Seasonal modeling analysis of nitrate formation pathways in Yangtze River Delta region, China

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Abstract

Nitrate (NO_3^-) has been the dominant and the least reduced chemical component of fine particulate matter ($PM_{2.5}$) since the stringent emission control implemented in China in 2013. The formation pathways of NO_3^- vary seasonally and differ substantially in daytime vs. nighttime. They are affected by precursor emissions, atmospheric oxidation capacity, and meteorological conditions. Understanding NO_3^- formation pathways provides insights for the design of effective emission control strategies to mitigate NO_3^- pollution. In this study, the Community Multiscale Air Quality (CMAQ) model was applied to investigate the impact of regional transport, predominant physical processes, and different formation pathways to NO_3^- and total nitrate (TNO_3, i.e., HNO_3+NO_3^-) production in the Yangtze River Delta (YRD) region during the four seasons of 2017. $NO_3^-/PM_{2.5}$ and NO_3^-/TNO_3 are the highest in the winter, reaching 21% and 94%, respectively. Adjusted gas ratio (adjGR~~)~~= ($[NH_3]$ + $[NO_3^-]$)/($[HNO_3]$ + $[NO_3^-]$))) in the YRD is generally greater than two in ~~different~~the four seasons across most areas in the YRD, indicating that YRD is mostly in the NH_3-rich regime and NO_3^- is limited by HNO_3 formation. Local emissions and regional transportation contribute to ~~YRD~~ NO_3^- concentrations throughout the YRD region by 50–62% and 38–50%, respectively. Majority of the regional transport of NO_3^- concentrations is contributed by indirect transport (i.e., NO_3^- formed by transported precursors reacting with local precursors). Aerosol (AERO, including condensation, coagulation, new particle formation and aerosol growth) processes are the dominant source of NO_3^- formation. In summer, NO_3^- formation is dominated by AERO and total transport (TRAN, sum of horizontal and vertical transport) processes. The OH+NO_2 pathway contributes to 60–83% of the TNO_3 production, and the N_2O_5 heterogeneous (HET N_2O_5) pathway contributes to 10–36% in the YRD region. HET N_2O_5 contribution becomes more important in cold seasons than warm seasons.

Within the planetary boundary layer in Shanghai, the TNO_3 production is dominated by the $OH+NO_2$ pathway during the day (98%) in the summer and spring, and by the HET N_2O_5 pathway during the night (61%) in the winter. Local contribution dominates the $OH+NO_2$ pathway for TNO_3 production during the day, while indirect transport dominates the HET N_2O_5 pathway at night.

Keywords: Nitrate formation pathways; chemical transport model, process analysis; local and transport contributions; Yangtze River Delta.

1. Introduction

The Yangtze River Delta (YRD) region, located in eastern China, is among the most populous and developed economic regions in China. Because of rapid population growth, economic advancement, urbanization, and industrialization during recent decades, the YRD region has been frequently suffering from both fine particulate matter ($PM_{2.5}$) and ozone (O_3) pollution problems (Qin et al., 2021;Sun et al., 2019;Dai et al., 2021). Particulate nitrate (NO_3^-) is a major $PM_{2.5}$ component and high concentrations of NO_3^- are often observed during cold seasons in the YRD region, due to high precursors emissions and regional transport contribution. Huang et al. (2014) reported that the daily average $PM_{2.5}$ concentrations in Shanghai were 91 $\mu g\,m^{-3}$ during haze pollution events of 5–25 January 2013, whereas NO_3^- accounted for 14% total $PM_{2.5}$ mass. Huang et al. (2020a) observed that $PM_{2.5}$ concentrations in Nanjing were 271 $\mu g\,m^{-3}$ on 30–31 December of 2017, and the fraction of NO_3^- was ~27%. Lin et al. (2020) found that the peak concentration of NO_3^- in Nanjing was 85 $\mu g\,m^{-3}$ during haze pollution events in the spring of 2016.

Owing to the stringent emission control strategies ~~implemented in China~~ since 2013, primary $PM_{2.5}$, the major precursors (i.e., sulfur dioxide (SO_2) and nitrogen oxides (NO_x = nitric oxide (NO) + nitrogen dioxide (NO_2)) emissions have decreased substantially in China, which led to significant decreases in ~~primary~~total $PM_{2.5}$ and sulfate (SO_4^{2-}) mass concentrations~~ in China~~ (Li et al., 2022;Chen et al., 2021). However, compared to SO_4^{2-} and other $PM_{2.5}$ components, the reduction rate of NO_3^- was much less slower (Wen et al., 2018;Zhai et al., 2021;Zhou et al., 2022;Wang et al., 2022). This led to a rise in the ratio of NO_3^- mass to total $PM_{2.5}$ in eastern China, rendering NO_3^- the dominant chemical component of $PM_{2.5}$ (accounting for 24–35 %, especially during the cold season and haze pollution events) (Ding et al., 2019;Wen et al., 2018;Lin et al., 2020;Fu et al., 2020;Zhou et al., 2022;Xie et al., 2022). High concentrations of NO_3^- influence the hygroscopicity and optical properties of particles, contributing to the formation of haze and to visibility degradation (Hu et al., 2021;Xie et al., 2020). Mitigating NO_3^- pollution has become an urgent concern in the YRD.

NO_3^- is formed in the atmosphere by a series of chemical reactions leading to the production of nitric acid (HNO_3) and then following gas-to-particle partitioning (Griffith et al., 2015;Guo et al., 2018;Lin et al., 2020). The key NO_3^- formation pathways include the gas-phase oxidation (hydroxyl (OH) and NO_2) and the heterogeneous hydrolysis of dinitrogen a dinitrogen pentoxide (HET N_2O_5) on the wet particles' surface (Fan et al., 2021;Wang et al., 2018;Chen et al., 2020). ~~Several studies investigated the importance of different pathways to NO_3^- formation in various locations using~~The chemical transport models (CTMs), field observations, ~~the~~ box model, ~~or~~as well as oxygen and nitrogen isotope techniques apply to quantify the contribution of different pathways to NO_3^- formation in various locations. For example, He et al. (2020) and Li et al. (2021b) reported that the OH+NO_2 pathway dominates daytime NO_3^- formation in the YRD, accounting for 60–92 % and 55–86 % in warm and cold seasons, respectively. The HET N_2O_5 pathway is the main nocturnal-NO_3^- formation in winter, especially in severe haze episodes, with contributions of 44–97 % at night (Fu et al., 2020;He et al., 2018). Furthermore, Tan et al. (2021) and Wang et al. (2018) indicated that the chemical formation cannot explain the variation of TNO_3 at the surface (sum of NO_3^- and HNO_3), due to the concentrations of N_2O_5 being close to zero and controlled by high NO emissions at night. Fan et al. (2021) and Kim et al. (2014) further emphasized the contributions of NO_3^- formation pathways differ significantly at vertical altitudes, owing to the vertical gradients of nocturnal NO_3 and total oxidant (NO_2+O_3) level within the planetary boundary layer (PBL). Prabhakar et al. (2017) revealed that the active nocturnal NO_3^- formation ~~via the HET N_2O_5 pathway~~ from the upper PBL contributed 80 % to daytime surface NO_3^- concentrations in winter of 2013 in California~~, accounting for 80 %.~~.

The complex NO_3^- formation chemistry involves the anthropogenic emission of precursors (i.e., NO_x, and ammonia (NH_3)) and atmospheric oxidants (i.e., OH, O_3, and ~~N_2O_5~~NO_3) (Chan et al., 2021;Womack et al., 2019). ~~Studies~~Previous studies suggested that NO_3^- responds nonlinearly to its precursors emissions reductions in major Chinese regions (i.e., the North China Plain (NCP) and YRD), emphasizing that the uncoordinated control of precursors (i.e., SO_2, NH_3, and NO_x) increase the atmospheric oxidant capacity (AOC) and enhance NO_3^- formation in NO_x-rich regimes (Li et al., 2021b;Huang et al., 2020b;Lu et al., 2021a). Coupled with the chemical formation, regional transport also plays important roles in NO_3^- pollution formation. Previous modeling studies using the CTMs highlighted the important role of the regional transport in NO_3^- concentrations in major regions of eastern China (Itahashi et al., 2017;Qu et al., 2021;Ying et al., 2014;Shen et al., 2020). For example, Huang et al. (2020a) reported that secondary pollutants are regionally transported between the NCP and YRD regions (a distance of 1000 km), and hence simultaneously exacerbate the levels of secondary inorganic aerosols (SIA) in two major Chinese regions. Ying et al. (2014) revealed that the regional air pollution transport from the north and central China contributed about 45 % to NO_3^- in

Shanghai during the winter of 2009. Wu et al. (2017) suggested that the regional transport plays a key role in NO_3^- sources in Shanghai (accounting for about 90 %), while local emission only contributed 10 % for NO_3^- in January 2013. ~~Shen et al. (2020)~~Shen et al. (2020) reported that the contribution of regional transport amounted to around 60–98 % to the high concentrations of NO_3^- under severe haze episodes in two winters of 2015 and 2016 in the YRD. Qu et al. (2021) found that the indirect transport made a contribution of 43 % to NO_3^- in the Pearl River Delta (PRD) region in cold season of 2015, mainly due to chemical reactions between the locally emitted NOx and transported O_3 at night. Du et al. (2020) also revealed that regional transport contributed about 56 % to NO_3^- in Beijing in winter 2017, mainly produced via indirect transport.

The NO_3^- ~~formation~~chemical pathways and formation controlling factors ~~can~~may be very different in different seasons ~~even~~ in the same studying ~~region~~locations. Most previous studies ~~on NO_3^-~~have focused on ~~one or~~only a few short period of NO_3^- pollution episodes, ~~but lack of~~and lacked the seasonal analysis for the full year. This study aims to obtain a comprehensive understanding of the seasonal variations in the NO_3^- formation mechanisms, as well as to determine key precursors, dominant processes and chemical pathways in the YRD. The Community Multiscale Air Quality (CMAQ) model was employed to investigate the contributions of various physical and chemical processes to NO_3^- and HNO_3 formation. Regional transport and chemical reaction pathways were quantified for the YRD region. The analyses were conducted in the four seasons of 2017 to compare and identify the key impact factors for NO_3^- in different seasons, and to provide a scientific basis for designing effective emissions control strategies to mitigate the urgent NO_3^- pollution in the YRD region.

2. Methods

2.1. Model configuration

The CMAQ v5.2 model (Wyat Appel et al., 2018;Liu et al., 2020b;Sheng et al., 2022) was applied to investigate the major chemical pathways and physical processes that contribute to NO_3^- and TNO_3 formation in the YRD region. Two nested domains were used, as shown in Fig. 1. The outer domain (36 km horizontal resolution) spanned eastern and southeastern China, while the inner domain (12 km horizontal resolution) spanned the entire YRD region. The simulation periods were January, April, July, and October 2017, representing the winter, spring, summer, and autumn, respectively. The simulation began three days prior to each of the study periods, and the results were not included in the model analysis as they served as a spin-up of the model.

The CMAQ model was configured using the photochemical mechanism of the State-wide Air Pollution Research Center version 07 (SAPRC07tic) and the sixth-generation aerosol (AERO6i) module (Fu et al., 2020;Sulaymon et al., 2021). Further details about the CMAQ modeling system provided in previous studies (Hu et al., 2016;Liu et al., 2020b). The Weather Research and Forecasting model (WRF v4.2, http://www.wrf-model.org) was used to simulate the required meteorological fields inputs, with initial and boundary meteorological conditions from the 1°×1° National Centers for Environmental Prediction Final (NCEP/FNL) reanalysis data (https://rda.ucar.edu/datasets/ds083.2/). ~~Detailed~~The detailed configurations of the WRF model ~~provided~~shown in ~~the studies of~~ Table S1, consistent with Hu et al. (2016) and Wang et al. (2021)~~, shown in Table S1,~~. The anthropogenic emissions ~~of~~for the 2017 ~~in the~~ YRD region were ~~released~~established by the Shanghai Academy of Environmental Sciences (SAES~~)~~), a high-resolution (4 km × 4 km) anthropogenic emission inventory across the entire YRD region (An et al., 2021)~~, and used for the entire YRD region.~~. The Multi-resolution Emission Inventory for China of the year

2017 with resolution of 0.25° × 0.25° (MEIC v1.3, http://meicmodel.org) served as the anthropogenic emissions for other Chinese regions outside the YRD (Zheng et al., 2018). Emissions from other regions outside China in the inner domain were calculated using the gridded Regional Emission inventory in ASia (REAS v3.2, 0.25° × 0.25° resolution) emissions of the year 2015. The global model of emissions of gases and aerosols from nature (MEGAN v2.1) was used to estimate biogenic emissions (Guenther et al., 2012). Biomass burning emissions were based on satellite observations including both gases and aerosols from the 2017 Fire Inventory from NCAR (FINN) (Wiedinmyer et al., 2011). Further descriptions of the emissions processing are provided in previous studies by Hu et al. (2016) and Qiao et al. (2015), and therefore not repeated here.

2.2. Contributions of transport

To quantify the contributions of local and regional transport to the surface concentrations of the nitrate-phase species (i.e., HNO_3 and NO_3^-), four scenarios were simulated under the same meteorological fields. Briefly, in the first (base) scenario, the anthropogenic emissions of 2017 in the YRD and outside regions were included. In the second (YRD-zero) scenario, anthropogenic emissions in the YRD were set to zero, while anthropogenic emissions in regions outside YRD were used. In the third (outside-zero) scenario, only anthropogenic emissions in the YRD were included, while the regions outside the YRD were set to zero. The fourth (all-zero) scenario represented the background case, where the anthropogenic emissions within the study domain were set to zero.

The predicted concentrations were denoted as C_{base}, $C_{YRD\text{-}zero}$, $C_{outside\text{-}zero}$, and $C_{all\text{-}zero}$, representing ~~concentration~~NO_3^- concentrations associated with the base, YRD-zero, outside-zero, and all-zero scenarios, respectively. ~~For NO_3^- in YRD, the~~ The contributions of local YRD emissions, regional transport (the sum of direct and indirect transport from outside regions), direct transport (NO_3^- contributed by transported precursors from outside regions), indirect transport (NO_3^- contributed by transported and local-emitted precursors via the $OH+NO_2$ and HET N_2O_5 chemical pathway), and background were defined as F_{Local}, F_{Region}, F_{Direct}, F_{Indirect}, and $F_{\mathrm{Background}}$, and they were ~~quantified~~calculated as follows:

$$F_{\mathrm{Local}} = (C_{\mathrm{outside\text{-}zero}} - C_{\mathrm{all\text{-}zero}})/C_{\mathrm{base}} \qquad (1)$$

$$F_{\mathrm{Region}} = (C_{\mathrm{base}} - C_{\mathrm{outside\text{-}zero}})/C_{\mathrm{base}} \qquad (2)$$

$$F_{\mathrm{Direct}} = (C_{\mathrm{YRD\text{-}zero}} - C_{\mathrm{all\text{-}zero}})/C_{\mathrm{base}} \qquad (\cancel{2}3)$$

$$F_{\mathrm{Indirect}} = [(C_{\mathrm{base}} - C_{\mathrm{outside\text{-}zero}}) - (C_{\mathrm{YRD\text{-}zero}} - C_{\mathrm{all\text{-}zero}})]/C_{\mathrm{base}} \qquad (\cancel{3}4)$$

$$F_{\mathrm{Background}} = C_{\mathrm{all\text{-}zero}}/C_{\mathrm{base}} \qquad (\cancel{4}5)$$

~~In addition to~~Besides NO_3^-, the major gases pollutants (i.e., ~~O_3,~~ NH_3, NO_2, and HNO_3), atmospheric oxidants (i.e., ~~OH,~~O_3 and ~~N_2O_5)~~OH,) and particulate pollutants (i.e., $PM_{2.5}$~~, SO_4^{2-},~~ and ~~SOC~~TNO_3) were also quantified. The values of the contributions of the local, direct and indirect transport emissions can be greater or less than zero, which represents the generation or depletion of pollutants through chemical reactions between local and non-local precursors.

2.3. Process analysis

In the CMAQ model system, the process analysis (PA) tool has two components, including the Integrated Process Rate (IPR) and Integrated Reaction Rate (IRR) (Liu et al., 2011;Byun and Schere, 2006). The IPR analysis was applied to investigate the cumulative effect of chemical and physical processes to NO_3^- and HNO_3 formation and their daily variation within the PBL (Chen et al., 2019;Yang et al., 2020;Kim et al., 2014). These processes, as explained in Table S2, include aerosol processes (AERO), gas chemistry (CHEM), emission (EMIS), horizontal transport (HTRA), vertical transport (VTRA), dry deposition (DDEP), and cloud processes (CLDS). Furthermore, the IRR analysis was employed to quantify the rates of TNO_3 chemical reactions pathways (Qu et al., 2021;Fu et al., 2020;Shen et al., 2020). The complex chemical production of TNO_3 involves eight reactions pathways, detailed in Table S3 (Qu et al., 2021;Fu et al., 2020;Chuang et al., 2022). In the latter analyses, these pathways are grouped into three major TNO_3 production pathways, including the $OH+NO_2$, HET N_2O_5, and “Others” pathways, according to their importance. Shanghai is selected as an example in the IPR and IRR analysis to explore the impacts of physical and chemical processes of NO_3^- and HNO_3 formation because it is the largest city in the YRD and has the most abundant measurement data.

2.4. Observation data

Hourly concentrations of six routine air pollutants (i.e., O_3, $PM_{2.5}$, NO_2, SO_2, and carbon monoxide (CO)) in five representative YRD cities (i.e., Shanghai, Nanjing, Hefei, Hangzhou, and Changzhou, shown in Fig. 1) during the four seasons were obtained from the China Ministry of Ecology and Environment (http://106.37.208.233:20035/, last accessed on April 30, 2022). Furthermore, hourly NO_3^- concentrations were measured by the Monitors for AeRosols and Gases (MARGA 1S ADI 2080, Netherlands) (Khezri et al., 2013) at four urban atmospheric environment supersites, including Shanghai (31.23 °N, 121.54 °E), Hefei (31.78 °N, 117.20 °E), Hangzhou (30.29 °N, 120.16 °E), and Changzhou (31.76 °N, 119.96 °E). Observation data of meteorological parameters (temperature (T2, °C), relative humidity (RH, %), wind speed (WS, m/s) and wind direction (WD, °)) for 75 weather stations in the YRD were downloaded from the Chinese Meteorological Agency (http://data.cma.cn/en, last accessed on November 30, 2021).

The statistical metrics used for the WRF-CMAQ model evaluation include the mean bias (MB), normalized mean bias (NMB), normalized mean error (NME), correlation coefficient (R), root mean square error (RMSE), and index of agreement (IOA). Definitions and criteria of all statistical metrics are illustrated in Table S4. The benchmarks of major air pollutants ($PM_{2.5}$, NO_2, O_3, and NO_3^-) concentrations are suggested by Emery et al. (2017) and Huang et al. (2021). The benchmarks of major meteorological parameters (T2, WS, and WD) are suggested by Emery and Tai (2001).

3. Results and discussion

3.1. Model evaluation

3.1.1. WRF model performance

Table 1 shows the modeling performance statistics of the meteorological parameters in the four seasons of 2017. Predicted T2 and WS values are slightly higher than the observations, and MB values of T2 and WS exceed the suggested benchmark (MB ≤ ±0.5) in all seasons. The seasonal and annual IOA values of T2 occur within the suggested benchmark (IOA ≥ 0.8). For WS, the seasonal and annual values of RMSE and IOA all meet the suggested criterion (RMSE ≤ 2.0 and IOA ≥ 0.6). The MB values of WD are slightly above the suggested benchmark (MB ≤ ±10) in the four seasons, except during spring. RH is generally under-estimated compared to the observations with averaged MB values of –6.96, –10.7, –9.06, and –5.98 in winter, spring, summer, and autumn, respectively. No suggested criterion for MB value of RH. In addition, high seasonal and annual values of R (0.85–0.95 for T; 0.87–0.91 for RH; 0.70–0.85 for WS; and 0.75–0.89 for WD) are found. The WRF performance in this study is comparable to WRF performance in our previous simulation studies (Wang et al., 2021;Hu et al., 2016;Sulaymon et al., 2021).

3.1.2. CMAQ model performance

Table 2 and Fig. S1 show the model performance and time series of major air pollutants in the four seasons. Overall, the CMAQ model has reasonably reproduced the observed $PM_{2.5}$, O_3, and NO_2 concentrations in the YRD region, especially in Shanghai. The daily concentrations of $PM_{2.5}$ are efficiently simulated in the five cities except Hefei, illustrated by the NMB, NME, and R values meeting the criteria established by Emery et al. (2017) (NMB ≤ ±0.30, NME ≤ 0.50, and R > 0.70).

MDA8 O_3 are slightly overestimated in Nanjing, Hefei, Hangzhou, and Changzhou. Predicted concentrations of NO_2 are generally lower than the observations in all five cities ($-0.15 < NMB \le -0.05$, $-10.37 < MB \le -1.89$). When compared to our previous ~~air quality simulation~~ studies (Hu et al., 2016;Wang et al., 2021;Ma et al., 2021;Sulaymon et al., 2021;Li et al., 2021a), the statistical results in this study show a better model performance.

Fig. 2 illustrates the comparison of predicted and observed NO_3^- concentrations at the four supersites on daily timescales~~ (Fig. S2 shows the hourly predicted and observed NO_3^- concentrations).~~. The general temporal variations of observed NO_3^- concentrations are efficiently captured by the model. The daily concentrations of NO_3^- are efficiently predicted in four supersites, all within the benchmark ($NMB \le \pm 0.60$, $NME \le 0.75$, and $R > 0.6$). But in Hefei (Fig. 2b), the wintertime NO_3^- measurement data is not available, when NO_3^- shows the highest concentrations and is of most concern. Good agreement between predicted and observed values is demonstrated on daily timescales, especially in Shanghai (NMB = –0.49, R = 0.70), Hangzhou (NMB = 0.11, MB = 0.64) and Changzhou (NMB = 0.36, R = 0.56). ~~The seasonal daily concentrations of NO_3^- are efficiently predicted in Shanghai, Hangzhou and Changzhou, within the benchmark ($NMB \le \pm 0.60$, $NME \le 0.75$, and $R > 0.6$).~~ ~~The~~Overall, the performance statistical metrics of predicted NO_3^- in this study are comparable to those of our previous ~~studies~~works (Shi et al., 2017;Qu et al., 2021;Xie et al., 2022). Fig. S2 shows the hourly predicted and observed NO_3^- concentrations in each season. NO_3^- concentrations are generally underestimated during the summer and autumn. One possible reason is that RH is slightly underestimated by the WRF model during these seasons (Table 1), which results in a lower buildup of NO_3^- concentrations. Other reasons could be associated with uncertainties in the NO_3^- formation mechanisms (~~i.e., ~~missing or insufficient heterogeneous reactions) in the current CMAQ model~~)~~ and uncertainties in NOx and NH_3 emissions (Zheng et al., 2020;Lu et al., 2021b;Zheng et al., 2015;Liu et al., 2019;Xie et al., 2022).

3.2. Regional transport contribution to nitrate in YRD

Fig. S3 shows the spatial distribution of the seasonal (winter, spring, summer and autumn) and annual ~~mean~~ (average of the four seasons) NO_3^-, HNO_3, and TNO_3 concentrations under four ~~different~~ emissions scenarios in the d02 domain. Under C_{base}, the seasonal and annual ~~predicted~~NO_3^- concentrations~~ of NO_3^-~~ for the entire YRD region were 16.0, 7.4, 1.0, 5.4, and 7.4 μg m^{-3}, respectively (Table S5). Compared to C_{base}, the seasonal and annual ~~YRD~~ NO_3^- concentrations in $C_{outside\text{-}zero}$ decreased by 8.0, 2.8, 0.4, 2.2, and 3.3 μg m^{-3}, respectively. Even more significant differences in NO_3^- are observed between C_{base} and $C_{YRD\text{-}zero}$. The NO_3^- ~~values~~ decreased by 12.0, 6.9, 0.9, 4.8 and 6.1 μg m^{-3} in winter, spring, summer, autumn, and ~~the~~a year, respectively, to become almost twice as high as those between C_{base} and $C_{outside\text{-}zero}$. The results suggest that the ~~YRD~~ local anthropogenic emissions contribute more to the seasonal NO_3^- concentrations~~.~~ in the YRD.

Fig. 3 shows the regional contributions of the background, local, direct and indirect transport to nitrate-related species in the four seasons (results for Shanghai are shown in Fig ~~S5~~S4). The local emissions dominate NO_3^- concentrations throughout the YRD~~ NO_3^-;~~, accounting for 50.4–62.0 % in the four seasons (Fig. 3a). Fig 3c suggests that the precursors (NO_2 and NH_3) are dominated by the local emissions (more than 93.0%). The contributions of the total regional transport ~~(sum of indirect and direct transport)~~ are 49.5, 38.0, 41.6, and 42.0 % in winter, spring, summer, and autumn, respectively. The indirect transport contributes 24.2–37.0% of NO_3^- concentrations, and exceeds the contributions from direct transport in the spring, summer, and autumn. Similarly, Qu et al. (2021) reported that the reaction between the locally emitted ~~NO_x~~NO_2 and transported O_3 dominates the production of indirect NO_3^- transport in the PRD region.

In Fig. 3b, the local emission and indirect transport have negative contributions to O_3 concentration, leading to the depletion of O_3 in the four seasons. ~~The~~For O_3, the local emissions have negative contribution ~~to O_3~~ in winter (–~~45.6~~46%) and autumn (–12~~.3%), and~~ %). The negative contributions of the indirect transport ~~has negative contribution~~are –6, –8, –8, and –4 % in winter, spring~~ (–8.5%)~~, summer, and autumn ~~(–8.7%). For O_3 and OH (~~, respectively. In Fig. ~~3b and~~ 3d~~),~~, the indirect transport contributes ~~about –8% and –~~from -42% to -12% ~~–42%~~ of OH concentrations in ~~all~~the four seasons~~, respectively.~~. The negative indirect transport contributions to O_3, N_2O_5, and OH suggest that the atmospheric oxidants are consumed in the YRD, which in turn enhances the chemical production of NO_3^-.

3.3. Formation processes of nitrate

Fig. 4 shows the modeled diurnal variations of three nitrate-phases (NO_3^-, HNO_3, and TNO_3), the major precursors (i.e., O_3, NO_2, and NH_3), and the major atmospheric oxidants (OH and N_2O_5) in the four seasons for the entire YRD region in the base scenario. Except for summer, higher predicted TNO_3 and NO_3^- concentrations are observed in early morning hours (6:00–8:00 am), while lower TNO_3 and NO_3^- concentrations are observed around 16:00–18:00 pm. Predicted concentrations of TNO_3, HNO_3, and O_3 show the same diurnal variations in the summer, and peak around 12:00 pm (the most active photochemical hours). The opposite profiles of TNO_3's diurnal variation between summer and non-summer are mainly attributed to the temperature effect on the gas-to-particle partitioning between NO_3^- and HNO_3. As shown in Fig. S3, NO_3^- dominates the TNO_3 concentrations and determines its diurnal variations in non-summer, while HNO_3 dominates the diurnal variation in summer. A two-peak mode diurnal variation of NO_2 and NH_3 is identified in the four seasons. High concentrations of NO_2 and NH_3 occur in the early morning (hours 6:00–8:00 am) and early evening (hours 18:00-19:00 pm), due to the local transportation emissions during rush hours. OH and N_2O_5 have a one-peak mode diurnal variation in the four seasons. OH peaks around 12:00 pm, similar to HNO_3, while N_2O_5 peaks around

18:00–20:00 pm.

Fig. ~~S7~~S6 shows seasonal variations in $NO_3^-/PM_{2.5}$, NO_3^-/TNO_3, nitrogen oxidation ratios (NOR = $[NO_3^-]/([NO_3^-] + [NO_2])$), and adjusted gas ratio (adjGR = $([NH_3] + [NO_3^-])/([HNO_3] + [NO_3^-])$) in the YRD. $NO_3^-/PM_{2.5}$ and NO_3^-/TNO_3 are the highest in the winter, accounting for 21 ±5% and 94 ±3%, respectively. The averaged NOR values for the entire YRD region are 0.24, 0.16, 0.03, and 0.13 mol/mol in winter, spring, summer, and autumn, respectively. The highest value of NOR in winter suggests a high conversion efficiency of NO_2 to NO_3^-. AdjGR values are generally greater than two in the four seasons across most areas in the YRD, indicating that YRD is mostly in the NH_3-rich regime. Therefore, NH_3 is not a limiting factor of NO_3^- formation in YRD.

~~Shanghai is selected as the example city in the IPRs analysis to explore the impacts of physical and chemical processes of NO_3^- and HNO_3 formation within the PBL.~~ Fig. 5 illustrates a two-peak mode diurnal variation of the net IPRs rates of NO_3^- production in the four seasons. Peak hours are around mid-noon (10:00–11:00 am) and early evening (19:00–21:00 pm), with peak rates of 1.2–1.5, 0.7–0.8, 0.4–0.6, and 0.1–0.2 μg m^{-3} h^{-1} in the winter, spring, summer, and autumn, respectively. AERO processes (including condensation, coagulation, and aerosol growth) are the dominant contributors of NO_3^- formation, with the peak rates of 2.1, 1.3, 1.5, and 0.4 μg m^{-3} h^{-1} in the winter, spring, summer, and autumn, respectively. The sharp decline hours of the net IPRs (around 11:00–18:00 pm) are mainly dominated by TRAN (sum of HTRA and VTRA) processes, with the mean rates of –1.4, –0.8, –0.7, and –0.3 μg m^{-3} h^{-1} in the winter, spring, summer, and autumn, respectively. However, in summer, TRAN processes constitute the dominant source during midnight (1:00–6:00 am), owing to ~~higher~~the stable PBL weakening the contribution of vertical transport and accelerating the accumulation of NO_3^- concentrations at the ~~upper PBL contributing to the~~ surface~~ through the vertical mixing and development of the PBL~~ (Huang et al., 2020c). In Fig. ~~S9~~S7, VTRA processes act as the main positive contributor to NO_3^- buildup production from 0:00 to 23:00 at layer 1 (surface layer), while AERO processes make the negative contribution to NO_3^- within layers 1–8 (from the surface to 800 m). Above layer 10, AERO processes for NO_3^- production are positive in the daytime, which is conducive to the accumulation of NO_3^-concentrations.

For HNO_3, a one-peak mode diurnal variation of the net IPRs rates is found, and peak times are at 20:00 pm in the winter and around 9:00–12:00 am in other seasons (Fig. 5). Meanwhile, CHEM (gas chemical processes) processes are the major contributor to HNO_3 formation, with the peak rates being 0.6, 1.4, 2.3, and 0.7 ppb h^{-1} in the winter, spring, summer, and autumn, respectively. In the spring, summer and autumn, the peak times of HNO_3 formation are consistent with the first-peak times of NO_3^-. The seasonal net IPRs rates reached a maximum of 0.3, 1.0, and 0.1 ppb h^{-1}, respectively. CHEM and VTRA processes are the dominant contributors of HNO_3^- production, especially during 7:00 to 13:00 (net IPRs rates > 0), with the seasonal peak rates of 1.5, 2.7, and 0.8 ppb h^{-1}, respectively. AERO, DDEP, and HTRA processes are the dominant contributors of the HNO_3^- sharp decline (14:00–17:00 pm), with the lowest net IPRs rates of –0.8, –0.7, and –0.3 μg m^{-3} h^{-1} in the spring, summer, and autumn, respectively. DDEP processes are the dominant sink of HNO_3 in summer (–0.64 ± 0.20 ppb h^{-1}). However, in the winter, the peak times of HNO_3 production are opposite with the first-peak time of NO_3^-~~;~~ production, but consistent with the second-peak time. HTRA make a positive contribution to HNO_3~~$^-$;~~, with peak rates of 0.18 ppb h^{-1} at 20:00 pm. In Fig. S12, the only-largest sink is the AERO process, consistent with efficient partitioning of HNO_3 into particle phase NO_3^- in cold seasons.

Table 3 illustrates that within the PBL, in cold seasons (winter and autumn), about 60–78 % of TNO_3 is produced through $OH+NO_2$, 21–36 % through HET N_2O_5, and 2–5 % through the "Others" pathways in the five representative YRD cities.

Meanwhile, 71–83 % of TNO_3 is produced through $OH+NO_2$, 10–23 % through HET N_2O_5, and 4–13 % through the "Others" pathways (mainly contributed by NO_3+Org and N_2O_5 H_2O) in warm seasons (summer and spring). Table 4 shows the comparison of the contribution of the major TNO_3 production pathways studies in China and other regions using different methods. The results are in agreement with the contribution of NO_3^- pathways in previous modeling and observational studies. For example, Li et al. (2021b) modeled that $OH+NO_2$ and HET N_2O_5 pathways dominate NO_3^- production in the YRD region in warm and cold seasons of 2016 by the CTM, accounting for 86–92 % and 8–14 % in the surface layer, respectively. He et al. (2020) reported that the $OH+NO_2$ pathway dominates NO_3^- production in Shanghai on the surface layer using nitrogen isotopes analysis, accounting for 84–92 % and 55–77 % in the warm and cold seasons of 2016, respectively. Alexander et al. (2020) highlighted that the $OH+NO_2$ and HET N_2O_5 pathways contribute the same proportion (both 41 % in the four seasons) to NO_3^- production in the global region using the CTM and oxygen isotopes analysis.

Fig. 6a shows the diurnal variations of TNO_3 formation reactions rates through three major pathways in Shanghai within the PBL. The average diurnal trends of TNO_3 production rates are consistent with the CHEM processes rates of HNO_3 production (Figs. 5–6). The chemical production of HNO_3 quickly transforms to particulate NO_3^-, through AERO processes in the presence of abundant NH_3. ~~In the winter, spring, summer, and autumn, the~~The averaged TNO_3 production rates are 0.31 ± 0.14, 0.65 ± 0.37, 1.09 ± 0.68, and 0.28 ± 0.22 ppb h^{-1}~~,~~ in the winter, spring, summer, and autumn, respectively (Table S6). Moreover, the seasonal peak rates of TNO_3 production are 0.6, 1.4, 2.3, and 0.7 ppb h^{-1} around 11:00 am –13:00 pm, respectively. In accordance with the seasonal variation of HNO_3 net IPRs rates, TNO_3 production rates are the fastest in summer.

In Shanghai, TNO_3 chemical production is dominated by the $OH+NO_2$ pathway on the daily timescale, accounting for 69.3–86.9 % of the total, while the HET N_2O_5 pathway is likewise a relatively important pathway (accounting for 11.1–28.4 %) in the four seasons (Fig. 6b). Notably, TNO_3 production rates are dominated by the OH+NO_2 pathway during the daytime (7:00 am–18:00 pm, accounting for 88.4–97.9 % of the total) in all seasons, while the HET N_2O_5 pathway becomes more important for the TNO_3 production during the nighttime (19:00 pm – 06:00 am, accounting for 42.5–61.6%). During winter, TNO_3 formation via the HET N_2O_5 pathway becomes dominant over the OH+NO_2 pathway, accounting for 62, 65, and 68% in Shanghai, Hangzhou and Nanjing at night, respectively. O_3 strongly coordinates TNO_3 production ~~in YRD~~ via the HET N_2O_5 pathway during the nighttime. Similarly, He et al. (2018) observed that the HET N_2O_5 pathway was the major contributor to NO_3^- production in the winter of Beijing at the surface layer, using oxygen and nitrogen isotopes analysis, accounting for 56–97 % of the total during the nighttime. In another CTM study in the NCP, the HET N_2O_5 pathway was the dominant contributor to nocturnal-NO_3^- production within the PBL in winter, with a contribution of 83 % at night (Liu et al., 2020a). In Fig. S8, the seasonal TNO_3 production rates (ppb/h) and contributions (%) of the major pathways have been compared between vertical layers and PBL. The OH+NO_2 pathway dominated TNO_3 production at all layers, accounting for more than 58%, 78%, 80%, and 83% in winter, spring, summer, and autumn, respectively. The OH+NO_2 pathway rate decreases with altitude at vertically layers, where its contribution decreases from 87% to 58%, from 91% to 78%, from 93% to 80%, and from 95% to 83% in the four seasons, respectively. The HET N_2O_5 pathway becomes more important for the TNO_3 production within layers 4~8 (250 to 580 m) in winter, accounting for 37% (Fig. S8b).

Fig. 7 displays the contributions of TNO_3 formation pathways from the local and transport (sum of indirect and direct transport) contributions. For the local contribution, the averaged TNO_3 production rates are 0.27 ± 0.14, 0.56 ± 0.37, 1.05 ±

0.69, and 0.26 ± 0.21 ppb h^{-1} in the winter, spring, summer, and autumn, respectively (Table ~~S8~~S7). During the daytime, the OH+NO_2 pathway contributes almost all TNO_3 production rates from the local contribution, accounting for about 89–98 % of the total, with mean rates of 0.33 ± 0.17, 0.83 ± 0.34, 1.55 ± 0.59, and 0.40 ± 0.22 ppb h^{-1} in the winter, spring, summer, and autumn, respectively. The results suggest that the locally-emitted NO_2 reacts with ~~locally formed~~ OH dominated TNO_3 production ~~rates~~ during the day in the ~~urban~~ YRD region.

For the transport contribution, the averaged TNO_3 production rates are 0.04 ± 0.01, 0.08 ± 0.02, 0.03 ± 0.02, and 0.02 ± 0.01 ppb h^{-1} in the winter, spring, summer, and autumn, respectively (Table ~~S9~~S8). The HET N_2O_5 pathway is noted as the dominant pathway for TNO_3 production of the transport contribution, accounting for around 72–86 % during the nighttime. Fig. ~~7b~~8 compares the seasonal TNO_3 production pathways rates between local, indirect and direct transport contributions. within the PBL. The regional production is mainly contributed by indirect transport, especially in the winter and summer. The results suggest that the transported O_3 from outside YRD region ~~can~~ react with the locally-emitted NO_2, supporting ~~HNO_3 formation~~TNO_3 production via the HET N_2O_5 ~~chemistry~~chemical pathway ~~at night~~during the nighttime.

Overall, our findings illustrate that local emissions dominate NO_3^- formation in the YRD (50–62%), more specifically, locally-emitted NOx reacting with OH and partitioning into particles with NH_3 (mostly from local sources, more than 93.0%), indicating that the uncoordinated control of precursors (i.e., NO_x and NH_3) and reduction of the oxidative capacity of the atmosphere is crucial for NO_3^- reduction. Furthermore, regional transport contributes 38–50% to NO_3^- formation in the YRD region. Indirect transport contributes 24–37% through transported O_3 reacting with local NO_x at night, indicating that the simultaneous controlling of O_3 and NO_3^- in the larger scale region is also important for NO_3^- reduction in the YRD.

This manuscript investigated the seasonal variations in the NO_3^- formation mechanisms, including local emission and regional transport contributions, as well as dominant processes and major chemical pathways in the YRD region. However, there are still some limitations in this manuscript, such as the insufficient heterogeneous chemistry on the dust particles' surface and uncertainties in precursors emissions in the model affect the model performance of NO_3^- during the spring and autumn (Xie et al., 2022). Furthermore, the Integrated Reaction Rate (IRR) analysis was employed to quantify the rates of TNO_3 (sum of NO_3^- and HNO_3) chemical pathways, which potentially lead to differences in chemical pathways rates and contributions between NO_3^- and TNO_3. Figure 6(b) illustrates that TNO_3 chemical production is dominated by the $OH+NO_2$ pathway on the daily timescale, accounting for 69.3–86.9 % in Shanghai. Notably, due to the higher temperature during the daytime, the potential production for NO_3^- is not as high as that of the nocturnal chemical pathway (mainly the HET N_2O_5 pathway at night), which potentially lead to underestimate in the nocturnal pathway contribution to NO_3^-.

4. Conclusions

This study investigates the contributions of regional transport and major chemical pathways to the of NO_3^- and HNO_3 formation in the YRD in different seasons using the WRF-CMAQ model. The modeled results show that local emissions dominate ~~YRD regional~~ NO_3^- concentrations in the YRD (50–62%), while regional transport contributes 38–50% to NO_3^- (indirect transport contributes 24–37%). Except for winter, HNO_3 was dominated by the contributions of local emissions (61–75%) and indirect transport contributed negatively –24 to –41%. In Shanghai, the IPRs analysis reveals that AERO processes were the predominant contributors in NO_3^- formation within the PBL. TRAN processes were the largest sinks in NO_3^- formation in the winter, spring and autumn, while the positive contributors at night in summer.

For HNO_3, CHEM processes were the only positive contributor during the day. The OH+NO_2 pathway is the predominant contributor (60–83%) among all chemical pathways, while the HET N_2O_5 pathway is also important (10–36%) in the YRD region. The TNO_3 production is dominated by the OH+NO_2 pathway during the day (98%) in summer, while the HET N_2O_5 pathway dominates during the night (61%) in winter. The TNO_3 production rates from the local and transport contributions were further elucidated. The OH+NO_2 pathway from the local contribution strongly dominates the TNO_3 production during the day (89–98%). At night, the HET N_2O_5 pathway mainly dominate by indirect transport (via reaction with transported O_3 at night).

Code and data availability

Hourly concentrations of O_3, $PM_{2.5}$, NO_2, SO_2, and CO used in this study are freely available through the website of http://106.37.208.233:20035/ (last accessed on April 30, 2022). Observation data of meteorological parameters used in this study are available from http://data.cma.cn/en (last accessed on November 30, 2021). The CMAQ outputs are currently available upon request, all python codes used to create any of the figures are available upon request.

Author contributions

JS, MQ and JH designed research. JS, MQ, XX, WF, YQ, LS, and LL contributed to model development, simulations, and data processing. JL, IS, LJ, LH, XY contributed to result discussion. JS prepared the manuscript and all coauthors helped improve the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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Tables and Figures

Table 1. Model performance for meteorological parameters for January, April, July, October and the annual average of 2017 in the entire YRD region. The values that do not meet the criteria are denoted in bold.

Parameters	Statistic(benchmarks)	January	April	July	October	Annual
T2(℃)	MB (≤ ±0.5)	**1.56**	**1.04**	**0.67**	**1.98**	**1.31**
	RMSE	1.99	1.76	1.57	2.24	1.89
	IOA (≥ 0.8)	0.89	0.93	0.85	0.89	0.89
	R	0.94	0.93	0.85	0.95	0.92
RH(%)	MB	-6.96	-10.70	-9.06	-5.98	-8.17
	RMSE	9.73	13.14	10.91	8.02	10.45
	IOA	0.88	0.83	0.72	0.82	0.81
	R	0.90	0.91	0.88	0.87	0.89
WD(°)	MB (≤ ±10)	**-12.78**	-0.92	**12.26**	**-24.42**	-6.46
	RMSE	37.68	36.04	26.61	55.85	39.05
	IOA	0.88	0.89	0.88	0.76	0.85
	R	0.85	0.82	0.85	0.70	0.81
WS(m/s)	MB (≤ ±0.5)	**0.61**	**0.76**	**1.03**	**0.69**	**0.77**
	RMSE (≤ 2.0)	0.82	1.06	1.31	0.96	1.04
	IOA (≥ 0.6)	0.84	0.71	0.65	0.82	0.76
	R	0.89	0.75	0.75	0.88	0.82

Notes: The following equations of MB, RMSE and IOA are defined in Table S4. The benchmarks are suggested by Emery and Tai (2001).

Table 2. Model performance of major pollutants for the full year of 2017 in five representative YRD cities [a].

[b] Pollutants	Shanghai				Nanjing				Hefei				Hangzhou				Changzhou			
	[c] NMB	NME	MB	R	NMB	NME	MB	R	NMB	NME	MB	R	NMB	NME	MB	R	NMB	NME	MB	R
MDA8 O_3	-0.01	0.20	-1.07	0.88	**0.17**	**0.28**	18.59	0.76	**0.17**	0.24	17.23	0.81	**0.25**	**0.31**	26.60	0.80	**0.19**	**0.26**	19.85	0.84
NO_2	-0.05	0.23	-1.89	0.71	-0.07	0.26	-3.20	0.50	-0.11	0.26	-5.21	0.67	-0.25	0.34	-10.37	0.51	-0.07	0.24	-2.67	0.56
SO_2	-0.38	0.43	-4.61	0.66	0.12	0.45	1.83	0.32	0.01	0.36	0.18	0.75	-0.28	0.40	-3.15	0.46	0.09	0.34	1.54	0.48
CO	-0.38	0.40	-0.29	0.67	-0.17	0.33	-0.17	0.45	-0.22	0.26	-0.19	0.76	-0.30	0.34	-0.25	0.55	0.06	0.25	0.05	0.64
$PM_{2.5}$	-0.08	0.30	-2.80	0.73	0.28	0.44	10.29	0.75	**0.41**	**0.51**	21.42	0.76	0.05	0.31	1.88	0.69	0.25	0.37	10.59	0.78
NO_3^-	-0.49	0.63	-3.25	0.70					0.07	0.65	0.32	0.59	0.11	0.79	0.64	0.43	-0.36	0.58	-3.34	0.56

Notes: [a] The year of 2017 includes the four typical months (January, April, July, and October). [b] MDA8 O_3, NO_2, SO_2 and $PM_{2.5}$ units (μg/m^3), CO units (mg/m^3).

[c] The equations of NMB, NME, MB and R are found in Table S4. The values that do not meet the criteria are highlighted in bold.

The recommended benchmarks for MDA8 O_3, 24-h $PM_{2.5}$ and NO_3^- are suggested by Emery et al. (2017) and Huang et al. (2021).

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Table 3. ~~Model performance for~~Seasonal TNO_3 production rates (ppb/h) and ~~daily~~ contributions ~~in percentage~~(%) of the major production pathways ~~(%) for the four seasons of 2017~~ in five representative ~~YRD~~ cities.

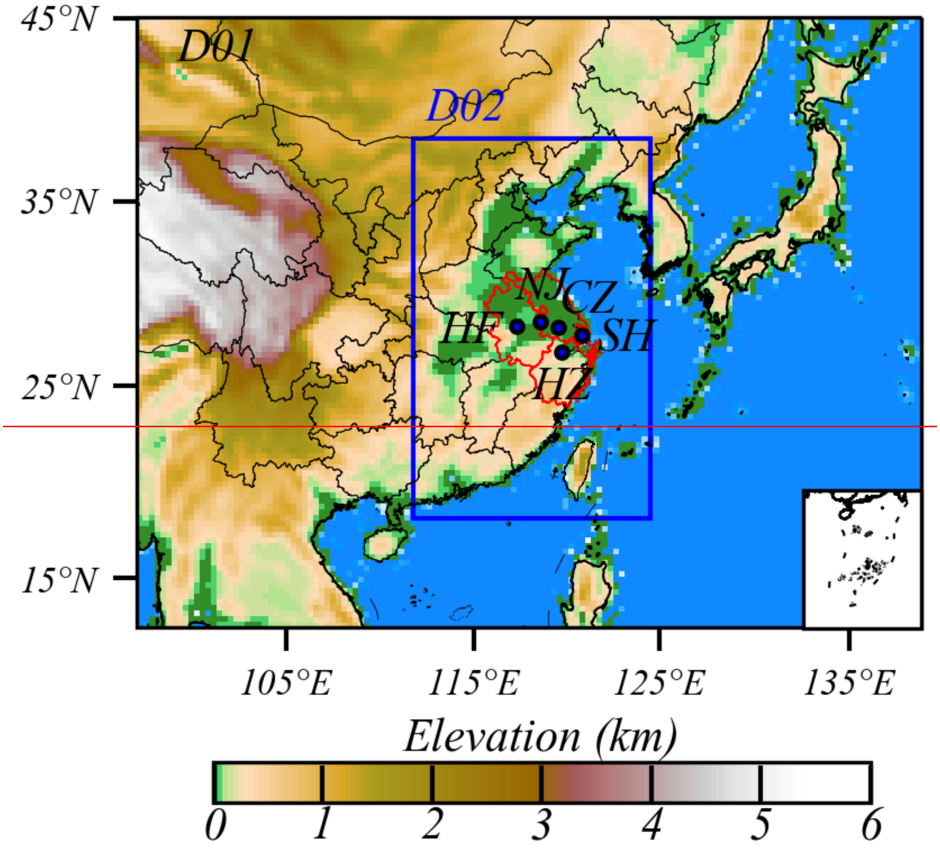
Selected cities	Seasons	TNO_3	OH NO_2	HET N_2O_5	OH NO_2 (%)	HET N_2O_5 (%)	Others (%)
Shanghai	Winter	0.31 ±0.13	0.21 ±0.18	0.09 ±0.06	69.3%	28.4%	2.2%
	Spring	0.65 ±0.35	0.52 ±0.43	0.10 ±0.09	81.8%	15.3%	2.9%
	Summer	1.09 ±0.68	0.90 ±0.80	0.13 ±0.15	82.9%	12.2%	4.9%
	Autumn	0.28 ±0.22	0.24 ±0.24	0.03 ±0.03	86.9%	11.1%	2.0%
Nanjing	Winter	0.38 ±0.13	0.23 ±0.20	0.14 ±0.11	59.2%	36.1%	4.7%
	Spring	0.65 ±0.29	0.48 ±0.40	0.14 ±0.12	73.1%	21.4%	5.4%
	Summer	0.83 ±0.41	0.62 ±0.55	0.15 ±0.17	74.7%	17.9%	7.4%
	Autumn	0.50 ±0.25	0.35 ±0.32	0.13 ±0.11	69.7%	25.4%	4.9%
Hefei	Winter	0.38 ±0.13	0.26 ±0.18	0.10 ±0.07	66.9%	27.1%	6.0%
	Spring	0.63 ±0.24	0.49 ±0.30	0.10 ±0.09	78.5%	16.5%	5.0%
	Summer	0.66 ±0.26	0.54 ±0.30	0.07 ±0.08	81.7%	10.4%	7.9%
	Autumn	0.48 ±0.18	0.35 ±0.24	0.11 ±0.08	72.5%	21.8%	5.7%
Changzhou	Winter	0.41 ±0.15	0.29 ±0.20	0.11 ±0.08	68.9%	26.8%	4.3%
	Spring	0.64 ±0.25	0.48 ±0.31	0.13 ±0.12	74.9%	20.9%	4.2%
	Summer	0.70 ±0.27	0.55 ±0.31	0.10 ±0.13	78.7%	14.3%	7.0%
	Autumn	0.46 ±0.19	0.36 ±0.24	0.08 ±0.07	77.6%	18.3%	4.1%
Hangzhou	Winter	0.43 ±0.15	0.26 ±0.21	0.15 ±0.12	59.7%	35.5%	4.8%
	Spring	0.57 ±0.24	0.40 ±0.33	0.13 ±0.12	70.5%	23.3%	6.2%
	Summer	0.47 ±0.23	0.36 ±0.29	0.05 ±0.05	76.4%	10.7%	12.9%
	Autumn	0.46 ±0.26	0.34 ±0.32	0.10 ±0.09	73.8%	21.3%	4.9%

Table 4. Comparison of contributions of major nitrate formation pathways in China and others regions [a].

References	Methods [b]	Study seasons	Year	Study regions	NO_3^- formation pathways [c]	Time metric	Contribution (%)
(Li et al., 2021b)	WRF-Chem	Warm (Aug –Sep)	2016	NCP, YRD	$OH+NO_2$ (layer 1)	season-mean	60-92%
		Cold (Nov-Dec)			HET N_2O_5 (layer 1)		8-40%
(Qu et al., 2021)	WRF-CMAQ PA	Transition season	2015	PRD	$OH+NO_2$ (layers 1-4)	day-mean	92-96%
		(Oct-Dec)			HET N_2O_5 (layers 1-4)	night- mean	64-72%
(Chuang et al., 2022)	WRF-CMAQ PA	Transition season	2017	Taiwan	$OH+NO_2$	day-mean	> 90%
		(Mar - Apr)			HET N_2O_5	night- mean	30-90%
(Wu et al., 2021)	WRF-Chem; Nitrogen Isotopes	Cold (Dec-Jan)	2017	Xi'an	HET N_2O_5 (surface)	season-mean	13-35 %
(Chan et al., 2021)	GEOS-Chem; Isotope tracing	Cold	2014-15	NCP	$OH+NO_2$&HET N_2O_5 (surface)	season-mean	34 % & 45 %
(Fu et al., 2020)	WRF-CMAQ PA	Cold (Dec)	2017	NCP	$OH+NO_2$ (HET N_2O_5) 10 layers	season-mean	43% (44%)
(Liu et al., 2020a)	WRF-Chem	Cold (Dec)	2016	NCP	HET N_2O_5 (surface)	haze-mean	52 %
					HET N_2O_5 (PBL)	night (day)	83% (10%)
(Zhang et al., 2022)	Nitrogen &Oxygen Isotopes	Cold (Jan)	2017-18	Nanjing	$OH+NO_2$ & HET N_2O_5 (surface)	season-peak	48% & 72%
(Zhang et al., 2021)	Nitrogen &Oxygen Isotopes	Cold (Nov-Jan)	2017-18	Nanchang	HET N_2O_5 (surface)	season-mean	60%
(Fan et al., 2021)	Nitrogen &Oxygen Isotopes	Warm and Cold	2016-17	Beijing	$OH+NO_2$&HET N_2O_5 (260 m)	Clean days	20% (80%)
(Luo et al., 2020a)	Nitrogen &Oxygen Isotopes	Spring(Mar-May)	2013	Beijing	$OH+NO_2$ (surface)	Clean days	24-50%
					$OH+NO_2$ (surface)	Polluted days	11-47%
(Luo et al., 2020b)	Nitrogen &Oxygen Isotopes	Four seasons	2018	Nanchang	$OH+NO_2$ (HET N_2O_5)	season-mean	12-59% (67-89%)
(Fan et al., 2020)	Nitrogen &Oxygen Isotopes	Cold (Nov-Dec)	2018	Beijing	HET N_2O_5	haze period	64%
(He et al., 2020)	Nitrogen &Oxygen Isotopes	Warm and	2016	Shanghai	$OH+NO_2$ (warm)	season-mean	84-92%
		Cold season			$OH+NO_2$ (cold)		48-74%
(Wang et al., 2019)	Nitrogen &Oxygen Isotopes	Warm and	2014	Beijing	$OH+NO_2$	annual-mean	32 ±10%
		Cold season			HET N_2O_5	annual-mean	68 ±23%
(He et al., 2018)	Nitrogen isotopic	Cold (Oct-Jan)	2014	Beijing	HET N_2O_5	night- haze	56-97 %
(Chen et al., 2020)	Field determination; Box model	Cold (Nov-Dec)	2016-17	Beijing	$OH+NO_2$& HET N_2O_5 (240 m)	haze period	74-76% & 34%

(Sun et al., 2018)	Field determination; Box model	Cold (Nov-Dec)	2015	Nanjing	HET N_2O_5 (surface)	haze period	80%
(Zang et al., 2022)	Field observations; Box model	Cold (Dec-Feb)	2018-19	Shanghai (urban & suburban areas)	OH+NO_2&HET N_2O_5 (surface)	haze period	69% & 29%
					OH+NO_2&HET N_2O_5 (surface)	haze period	63% & 35%
(Womack et al., 2019)	Box model	Cold (Dec)	2016-17	Salt Lake Valley	HET N_2O_5 (RL)	season-mean	43%
(Vrekoussis et al., 2004)	Field determination, Box model	Summer(Jul-Aug)	2001	South-East Europe	HET N_2O_5 (surface)	season-mean	21%
(Kim et al., 2014)	WRF-CMAQ PA	Cold (Dec)	2009	The Great Lakes	OH+NO_2&HET N_2O_5 (surface)	season-mean	28% & 57%
(Shah et al., 2018)	GEOS-Chem	Cold (Feb-Mar)	2015	Eastern US	OH+NO_2&HET N_2O_5 (surface)	season-mean	36% & 62%
(Alexander et al., 2020)	GEOS-Chem; Oxygen Isotopes	Four seasons	2000-15	Global	OH+NO_2 (below 1 km)	annual-mean	41-42%
					HET N_2O_5 (below 1 km)		28-41%

Notes: [a] The ~~above studies~~24 peer-reviewed publications are conducted in the major regions and megalopolises of China (the North China Plain (NCP), Yangtze River Delta (YRD), Pearl River Delta (PRD)), the United States, and the Global region. The comparison serves to quantify the relative contribution of two main nitrate formation pathways in different seasons. [b] Methods include the 3-D CTMs, nitrogen and oxygen isotopes analysis, field determination, and box model. [c] Surface represents the surface layer.


D01
D02
NJ
CZ
HF
SH
HZ
45°N
35°N
25°N
15°N
105°E
115°E
125°E
135°E
Elevation (km)
0
1
2
3
4
5
6

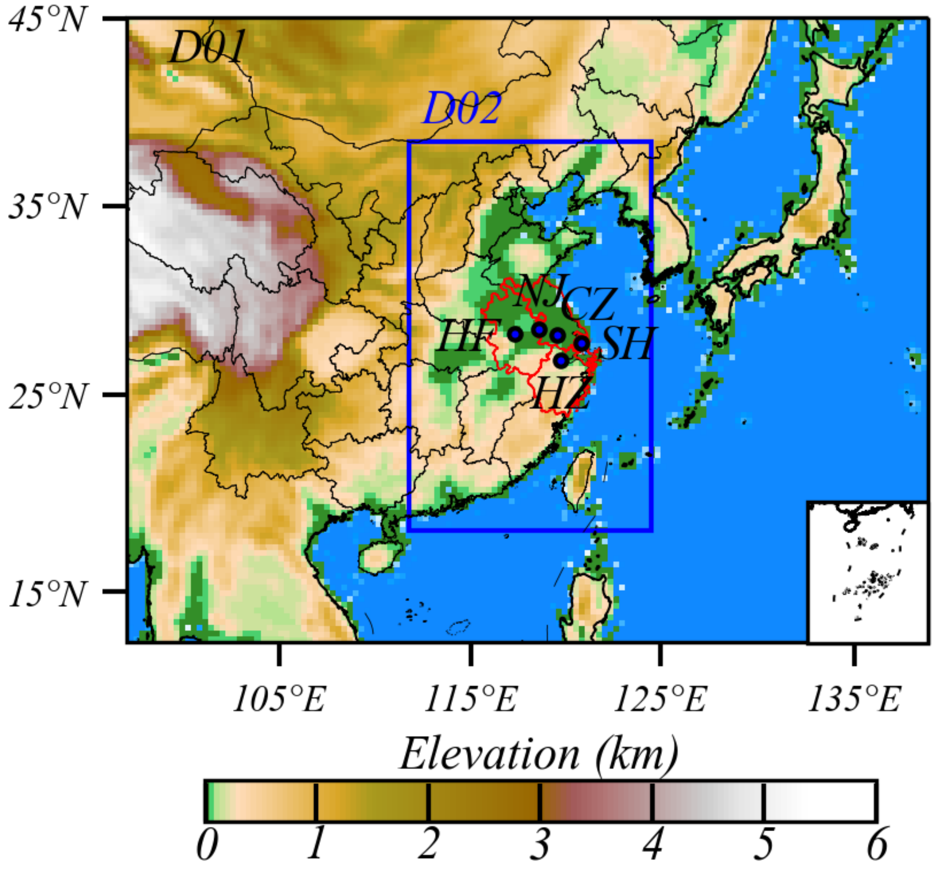

D01
D02
NJ
CZ
HF
SH
HZ
45°N
35°N
25°N
15°N
105°E
115°E
125°E
135°E
Elevation (km)
0
1
2
3
4
5
6

Fig 1. Entire YRD region as the target region (marked as red) in two nested simulation domains (36 and 12 km resolutions), and location of five representative YRD cities used in modeling evaluations in the d02 modeling domain.

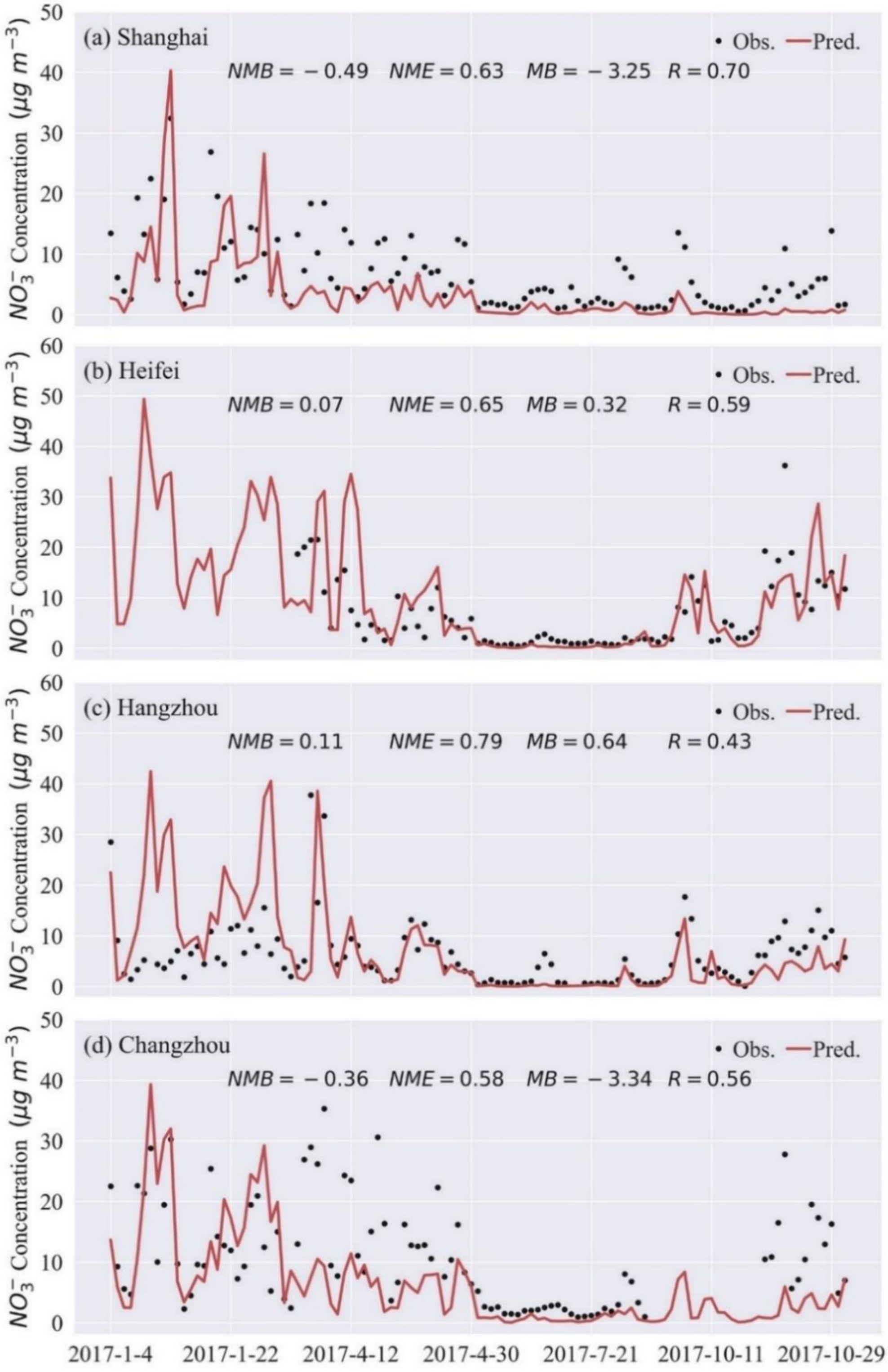
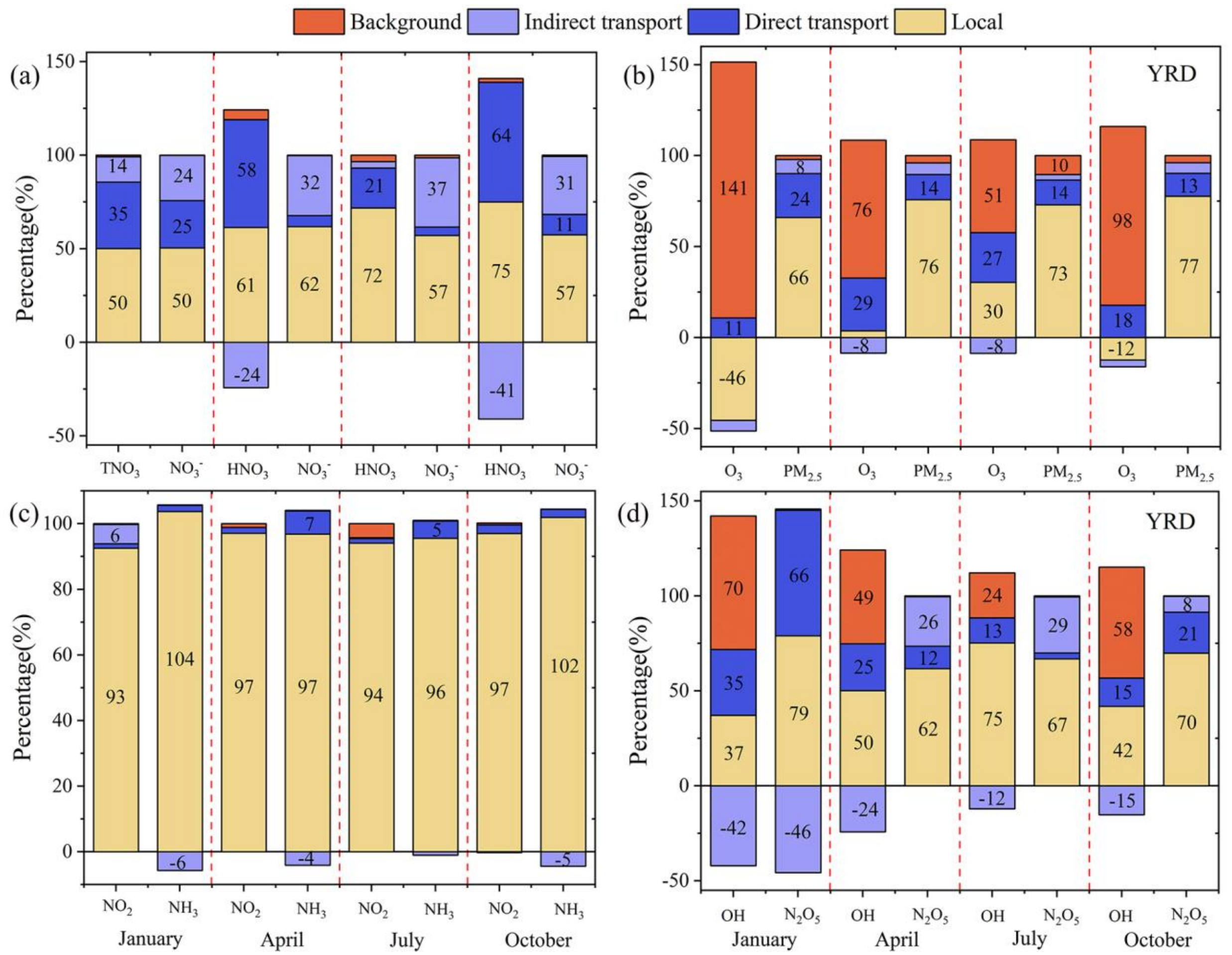


Fig 2. Time series of predicted (red) and observed (black) daily NO_3^- concentrations in four atmospheric environment supersites (a–d) in January, April, July, and October 2017.


Background
Indirect transport
Direct transport
Local
(a)
Percentage(%)
150
100
50
0
-50
TNO$_3$
NO$_3^-$
HNO$_3$
NO$_3^-$
HNO$_3$
NO$_3^-$
HNO$_3$
NO$_3^-$
14
35
50
24
25
50
58
61
-24
32
62
21
72
37
57
64
75
-41
31
11
57
(b)
YRD
O$_3$
PM$_{2.5}$
O$_3$
PM$_{2.5}$
O$_3$
PM$_{2.5}$
O$_3$
PM$_{2.5}$
141
11
-46
8
24
66
76
29
-8
14
76
51
27
30
-8
10
14
73
98
18
-12
13
77
(c)
100
80
60
40
20
0
NO$_2$
NH$_3$
NO$_2$
NH$_3$
NO$_2$
NH$_3$
NO$_2$
NH$_3$
6
93
104
-6
97
7
97
-4
94
5
96
97
102
-5
January
April
July
October
(d)
YRD
OH
N$_2$O$_5$
OH
N$_2$O$_5$
OH
N$_2$O$_5$
OH
N$_2$O$_5$
70
35
37
-42
66
79
-46
49
25
50
-24
26
12
62
24
13
75
-12
29
67
58
15
42
-15
8
21
70

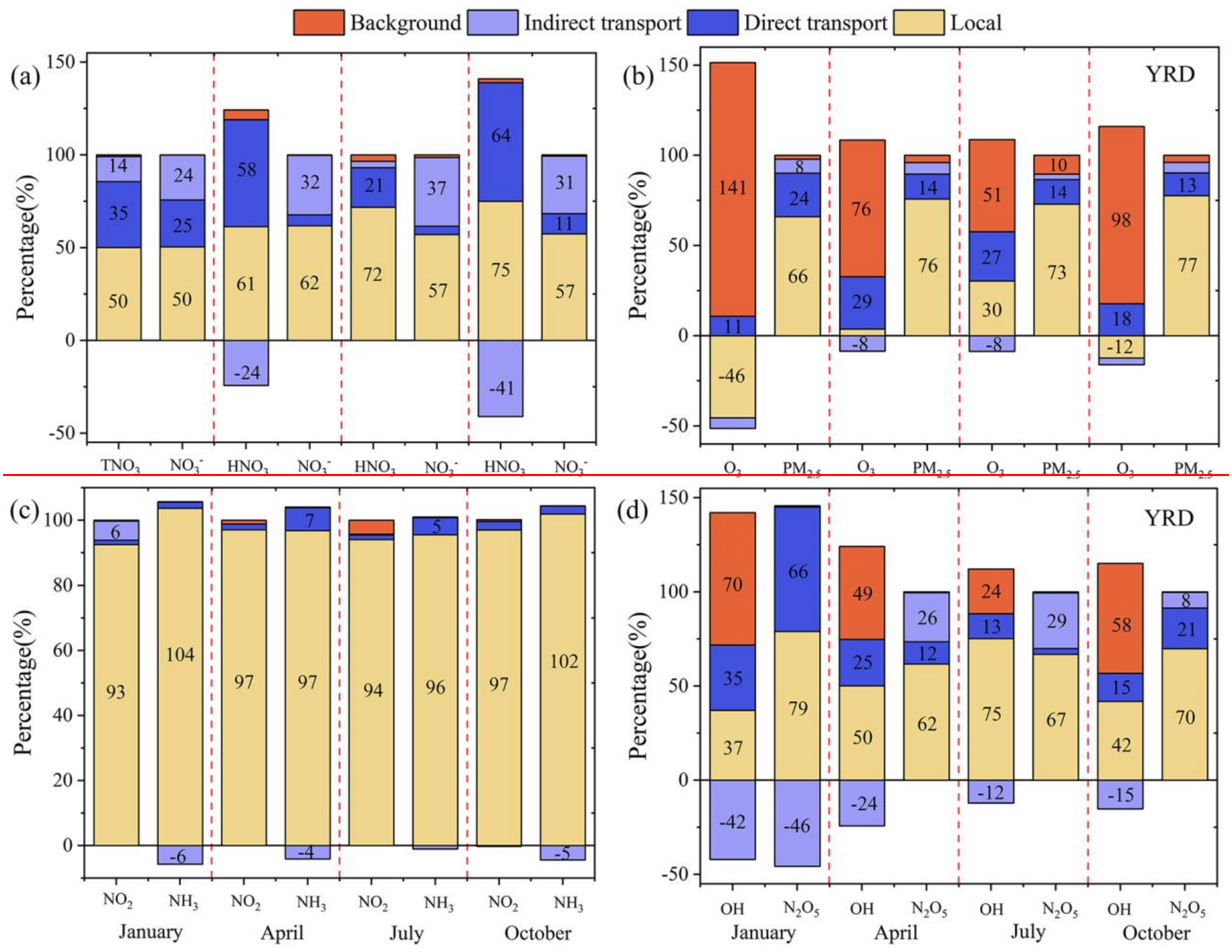
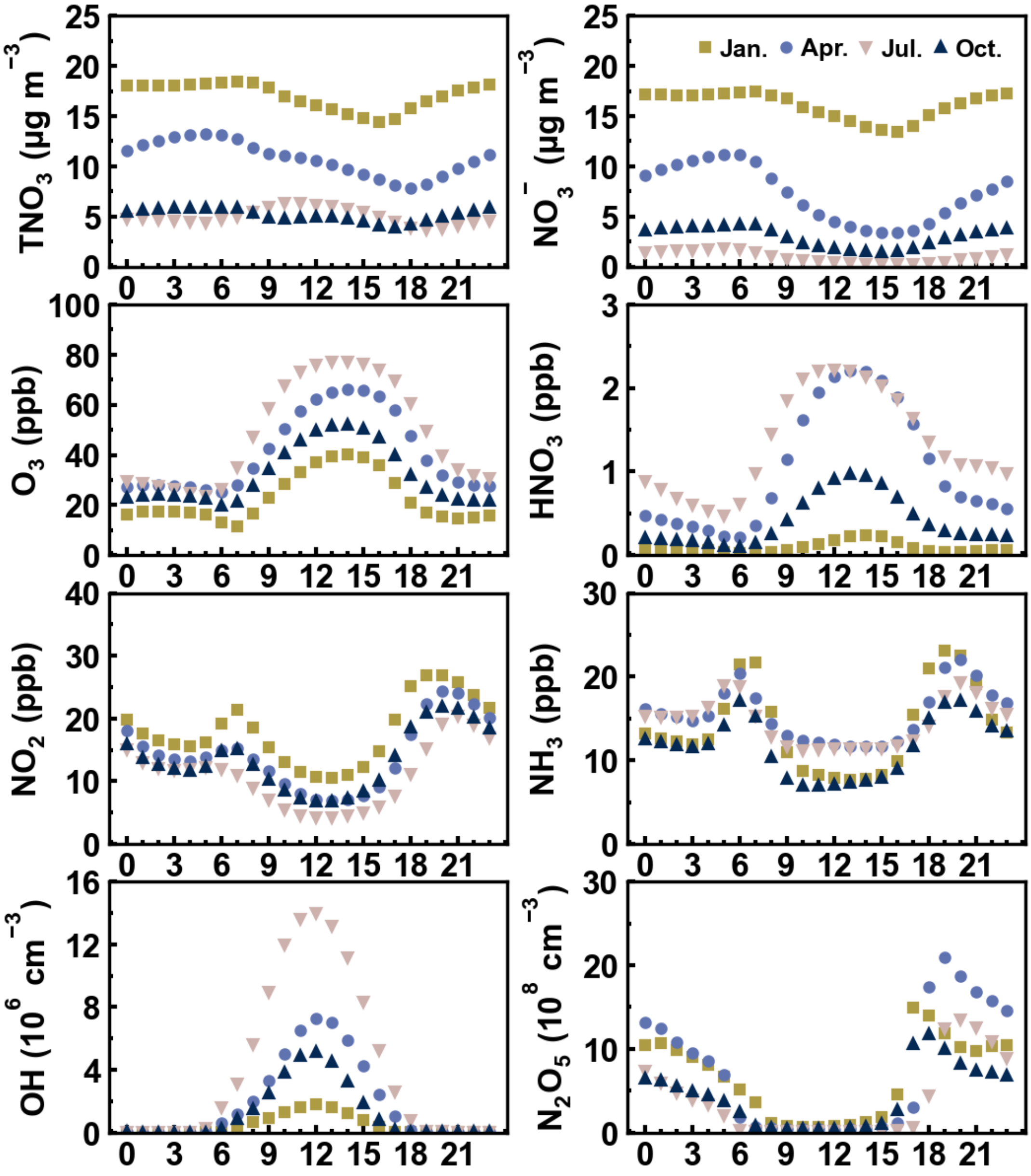


Fig 3. (a–d) Contributions of Background, Local, Indirect, and Direct transport to nitrate-related species in four months of 2017 for the entire YRD region.

Notes: Nitrate-related species represent NO_3^-, HNO_3, $PM_{2.5}$, O_3, NO_2, NH_3, OH, and N_2O_5. The contributions of HNO_3 in January 2017 are shown in Fig. S6.


TNO$_3$ (μg m^{-3})
NO$_3^-$ (μg m^{-3})
Jan.
Apr.
Jul.
Oct.
O$_3$ (ppb)
HNO$_3$ (ppb)
NO$_2$ (ppb)
NH$_3$ (ppb)
OH (10^6 cm^{-3})
N$_2$O$_5$ (10^8 cm^{-3})
0
3
6
9
12
15
18
21
25
20
15
10
5
0
100
80
60
40
20
3
2
1
40
30
30
16
12
8
4

881

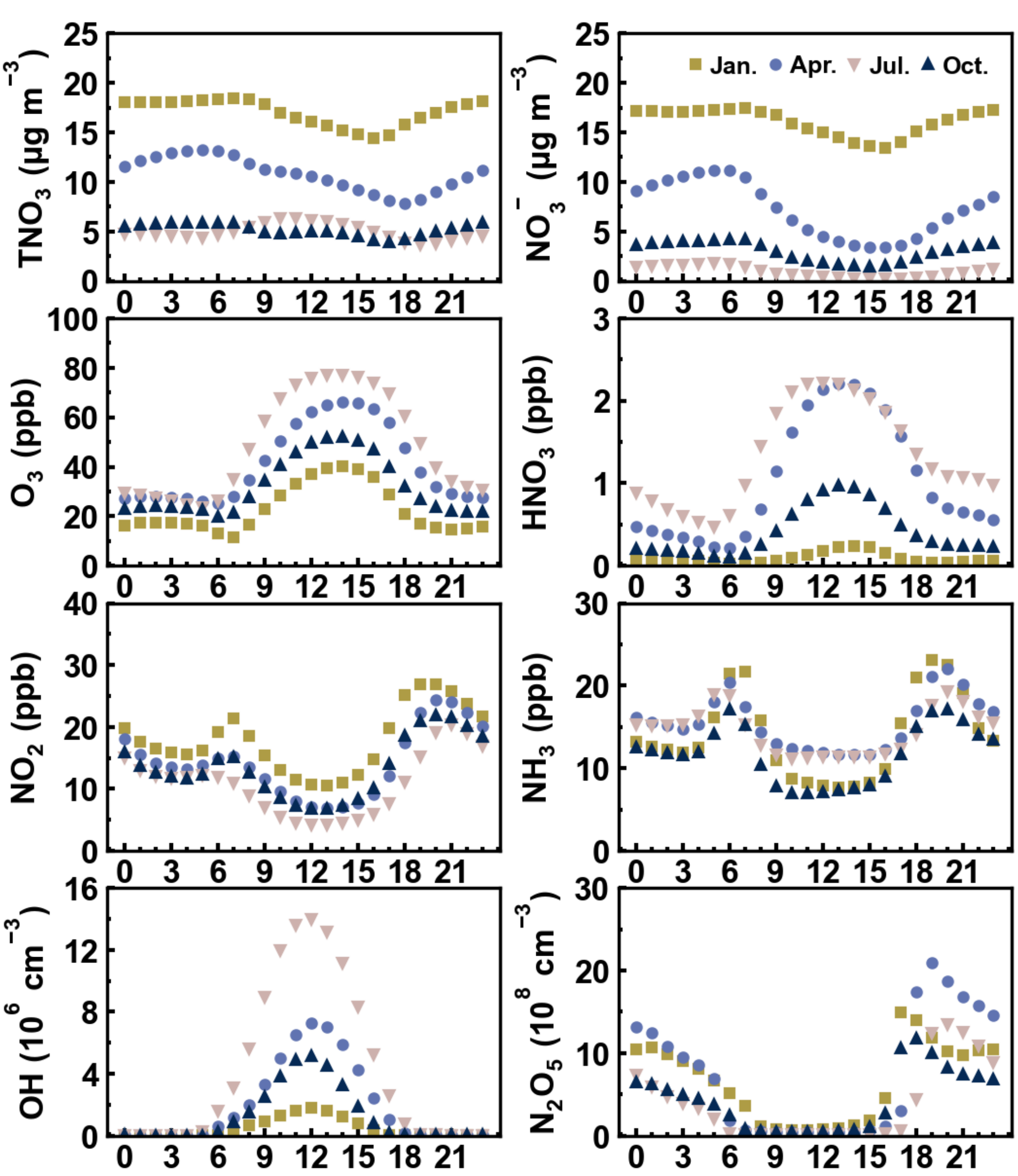
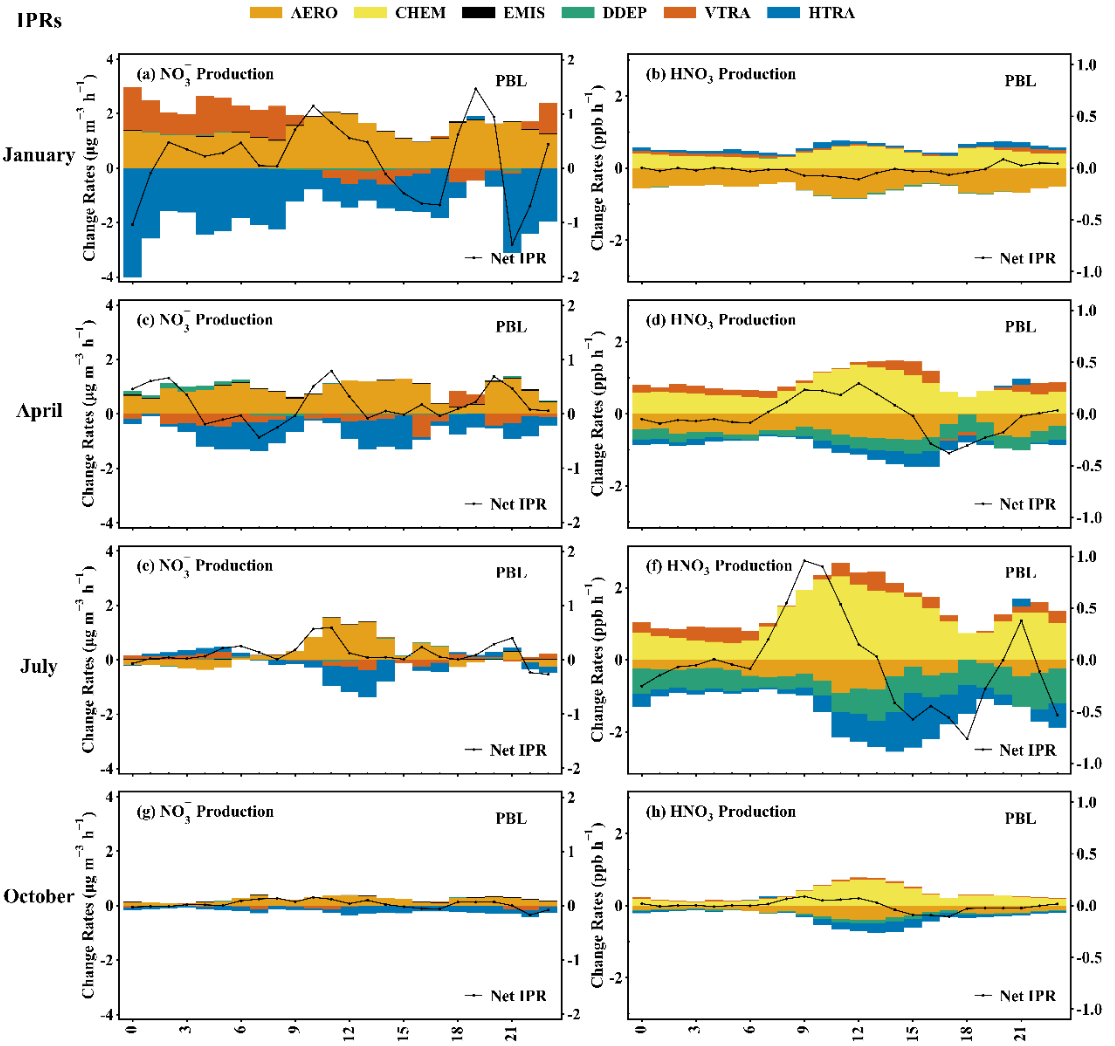


Fig 4. Monthly diurnal variations of three nitrate-phases (NO_3^-, HNO_3, and TNO_3), the major nitrate-precursors (~~O_3,~~ NO_2, NH_3, and ~~NH_3~~N_2O_5) and ~~major~~ atmospheric oxidants (~~OH~~O_3 and ~~N_2O_5~~OH) for the entire YRD region under the base scenario. The X axis marks each hour of the day (Beijing time).


IPRs
AERO
CHEM
EMIS
DDEP
VTRA
HTRA
January
April
July
October
(a) NO$_3^-$ Production
(b) HNO$_3$ Production
(c) NO$_3^-$ Production
(d) HNO$_3$ Production
(e) NO$_3^-$ Production
(f) HNO$_3$ Production
(g) NO$_3^-$ Production
(h) HNO$_3$ Production
PBL
Net IPR
Change Rates (μg m^{-3} h^{-1})
Change Rates (ppb h^{-1})
4
2
0
-2
-4
1.0
0.5
0.0
-0.5
-1.0
0
3
6
9
12
15
18
21

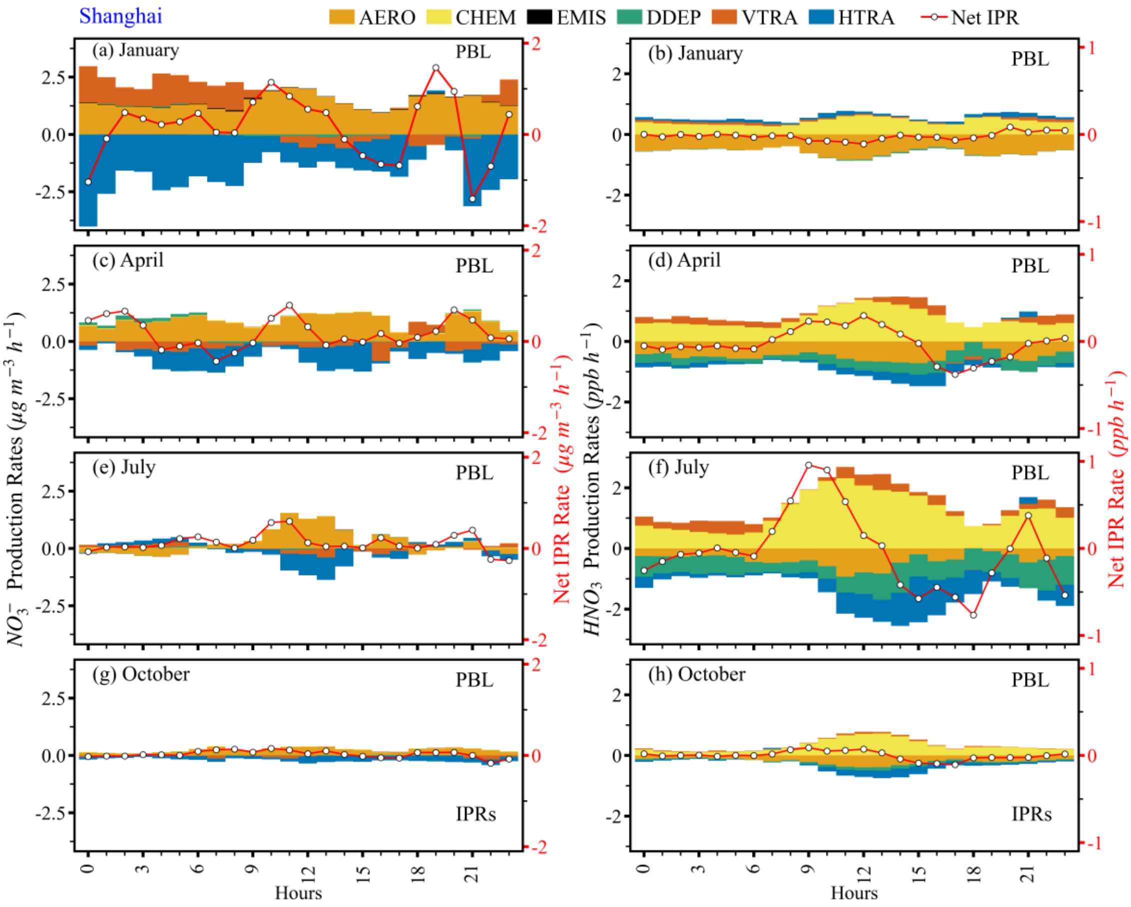
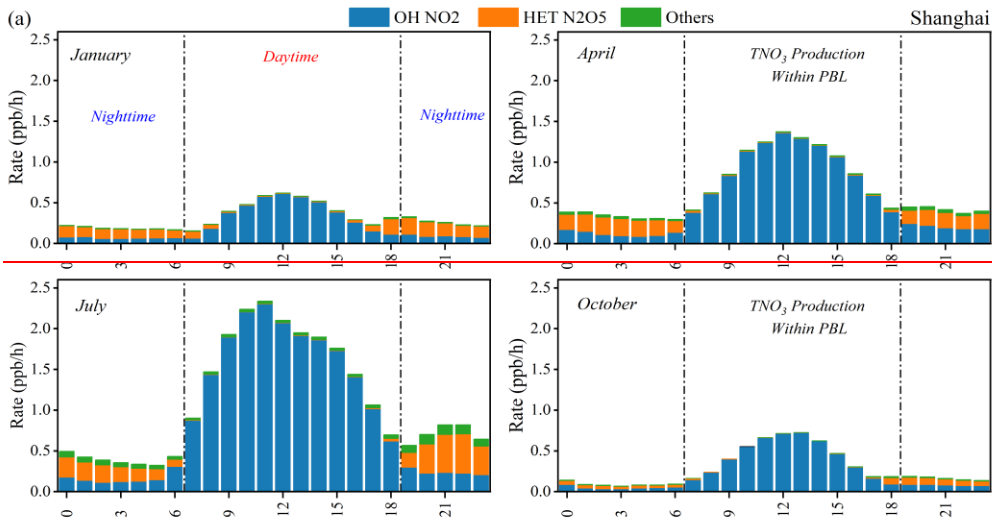
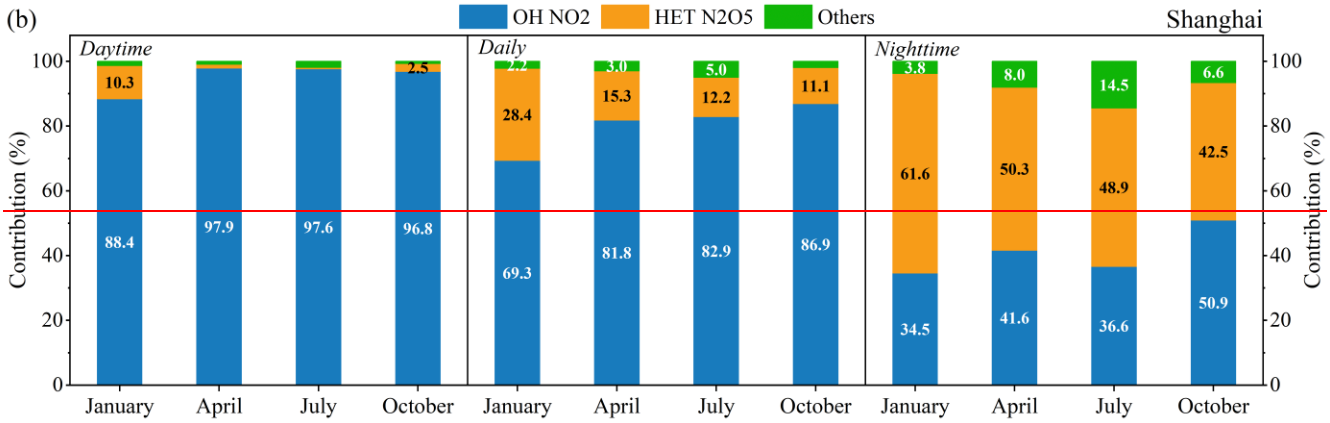
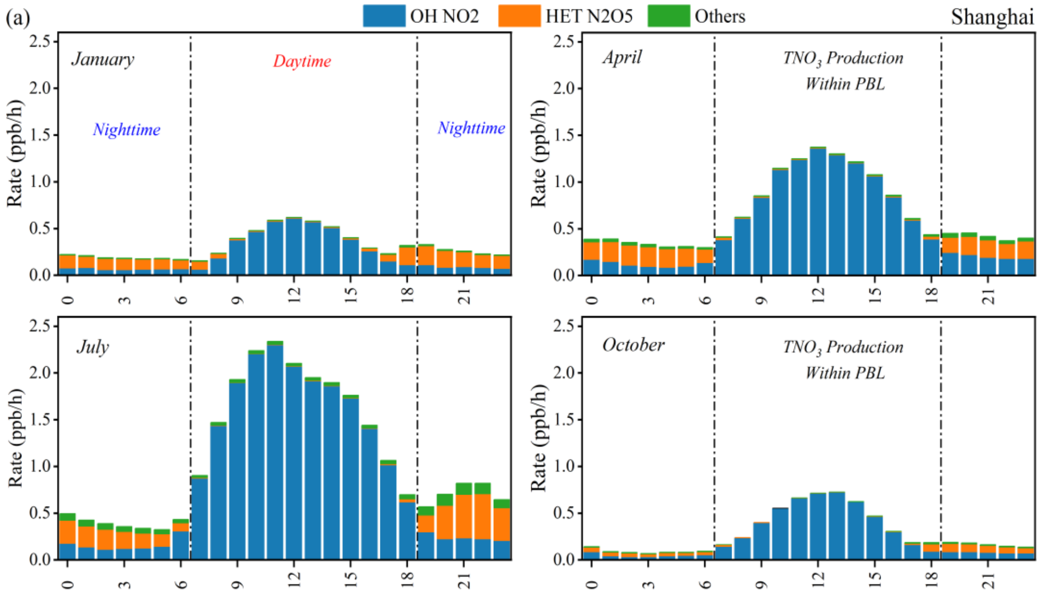


Fig 5. Diel variations in physical and chemical processes rates of NO_3^- and HNO_3 production (a–h) within the PBL in Shanghai. ~~Black~~Red line represents the net IPR value for each hour of the day; its value scale is on the right Y axis.


(a)
OH NO2
HET N2O5
Others
Shanghai
January
Daytime
Nighttime
Nighttime
April
TNO_3 Production Within PBL
July
October
TNO_3 Production Within PBL
Rate (ppb/h)
0.0
0.5
1.0
1.5
2.0
2.5
0
3
6
9
12
15
18
21


(b)
OH NO2
HET N2O5
Others
Shanghai
Daytime
Daily
Nighttime
Contribution (%)
0
20
40
60
80
100
88.4
10.3
97.9
97.6
96.8
2.5
69.3
28.4
2.2
81.8
15.3
3.0
82.9
12.2
5.0
86.9
11.1
34.5
61.6
3.8
41.6
50.3
8.0
36.6
48.9
14.5
50.9
42.5
6.6
January
April
July
October
January
April
July
October
January
April
July
October


(a)
OH NO2
HET N2O5
Others
Shanghai
January
Daytime
Nighttime
Nighttime
April
TNO_3 Production Within PBL
July
October
TNO_3 Production Within PBL
Rate (ppb/h)
0.0
0.5
1.0
1.5
2.0
2.5
0
3
6
9
12
15
18
21

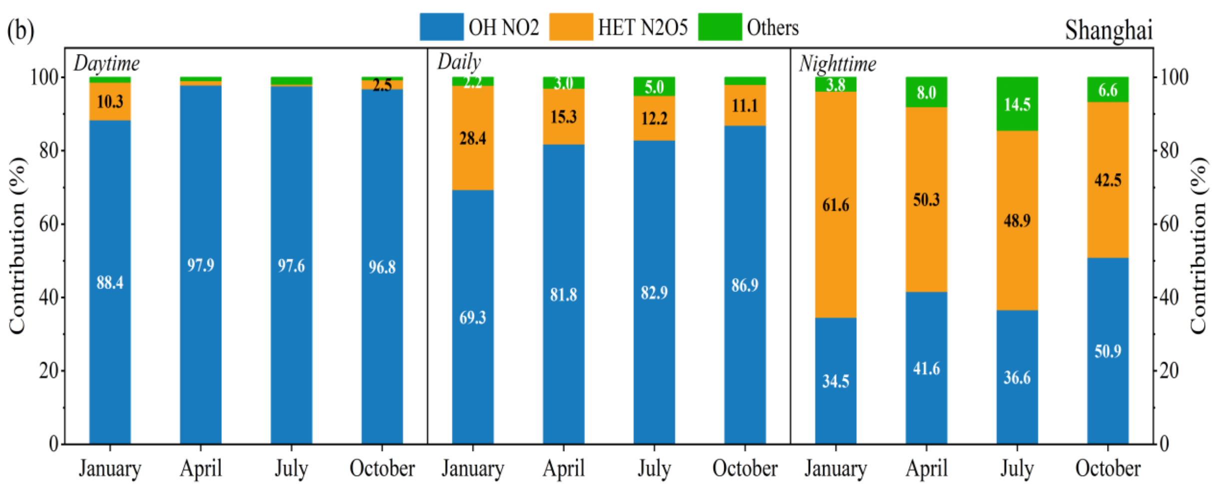
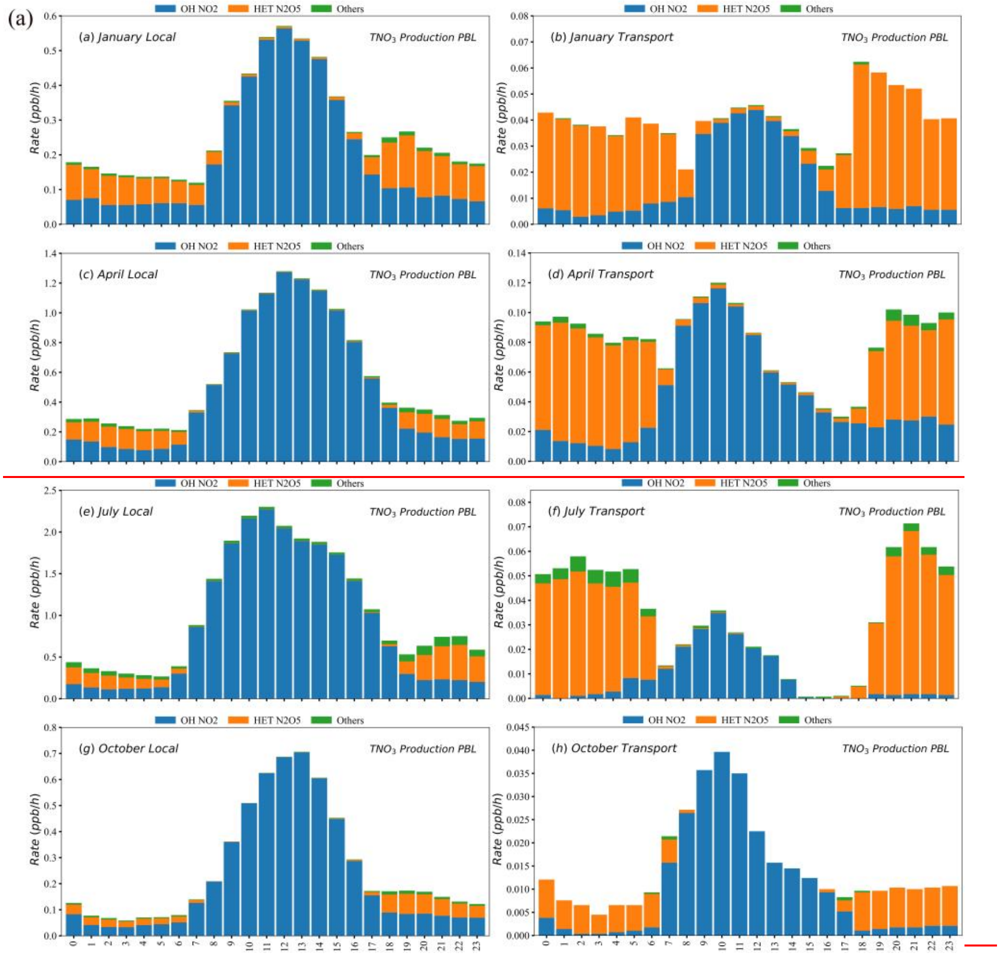
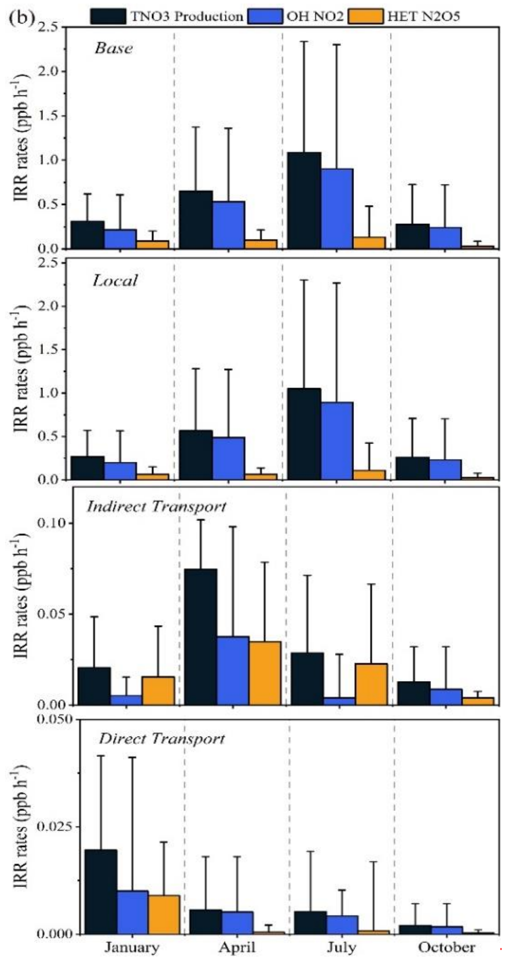


Fig 6. (a) Mean diurnal variations of TNO_3 production rates in different pathways in 2017 in Shanghai. (b) Average potential contribution of OH + NO_2, HET N_2O_5 and Others pathways to TNO_3 chemical production in Shanghai within the PBL under base case simulation.

Notes: Daytime (7:00–18:00), Nighttime (19:00–6:00). OH + NO_2 and HET N_2O_5 pathways are noted as "OH NO2" and "HET N2O5" in Figs.6 and 7.




(b)
TNO3 Production
OH NO2
HET N2O5
Base
Local
Indirect Transport
Direct Transport
IRR rates (ppb h^{-1})
0.0
0.5
1.0
1.5
2.0
2.5
0.00
0.05
0.10
0.000
0.025
0.050
January
April
July
October

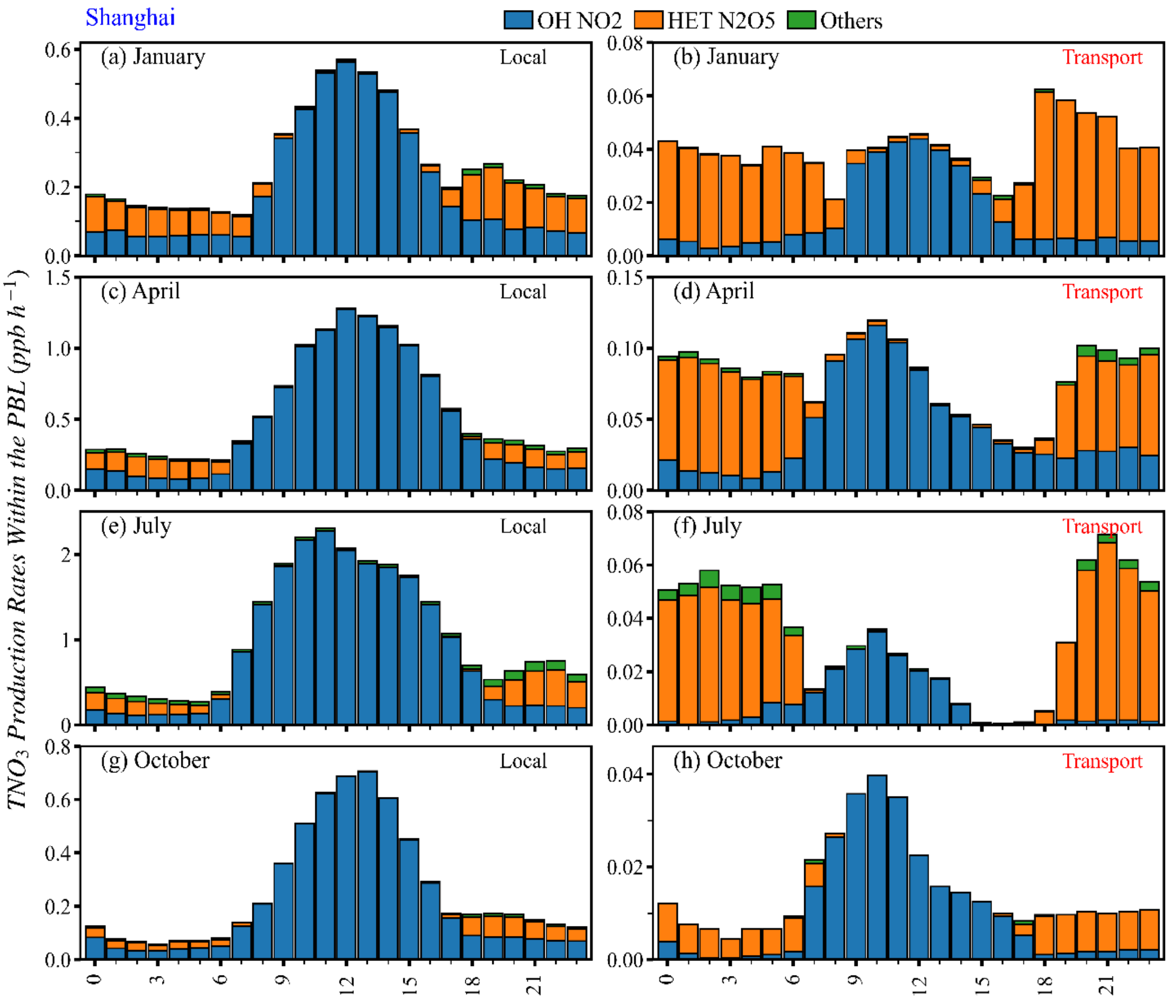


Fig 7.~~ (a)~~ Mean diurnal variations of TNO$_3$ production rates in major pathways from the local and transport (sum of indirect and direct transport) contributions.~~ (b) Total IRRs~~

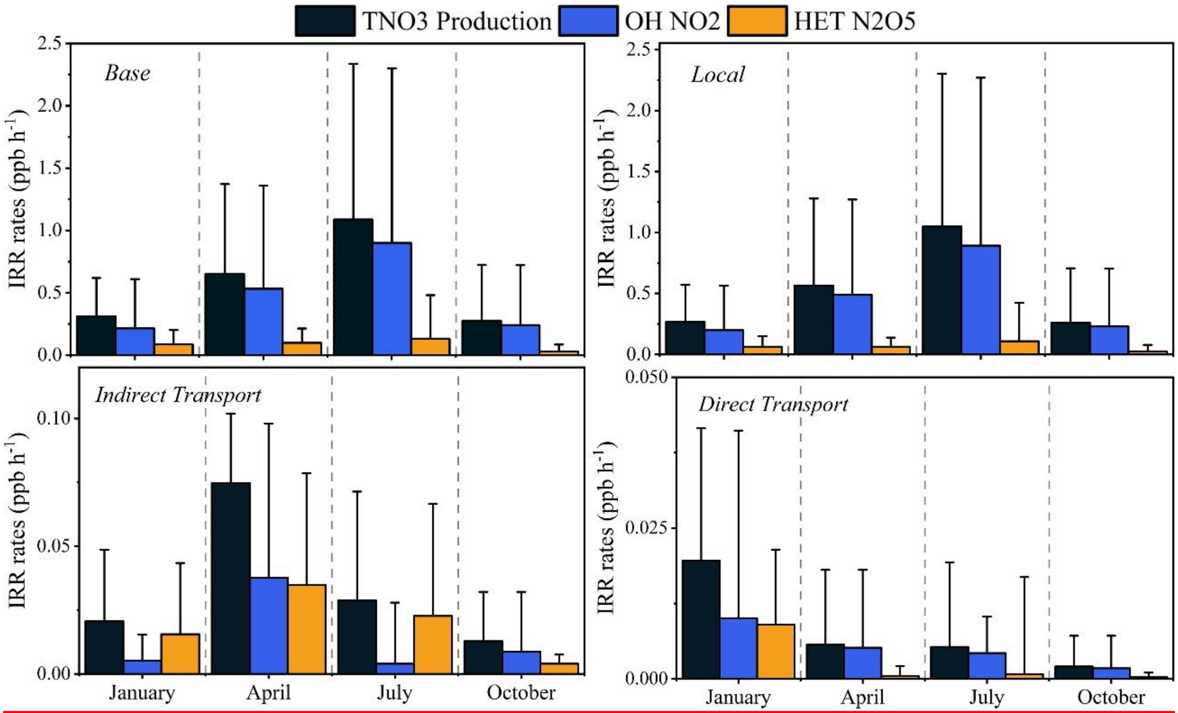


Fig 8. The seasonal rates of TNO$_3^-$ production ~~rates~~and the major pathways in the base case, and from the local and transport contributions within the PBL. The error bar indicates one standard deviation.