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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.

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1. Introduction

Surface ozone (O_3) 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 O_3 pollution, with the surface O_3 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 (NO_x = NO + NO_2), the summertime O_3 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 O_3 pollution from the perspective of changes in meteorology and anthropogenic emissions, and attributed the O_3 increase to decreased PM levels and anthropogenic NO_x 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 N_2O, NO_x, HONO and NH_3, 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 NO_x 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 O_3 and NO_2 concentrations in US (Almaraz, 2018; Romer et

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al., 2018; Sha et al., 2021; Wang et al., 2021a), Europe (Skiba et al., 2020) and sub-Saharan Africa (Huang et al., 2018).

China has a large area of cultivated land (~1.276 $\times 10^6$ km^2, 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 μg 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 (·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

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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

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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 O_3 and $PM_{2.5}$ pollutions. In addition, by quantitatively analyzing the difference in the response of surface 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 O_3 mitigation strategies and climate change are also studied. Our study is designed to address the underestimated role of soil Nr emission in O_3 pollution, thereby providing the scientific basis for 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

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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 31th July in 2018 with the first 2 days as the spin-up period. The model outputs from 1th to 31th July in 2018 are analyzed.

The default WRF-Chem model only considers the gas-phase formation of HONO ($NO + OH \rightarrow HONO$), thus underestimating the HONO concentrations. In this study, in

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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

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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):

$$F_N(\mathrm{HONO}) = F_{N,opt}(\mathrm{HONO}) \cdot f(T) \cdot f(SWC)$$

where $F_{N,opt}(\mathrm{HONO})$ 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).

$$f(T) = e^{\frac{Ea}{R}\left(\frac{T}{T_{opt}}-\frac{1}{T}\right)}$$

E_a is the activation energy of HONO (80 kJ mol^{-1}), R is the gas constant, T_{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:

$$f(SWC) = 1.04 \times exp^{\left(-e^{-\frac{\mathrm{SWC}-11.32586}{5.27335}}-\frac{\mathrm{SWC}-11.32586}{5.27335}+1\right)}$$

2.2 Model experiment design

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The descriptions of the sensitivity simulations are shown in Table S5. Default simulation uses MEGAN scheme to estimate SNO_x and no SHONO is considered. Base simulation uses soil Nr emissions schemes with the improvement of using BDISNP scheme for SNO_x 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 O_3 and secondary pollutants, we conduct a series of sensitivity simulations with soil NO_x and HONO emissions turned on/off separately and jointly (anthropogenic emissions for the year 2017), i.e., NoSoilNr, NoSHONO and $NoSNO_x$. To evaluate the role of soil Nr emissions on O_3 mitigation strategies and air temperature change under different anthropogenic emission reduction scenarios, we further conduct the Base_redANO_x and NoSoil_redANO_x simulations with anthropogenic NO_x emissions reduced by 20%, 40%, 60%, 80% and 100%, respectively.

2.3 Observational data

The tropospheric column densities of NO_2 from TROPOMI (TROPOspheric Monitoring Instrument) level-2 in version 1 with the horizontal spatial resolution of 3.5 × 7 km^2 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 NO_2 vertical column densities (defined as NO_2 VCD).

To evaluate the model performance on simulating surface air pollutants, we use

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the hourly surface O_3 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) (32.2º N, 118.7º 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 SNO_x and SHONO fluxes in July 2018 across North China. In most regions, SNO_x flux is nearly doubled that of SHONO, and higher SNO_x 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 NO_x and 52.7 (45.9) Gg N mon^{-1} for HONO. In the densely populated BTH region, the monthly total SNO_x are 18.7 Gg N mon^{-1}, which is equivalent to 37.3% of anthropogenic NO_x emissions for the year 2017. For the FEW region, where also experiences severe O_3 and $PM_{2.5}$ pollution, the monthly total SNO_x (7.0 Gg N mon^{-1}) account for 29.2% of anthropogenic NO_x emissions. The monthly total SHONO in both study regions are much lower than their SNO_x counterparts, with the emissions of 6.9 and 4.6 Gg N mon^{-1}, accounting for 13.5% and 19.2% of anthropogenic NO_x emissions in BTH and FWP regions, respectively.

To evaluate the model performance, Figure 2 shows the tropospheric NO_2 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

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NO_2 VCD in urban areas shown in the TROPOMI observations. However, the Default significantly underestimates the NO_2 VCD, especially in regions surrounding urban areas. It is found that Default underestimates NO_2 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 NO_2 VCD in comparison to Default with a decreasing bias from -30% (-21%) to +4% (+17%) in the study region (cropland). The overestimated NO_2 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 NO_2 VCD and AK caused the retrieval errors (Van Geffen et al., 2020). Additionally, the estimated SNO_x 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 SNO_x. 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 SNO_x 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 SNO_x based

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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 μg m^{-3} in Default and 132.5 μg m^{-3} in Base, respectively, which are both slightly higher than the observed concentrations (120.7 μg 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

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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

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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

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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 SNO_x results in a significant reduction of 31.3% in the max-1h ·OH across the entire study domain. Considering the combined effect of SNO_x 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 NO_x and HONO led to a 7.5% increase in max-1h ·OH in China (Wang et al., 2023b). We stress the crucial role of SNO_x in influencing ·OH concentrations and highlight the varying impacts across different regions. For secondary pollutants, substantial O_3 enhancement is found in Henan and Hubei provinces, while the increase in nitrate is consistent with the spatial pattern of surface NO_2 from soil emissions. Specifically, soil Nr emissions increase the monthly average MDA8 O_3 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 NO_x have a stronger effect on O_3 and nitrate in North China than those of SHONO.

The ratio of surface H_2O_2 to HNO_3 concentrations (hereafter H_2O_2/HNO_3) was used as an indicator of the O_3 formation regime to study the changes in sensitivity of summer O_3 to its precursors after considering the soil Nr emissions. The threshold of H_2O_2/HNO_3 for determining O_3 formation regime varies regionally (Sillman, 1995), thus in this study, we identify the regions with H_2O_2/HNO_3 values greater than 0.65 as

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NO_x-sensitive regime, H_2O_2/HNO_3 values lower than 0.35 as VOCs-sensitive regime, and H_2O_2/HNO_3 values between 0.35 and 0.65 as VOCs-NO_x mixed sensitive regime (Shen et al., 2023). Figure 6 illustrates that the majority of BTH region has H_2O_2/HNO_3 values lower than 0.35 in Base simulation, indicating a VOCs-sensitive regime or NO_x-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 O_3 to precursor emission in FWP regions are more complex with a mix of three O_3 formation regimes, which is attributed to the large population, regional urbanization and industrialization. However, when soil nitrogen emissions are excluded, the H_2O_2/HNO_3 values mostly increase within 40% and the O_3 formation regime shifts to VOCs-NO_x mixed sensitive regime and NO_x-sensitive regime in both BTH and FWP regions. Although soil Nr emissions are lower than anthropogenic emissions, they still could affect the sensitivity of O_3 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 O_3 pollution.

3.3 Implication on O_3 mitigation strategies and temperature rise

Due to the influence of soil Nr emissions, the sensitivity of O_3 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 O_3 pollution regulation for improving the effectiveness of air control measures. We conduct a series of sensitivity experiments with anthropogenic NO_x emissions reduced by 20%, 40%, 60%, 80% and

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100%, respectively, relative to the Base simulation (Table S5), and analyze the difference in the response of surface O_3 concentrations to the anthropogenic NO_x emissions reductions in the presence and absence of soil Nr emissions. Figure 7 shows that with the reduction of anthropogenic NO_x emissions, MDA8 O_3 concentrations show an accelerated decreasing trend, suggesting increasing efficiency of anthropogenic NO_x control measures. And MDA8 O_3 response to anthropogenic NO_x 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 NO_x-saturated O_3 production (Figure 6).

It is noted that the reduction of anthropogenic NO_x emissions in the presence of soil Nr emissions leads to a slower decrease in MDA8 O_3 compared to when soil Nr emissions are excluded. We further analyze the details of the domain-averaged MDA8 O_3 changes under different anthropogenic reduction scenarios for the two key regions. Specifically, in the BTH region, MDA8 O_3 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 NO_x 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 O_3 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 NO_x emissions, MDA8 O_3 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 NO_x emissions are removed

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entirely, MDA8 O_3 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 O_3 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 O_3 pollution, and this effect becomes more significant as anthropogenic emissions increase.

We also quantify the O_3 generated from soil Nr emission source (denoted as the soil O_3) under the different anthropogenic NO_x emission scenarios. Overall, soil O_3 concentrations in croplands are higher than in non-croplands. Regionally, in the BTH region, the soil O_3 concentrations are 19.8 μg m^{-3} under high anthropogenic emissions level (referred to as the Base simulation), while the soil O_3 concentrations significantly increase to 46.4 μg m^{-3} when all anthropogenic NO_x emissions are cut down (shown as red bar in Figure 7b). A similar trend is also found in the FWP region, although soil O_3 concentrations are relatively lower than that in the BTH region, the soil O_3 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 NO_x emissions are excluded (shown as red bar in Figure 7c). The reduction in anthropogenic NO_x emissions results in a shift of the O_3 formation regime

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towards a more NO_x-sensitive chemical regime, leading to a higher contribution of O_3 from soil sources. We conclude that with stricter anthropogenic emission reduction measures, the contributions of soil Nr emissions to O_3 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_3 concentrations, it is necessary to implement much stricter control measures for anthropogenic emissions due to the synergistic effects of SNO_x and SHONO.

Here we show that the substantial soil Nr emissions present an additional challenge for O_3 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_x emissions are eliminated, T2 increases by 0.056 ℃ in the presence of soil Nr emissions, compared to 0.092 ℃ in the absence of soil Nr emissions. In the BTH region, which has relatively high anthropogenic emissions, reducing anthropogenic NO_x emissions by the same proportion could result in relatively greater warming, and T2 increases by 0.084 ℃ in the presence of soil Nr emissions, compared to 0.15 ℃ in the absence of soil Nr emissions when anthropogenic NO_x emissions are excluded. This is attributed to aerosols (such as sulfate and nitrate) and NO_x emissions and their effective radiative

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forcing (ERF) associated with a cooling effect (high confidence) (Liao and Xie, 2021; Bellouin et al., 2020). Decreases in aerosol concentrations and NO_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_x emissions (Figure S5). Therefore, although soil Nr emissions are relatively low compared to anthropogenic emissions, the combined effects of NO_x and HONO emissions from natural soil and agricultural land should be considered when assessing climate change and implementing strategies to mitigate O_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_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_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_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_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_x or SHONO effect. The presence of soil Nr emissions, acting as precursors of O_3 and secondary inorganic aerosols, has a suppressing effect on efforts

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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.

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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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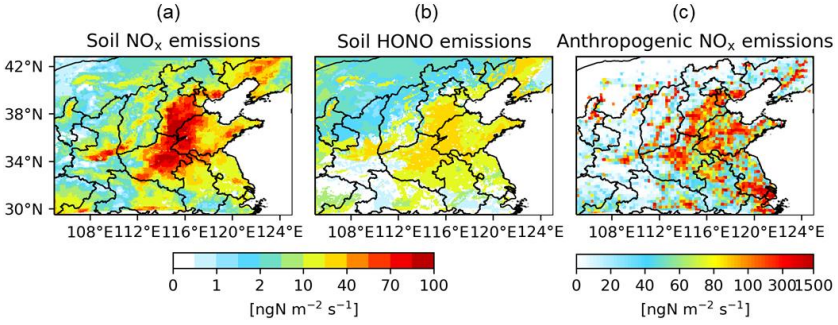

753

754 **Figure 1.** Distribution of the simulated monthly mean (a) soil NO_x emissions, (b) soil

755 HONO emissions, and (c) anthropogenic NO_x emissions in July 2018.

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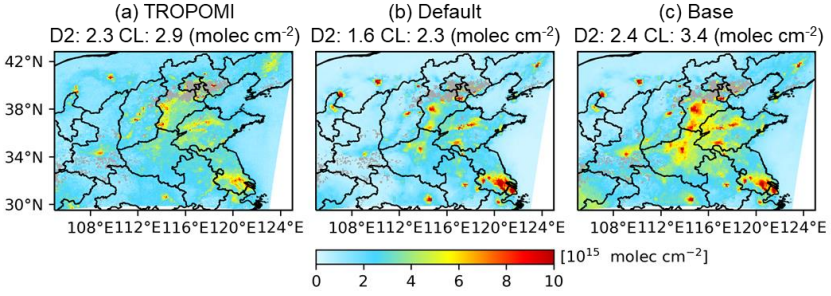

757

758 **Figure 2.** (a) Monthly mean tropospheric NO_2 VCD retrieved by TROPOMI measured

759 at 12:00−14:00 LT and simulated by (e) Default and (f) Base averaged over the same

760 periods in July 2018.

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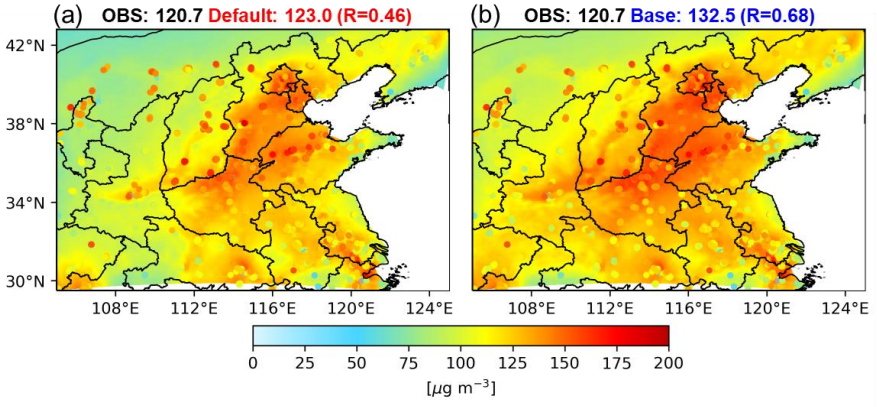

762

763 **Figure 3.** Distribution of observed (dots) and simulated (shaded) surface MDA8 O_3

764 from (a) Default and (b) Base in July 2018. Statistics in the upper corner of panels are

765 the monthly mean MDA8 O_3 concentrations averaged over the study region and the

766 spatial correlation coefficient R between observations and simulations.

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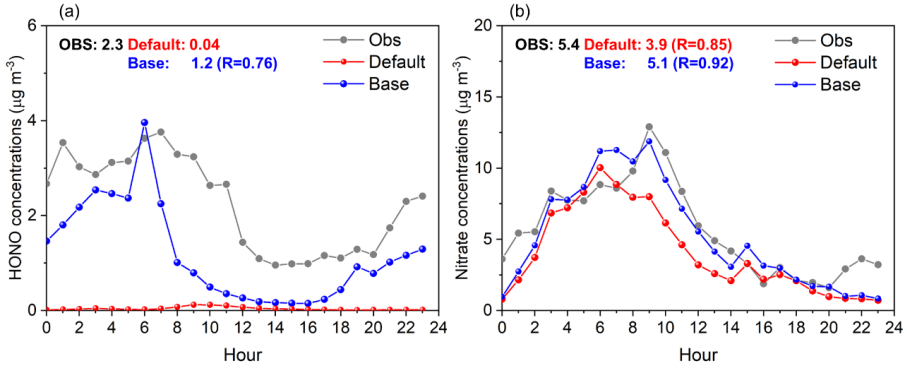

768

769 **Figure 4.** Diurnal variation of observed (in grey) and simulated (Default in red and

770 Base in blue) surface (a) HONO and (b) nitrate concentrations at a rural station in

771 Nanjing, with the mean value and temporal correlation coefficients (R) shown in the

772 upper right corner.

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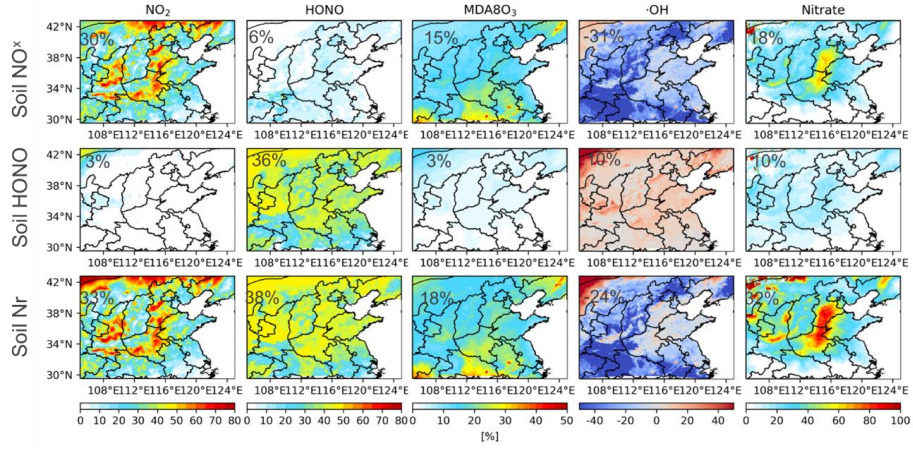

775

776 **Figure 5.** Simulated effects of soil Nr emissions on air quality. The first and second
777 rows show the contributions of soil NO_x and soil HONO emissions on monthly average
778 concentrations of NO_2, HONO, $MDA8O_3$, max-1h ·OH, and nitrate, respectively. The
779 third row shows the combined effect of soil Nr emissions on the species listed above.
780 Statistics in the upper right corner of each panel are the mean values averaged over the
781 study region.

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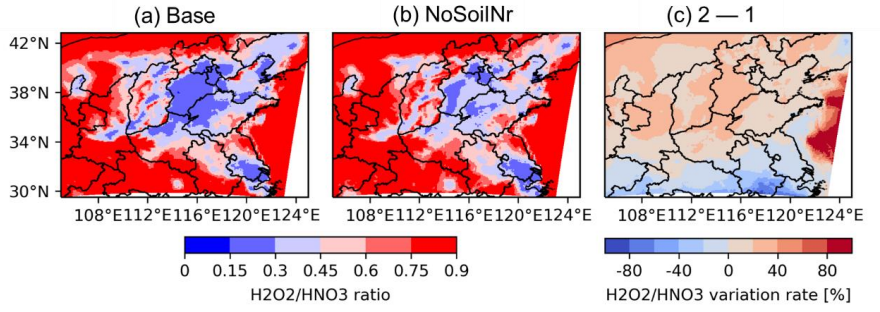

783

784 **Figure 6.** Distribution of the O_3 formation regimes (represented as H_2O_2/HNO_3 ratios)

785 for (a) Base simulation with the addition of soil Nr emissions and (b) NoSoilNr

786 simulation without the addition of soil Nr emissions. (c) Changes in the distribution of

787 O_3 formation regimes due to the soil Nr emissions

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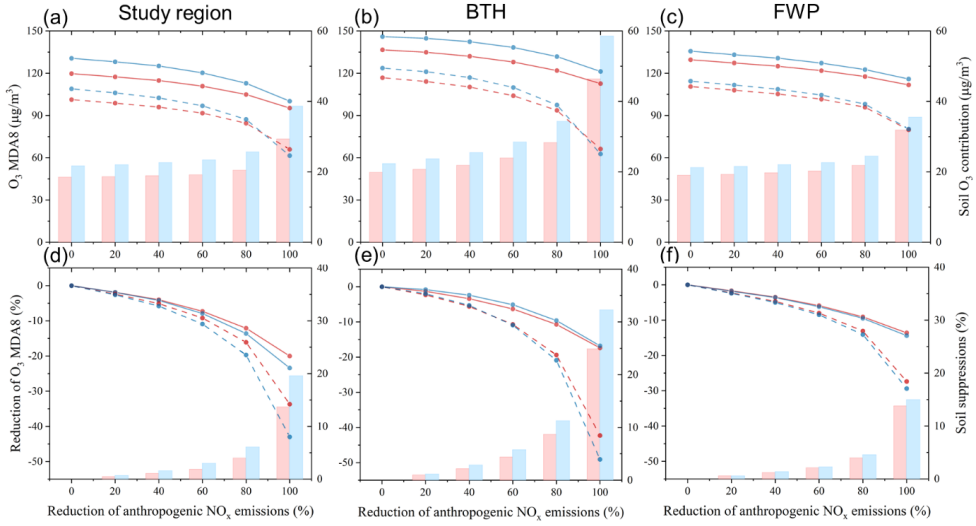

Figure 7. Role of soil Nr emissions in O_3 pollution regulation. The responses of MDA8 O_3 concentrations to the reductions of anthropogenic NO_x emissions (20%, 40%, 60%, 80% and 100%) relative to July 2018 levels, in the presence (solid line) and absence (dotted line) of soil Nr emissions in the study region, BTH and FWP region. (The lines in panels a-c and d-f are MDA8 O_3 concentrations and the relative reductions in MDA8 O_3 under different anthropogenic NO_x emission reductions, respectively. The red bars (right y-axis) in panels a-c show the corresponding O_3 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 O_3 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.)

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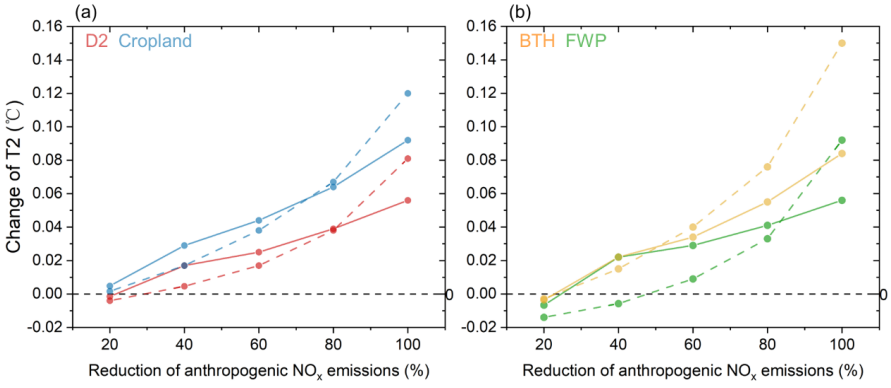

804

805 **Figure 8.** The responses of air temperature at 2m (T2) to the reductions of

806 anthropogenic NO_x emissions (20%, 40%, 60%, 80% and 100%) relative to July 2018

807 levels in the presence (solid line) and absence (dotted line) of soil Nr emissions (a) in

808 the study region, (b) BTH and FWP region.

809