Large contribution of soil emissions to the atmospheric nitrogen budget and their impacts on air quality and temperature rise in North China

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Abstract

Soil emissions of nitrogen compounds, including NO and HONO, play a significant role in atmospheric nitrogen budget. However, HONO has been overlooked in previous research on soil reactive nitrogen (Nr) emissions and their impacts on air quality in China. This study estimates both soil NO\(_x\) and HONO emissions (SNO\(_x\) and SHONO) in North China with an updated soil Nr emissions scheme in a chemical transport model, the Unified Inputs for WRF-Chem (UI-WRF-Chem). The effects of soil Nr emissions on O\(_3\) pollution, air quality and temperature rise are also studied, with a focus on two key regions, Beijing-Tianjin-Hebei (BTH) and Fenwei Plain (FWP), known for high soil Nr and anthropogenic emissions. We find that the flux of SNO\(_x\) is nearly doubled those of SHONO; the monthly contributions of SNO\(_x\) and SHONO account for 37.3% and 13.5% of anthropogenic NO\(_x\) emissions in the BTH, and 29.2% and 19.2% in the FWP during July 2018, respectively. Soil Nr emissions have a significant impact on surface O\(_3\) and nitrate, exceeding SNO\(_x\) or SHONO effects alone. On average, soil Nr emissions increase MDA8 O\(_3\) by 16.9% and nitrate concentrations by 42.4% in the BTH, 17.2% for MDA8 O\(_3\) and 42.7% for nitrate in the FWP. Reducing anthropogenic NO\(_x\) emissions leads to a more substantial suppressive effect of soil Nr emissions on O\(_3\) mitigation, particularly in BTH. Soil Nr emissions, via their role as precursors for secondary inorganic aerosols, can result in a slower increase rate of surface air temperature. This study suggests that mitigating O\(_3\) pollution and addressing climate change in China should consider the role of soil Nr emission, and their regional differences.
1. Introduction

Surface ozone (O₃) is a major air pollutant harmful to human health, terrestrial vegetation, and crop growth (Feng et al., 2022b; Turner et al., 2016; Unger et al., 2020; Yue et al., 2017). China is confronting serious O₃ pollution, with the surface O₃ concentrations routinely exceeding air quality standards (Li et al., 2019). Although the Chinese Action Plan on Air Pollution Prevention and Control implemented in 2013 has significantly reduced the nationwide anthropogenic emissions of primary pollutants including particulate matter (PM) and nitrogen oxides (NOₓ = NO + NO₂), the summertime O₃ concentrations observed by national ground sites and satellite observations both show an increasing trend of 1-3 ppbv a⁻¹ in megacity clusters of eastern China from 2013 to 2019 (Wang et al., 2022b; Wei et al., 2022). Many studies have explored the causes of O₃ pollution from the perspective of changes in meteorology and anthropogenic emissions, and attributed the O₃ increase to decreased PM levels and anthropogenic NOₓ emissions, and adverse meteorological conditions (Li et al., 2021b; Li et al., 2019; Li et al., 2020; Liu and Wang, 2020a, b; Lu et al., 2019).

Soil emissions are an important natural source of reactive nitrogen species, including N₂O, NOₓ, HONO and NH₃, and can strongly affect the atmospheric chemistry, air pollution and climate change (Elshorbany et al., 2012; Pinder et al., 2012). It has been acknowledged that the soils emissions account for 12-20% of total emissions of NOₓ in global average (Vinken et al., 2014; Yan et al., 2005), and 40-51% in agricultural regions during periods in which fertilizers are applied to soils, resulting in a significant increase in O₃ and NO₂ concentrations in US (Almaraz, 2018; Romer et
China has a large area of cultivated land (~1.276 ×10^6 km², \[\text{http://gi.mnr.gov.cn/202304/t20230414_2781724.html, last access: 18th December 2023}\]), which contributes to one-third of the global nitrogen fertilizer use and has extensive nitrogen deposition (Liu et al., 2013; Lu and Tian, 2017; Reay, 2008). So far, only a limited studies focused on the impact of soil NO\(_x\) emissions (denoted as SNO\(_x\)) on O\(_3\) pollution in China (Huang et al., 2023; Lu et al., 2021; Shen et al., 2023; Wang et al., 2008; Wang et al., 2023a; Wang et al., 2022a). Lu et al. (2021) demonstrated that the presence of SNO\(_x\) in the North China Plain significantly reduced the sensitivity of surface O\(_3\) to anthropogenic emissions. Huang et al. (2023) suggested that substantial SNO\(_x\) could increase the maximum daily 8 h (MDA8) O\(_3\) concentrations by 8.0–12.5 \(\mu\text{g m}^{-3}\) on average for June 2018 in China. These studies focused only on NO\(_x\) emitted from soils, and neglected that similar soil microbial activities also emit nitrous acid (HONO). The measurements in laboratory showed that the emission rates of soil HONO were comparable to those of NO (Oswald et al., 2013; Weber B, 2015). The photolysis of HONO has been identified to be an important source of atmospheric hydroxyl radical (\(^{\cdot}\text{OH}\)), which enhances concentrations of hydroperoxyl (HO\(_2\)) and organic peroxy radicals (RO\(_2\)), accelerating the conversion of NO to NO\(_2\), resulting in more concentrations of O\(_3\) and secondary pollutants. Although the sources and formation mechanisms of HONO are still not fully understood, recent model studies suggested that HONO emission from soils in the agriculture-intensive North China Plain could...
increase the regionally averaged daytime ·OH, \(O_3\), and daily fine particulate nitrate concentrations (Feng et al., 2022a; Wang et al., 2021b).

Only a few studies simultaneously considered the impact of soil HONO emissions (denoted as SHONO) along with \(SNO_x\) on \(O_3\) and other secondary pollutants (Tan et al., 2023; Wang et al., 2023b). Wang et al. (2023b) found that the \(NO_x\) and HONO emissions from natural soils (i.e., soil background emissions) increased daily average \(O_3\) concentrations by 2.0% in Northeast Plain during August 2016 without considering the contribution from fertilized croplands. Tan et al. (2023) believed that the contribution of soil \(NO_x\) and HONO to \(O_3\) pollution has been in an increasing trend from 2013 (5.0 pptv) to 2019 (8.0 pptv) in the summer season over the North China Plain by using the GEOS-Chem model; however the coarse resolution of GEOS-Chem simulation may not insufficient to resolve the spatial heterogeneity in soil emission distribution (Lu et al., 2021). Associated with the decreasing anthropogenic emissions is the increasing contribution of soil emissions to the atmospheric nitrogen budget in China. Therefore, it is critical to quantify the impact of soil reactive nitrogen (Nr: \(NO_x\) and HONO) emissions on \(O_3\) and secondary pollutants.

In this study, we improve the soil Nr emissions scheme in the Unified Inputs (initial and boundary conditions) for Weather Research and Forecasting model coupled with Chemistry (UI-WRF-Chem) by considering all potential sources of HONO published in the literature. Since serious \(O_3\) pollution and high soil emissions always occurred in summer, a series of sensitivity experiments are conducted to quantify the coupled and separate impact of \(SNO_x\) and SHONO on \(O_3\) and secondary pollutants.
during July over the North China, focusing on two city clusters, the Beijing-Tianjin-Hebei (BTH) region and Fenwei Plain (FWP) region, both of which have the vast areas of croplands and dense populations and experiencing severe \( \text{O}_3 \) and PM\(_{2.5} \) pollutions.

In addition, by quantitatively analyzing the difference in the response of surface \( \text{O}_3 \) concentrations and surface air temperature to the anthropogenic NO\(_x\) emissions reductions in the presence vs. absence of soil Nr emissions, the roles of soil Nr emissions on \( \text{O}_3 \) mitigation strategies and climate change are also studied. Our study is designed to address the underestimated role of soil Nr emission in \( \text{O}_3 \) pollution, thereby providing the scientific basis for \( \text{O}_3 \) mitigation strategies and climate change.

2. Methodology

2.1 Model description

2.1.1 Model configurations, input data, and non-soil HONO emission

The UI-WRF-Chem model, developed upon the standard version of WRF-Chem 3.8.1 (Grell et al., 2005), was used in this study. The 0.625°×0.5° Modern-Era Retrospective analysis for Research and Applications, Version 2 (MERRA-2) reanalysis data provide both the meteorological and chemical boundary and initial conditions (Gelaro et al., 2017). The 0.25° × 0.25° Global Land Data Assimilation System (GLDAS) data provides the initial and boundary conditions of soil properties, i.e., soil moisture and temperature (Rodell, 2004). Details of Unified Inputs of meteorological and chemical position data for UI-WRF-Chem, can be found in recent publications (Li et al., 2024; Wang et al., 2023c). Anthropogenic emissions are imported from the Multi-resolution Emission Inventory for China (MEIC: http://www.meicmodel.org/) with a
The spatial resolution of 0.25° × 0.25° for the year 2017. Biomass burning emissions are from the Fire Inventory from NCAR version (FINN, version 1.5, https://www.acom.ucar.edu/Data/fire/). Biogenic emissions are calculated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2.1 (Guenther et al., 2012).

The physical and chemical schemes include the Morrison 2-moment microphysical scheme (Morrison et al., 2009), Grell 3-D cumulus scheme (Grell and Dévényi, 2002), RRTMG for both longwave and shortwave radiation scheme (Iacono et al., 2008), Yonsei University planetary boundary layer scheme (Hong, 2006), Noah land surface model (Tewari, 2004), and the Carbon Bond Mechanism (CBMZ) for gas-phase chemistry and the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) aerosol module with four sectional aerosol bins and aqueous reactions (Zaveri et al., 2008; Zaveri and Peters, 1999) are adopted in the UI-WRF-Chem model.

Two nested domains are used, domain one covers China with a horizontal resolution of 27 km and contains 112×112 grid cells, and domain two covers central and eastern China and its surrounding area with a horizontal resolution of 9 km, containing 196×166 grid cells (study region are shown in Figure S1), both domains have 74 vertical levels from surface to 50 hPa and 4 levels of soil. The simulations are conducted from 29th June to 31st July in 2018 with the first 2 days as the spin-up period. The model outputs from 1st to 31st July in 2018 are analyzed.

The default WRF-Chem model only considers the gas-phase formation of HONO (NO + OH → HONO), thus underestimating the HONO concentrations. In this study, in
addition to considering SHONO (details in Section 2.1.2), potential sources of HONO recognized in recent studies are also taken into account in the current model (Fu et al., 2019; Li et al., 2010; Ye et al., 2016; Ye et al., 2017; Zhang et al., 2022b; Zhang et al., 2022a; Zhang et al., 2016; Zhang et al., 2021; Zhang et al., 2020), including traffic emissions, NO$_2$ heterogeneous reactions on ground and aerosol surfaces, and inorganic nitrate photolysis in the atmosphere. Through a series of tests and comparisons with observed surface HONO concentrations, the specific parameterization schemes of HONO sources adopted in this study are shown in Text S1.

### 2.1.2 Parameterization of soil Nr emissions

The soil Nr emissions schemes in the UI-WRF-Chem model are updated in this study. The default SNO$_x$ scheme in UI-WRF-Chem, MEGAN v2.1, is replaced by the Berkeley–Dalhousie–Iowa Soil NO Parameterization (BDISNP), and the implementation of BDISNP can be found in Sha et al. (2021). Considering that the baseline year of N fertilizer data is 2006, and the amount of N fertilizer application in China has changed in the past ten years, we update the N fertilizer data to the year 2018 based on the N fertilizer application data at the province level from the statistical yearbook (Table S1).

The process of soil HONO emission is similar to that of NO$_x$, as both are influenced by the physical and chemical characteristics of soils. Consequently, soil emissions of HONO with consideration of their dependence on land type, soil humidity, and temperature are also parameterized into the UI-WRF-Chem model. We first map the soil types measured in Oswald et al. (2013) (collected from 17 ecosystems in Table...
S2) into the most closely matching MODIS land cover types in the model following Feng et al. (2022a), described in Table S3. The optimal emission flux for each MODIS land cover type is calculated as the average of the measured fluxes from the category/categories in Oswald et al. (2013) that is/are been mapped into a specific MODIS classification. We also collect the SHONO data from various ecosystems in China published in different studies to correct the optimal SHONO fluxes in the model (Table S4). These ecosystems include semi-arid, fertilized and irrigated farmland in China. Consequently, the parameterization scheme takes into account the effect of fertilizer application on the SHONO. After that, the optimal fluxes over the domains are digested into the model and further scaled online according to the soil temperature and water content in each model grid at each time step throughout the simulation period by the following of equation from (Zhang et al., 2016):

\[ F_N(\text{HONO}) = F_{N,\text{opt}}(\text{HONO}) \cdot f(T) \cdot f(SWC) \]

where \( F_{N,\text{opt}}(\text{HONO}) \) is the optimum flux of SHONO in terms of nitrogen. \( f(T) \) and \( f(SWC) \) are the scaling factors of soil temperature \( (T) \) and water content \( (SWC) \).

\[ f(T) = e^{\frac{E_a}{R(T_{\text{opt}} - T)}} \]

\( E_a \) is the activation energy of HONO (80 kJ mol\(^{-1}\)), \( R \) is the gas constant, \( T_{\text{opt}} \) is the temperature at which optimum flux is emitted (298.15 K), \( T \) is the soil temperature calculated online by the model, \( f(SWC) \) is fitted based on the data curves in Figures 1 and 3 in (Oswald et al., 2013) and the equation is as follows:

\[ f(SWC) = 1.04 \times e^{x \left( -\frac{\text{SWC} - 11.32586}{5.27335} \right)} \]

2.2 Model experiment design
The descriptions of the sensitivity simulations are shown in Table S5. Default simulation uses MEGAN scheme to estimate SNOx and no SHONO is considered. Base simulation uses soil Nr emissions schemes with the improvement of using BDISNP scheme for SNOx and consideration of SHONO and other four HONO sources (as described above). Comparison of results from Default and Base simulations is used to show the improvement in the model performance after updating the soil Nr emissions schemes and incorporating HONO potential sources. To explore the impact of soil Nr emissions on O3 and secondary pollutants, we conduct a series of sensitivity simulations with soil NOx and HONO emissions turned on/off separately and jointly (anthropogenic emissions for the year 2017), i.e., NoSoilNr, NoSHONO and NoSNOx. To evaluate the role of soil Nr emissions on O3 mitigation strategies and air temperature change under different anthropogenic emission reduction scenarios, we further conduct the Base_redANOx and NoSoil_redANOx simulations with anthropogenic NOx emissions reduced by 20%, 40%, 60%, 80% and 100%, respectively.

2.3 Observational data

The tropospheric column densities of NO2 from TROPOMI (TROPOspheric Monitoring Instrument) level-2 in version 1 with the horizontal spatial resolution of 3.5 × 7 km² are used. The quality controls, i.e., cloud-screened (cloud fraction below 30%) and quality-assured (qa_value above 0.50), and averaging kernels (AK) are applied in the comparison of the TROPOMI and UI-WRF-Chem simulated tropospheric NO2 vertical column densities (defined as NO2 VCD).

To evaluate the model performance on simulating surface air pollutants, we use
the hourly surface O₃ concentrations at 888 monitoring sites from the China National Environmental Monitoring Center (CNEMC), and hourly surface HONO concentrations measured by the In-situ Gas and Aerosol Compositions monitor (IGAC) (Zhan et al., 2021) at Nanjing University of Information Science & Technology (NUIST) (32.2° N, 118.7° E; 22m above sea level) (Xu et al., 2019).

3. Results and discussions

3.1 Soil nitrogen emissions and air pollution evaluation

Figure 1 shows the spatial distribution of simulated monthly mean SNOₓ and SHONO fluxes in July 2018 across North China. In most regions, SNOₓ flux is nearly doubled that of SHONO, and higher SNOₓ and SHONO are concentrated in areas dominated by cropland. The monthly total soil emissions over the whole study domain (cropland) are 104.5 (82.4) Gg N mon⁻¹ for NOₓ and 52.7 (45.9) Gg N mon⁻¹ for HONO. In the densely populated BTH region, the monthly total SNOₓ are 18.7 Gg N mon⁻¹, which is equivalent to 37.3% of anthropogenic NOₓ emissions for the year 2017. For the FEW region, where also experiences severe O₃ and PM₂.₅ pollution, the monthly total SNOₓ (7.0 Gg N mon⁻¹) account for 29.2% of anthropogenic NOₓ emissions. The monthly total SHONO in both study regions are much lower than their SNOₓ counterparts, with the emissions of 6.9 and 4.6 Gg N mon⁻¹, accounting for 13.5% and 19.2% of anthropogenic NOₓ emissions in BTH and FWP regions, respectively.

To evaluate the model performance, Figure 2 shows the tropospheric NO₂ VCD from TROPOMI satellite products and UI-WRF-Chem simulations (Default and Base) during July 2018 in North China. Default and Base can both reproduce the hot spots of...
NO₂ VCD in urban areas shown in the TROPOMI observations. However, the Default significantly underestimates the NO₂ VCD, especially in regions surrounding urban areas. It is found that Default underestimates NO₂ VCD by 48% over the regions where soil emissions dominate (i.e., soil Nr emissions contribute more than half to the atmospheric nitrogen emissions), while the Base reduced the bias to 13% (Figure S2). Overall, Base shows the improved performance in simulating NO₂ VCD in comparison to Default with a decreasing bias from -30% (-21%) to +4% (+17%) in the study region (cropland). The overestimated NO₂ VCD in Base is most likely attributed to the time lag in anthropogenic emissions inventory used in the study (Chen et al., 2021), uncertainties in the stratospheric portion of NO₂ VCD and AK caused the retrieval errors (Van Geffen et al., 2020). Additionally, the estimated SNOₓ are also subjected to certain limitations and uncertainties. The first uncertainty comes from the amount of N fertilizer application, which has been identified as the dominant contributor to SNOₓ. In this study, we use the amount of agricultural N fertilizer application at the province level from the statistical yearbook to update the default N fertilizer application data in the model (the baseline year for 2006), but a recent study showed that compound fertilizer, usually with nitrogen (N), phosphorus (P), and potassium (K), were more commonly used in China; if only N fertilizer is considered to nudge the N fertilizer application data in the model, the estimated SNOₓ may be underestimated by 11.1%–41.5% (Huang et al., 2023). Furthermore, although we use the modeled green vegetation fraction (GVF) to determine the distribution of arid (GVF ≤ 30%) and non-arid (GVF > 30%) regions. Huber et al. (2023) showed that the estimated SNOₓ based
on the static classification of arid vs. non-arid is very sensitive to the soil moisture, and thus could not produce self-consistent results when using different input soil moisture products unless a normalized soil moisture index to represent. Therefore, more direct measurements of soil Nr fluxes are crucial to better constrain soil emissions and improve the parametrization in the model.

We evaluate the simulation with the surface O$_3$ observations from the China National Environmental Monitoring Centre (CNEMC) network (http://www.cnemc.cn/en/) (Figure 3). Over the whole study region, the Base can better capture the spatial distribution of observed surface MDA8 O$_3$ with a relatively higher spatial correlation of $R = 0.68$ than that in Default ($R = 0.46$). The simulated monthly averaged MDA8 O$_3$ concentrations across the 888 sites in the study region are 123.0 $\mu$g m$^{-3}$ in Default and 132.5 $\mu$g m$^{-3}$ in Base, respectively, which are both slightly higher than the observed concentrations (120.7 $\mu$g m$^{-3}$). Overprediction is also observed for the FWP and BTH regions in the Base simulation, with the normalized mean bias (NMB) of 6.1% and 4.9%, respectively (Figure S3). These positive biases are mainly due to overestimated transport of boundary O$_3$ in both horizontal and vertical directions (Huang et al., 2023) and underestimated precipitation and cloud cover in the current model (Sun et al., 2019).

We also compare the simulated surface HONO and nitrate concentrations to the observations at a rural station in Nanjing during July 2018. Figure 4 shows that the simulated HONO concentrations in Default are 98.3% lower than the observations. In comparison, the Base with considering SHONO and other HONO potential sources
significantly improves the simulation performance and reduces the bias to 47.8%, and also reproduces the diurnal variation of HONO with the temporal correlation of $R = 0.76$. It is worth noting that the concentrations of HONO from 08 am to 18 pm are lower than the observations, this discrepancy may be attributed to the underestimated contribution from the predominant sources of HONO during the daytime, such as NO$_2$ heterogeneous reactions on ground and aerosol surfaces. Moreover, the contributions of different sources to ambient HONO concentrations at this rural station are also evaluated, the soil emissions could contribute almost 25.8% to the surface HONO, which may be partially attributed to the high emissions of HONO from croplands around the city of Nanjing (Figure S4). The results that soil emissions contribute less to the daytime positive flux than the other source is consistent with previous studies (Skiba et al., 2020; Wang et al., 2023b). For nitrate concentration, the Base simulation shows a lower bias (5.6%) and an improved diurnal variation (temporal correlation of $R = 0.92$) compared to the Default simulation (bias = 27.8%, $R = 0.85$). We acknowledge that there are certain uncertainties in the current model. Nevertheless, the improved simulation performance compared to the Default illustrates the credibility of the results obtained from the Base simulation.

### 3.2 Impact on O$_3$ formation and air quality

To quantify the effects of SNO$_x$ and SHONO on atmospheric oxidation capacity, O$_3$ formation and air quality as well as their combined effect, the conventional brute-force method was used, i.e., the impact of a specific source is determined in atmospheric chemistry models as the differences between the standard/base simulation with all
emissions turned on and a sensitivity simulation with this source turned off or perturbed (Table S5). As shown in Figure 5, the contribution of SNO$_x$ and SHONO to surface NO$_2$ and HONO has a different spatial pattern from that of the fluxes of SNO$_x$ and SHONO. Overall, the maximum contribution of SNO$_x$ to the monthly average surface NO$_2$ concentrations is 78.6%, with a domain-averaged value of 30.3%. Regionally, SNO$_x$ contribute 5.5 µg m$^{-3}$ (37.1%) and 2.5 µg m$^{-3}$ (31.8%) to the surface NO$_2$ in the BTH and FWP regions, respectively, which are both higher than the domain-averaged contribution. Although SHONO fluxes are lower than that of SNO$_x$, its effect on ambient HONO cannot be ignored. Over the study region, the contribution of SHONO to surface HONO concentration ranges from 0 to 49.0%, with a domain-averaged value of 35.6%. For the selected key regions, there are 1.8 µg/m$^3$ (36.7%) and 1.5 µg/m$^3$ (38.0%) of the monthly average HONO concentrations in the BTH and FWP regions, respectively, from soil emissions. It is noteworthy that, despite the surface NO$_2$ (HONO) concentrations in the study regions being impacted by less than 13% (17%) due to SHONO (SNO$_x$), the combined effects of soil Nr emissions on surface NO$_2$ (HONO) are found to be greater than the individual effects, which are 38.4% (40.3%) for BTH and 33.9% (40.1%) for FWP region, respectively (Table S6). These results highlight the importance of considering the cumulative impacts of multiple reactive nitrogen emissions from soils on air pollution.

Consequently, substantial soil Nr emissions have a non-negligible effect on atmospheric oxidation and the formation of secondary pollutants. For atmospheric oxidation, we assess the impact of soil Nr emission on the maximum 1 h (max-1h) ·OH
levels and find that SHONO have a potential to increase the max-1h ·OH in most areas, with a domain-averaged increase of 10.0%. On the contrary, the inclusion of SNOx results in a significant reduction of 31.3% in the max-1h ·OH across the entire study domain. Considering the combined effect of SNOx and SHONO, there is an overall decrease of 24.3% in the max-1h ·OH over the study domain, with the BTH region experiencing a decrease of 22.6% and FWP region showing a relatively greater reduction of 32.2% (Table S7). These findings are different from the previous study, which showed that soil background emissions including NOx and HONO led to a 7.5% increase in max-1h ·OH in China (Wang et al., 2023b). We stress the crucial role of SNOx in influencing ·OH concentrations and highlight the varying impacts across different regions. For secondary pollutants, substantial O3 enhancement is found in Henan and Hubei provinces, while the increase in nitrate is consistent with the spatial pattern of surface NO2 from soil emissions. Specifically, soil Nr emissions increase the monthly average MDA8 O3 and nitrate concentrations by 18.2% and 31.8%, respectively, across the study domain, with the increase of 16.9% and 42.4% in the BTH region and 17.2% and 42.7% in the FWP region. Moreover, soil emissions of NOx have a stronger effect on O3 and nitrate in North China than those of SHONO.

The ratio of surface H2O2 to HNO3 concentrations (hereafter H2O2/HNO3) was used as an indicator of the O3 formation regime to study the changes in sensitivity of summer O3 to its precursors after considering the soil Nr emissions. The threshold of H2O2/HNO3 for determining O3 formation regime varies regionally (Sillman, 1995), thus in this study, we identify the regions with H2O2/HNO3 values greater than 0.65 as
NOx-sensitive regime, H2O2/HNO3 values lower than 0.35 as VOCs-sensitive regime,  
and H2O2/HNO3 values between 0.35 and 0.65 as VOCs-NOx mixed sensitive regime  
(Shen et al., 2023). Figure 6 illustrates that the majority of BTH region has H2O2/HNO3  
values lower than 0.35 in Base simulation, indicating a VOCs-sensitive regime or NOx-  
saturated regime, which is consistent with the previous studies based on satellite  
observations and model simulations (Wang et al., 2019; Wang et al., 2017). The  
distribution of sensitivity of O3 to precursor emission in FWP regions are more complex  
with a mix of three O3 formation regimes, which is attributed to the large population,  
regional urbanization and industrialization. However, when soil nitrogen emissions are  
excluded, the H2O2/HNO3 values mostly increase within 40% and the O3 formation  
regime shifts to VOCs-NOx mixed sensitive regime and NOx-sensitive regime in both  
BTH and FWP regions. Although soil Nr emissions are lower than anthropogenic  
emissions, they still could affect the sensitivity of O3 to its precursors and thus have an  
impact on the effectiveness of emission reduction policies. Therefore, soil emissions  
must be considered in formatting policies for the prevention and management of O3  
pollution.  

3.3 Implication on O3 mitigation strategies and temperature rise  

Due to the influence of soil Nr emissions, the sensitivity of O3 pollution to its  
precursors varies spatially, depending on the local levels of anthropogenic emissions. It  
is thus important to quantify the role of soil Nr emissions in O3 pollution regulation for  
improving the effectiveness of air control measures. We conduct a series of sensitivity  
experiments with anthropogenic NOx emissions reduced by 20%, 40%, 60%, 80% and
100%, respectively, relative to the Base simulation (Table S5), and analyze the difference in the response of surface O₃ concentrations to the anthropogenic NOₓ emissions reductions in the presence and absence of soil Nr emissions. Figure 7 shows that with the reduction of anthropogenic NOₓ emissions, MDA8 O₃ concentrations show an accelerated decreasing trend, suggesting increasing efficiency of anthropogenic NOₓ control measures. And MDA8 O₃ response to anthropogenic NOₓ emissions in the BTH region is more curved (nonlinear) than that in the FWP region, which is consistent with the fact that the BTH tends to have more NOₓ-saturated O₃ production (Figure 6).

It is noted that the reduction of anthropogenic NOₓ emissions in the presence of soil Nr emissions leads to a slower decrease in MDA8 O₃ compared to when soil Nr emissions are excluded. We further analyze the details of the domain-averaged MDA8 O₃ changes under different anthropogenic reduction scenarios for the two key regions. Specifically, in the BTH region, MDA8 O₃ decrease by 1.3% (1.8 µg m⁻³), 3.4% (4.6 µg m⁻³), 6.3% (8.7 µg m⁻³), 10.7% (14.7 µg m⁻³), and 17.4% (24.0 µg m⁻³) with anthropogenic NOₓ emission reductions by 20%, 40%, 60%, 80%, and 100%, respectively, in the present of soil Nr emissions. Comparatively, in the absence of soil Nr emissions, the reductions in MDA8 O₃ are more pronounced and decrease by 2.3% (2.7 µg m⁻³), 5.6% (6.6 µg m⁻³), 10.7% (12.8 µg m⁻³), 19.4% (23.2 µg m⁻³), and 42.3% (50.6 µg m⁻³), respectively. In the FWP region, with a 20% reduction in anthropogenic NOₓ emissions, MDA8 O₃ levels only exhibit a slight decrease of 1.7% (2.3 µg m⁻³) in the presence of soil Nr emissions, whereas a decrease of 2.3% (2.6 µg m⁻³) is found in the absence of soil Nr emissions. When anthropogenic NOₓ emissions are removed...
entirely, MDA8 O₃ decreases by 13.6% (17.7 µg m⁻³) in the presence of soil Nr emissions, and more significant decreases are found in the absent of soil Nr emissions with a reduction of 27.4% (34.0 µg m⁻³) (as shown in Figure 7b-c, e-f). We conclude that the existence of soil Nr emissions could contribute to an additional part of O₃ production, amounting to a range of 0-24.9% in the BTH and 0-13.8% in the FWP region, and these suppressions could be enlarged over the rural areas where have more substantial soil Nr emissions (e.g. 0-32.3% in cropland over the BTH and 0-15.0% in croplands over the FWP region). These findings suggest that soil Nr emissions have the potential to suppress the effectiveness of measures implemented to mitigate O₃ pollution, and this effect becomes more significant as anthropogenic emissions increase.

We also quantify the O₃ generated from soil Nr emission source (denoted as the soil O₃) under the different anthropogenic NOₓ emission scenarios. Overall, soil O₃ concentrations in croplands are higher than in non-croplands. Regionally, in the BTH region, the soil O₃ concentrations are 19.8 µg m⁻³ under high anthropogenic emissions level (referred to as the Base simulation), while the soil O₃ concentrations significantly increase to 46.4 µg m⁻³ when all anthropogenic NOₓ emissions are cut down (shown as red bar in Figure 7b). A similar trend is also found in the FWP region, although soil O₃ concentrations are relatively lower than that in the BTH region, the soil O₃ concentrations are 19.0 µg m⁻³ in the Base simulation, and do not change significantly with the reduction of anthropogenic emissions, but increase to 31.9 µg m⁻³ when anthropogenic NOₓ emissions are excluded (shown as red bar in Figure 7c). The reduction in anthropogenic NOₓ emissions results in a shift of the O₃ formation regime.
towards a more NO<sub>x</sub>-sensitive chemical regime, leading to a higher contribution of O<sub>3</sub> from soil sources. We conclude that with stricter anthropogenic emission reduction measures, the contributions of soil Nr emissions to O<sub>3</sub> production in both absolute and relative value would increase and further hamper the effectiveness of anthropogenic emission reductions. To effectively mitigate the desired level of O<sub>3</sub> concentrations, it is necessary to implement much stricter control measures for anthropogenic emissions due to the synergistic effects of SNO<sub>x</sub> and SHONO.

Here we show that the substantial soil Nr emissions present an additional challenge for O<sub>3</sub> pollution regulation in the North China. We further assess the impact of soil Nr emissions on air temperature change under different anthropogenic emission reduction scenarios. By comparing changes in air temperature at 2m (T2) with and without soil Nr emissions under different anthropogenic emission reduction scenarios, Figure 8 shows that incorporating soil Nr emissions results in a slower rate of T2 increase compared to scenarios without soil Nr emissions, and this phenomenon is consistent across all study regions. In the FWP region, when anthropogenic NO<sub>x</sub> emissions are eliminated, T2 increases by 0.056 °C in the presence of soil Nr emissions, compared to 0.092 °C in the absence of soil Nr emissions. In the BTH region, which has relatively high anthropogenic emissions, reducing anthropogenic NO<sub>x</sub> emissions by the same proportion could result in relatively greater warming, and T2 increases by 0.084 °C in the presence of soil Nr emissions, compared to 0.15 °C in the absence of soil Nr emissions when anthropogenic NO<sub>x</sub> emissions are excluded. This is attributed to aerosols (such as sulfate and nitrate) and NO<sub>x</sub> emissions and their effective radiative
forcing (ERF) associated with a cooling effect (high confidence) (Liao and Xie, 2021; Bellouin et al., 2020). Decreases in aerosol concentrations and NO\textsubscript{x} emissions could weaken the cooling effect and potentially accelerate warming to some extent, while soil Nr emissions can offset temperature rise caused by declining anthropogenic NO\textsubscript{x} emissions (Figure S5). Therefore, although soil Nr emissions are relatively low compared to anthropogenic emissions, the combined effects of NO\textsubscript{x} and HONO emissions from natural soil and agricultural land should be considered when assessing climate change and implementing strategies to mitigate O\textsubscript{3} pollution.

4. Conclusions

In this study, the updated soil Nr emission scheme was implemented in the UI-WRF-Chem model and used to estimate the combined and individual impact of SNO\textsubscript{x} and SHONO on subsequent changes in air quality and air temperature rise in North China, with a focus on two key regions (the BTH and FWP regions) because of high levels of soil Nr and anthropogenic emissions. We show that the SNO\textsubscript{x} flux is nearly doubled that of SHONO during July 2018, with higher soil emissions in areas with extensive cropland. The contribution of soil Nr emissions to average surface NO\textsubscript{2} and HONO are 38.4% and 40.3% in the BTH, and 33.9% and 40.1% in the FWP region, respectively, and the substantial soil Nr emissions lead to a considerable increase in the monthly average MDA8 O\textsubscript{3} and nitrate concentrations, with the values of 16.9% and 42.4% in the BTH region and 17.2% and 42.7% in the FWP region, which both exceed the individual SNO\textsubscript{x} or SHONO effect. The presence of soil Nr emissions, acting as precursors of O\textsubscript{3} and secondary inorganic aerosols, has a suppressing effect on efforts
to mitigate O$_3$ pollution, particularly in the BTH region, and also leads to a slower
increase rate of T2 compared to scenarios without soil Nr emissions. We note that the
effect of soil Nr emissions shows spatial heterogeneity under different anthropogenic
NO$_x$ emissions reduction scenarios.

However, we admit that uncertainties in both soil Nr and anthropogenic emissions,
as well as the parameterization scheme of HONO sources. The agricultural emissions
of another important reactive nitrogen gas, NH$_3$, may also be underestimated due to
uncertainties in agricultural fertilizer application and livestock waste in MEIC
inventory (Li et al., 2021a). These uncertainties could impact the aerosol formation and
local cooling effect. Also, the discrepancies between simulated and observed NO$_2$, O$_3$
and other air pollutants in the model may affect the assessment of the role of soil Nr
emissions in O$_3$ mitigation strategies and their impact on climate change. Thus, more
direct measurements of soil Nr fluxes are crucial to better constrain soil emissions and
improve the parametrization in the model.

Our study highlights that despite soil Nr emissions being lower than anthropogenic
emissions, they still have a substantial impact on the effectiveness of O$_3$ pollution
mitigation measures, and this effect becomes more significant as anthropogenic
emissions decrease. Therefore, reactive nitrogen from soil emission source must be
considered in formatting measures for the prevention and management of O$_3$, as well
as addressing climate change.
Code and data availability. Some of the data repositories have been listed in Section 2. The other data, model outputs and codes can be accessed by contacting Tong Sha via tong-sha@sust.edu.cn.

Author contributions. TS performed the model simulation, data analysis and manuscript writing. TS and JW proposed the idea. SY, QC and LL supervised this work and revised the manuscript. XM, ZF and KB helped the revision of the manuscript. YZ provided and analyzed the observation data.

Competing interests. The authors declare that they have no conflict of interest.

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Figure 1. Distribution of the simulated monthly mean (a) soil NO\textsubscript{x} emissions, (b) soil HONO emissions, and (c) anthropogenic NO\textsubscript{x} emissions in July 2018.
Figure 2. (a) Monthly mean tropospheric NO$_2$ VCD retrieved by TROPOMI measured at 12:00−14:00 LT and simulated by (e) Default and (f) Base averaged over the same periods in July 2018.
Figure 3. Distribution of observed (dots) and simulated (shaded) surface MDA8 O$_3$ from (a) Default and (b) Base in July 2018. Statistics in the upper corner of panels are the monthly mean MDA8 O$_3$ concentrations averaged over the study region and the spatial correlation coefficient R between observations and simulations.
Figure 4. Diurnal variation of observed (in grey) and simulated (Default in red and Base in blue) surface (a) HONO and (b) nitrate concentrations at a rural station in Nanjing, with the mean value and temporal correlation coefficients (R) shown in the upper right corner.
Figure 5. Simulated effects of soil Nr emissions on air quality. The first and second rows show the contributions of soil NO\textsubscript{x} and soil HONO emissions on monthly average concentrations of NO\textsubscript{2}, HONO, MDA8O\textsubscript{3}, max-1h ·OH, and nitrate, respectively. The third row shows the combined effect of soil Nr emissions on the species listed above. Statistics in the upper right corner of each panel are the mean values averaged over the study region.
Figure 6. Distribution of the O₃ formation regimes (represented as H₂O₂/HNO₃ ratios) for (a) Base simulation with the addition of soil Nr emissions and (b) NoSoilNr simulation without the addition of soil Nr emissions. (c) Changes in the distribution of O₃ formation regimes due to the soil Nr emissions.
Figure 7. Role of soil Nr emissions in O₃ pollution regulation. The responses of MDA8 O₃ concentrations to the reductions of anthropogenic NOₓ emissions (20%, 40%, 60%, 80% and 100%) relative to July 2018 levels, in the presence (solid line) and absence (dotted line) of soil Nr emissions in the study region, BTH and FWP region. (The lines in panels a-c and d-f are MDA8 O₃ concentrations and the relative reductions in MDA8 O₃ under different anthropogenic NOₓ emission reductions, respectively. The red bars (right y-axis) in panels a-c show the corresponding O₃ contribution from soil Nr emissions, which is determined as the difference between the solid and dotted lines, and the blue bars are the same as the red bars but for statistics in cropland. The red bars (right y-axis) in panels d-f show the suppression of O₃ pollution mitigated due to the existence of soil Nr emissions, which are determined as the difference between the solid and dotted lines, and the blue bars are the same as the red bars but for statistics in cropland.)
Figure 8. The responses of air temperature at 2m (T2) to the reductions of anthropogenic NOx emissions (20%, 40%, 60%, 80% and 100%) relative to July 2018 levels in the presence (solid line) and absence (dotted line) of soil Nr emissions (a) in the study region, (b) BTH and FWP region.