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 YRD is generally greater than two in different seasons across most areas in 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 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$_2$O$_5$ heterogeneous (HET N$_2$O$_5$) pathway contributes to 10–36% in YRD. HET N$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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 µg 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 µg 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 µg m$^{-3}$ during haze pollution events in the spring of 2016.

Owing to the stringent emission control strategies implemented in China since 2013, PM$_{2.5}$, sulfur dioxide (SO$_2$) and nitrogen oxides (NO$_x$ = nitric oxide (NO) + nitrogen dioxide (NO$_2$)) emissions have decreased substantially, which led to significant decreases in primary PM$_{2.5}$ and sulfate (SO$_4^{2-}$) 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 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). 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 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 (HET N$_2$O$_5$) 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 chemical transport models (CTMs), field observations, the box model, or oxygen and nitrogen isotope techniques. 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ pathway from the upper PBL contributed to daytime surface NO$_3^-$ concentrations 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$_2$O$_5$) (Chan et al., 2021; Womack et al., 2019). 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) 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 O₃ at night. Du et al. (2020) also revealed that regional transport contributed about 56% to NO₃⁻ in Beijing in winter 2017, mainly produced via indirect transport.

The NO₃⁻ formation pathways and controlling factors can be very different in different seasons even in the same studying region. Most previous studies on NO₃⁻ focused on one or a few short period of pollution episodes, but lack of seasonal analysis. This study aims to obtain a comprehensive understanding of the seasonal variations in the NO₃⁻ formation mechanisms, as well as to determine key precursors, dominant processes and chemical pathways in YRD. The Community Multiscale Air Quality (CMAQ) model was employed to investigate the contributions of various physical and chemical processes to NO₃⁻ and HNO₃ 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 NO₃⁻ in different seasons, and to provide a scientific basis for designing effective emissions control strategies to mitigate the urgent NO₃⁻ 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 NO₃⁻ and TNO₃ 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 configurations of the WRF model provided in the studies of Hu et al. (2016) and Wang et al. (2021), shown in Table S1.

The anthropogenic emissions of 2017 in the YRD region were released by the Shanghai Academy of Environmental Sciences (SAES) (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., HNO₃ and NO₃⁻), 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 \( C_{\text{base}} \), \( C_{\text{YRD-zero}} \), \( C_{\text{outside-zero}} \), and \( C_{\text{all-zero}} \), representing concentration associated with the base, YRD-zero, outside-zero, and all-zero scenarios, respectively. For NO₃⁻ in YRD, the contributions of local YRD emissions, direct transport (NO₃⁻ contributed by transported precursors from outside regions), indirect transport (NO₃⁻ contributed by transported and local-emitted precursors), and background were defined as \( F_{\text{Local}} \), \( F_{\text{Direct}} \), \( F_{\text{Indirect}} \), and \( F_{\text{Background}} \), and they were quantified as follows:

\[
F_{\text{Local}} = \frac{(C_{\text{outside-zero}} - C_{\text{all-zero}})}{C_{\text{base}}} \quad (1)
\]

\[
F_{\text{Direct}} = \frac{(C_{\text{YRD-zero}} - C_{\text{all-zero}})}{C_{\text{base}}} \quad (2)
\]

\[
F_{\text{Indirect}} = \frac{[(C_{\text{base}} - C_{\text{outside-zero}}) - (C_{\text{YRD-zero}} - C_{\text{all-zero}})]}{C_{\text{base}}} \quad (3)
\]

\[
F_{\text{Background}} = \frac{C_{\text{all-zero}}}{C_{\text{base}}} \quad (4)
\]

In addition to NO₃⁻, the major gases (i.e., O₃, NH₃, NO₂, and HNO₃), atmospheric oxidants (i.e., OH, and N₂O₅) and particulate pollutants (PM₂·₅, SO₄²⁻, and SOC) 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 NO₃⁻ and HNO₃ 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 TNO₃ chemical reactions pathways (Qu et al., 2021; Fu et al., 2020; Shen et al., 2020). The complex chemical production of TNO₃ 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 TNO₃ production pathways, including the OH+NO₂, HET N₂O₅, 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 NO₃⁻ and HNO₃ formation because it is the largest city in YRD and has the most abundant measurement data.

2.4. Observation data

Hourly concentrations of six routine air pollutants (i.e., O₃, PM₂.₅, NO₂, SO₂, 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 NO₃⁻ 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 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 previous 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 $\leq \pm 0.30$, NME $\leq 0.50$, 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 ($-0.15 < \text{NMB} \leq -0.05$, $-10.37 < \text{MB} \leq -1.89$). When compared to 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 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. 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 $\leq \pm 0.60$, NME $\leq 0.75$, and $R > 0.6$). The performance statistical metrics of predicted NO$_3^-$ in this study are comparable to those of previous studies (Shi et al., 2017; Qu et al., 2021). 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 NH3 emissions (Zheng et al., 2020; Lu et al., 2021b; Zheng et al., 2015; Liu et al., 2019).

### 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 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$_{outside-zero}$ 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$_{YRD-zero}$. 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 year respectively, to become almost twice as high as those between C$_{base}$ and C$_{outside-zero}$. The results suggest that the YRD local anthropogenic emissions contribute more to the seasonal NO$_3^-$ concentrations.

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). The local emissions dominate 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 NOx 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 local emissions
have negative contribution to O₃ in winter (–45.6%) and autumn (–12.3%), and the
indirect transport has negative contribution in spring (–8.5%) and autumn (–8.7%). For
O₃ and OH (Fig. 3b and 3d), indirect transport contributes about –8% and –12% – –42%
in all seasons, respectively. The negative contributions to O₃, N₂O₅, and OH suggest that
the atmospheric oxidants are consumed in YRD, which in turn enhances the chemical
production of NO₃⁻.

3.3. Formation processes of nitrate

Fig. 4 shows the modeled diurnal variations of three nitrate-phases (NO₃⁻, HNO₃,
and TNO₃), the major precursors (i.e., O₃, NO₂, and NH₃), and the major atmospheric
oxidants (OH and N₂O₅) in the four seasons for the entire YRD region in the base
scenario. Except for summer, higher predicted TNO₃ and NO₃⁻ concentrations are
observed in early morning hours (6:00–8:00 am), while lower TNO₃ and NO₃⁻
concentrations are observed around 16:00–18:00 pm. Predicted concentrations of TNO₃,
HNO₃, and O₃ show the same diurnal variations in the summer, and peak around 12:00
pm (the most active photochemical hours). The opposite profiles of TNO₃’s diurnal
variation between summer and non-summer are mainly attributed to the temperature
effect on the gas-to-particle partitioning between NO₃⁻ and HNO₃. As shown in Fig. S3,
NO₃⁻ dominates the TNO₃ concentrations and determines its diurnal variations in non-
summer, while HNO₃ dominates the diurnal variation in summer. A two-peak mode
diurnal variation of NO₂ and NH₃ is identified in the four seasons. High concentrations
of NO₂ and NH₃ 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 N₂O₅ have a one-peak mode diurnal variation in the four seasons. OH peaks
around 12:00 pm, similar to HNO₃, while N₂O₅ peaks around 18:00–20:00 pm.

Fig. S7 shows seasonal variations in NO₃⁻/PM₁.₅, NO₃⁻/TNO₃, nitrogen oxidation
ratios (NOR = [NO₃⁻]/([NO₃⁻] + [NO₂])), and adjusted gas ratio (adjGR = ([NH₃] +
[NO₃⁻])/([HNO₃] + [NO₃⁻])) in YRD. NO₃⁻/PM₁.₅ and NO₃⁻/TNO₃ 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 NO₂ to NO₃⁻. AdjGR values are generally greater than two in the four seasons across most areas in YRD, indicating that YRD is mostly in the NH₃-rich regime. Therefore, NH₃ is not a limiting factor of NO₃⁻ formation in YRD.

Fig. 5 illustrates a two-peak mode diurnal variation of the net IPRs rates of NO₃⁻ 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 NO₃⁻ 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 NO₃⁻ 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, VTRA processes act as the main positive contributor to NO₃⁻ buildup production from 0:00 to 23:00 at layer 1 (surface layer), while AERO processes make the negative contribution to NO₃⁻ within layers 1–8 (from the surface to 800 m). Above layer 10, AERO processes for NO₃⁻ production are positive in the daytime, which is conducive to the accumulation of NO₃⁻ concentrations.

For HNO₃, 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 HNO₃ 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 HNO₃ formation are consistent with the first-peak times of NO₃⁻. 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 HNO₃ 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. CHEM and VTRA processes are the dominant contributors of HNO₃ 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 HNO₃ 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 HNO₃ in summer (−0.64 ± 0.20 ppb h⁻¹). However, in the winter, the peak times of HNO₃ production are opposite with the first-peak of NO₃⁻, but consistent with the second-peak. HTRA make a positive contribution to HNO₃⁻ 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 HNO₃ into particle phase NO₃⁻ in cold seasons.

Table 3 illustrates that within the PBL, in cold seasons (winter and autumn), about 60–78 % of TNO₃ is produced through OH+NO₂, 21–36 % through HET N₂O₅, and 2–5 % through the “Others” pathways in the five representative YRD cities. Meanwhile, 71–83 % of TNO₃ is produced through OH+NO₂, 10–23 % through HET N₂O₅, and 4–13 % through the “Others” pathways (mainly contributed by NO₃⁻+Org and N₂O₅ H₂O) in warm seasons (summer and spring). Table 4 shows the comparison of the contribution of the major TNO₃ production pathways studies in China and other regions using different methods. The results are in agreement with the contribution of NO₃⁻ pathways in previous modeling and observational studies. For example, Li et al. (2021b) modeled that OH+NO₂ and HET N₂O₅ pathways dominate NO₃⁻ 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+NO₂ 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$_2$O$_5$ 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 averaged TNO$_3$ production rates are $0.31 \pm 0.14$, $0.65 \pm 0.37$, $1.09 \pm 0.68$, and $0.28 \pm 0.22$ ppb h$^{-1}$, 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ 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$_2$O$_5$ pathway during the nighttime. Similarly, He et al. (2018) observed that the HET N$_2$O$_5$ 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$_2$O$_5$ 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).

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 $0.27 \pm 0.14$, $0.56 \pm 0.37$, $1.05 \pm 0.69$, and $0.26 \pm 0.21$ ppb h$^{-1}$ in the winter, spring, summer, and autumn, respectively (Table S8). 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 $0.33 \pm 0.17$, $0.83 \pm 0.34$, $1.55 \pm 0.59$, and $0.40 \pm 0.22$ 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 $0.04 \pm 0.01$, $0.08 \pm 0.02$, $0.03 \pm 0.02$, and $0.02 \pm 0.01$ ppb h$^{-1}$ in the winter, spring, summer, and autumn, respectively (Table S9). The HET N$_2$O$_5$ 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 compares the TNO$_3$ production pathways rates between indirect and direct transport contributions. 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 production via the HET N$_2$O$_5$ chemistry pathway at night.

4. Conclusions

This study investigates the contributions of regional transport and major chemical pathways to the of NO$_3^-$ and HNO$_3$ formation in YRD in different seasons using the
WRF-CMAQ model. The modeled results show that local emissions dominate YRD-regional NO$_3^-$ concentrations (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$_2$O$_5$ pathway is also important (10–36%) in YRD. The TNO$_3$ production is dominated by the OH+NO$_2$ pathway during the day (98%) in summer, while the HET N$_2$O$_5$ 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$_2$O$_5$ 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.

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

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.

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Shanghai</th>
<th>Nanjing</th>
<th>Hefei</th>
<th>Hangzhou</th>
<th>Changzhou</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NMB</td>
<td>NME</td>
<td>MB</td>
<td>R</td>
<td>NMB</td>
</tr>
<tr>
<td>MDA8 O₃</td>
<td>-0.01</td>
<td>0.20</td>
<td>-1.07</td>
<td>0.88</td>
<td>0.17</td>
</tr>
<tr>
<td>NO₂</td>
<td>-0.05</td>
<td>0.23</td>
<td>-1.89</td>
<td>0.71</td>
<td>-0.07</td>
</tr>
<tr>
<td>SO₂</td>
<td>-0.38</td>
<td>0.43</td>
<td>-4.61</td>
<td>0.66</td>
<td>0.12</td>
</tr>
<tr>
<td>CO</td>
<td>-0.38</td>
<td>0.40</td>
<td>-0.29</td>
<td>0.67</td>
<td>-0.17</td>
</tr>
<tr>
<td>PM₂.₅</td>
<td>-0.08</td>
<td>0.30</td>
<td>-2.80</td>
<td>0.73</td>
<td>0.28</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>-0.49</td>
<td>0.63</td>
<td>-3.25</td>
<td>0.70</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Notes: * The year of 2017 includes the four typical months (January, April, July, and October). ** MDA8 O₃, NO₂, SO₂ and PM₂.₅ units (μg/m³), CO units (mg/m³). 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 O₃, 24-h PM₂.₅ and NO₃⁻ are suggested by Emery et al. (2017) and Huang et al. (2021).
Table 3. Model performance for 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.

<table>
<thead>
<tr>
<th>Selected cities</th>
<th>Seasons</th>
<th>TNO$_3$</th>
<th>OH NO$_2$</th>
<th>HET N$_2$O$_5$</th>
<th>OH NO$_2$ (%)</th>
<th>HET N$_2$O$_5$ (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shanghai</td>
<td>Winter</td>
<td>0.31 ± 0.13</td>
<td>0.21 ± 0.18</td>
<td>0.09 ± 0.06</td>
<td>69.3%</td>
<td>28.4%</td>
<td>2.2%</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>0.65 ± 0.35</td>
<td>0.52 ± 0.43</td>
<td>0.10 ± 0.09</td>
<td>81.8%</td>
<td>15.3%</td>
<td>2.9%</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>1.09 ± 0.68</td>
<td>0.90 ± 0.80</td>
<td>0.13 ± 0.15</td>
<td>82.9%</td>
<td>12.2%</td>
<td>4.9%</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>0.28 ± 0.22</td>
<td>0.24 ± 0.24</td>
<td>0.03 ± 0.03</td>
<td>86.9%</td>
<td>11.1%</td>
<td>2.0%</td>
</tr>
<tr>
<td>Nanjing</td>
<td>Winter</td>
<td>0.38 ± 0.13</td>
<td>0.23 ± 0.20</td>
<td>0.14 ± 0.11</td>
<td>59.2%</td>
<td>36.1%</td>
<td>4.7%</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>0.65 ± 0.29</td>
<td>0.48 ± 0.40</td>
<td>0.14 ± 0.12</td>
<td>73.1%</td>
<td>21.4%</td>
<td>5.4%</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>0.83 ± 0.41</td>
<td>0.62 ± 0.55</td>
<td>0.15 ± 0.17</td>
<td>74.7%</td>
<td>17.9%</td>
<td>7.4%</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>0.50 ± 0.25</td>
<td>0.35 ± 0.32</td>
<td>0.13 ± 0.11</td>
<td>69.7%</td>
<td>25.4%</td>
<td>4.9%</td>
</tr>
<tr>
<td>Hefei</td>
<td>Winter</td>
<td>0.38 ± 0.13</td>
<td>0.26 ± 0.18</td>
<td>0.10 ± 0.07</td>
<td>66.9%</td>
<td>27.1%</td>
<td>6.0%</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>0.63 ± 0.24</td>
<td>0.49 ± 0.30</td>
<td>0.10 ± 0.09</td>
<td>78.5%</td>
<td>16.5%</td>
<td>5.0%</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>0.66 ± 0.26</td>
<td>0.54 ± 0.30</td>
<td>0.07 ± 0.08</td>
<td>81.7%</td>
<td>10.4%</td>
<td>7.9%</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>0.48 ± 0.18</td>
<td>0.35 ± 0.24</td>
<td>0.11 ± 0.08</td>
<td>72.5%</td>
<td>21.8%</td>
<td>5.7%</td>
</tr>
<tr>
<td>Changzhou</td>
<td>Winter</td>
<td>0.41 ± 0.15</td>
<td>0.29 ± 0.20</td>
<td>0.11 ± 0.08</td>
<td>68.9%</td>
<td>26.8%</td>
<td>4.3%</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>0.64 ± 0.25</td>
<td>0.48 ± 0.31</td>
<td>0.13 ± 0.12</td>
<td>74.9%</td>
<td>20.9%</td>
<td>4.2%</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>0.70 ± 0.27</td>
<td>0.55 ± 0.31</td>
<td>0.10 ± 0.13</td>
<td>78.7%</td>
<td>14.3%</td>
<td>7.0%</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>0.46 ± 0.19</td>
<td>0.36 ± 0.24</td>
<td>0.08 ± 0.07</td>
<td>77.6%</td>
<td>18.3%</td>
<td>4.1%</td>
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<tr>
<td>Hangzhou</td>
<td>Winter</td>
<td>0.43 ± 0.15</td>
<td>0.26 ± 0.21</td>
<td>0.15 ± 0.12</td>
<td>59.7%</td>
<td>35.5%</td>
<td>4.8%</td>
</tr>
<tr>
<td></td>
<td>Spring</td>
<td>0.57 ± 0.24</td>
<td>0.40 ± 0.33</td>
<td>0.13 ± 0.12</td>
<td>70.5%</td>
<td>23.3%</td>
<td>6.2%</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>0.47 ± 0.23</td>
<td>0.36 ± 0.29</td>
<td>0.05 ± 0.05</td>
<td>76.4%</td>
<td>10.7%</td>
<td>12.9%</td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>0.46 ± 0.26</td>
<td>0.34 ± 0.32</td>
<td>0.10 ± 0.09</td>
<td>73.8%</td>
<td>21.3%</td>
<td>4.9%</td>
</tr>
<tr>
<td>References</td>
<td>Methods</td>
<td>Study seasons</td>
<td>Year</td>
<td>Study regions</td>
<td>NO$_3^-$ formation pathways$^c$</td>
<td>Time metric</td>
<td>Contribution (%)</td>
</tr>
<tr>
<td>------------</td>
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</tr>
<tr>
<td>(Li et al., 2021b)</td>
<td>WRF-Chem</td>
<td>Warm (Aug-Sep); Cold (Nov-Dec)</td>
<td>2016</td>
<td>NCP, YRD</td>
<td>OH$^\cdot$NO$_2$ (layer 1); HET N$_2$O$_5$ (layer 1)</td>
<td>season-mean</td>
<td>60-92%</td>
</tr>
<tr>
<td>(Qu et al., 2021)</td>
<td>WRF-CMAQ PA</td>
<td>Transition season (Oct-Dec)</td>
<td>2015</td>
<td>PRD</td>
<td>OH$^\cdot$NO$_2$ (layers 1-4); HET N$_2$O$_5$ (layers 1-4)</td>
<td>day-mean</td>
<td>92-96%</td>
</tr>
<tr>
<td>(Chuang et al., 2022)</td>
<td>WRF-CMAQ PA</td>
<td>Transition season (Mar-Apr)</td>
<td>2017</td>
<td>Taiwan</td>
<td>OH$^\cdot$NO$_2$</td>
<td>day-mean</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>(Wu et al., 2021)</td>
<td>WRF-Chem; Nitrogen Isotopes</td>
<td>Cold (Dec-Jan)</td>
<td>2017</td>
<td>Xi’an</td>
<td>HET N$_2$O$_5$ (surface)</td>
<td>season-mean</td>
<td>13-35%</td>
</tr>
<tr>
<td>(Chan et al., 2021)</td>
<td>GEOS-Chem; Isotope tracing</td>
<td>Cold</td>
<td>2014-15</td>
<td>NCP</td>
<td>OH$^\cdot$NO$_2$ &amp; HET N$_2$O$_5$ (surface)</td>
<td>season-mean</td>
<td>34% &amp; 45%</td>
</tr>
<tr>
<td>(Fu et al., 2020)</td>
<td>WRF-CMAQ PA</td>
<td>Cold (Dec)</td>
<td>2017</td>
<td>NCP</td>
<td>OH$^\cdot$NO$_2$ (HET N$_2$O$_5$ 10 layers)</td>
<td>season-mean</td>
<td>43% (44%)</td>
</tr>
<tr>
<td>(Liu et al., 2020a)</td>
<td>WRF-Chem</td>
<td>Cold (Dec)</td>
<td>2016</td>
<td>NCP</td>
<td>HET N$_2$O$_5$ (surface)</td>
<td>haze-mean</td>
<td>52%</td>
</tr>
<tr>
<td>(Zhang et al., 2021)</td>
<td>Nitrogen &amp; Oxygen Isotopes</td>
<td>Cold (Nov-Jan)</td>
<td>2017-18</td>
<td>Nanchang</td>
<td>HET N$_2$O$_5$ (surface)</td>
<td>season-mean</td>
<td>60%</td>
</tr>
<tr>
<td>(Fan et al., 2021)</td>
<td>Nitrogen &amp; Oxygen Isotopes</td>
<td>Warm and Cold</td>
<td>2016-17</td>
<td>Beijing</td>
<td>OH$^\cdot$NO$_2$ &amp; HET N$_2$O$_5$ (260 m)</td>
<td>Clean days</td>
<td>20% (80%)</td>
</tr>
<tr>
<td>(Luo et al., 2020a)</td>
<td>Nitrogen &amp; Oxygen Isotopes</td>
<td>Spring (Mar-May)</td>
<td>2013</td>
<td>Beijing</td>
<td>OH$^\cdot$NO$_2$ (surface)</td>
<td>Clean days</td>
<td>24-50%</td>
</tr>
<tr>
<td>(Luo et al., 2020b)</td>
<td>Nitrogen &amp; Oxygen Isotopes</td>
<td>Four seasons</td>
<td>2018</td>
<td>Nanchang</td>
<td>OH$^\cdot$NO$_2$ (HET N$_2$O$_5$)</td>
<td>season-mean</td>
<td>12-59% (67-89%)</td>
</tr>
<tr>
<td>(Fan et al., 2020)</td>
<td>Nitrogen &amp; Oxygen Isotopes</td>
<td>Cold (Nov-Dec)</td>
<td>2018</td>
<td>Beijing</td>
<td>HET N$_2$O$_5$</td>
<td>haze period</td>
<td>64%</td>
</tr>
<tr>
<td>(He et al., 2020)</td>
<td>Nitrogen &amp; Oxygen Isotopes</td>
<td>Warm and Cold</td>
<td>2016</td>
<td>Shanghai</td>
<td>OH$^\cdot$NO$_2$ (warm)</td>
<td>season-mean</td>
<td>84-92%</td>
</tr>
<tr>
<td>(Wang et al., 2019)</td>
<td>Nitrogen &amp; Oxygen Isotopes</td>
<td>Warm and Cold</td>
<td>2014</td>
<td>Beijing</td>
<td>OH$^\cdot$NO$_2$ (cold)</td>
<td></td>
<td>48-74%</td>
</tr>
<tr>
<td>(He et al., 2018)</td>
<td>Nitrogen isotopic</td>
<td>Cold (Oct-Jan)</td>
<td>2014</td>
<td>Beijing</td>
<td>HET N$_2$O$_5$</td>
<td>annual-mean</td>
<td>32 ± 10%</td>
</tr>
<tr>
<td>(Chen et al., 2020)</td>
<td>Field determination; Box model</td>
<td>Cold (Nov-Dec)</td>
<td>2016-17</td>
<td>Beijing</td>
<td>OH$^\cdot$NO$_2$ &amp; HET N$_2$O$_5$ (240 m)</td>
<td>haze period</td>
<td>74-76% &amp; 34%</td>
</tr>
<tr>
<td>(Zang et al., 2022)</td>
<td>Field observations; Box model</td>
<td>Cold (Dec-Feb)</td>
<td>2018-19</td>
<td>Shanghai (urban)</td>
<td>OH$^\cdot$NO$_2$ &amp; HET N$_2$O$_5$ (surface)</td>
<td>haze period</td>
<td>69% &amp; 29%</td>
</tr>
<tr>
<td>Study</td>
<td>Model</td>
<td>Season</td>
<td>Year</td>
<td>Region</td>
<td>Formation Pathway</td>
<td>Measurement Period</td>
<td>Haze Period</td>
</tr>
<tr>
<td>--------------------------------------------</td>
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</tr>
<tr>
<td>Womack et al., 2019</td>
<td>Box model</td>
<td>Cold</td>
<td>2016-17</td>
<td>Salt Lake Valley</td>
<td>OH+NO2 &amp; HET N2O5 (surface)</td>
<td>haze period</td>
<td>63% &amp; 35%</td>
</tr>
<tr>
<td>Vrekoussis et al., 2004</td>
<td>Field determination, Box model</td>
<td>Summer(Jul-Aug)</td>
<td>2001</td>
<td>South-East Europe</td>
<td>HET N2O5 (RL)</td>
<td>season-mean</td>
<td>43%</td>
</tr>
<tr>
<td>Kim et al., 2014</td>
<td>WRF-CMAQ PA</td>
<td>Cold</td>
<td>2009</td>
<td>The Great Lakes</td>
<td>OH+NO2 &amp; HET N2O5 (surface)</td>
<td>season-mean</td>
<td>28% &amp; 57%</td>
</tr>
<tr>
<td>Shah et al., 2018</td>
<td>GEOS-Chem</td>
<td>Cold (Feb-Mar)</td>
<td>2015</td>
<td>Eastern US</td>
<td>OH+NO2 &amp; HET N2O5 (surface)</td>
<td>season-mean</td>
<td>36% &amp; 62%</td>
</tr>
<tr>
<td>Alexander et al., 2020</td>
<td>GEOS-Chem; Oxygen Isotopes</td>
<td>Four seasons</td>
<td>2000-15</td>
<td>Global</td>
<td>OH+NO2 &amp; HET N2O5 (surface)</td>
<td>annual-mean</td>
<td>41-42%</td>
</tr>
</tbody>
</table>

Notes: 

a The above studies 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.
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.
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$_2$O$_5$. The contributions of HNO$_3$ in January 2017 are shown in Fig. S6.
Fig 4. Monthly diurnal variations of three nitrate-phases (NO$_3^-$, HNO$_3$, and TNO$_3$), major nitrate-precursors (O$_3$, NO$_2$, and NH$_3$) and major atmospheric oxidants (OH and N$_2$O$_5$) for the entire YRD region under the base scenario. The X axis marks each hour of the day (Beijing time).
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 line represents the net IPR value for each hour of the day; its value scale is on the right Y axis.
Fig 6. (a) Mean diurnal variations of TNO₃ production rates in different pathways in 2017 in Shanghai. (b) Average potential contribution of OH + NO₂, HET N₂O₅ and Others pathways to TNO₃ chemical production in Shanghai within the PBL under base case simulation.

Notes: Daytime (7:00–18:00), Nighttime (19:00–6:00). OH + NO₂ and HET N₂O₅ pathways are noted as “OH NO₂” and “HET N₂O₅” in Figs. 6 and 7.
Fig 7. (a) Mean diurnal variations of TNO3 production rates in major pathways from the local and transport (sum of indirect and direct transport) contributions. (b) Total IRRs rates of TNO3⁻ production rates in the base case and from the local and transport contributions within the PBL. The error bar indicates one standard deviation.