData/HEMCO/CEDS/. The NMIP2 model outputs can be downloaded through the open-accessed data in Gong et al. (2024).

Author contributions

C.G. designed the study. C.G. performed the GEOS-Chem simulations and data analysis. Y.W. helps the non-linear EF analysis. H.T. led the NMIP2 projects. S.K, N.V., and S.Z. together contributed to the simulation of terrestrial biosphere models in NMIP2. C.G. wrote the manuscript. All of the authors contributed to reviewing or editing the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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