O$_3$ and PAN in southern Tibetan Plateau determined by distinct physical and chemical processes

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Abstract. Tropospheric ozone (O$_3$) and peroxyacetyl nitrate (PAN) are both photochemical pollutants harmful to the ecological environment and human health. In this study, measurements of O$_3$ and PAN as well as their precursors were conducted from May to July 2019 at Nam Co station (NMC), a highly pristine high-altitude site in the southern Tibetan Plateau (TP), to investigate how distinct transport processes and photochemistry contributed to their variations. Results revealed that, despite highly similar diurnal variations with steep morning rises and flat daytime plateaus that were caused by boundary layer development and downmixing of free-tropospheric air, day-to-day variations in O$_3$ and PAN were in fact controlled by distinct physicochemical processes. During the dry spring season, air masses rich in O$_3$ were associated with high-altitude westerly air masses that entered the TP from the west or the south, which frequently carried high loadings of stratospheric O$_3$ to NMC. During the summer monsoon season, a northward shift of the subtropical jet stream shifted the stratospheric downward entrainment pathway also to the north, leading to direct stratospheric O$_3$ entrainment into the troposphere of the northern TP, which traveled southwards to NMC within low altitudes via northerly winds in front of ridges or closed high pressures over the TP. Westerly and southerly air masses, however, revealed low O$_3$ levels due to the overall less stratospheric O$_3$ within the troposphere of low-latitude regions. PAN, however, was only rich in westerly or southerly air masses that crossed over polluted regions such as northern India, Nepal or Bangladesh before entering the TP and arriving at NMC from the south during both spring and summer. Overall, the O$_3$ level at NMC was mostly determined by stratosphere–troposphere exchange (STE), which explained 77% and 88% of the observed O$_3$ concentration in spring and summer, respectively. However, only 0.1% of the springtime day-to-day O$_3$ variability could be explained by STE processes, while 22% was explained during summertime. Positive net photochemical formation was estimated for both O$_3$ and PAN based on observation-constrained box modeling. Near-surface photochemical formation was unable to account for the high O$_3$ level observed at NMC, nor was it the determining factor for the day-to-day variability of O$_3$. However, it was able to capture events with elevated PAN concentrations and explain its day-to-day variations. O$_3$ and PAN formation were both highly sensitive to NO$_x$ levels, with PAN being also quite sensitive to volatile organic compound (VOC) concentrations. The rapid development of transportation networks and urbanization within the TP may lead to increased emissions and loadings in NO$_x$ and VOCs, resulting in strongly enhanced O$_3$ and PAN formation in downwind pristine regions, which should be given greater attention in future studies.
1 Introduction

Ozone (O$_3$) and peroxyacetyl nitrate (PAN) are key photochemical pollutants in the troposphere that are harmful to vegetation and human health (Kleindienst et al., 1990; Yukihiro et al., 2012; Taylor, 1969; Lefohn et al., 2017). Since O$_3$ and PAN are both produced during the oxidation of volatile organic compounds (VOCs) in the presence of nitrogen oxides (NO$_x$), they often share highly similar variational characteristics (Fischer et al., 2014). However, PAN is formed only from a limited number of oxygenated VOCs (OVOCs), which are typically oxidation products of alkenes (with low carbon numbers), aromatics and isoprene (Xu et al., 2021), while O$_3$ can be practically formed from all VOCs. Additionally, the photochemical formation of O$_3$ depends highly nonlinearly on its precursor concentrations, being insensitive to VOC changes under NO$_x$-limited conditions and vice versa, while PAN varied nearly proportionally to its OVOC precursors, with additional influences from the NO$_2$ to NO ratio (Xu et al., 2021). Thus, photochemistry can sometimes result in distinct variations of O$_3$ and PAN, especially during cold seasons (Xu et al., 2021; Zhang et al., 2020). From the aspect of physical transport, O$_3$ and PAN can both be transported over large distances. Since PAN is easily thermal decomposed under high temperatures, its transport is more favored in cold seasons or at higher altitudes. Early simulation studies suggested PAN to be an important reservoir for NO$_x$ in the troposphere and lower stratosphere (Singh and Hansn, 1981), redistributing NO$_x$ far from its source regions (Moxim et al., 1996). Different from PAN, O$_3$ is naturally produced within the stratosphere and can be transported into the troposphere via stratosphere–troposphere exchange (STE) processes that are often associated with the occurrence of tropopause folds, cut-off lows, streamers near the polar-front jet or subtropical jet stream, and mid-latitude cyclones (Langford, 1999; Stohl et al., 2003; Sprenger et al., 2007; Tang et al., 2011). STE elevates tropospheric O$_3$ and oxidation capacity at distinct latitudes during different seasons, with the largest mass fluxes in summer occurring mostly in higher mid-latitudes, followed by spring occurring mostly in lower mid-latitudes (Tang et al., 2011; Škerlak et al., 2014). Deep STE intrusions reaching the planetary boundary layer (PBL) and associated mass fluxes are largest during spring in China and the western part of North America.

While the variational characteristics, influence of photochemical formation, and transport on O$_3$ and PAN have been widely investigated in polluted urban regions of China (Liu et al., 2018; Yao et al., 2019; Hu et al., 2020; Wei et al., 2020; Qiu et al., 2021; Zhang et al., 2021; Xu et al., 2021), those at remote background sites received less attention, especially for PAN. The Tibetan Plateau (TP), located in western China, is often called the “Third Pole” with its average altitude over 4000 m. Due to its harsh environment, the TP is only scarcely populated and thus highly pristine. The topography of the TP affects large-scale circulations with its strong thermal forcing, thereby influencing the weather, climate and air quality in eastern China (Yang et al., 2014). Surface O$_3$ as a crucial greenhouse gas and with its deterministic role on atmospheric oxidation capacity has been paid certain attention in the TP, and special attention has been given to the photochemical formation of O$_3$ under the strong radiative conditions at such high altitudes. Ma et al. (2002) investigated the photochemical formation of O$_3$ at Mt. Waliguan (WLG) in the northeastern TP through box modeling and suggested wintertime net production and summertime net loss in O$_3$. Xue et al. (2013) further constrained the box model with VOC sampling results, mainly including hydrocarbons and aromatic compounds (no oxygenated compounds), and found net O$_3$ formation at WLG during both spring and summer 2003. Air-mass transport from central and eastern China was found to be frequent during summertime (Xue et al., 2011; W. Xu et al., 2018), revealing higher O$_3$ production efficiencies (Xue et al., 2011) and being held responsible for rising O$_3$ trends during summer and autumn (Xu et al., 2016; W. Xu et al., 2018). Due to its high altitude, the TP revealed the largest deep STE O$_3$ mass fluxes, with higher fluxes in spring and winter and lower ones in summer and autumn, especially in the southeastern TP (Škerlak et al., 2014). At WLG, O$_3$ was observed to be strongly influenced by STE associated with the subtropical jet during spring and summer in 2003, with stronger impacts during summer than spring (Ding and Wang, 2006; Zheng et al., 2008). STE was estimated to contribute an annual average of 10.2 % to tropospheric O$_3$ at WLG based on the numerical global atmosphere–chemistry model EMAC (ECHAM/MESSy Atmospheric Chemistry) simulations using tagged tracers, revealing a peak contribution in June (Liu et al., 2020). At Nam Co station (NMC) in the southern TP stratrophic influence was also mainly observed during spring and summer, which was estimated to contribute 20% and 10%, respectively, based on model simulations (Yin et al., 2017). Measurements from Dangxiong, a lower site not far from NMC, also revealed significant stratrophic impacts on surface O$_3$ (Lin et al., 2015). At Xianggelila station in the southeastern TP, the STE impact was suggested to be most pronounced during winter and weakest during spring and summer based on surface observations (Ma et al., 2014), which however was in disagreement with modeling results revealing strongest STE during April and May, with an annual average contribution of 4.3 %. In comparison, PAN was far less investigated, and the few existing studies mainly focused on the impact of transport on local PAN variations. Zhang et al. (2009) made measurements of O$_3$ and PAN at WLG station during summer 2006 and found that the two oxidants exhibited distinct diurnal variations and only weak correlations to each other, suggesting they were controlled by different processes, with PAN being strongly
influenced by regional transport of polluted air plumes. Xue et al. (2011) analyzed the same set of observations and reported PAN to be one of the most abundant reactive nitrogen species (NO$_3$) at WLG, contributing 32% to total NO$_x$. X. Xu et al. (2018) made measurements of O$_3$ and PAN at NMC station in summer 2011 and late spring to early summer 2012, detecting highly similar diurnal variations in both gases caused by boundary layer development and elevated PAN in connection with transport of air plumes crossing over Nepal, northern Pakistan or northern India.

Despite the findings in previous literature, the physicochemical factors determining the variation of O$_3$ and PAN in the TP and their relative contributions have not been comprehensively investigated mainly due to the lack of comprehensive online VOC observations and accurate NO$_x$ measurements. In this study, we present integrated real-time measurements of O$_3$, PAN, NO$_2$, VOCs, CH$_4$, CO, photolysis rates and other meteorological parameters during spring and summer 2019 at NMC station and analyzed them in combination with reanalysis data, utilizing trajectory modeling and box-modeling approaches. The different impact of distinct transport processes and photochemical formation on O$_3$ and PAN, as well as differences in sensitivities towards their precursors, are intercompared using improved box-model constraints, and the relative contributions of physical and chemical processes to O$_3$ and PAN variability are evaluated.

2 Experimental and analysis methods

2.1 Site, observations and data

As the first part of the @Tibet series campaign, a campaign was carried out at NMC station (30.77° N, 90.95° E; 4730 m a.s.l.), which is a highly pristine site in the southern TP (Fig. 1). The site campus is located within the natural reserve of NMC lake, thus far away from anthropogenic activities and emissions. The nearest county (Dangxiong) and city (Lhasa) are located 40 and 125 km to the southeast of NMC, respectively. The NMC lake was ~1 km to the north of our observation site, while the foothills of the northern Nyainqêntanglha Mountains were ~15 km to the south.

Measurements were performed from 1 May to 31 July 2019. Instruments for gases (including O$_3$, PAN, NO$_2$, CO, CH$_4$ and non-methane volatile organic compounds (NMVOCs)) were housed in an air-conditioned container. O$_3$ was measured alternately at the heights of 1.8 and 6.8 m (switching between two heights at 15 min intervals) using a Model TE-49C commercial O$_3$ analyzer, which was calibrated with a TE-49iPS O$_3$ calibrator (both from Thermo Electronics, USA). A Los Gatos Research (LGR) NO$_2$ analyzer was adopted for the measurements of NO$_2$, which has a measurement range of 0.01–1000 ppb and was calibrated using NO$_2$ standard gas at the beginning and end of the experiment. PAN measurements were made using a GC-ECD analyzer (Meteorologie Consult GmbH, Germany), which was calibrated using PAN instantly formed in the reaction of a NO reference gas with acetone in the internal calibration unit of the instrument. CO and CH$_4$ were measured (until 2 July) by a cavity ring-down spectroscopy (CRDS) analyzer (Model G2401, Picarro, USA) at a high precision (0.4 and 0.04 ppb, respectively, for CO and CH$_4$). The CRDS instrument was calibrated twice using a mixed CO and CH$_4$ standard gas, which was pressurized in 29.5 L treated aluminum alloy cylinders (Scott-Marrin Inc.) fitted with high-purity, two-stage gas regulators and calibrated with cylinders assigned by the Global Atmosphere Watch (GAW) CO Central Calibration Laboratory operated by National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL). NMVOCs were measured (only from 29 April to 21 May) using an online GC-MS/FID analysis system (TH-PKU 300B, Wuhan Tianhong Instrument Co. Ltd., China) at a 1 h time resolution, with detection limits in the range of 0.004 to 0.066 ppb. Multipoint calibrations were performed using Photochemical Assessment Monitoring Stations (PAMS) standard mixture and TO-15 standard mixture (100 ppb, Spectra Gases Inc., New Jersey, USA). To account for the reactivity of different VOC species, propy-equivalent VOC concentrations were calculated as

\[
C_{\text{Propy-Equiv}}(i) = C(i) \cdot \frac{k_{\text{OH}}(i)}{k_{\text{OH}}(C_3H_6)},
\]

where $C(i)$ is the ppbC concentration of species $i$ (calculated using ppb mixing ratios multiplied by carbon numbers of species $i$), $k_{\text{OH}}(i)$ the reaction rate of species $i$ with OH radicals (obtained from master chemical mechanism, MCM, http://mcm.york.ac.uk/MCM/, last access: 17 May 2023), and $k_{\text{OH}}(C_3H_6)$ the reaction rate of propene with OH.

Photolysis rates ($J$ values) were obtained using a Metcon CCD spectrophotograph (Meteorologie Consult GmbH, Germany), whose receptor optics were mounted on top of the container at the height of 2 m. Conventional meteorological parameters including temperature ($T$), relative humidity (RH), surface pressure ($P$), wind speed (WS) and wind direction (WD) were recorded by an automatic weather station. In addition, meteorological reanalysis data (ERA5) from the European Centre for Medium-Range Weather Forecasts (ECMWF) were used for complementary analysis (https://cds.climate.copernicus.eu/#/home, last access: 24 June 2023).

2.2 Backward trajectory analysis and PSCF calculations

The HYSPLIT model (version 5) from NOAA Air Resources Laboratory (Draxler and Hess, 1997, 1998; Draxler, 1999) was used for backward trajectory calculations, with 0.25° resolution Global Forecast System (GFS) model data from the National Center for Environmental Prediction (NCEP) adopted as input. The trajectory endpoint was set at 250 m a.g.l. (above ground level) of NMC station; 7 d (168 h)
backward trajectories were calculated at an hourly interval for the entire period of the campaign.

The potential sources of high \( \text{O}_3 \) and PAN were studied using the potential source contribution function (PSCF) analysis, which has been widely applied to detect possible source regions (Ara Begum et al., 2005; Lucey et al., 2001; Zhou et al., 2004). The PSCF on grid \( (i, j) \) is defined as

\[
PSCF = \frac{m(i, j)}{n(i, j)},
\]

where \( m(i, j) \) is the residence time of a subset of trajectories, whereas \( n(i, j) \) is the residence time of all the trajectories in that grid. Each trajectory was associated with \( \text{O}_3 \) and PAN concentrations observed at its time of arrival. To pin out the potential source regions for high \( \text{O}_3 \) and PAN, the \( m(i, j) \) was calculated using the subset of trajectories that were associated with \( \text{O}_3 \) or PAN concentrations higher than their respective 75th percentiles.

Abnormally high PSCF values may be produced for certain grids with very small \( n(i, j) \) values, which would induce large uncertainties. Thus, a weighting factor \( W(n_{i,j}) \) is introduced that was proposed by Zeng and Hopke (1989), giving grids with few trajectories passing through less weight:

\[
W(n_{i,j}) = \begin{cases} 
1.0, & n_{i,j} > \bar{n}_{i,j} \\
0.7, & 0.1 \cdot \bar{n}_{i,j} < n_{i,j} \leq \bar{n}_{i,j} \\
0.4, & 0.05 \cdot \bar{n}_{i,j} < n_{i,j} \leq 0.1 \cdot \bar{n}_{i,j} \\
0.2, & n_{i,j} \geq 0.05 \cdot \bar{n}_{i,j}
\end{cases},
\]

where \( \bar{n}_{i,j} \) is the average number of \( n_{i,j} \).

The PSCF analysis was respectively performed for \( \text{O}_3 \) and PAN, separately for spring and summer periods. Based on meteorological variations, spring and summer periods were defined as 1 May to 15 June and 15 June to 31 July, respectively.

### 2.3 Box modeling of local photochemistry

The Master Chemical Mechanism (version 3.2) was used within the F0AM (version 3.1) box-model framework developed by Wolfe et al. (2016), to simulate the impacts of local photochemistry on \( \text{O}_3 \) and PAN and to evaluate how much of their variations could be explained through local photochemistry. Observation data of VOCs, \( \text{NO}_2 \), \( \text{J} \) values and meteorological parameters were either averaged or interpolated into 10 min averages and used as constraints in the model. Model simulations were only performed for the period from 1 to 21 May, when VOC observation data were available. To evaluate local \( \text{O}_3 \) and PAN formation, three sets...
of simulations were performed for each, respectively, using measurement constraints on OVOCs, NO2 or both of them. In O3 simulation cases, PAN was constrained by observations, while in PAN simulations O3 was constrained. Daytime O3 and PAN increments (ΔO3\text{mod} and ΔPAN\text{mod}) were calculated and compared against observed ones (ΔO3\text{obs} and ΔPAN\text{obs}), with their ratios used to reflect how much modeled local photochemistry can explain observed daytime increases in O3 and PAN. Simulated O3 and PAN net formation rates in distinct modeling scenarios were intercompared and evaluated the sensitivity of their formation to VOCs and NOx concentrations.

### 2.4 Impact of stratospheric–tropospheric exchange

A Y index was defined as the ratio between normalized O3 and water vapor concentrations, calculated using the following equation:

\[
Y_{\text{ind}} = \frac{O_3}{H_2O}/\frac{O_3}{H_2O}.
\]

(4)

The Y index adopted in previous studies for the identification of stratospheric air intrusions has additionally divided Eq. (3) by normalized CO concentrations (Ma et al., 2014). Due to the lack of CO measurements after 2 July, the Y index was modified to the current form (in Eq. 4), which compared well with those calculated when incorporating normalized CO concentrations (Fig. S1 in the Supplement), since CO revealed very small variability during the entire observation period.

Additionally, O3 mass mixing ratios from the ERA5 hourly reanalysis dataset were converted to volume mixing ratios and applied in the investigation of STE impacts, since the ERA5 data are simulated with simple stratospheric O3 chemistry consideration and thus mainly represent the physical transport of stratospheric O3 (Sprenger and Wernli, 2003). Additionally, ERA5 O3 data have been verified to be well representative of observed O3 profiles and ground concentration levels in remote polar regions (Wang et al., 2021), indicating that it can well represent stratospheric O3 and the influence of its transport.

### 3 Results and discussions

#### 3.1 Variational characteristics of O3, PAN and their precursors

The time series of observed O3, PAN, NO2, CO, photolysis rates of O3 (jO3\text{D}) and NO2 (jNO2), and meteorological parameters observed at NMC from 1 May to 31 July are displayed in Fig. 2. From 1 May to 15 June (defined hereafter as the spring period), NMC experienced cold temperatures, strong winds, and dry conditions with low relative humidity (RH) and hardly any precipitation except for three small

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Figure 2: Time series of (a, g) O3 (black), PAN (red), (b, h) VOCs (bars), Y index (black), PBLH (blue), (c, i) NO2 (black), CO (red), (d, j) jO3\text{D} (black), jNO2 (red), (e, k) RH (blue), T (red), (f, j) wind speed and wind direction (colored dots) during the spring (a–f, 1 May to 15 June) and summer (g–j, 15 June to 31 July) period at Nam Co.
Table 1. Statistics of trace gases (including O$_3$, PAN, NO$_2$, CO, OVOCs, aromatics, alkanes and alkenes), photolysis rates ($j$O$_1^+$ and $j$NO$_2$), meteorological variables, as well as the $Y$ index.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Unit</th>
<th>Spring</th>
<th>Summer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>all day (08:00–20:00 LT)</td>
<td>night (20:00–08:00 LT)</td>
</tr>
<tr>
<td>O$_3$ ppb</td>
<td>59.8 ± 13.4</td>
<td>67.8 ± 9.0</td>
<td>52.2 ± 12.4</td>
</tr>
<tr>
<td>PAN ppb</td>
<td>0.27 ± 0.08</td>
<td>0.30 ± 0.07</td>
<td>0.24 ± 0.07</td>
</tr>
<tr>
<td>NO$_2$ ppb</td>
<td>0.12 ± 0.05</td>
<td>0.11 ± 0.07</td>
<td>0.13 ± 0.04</td>
</tr>
<tr>
<td>CO ppb</td>
<td>108 ± 26</td>
<td>108 ± 16</td>
<td>107 ± 33</td>
</tr>
<tr>
<td>CH$_4$ ppm</td>
<td>1.890 ± 0.024</td>
<td>1.884 ± 0.012</td>
<td>1.895 ± 0.030</td>
</tr>
<tr>
<td>OVOCs Propy-Equiv.</td>
<td>2.49 ± 2.16</td>
<td>3.10 ± 2.60</td>
<td>1.88 ± 1.34</td>
</tr>
<tr>
<td>Aromatics ppbC</td>
<td>0.56 ± 1.29</td>
<td>0.61 ± 1.74</td>
<td>0.51 ± 0.55</td>
</tr>
<tr>
<td>Alkenes</td>
<td>0.47 ± 0.50</td>
<td>0.48 ± 0.59</td>
<td>0.46 ± 0.40</td>
</tr>
<tr>
<td>Alkanes</td>
<td>0.59 ± 0.57</td>
<td>0.71 ± 0.68</td>
<td>0.47 ± 0.39</td>
</tr>
<tr>
<td>$j$O$_1^+$ s$^{-1}$</td>
<td>–</td>
<td>277 ± 183</td>
<td>–</td>
</tr>
<tr>
<td>$j$NO$_2$ s$^{-1}$</td>
<td>–</td>
<td>70 ± 27</td>
<td>–</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>4.2 ± 4.1</td>
<td>6.6 ± 3.4</td>
<td>2.0 ± 3.5</td>
</tr>
<tr>
<td>RH %</td>
<td>50 ± 19</td>
<td>41 ± 18</td>
<td>59 ± 17</td>
</tr>
<tr>
<td>Cumulated rain mm</td>
<td>1.0</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Wind speed m$^{-1}$</td>
<td>4.0 ± 2.6</td>
<td>4.8 ± 2.3</td>
<td>3.3 ± 2.6</td>
</tr>
<tr>
<td>$Y$ index</td>
<td>1.7 ± 0.9</td>
<td>2.1 ± 0.9</td>
<td>1.4 ± 0.6</td>
</tr>
</tbody>
</table>

Snow events, while during 15 June to 31 July (defined hereafter as the summer period), temperatures increased, average wind speeds were smaller and frequent precipitation events occurred under the influence of the Asian summer monsoon (Fig. 2a, Table 1). Despite more frequent precipitation events, observed average daytime photolysis rates were similar between spring and summer periods.

Under such meteorological variations, O$_3$ and PAN exhibited higher average concentrations in the spring (59.8 ± 13.4 and 0.27 ± 0.08 ppb) and lower ones in the summer period (53.6 ± 13.2 and 0.20 ± 0.05 ppb), with O$_3$ levels being overall in accordance with previous observations (X. Xu et al., 2018; Yin et al., 2017), while PAN levels were significantly lower than those observed in 2012 (X. Xu et al., 2018). VOC concentrations were only obtained for the first half of the spring period, reaching average concentrations of 4.9 ± 3.3 Propy-Equiv. ppbC (10.5 ± 3.2 ppbC), to which OVOCs contributed 61 ± 12% (reaching 2.5 ± 2.2 Propy-Equiv. ppbC on average), followed by alkenes (0.6 ± 0.6 Propy-Equiv. ppbC), aromatics (0.6 ± 1.3 Propy-Equiv. ppbC) and alkanes (0.5 ± 0.5 Propy-Equiv. ppbC), which made up similar fractions (14 ± 6%, 13 ± 7%, and 11 ± 4%, respectively), while other components (including alkynes, halogenated VOCs and nitriles) had negligible impacts (1 ± 1%) on the overall VOC concentration and reactivity (Fig. S2). Alkanes, alkenes and aromatics observed at the Dinghu Mountain (1000 m a.s.l.) background site in southern China were 48, 40 and 29 times those observed at the Nam Co site (Wu et al., 2016). Those in the Rocky Mountain National Park (3498 m a.s.l.) were 1.2, 3.6 and 1.3 times those observed in this study (Benedict et al., 2019), while those observed during summertime (1994–1996) were 0.9, 14 and 1.6 times those in Nam Co (Ma et al., 2002), revealing the extremely low primary VOC emissions at our site. However, OVOC concentrations at Nam Co were 1.3 times those observed in the Rocky Mountains, while only 0.24 times those previously observed at Mt. Waliguan (Mu et al., 2007), indicating that air masses in the TP were strongly photochemically aged due to the strong radiation and high atmospheric oxidative capacity at high altitudes, with additional influences from natural sources such as plant emissions or animal excrement (mostly from yak and sheep). At Nam Co, concentrations of isoprene and its oxidation products (e.g., MVK and MACR) were very low (0.034 ppb in total), with OVOCs being mostly dominated by formaldehyde, acetaldehyde and acetone (3.2 ppb in total), which have shown elevated concentrations over animal excrement (Mu et al., 2007). While daytime concentrations of OVOCs and alkenes were significantly higher than those during nighttime, other VOC species did not display much day–night discrepancy.

NO$_2$ revealed averaged concentrations 0.12 ± 0.05 and 0.09 ± 0.05 ppb during spring and summer periods, respectively, with no evident day to night differences. NO$_2$ levels were only scarcely reported for remote high-altitude locations, mainly due to instrument limitations. NO$_2$ levels were only slightly higher than the average NO$_2$ and NO level reported at Mt. Waliguan during summer 1994–1996 (0.048 ± 0.017 ppb) based on filter-pack sampling and spring 2003 (0.043 ± 0.069 ppb) based on chemiluminescence (Ma et al., 2002; Wang et al., 2006). Since Nam Co is located far away from anthropogenic emission sources, NO$_2$ levels here are mainly determined by natural emissions, such as those from soil microbial activities or lightning processes. Additionally, a latest study has proposed that lakes in the...
Figure 3. Averaged diurnal variations of (a) O$_3$ (blue), PAN (brown), (b) VOCs (bars), PBLH (solid line black line: average value, dashed black lines: minimum and maximum value) (c) NO$_2$ (yellow), CO (black), (d) $j$O$_3^D$ (green), $j$NO$_2$ (orange), (e) H$_2$O (light blue), RH (dark blue) and (f) temperature (red), wind speed and wind direction (colored dots) during the (1) spring and (2) summer period, respectively.

TP are strong natural NO$_x$ emission sources (Kong et al., 2023). Averaged diurnal variations of O$_3$ and PAN resembled each other (Fig. 3a1–2), both revealing decreases after sunset, reaching daily minimum concentrations near 07:00 Beijing local time (LT) and increasing quickly after sunrise simultaneous to PBL height (PBLH, Fig. 3b1–2) and exhibiting a flat plateau afterwards. Daily minimum O$_3$ concentrations were $52.8 \pm 10.9$ and $48.3 \pm 12.8$ ppb, while those of PAN were $0.21 \pm 0.06$ and $0.17 \pm 0.04$ ppb during spring and summer, respectively. Daily maximum O$_3$ reached $74.3 \pm 6.7$ and $63.5 \pm 13.0$ ppb, while those of PAN reached $0.31 \pm 0.08$ and $0.22 \pm 0.06$ ppb during spring and summer, respectively. Thus, O$_3$ and PAN both revealed higher levels in spring and lower ones in summer; however, PAN concentrations have decreased more significantly than O$_3$ (26% versus 10%), revealing a very flat and broad plateau during the day. OVOCs, aromatics and alkenes determined the variations of VOCs, with OVOCs and alkenes displaying diel variations similar to those of O$_3$ and PAN, revealing increases from 07:00 to 09:00 LT, fluctuating around its daily maximum value over daytime and decreasing after 17:00 LT (Fig. 3b1–2). NO$_2$ was typically higher during nighttime and lower during daytime, which is caused by combined effects of weakened dilution under nighttime shallow boundary layers, natural and anthropogenic NO$_x$ emissions, as well as chemical transformations. Additionally, springtime NO$_2$ concentrations ($0.12 \pm 0.04$ ppb) were higher than those during the summer period ($0.09 \pm 0.05$ ppb, Fig. 3c1–2). CO, however, revealed only slightly higher concentrations during the spring period ($107 \pm 26$ and $117 \pm 29$ ppb in spring and summer, respectively), staying overall flat during the day, without any diurnal variations (Fig. 3c1–2). Both RH and absolute water vapor concentrations were higher during the summer period. RH revealed a diurnal maximum by 07:00 LT during both periods, decreased rapidly after sunrise and reached its diurnal minimum at 16:00 and 18:00 LT in spring and summer, respectively (Fig. 3e1–2). Water vapor, however, increased further after sunrise, possibly due to surface evaporation processes of frost and dew during the morning. While the diurnal peak in photolysis rates were similar between spring and summer periods, the averaged diurnal variations displayed a
narrower peak during summer, especially for $j_{NO_2}$, due to more frequent precipitation and higher cloud coverage.

The day-to-day evolution of diurnal $O_3$ and PAN variations as well as those of winds and PBLH are more clearly displayed by Fig. 4. Downward winds were strongest during the afternoon under high PBLH (Fig. 4a and d). Due to the local topography with the NMC lake to its west and north and the Nyainqên Tanglha Mountains to its south, the site was susceptible to both influences from land–lake and mountain–valley breezes. Accordingly, local surface winds displayed clear diurnal variations with southeasterly nighttime winds shifting to northwesterly winds during daytime (Fig. S3b–d, Fig. S3 is the same as Fig. 4, with winds replaced by 2 m wind measurements); 550 hPa winds from ERA5 over the 0.25° grid containing NMC station (representing near surface conditions, since surface pressure was on average 573 ± 2 hPa) revealed stronger diurnal variations in zonal winds (Fig. 4b), overall agreeing with variations in surface winds, while meridional winds were dominated by southerly wind directions (Fig. 4c), with occasional changes to northerly winds, suggesting that local circulations had stronger impacts on zonal winds.

Broad peaks in $O_3$ often lasted until late evening hours, while nighttime $O_3$ frequently revealed increases under westerly winds and could reach daytime concentration levels, which can only be attributed to transport processes. High nighttime $O_3$ was not always accompanied by simultaneous PAN increases, while vice versa, elevated nighttime PAN was also not always synchronized with those of $O_3$, indicating that they might have originated from distinct sources and processes. $O_3$ levels were continuously high throughout the spring period, especially during 6–13 May. Despite overall lower levels in the summer period, two $O_3$ episodes occurred during 7–8 July and 24–25 July, respectively, exhibiting the highest concentrations (daily maximum concentrations ranging from 85.9 to 91.9 ppb) observed during the entire campaign (Figs. 2a and 4e). Compared to $O_3$, PAN displayed much larger day-to-day variability, with an evident high PAN episode occurring from 13 to 16 May (0.42±0.08 ppb on average) under southeasterly winds from aloft (Fig. 4f). Summitertime PAN was distinctly lower than that during spring season, with no increases detected during the two high $O_3$ episodes.

Overall, while $O_3$ and PAN revealed highly similar average diurnal variation patterns, their temporal variations often differed from each other, suggesting that they were determined by distinct transport or formation processes, which will be further investigated in the following sections.

3.2 Impact of local circulation

In previous studies, diurnal variations in $O_3$ and PAN were mainly attributed to local circulations, particularly the development of the PBL. At pristine mountain sites such as WLG, surface $O_3$ was influenced by free-tropospheric air during nighttime and by boundary layer air masses during daytime, which resulted in a diurnal cycle with lower daytime and higher nighttime $O_3$ with very small diurnal variation amplitudes. Despite its high altitudes, NMC is located at the foot of the northern Nyainqên Tanglha Mountains and thus experienced local circulation distinct from those at WLG. Free-tropospheric air was suggested to be richer in $O_3$ and PAN concentrations and was mixed down upon the rapid development of the convective boundary layer (CBL) after sunrise, while $O_3$ and PAN concentrations decreased upon the establishment of the nocturnal boundary layer (NBL), due to the dominance of local boundary layer air masses during nighttime, which were low in $O_3$ and PAN, since barely any surface $O_3$ and PAN precursor emission sources existed at NMC, added by effects of dry deposition (X. Xu et al., 2018). The broad $O_3$ peaks that often lasted until late evenings and the frequent events of elevated nighttime $O_3$ (occurrence frequency of 38 %, Fig. 4e) both supported the idea that under favorable meteorological conditions, high surface $O_3$ levels after sunlight hours could be sustained by continuous downmixing of free-tropospheric air (average daily maximum nighttime $O_3$ reaching 67.6 ± 10.1 and 62.9 ± 6.4 ppb during spring and summer, respectively). The fact that nighttime $O_3$ could reach the same level as noontime $O_3$ is why previous studies suggested that physical transport was determining $O_3$ variations at NMC, while photochemistry played a minor role.

Diurnal variations of $O_3$ and PAN followed their averaged diel pattern on 72 % and 75 % out of the days with valid records, respectively. While $O_3$ diurnal cycles revealed more days with such daytime increases during summer (69 % in spring vs. 74 % in summer), PAN conformed better to its averaged diurnal cycle in spring (90 % in spring vs. 63 % in summer), suggesting that despite being under the same meteorological influences and despite highly similar average diurnal concentration profiles, $O_3$ and PAN often revealed different variations. $O_3$ and PAN increasing rates (on days with daytime increases) between 07:30 and 10:30 LT both displayed linear correlations to temperature increasing rates ($r=0.45$ and 0.52 for $O_3$ and PAN, respectively, Fig. S4), confirming again that their morning increases were closely connected to boundary layer development upon radiative heating. Prenoon (06:00 to 12:00 LT) $O_3$ concentrations also increased with PBLH during both spring (Fig. 5a) and summer (Fig. 5b), however, revealing slightly distinct slopes during distinct seasons. Weaker prenoon winds that mainly occurred during early morning under low PBLH conditions were associated with evidently lower $O_3$ concentrations. During early morning hours when PBLH was still low, strong winds that mostly came from the W–NW direction were associated with $O_3$ concentrations as high as those observed during noontime in the spring period (Fig. 5a). During the afternoon (12:00 to 18:00 LT), when the CBL has fully established, $O_3$ hardly displayed any more variation with PBLH (Fig. S5a), indicating that once boundary layer
and free-tropospheric air was fully mixed, \( \text{O}_3 \) did not further increase with PBLH. In the summer period, W–NW winds were less frequent and \( \text{O}_3 \) associated with these winds only increased weakly with PBLH, whereas N–NE winds resulted in more significant rise in \( \text{O}_3 \) over prenoon hours. Summertime afternoon PBLH was significantly lower than during spring due to frequent cloudy and rainy conditions, mostly falling into the range of 0.5–1.5 km (Fig. S5b). \( \text{O}_3 \) still increased with PBLH, however, revealing large variability under the same PBLH, indicating that PBLH was not the deterministic factor for afternoon \( \text{O}_3 \) levels. PAN did not replicate the variation of \( \text{O}_3 \) with PBLH during prenoon hours, displaying large variability at lower PBLH and moderate concentration levels under high PBLH. This suggests that free-tropospheric \( \text{O}_3 \) levels were consistently and significantly higher than boundary layer \( \text{O}_3 \) levels, indicating weak surface formation of \( \text{O}_3 \) (further discussed in Sect. 3.3), which resulted in significant increases in observed surface \( \text{O}_3 \) upon down mixing. Whereas free-tropospheric PAN or the surface formation of PAN might have had higher variability, which resulted in largely different responses of PAN with the down mixing of free-tropospheric air. Intensive downmixing for free-tropospheric air under high PBLH might have even diluted boundary layer PAN concentrations.

To investigate what has caused the discrepancies in free-tropospheric \( \text{O}_3 \) and PAN over NMC, the variations of surface \( \text{O}_3 \) and PAN with free-tropospheric (500–550 hPa) winds during spring and summer are depicted in Fig. 6. At lower wind speeds, both \( \text{O}_3 \) and PAN typically revealed lower concentrations. With increasing wind speeds, high concentrations of \( \text{O}_3 \) and PAN were associated with distinct wind directions, in both spring and summer. During springtime, high concentrations of \( \text{O}_3 \) and PAN both occurred with W winds; however, low \( \text{O}_3 \) and high PAN concentrations were detected under strong S winds. During summertime, high \( \text{O}_3 \) dominantly occurred with N–NE winds, while PAN mainly revealed elevated concentrations under S–SW winds. The distinct variation of \( \text{O}_3 \) and PAN with wind speed and wind direction suggests that the concentrations of both gases might have been impacted by different long-range transport processes, which will be investigated in the next section.
et al., 2018). However, the source regions of O$_3$ and PAN in the TP have not been systematically investigated before. NO$_2$ and CO columns from TROPOMI revealed high concentrations in South Asian regions south of the TP contrasting to the pristine environment within the TP (Fig. 7). CO pollution was more severe and widespread outside of the TP during the spring period, while NO$_2$ pollution was more severe during the summer period both in South Asia and to the east of the TP in China. Inside the TP, NO$_2$ and CO columns were both higher during the summer period, suggesting that summertime atmospheric circulations might have been more favorable for pollution transport into the TP. The high-altitude Himalayas along the southern border of the TP are highly effective in blocking out direct intrusion of South Asian pollution, leading mostly to pollutant accumulation on its southern slope. High-resolution satellite observations clearly reveal high NO$_2$ and CO along mountain and river valleys, indicating that pollution might have been transported into the TP through these passageways. Belts of elevated CO extend from the western side (Kashmir) to the southeastern corner of the TP, indicating that pollution from South Asia could not directly cross over the Himalayas, especially not over those regions with very high altitudes, but it had entered the TP by crossing either to its west or southeast.

To further identify possible source regions for high O$_3$ and PAN at NMC station, the PSCF for both gases was calculated for spring and summer, respectively (Fig. 8). Springtime high O$_3$ concentrations were mainly associated with westerly trajectories, which crossed over northern India and Nepal before arriving at NMC (Fig. 8a). Although trajectories associated with high springtime O$_3$ crossed over vast areas outside the southern TP border, they mainly entered the TP from two passageways: one from the west and another from the southeast (near the border of Bhutan). Before entering the TP, the majority of the air masses associated with high O$_3$ came from higher altitudes (> 6 km), diving downwards to heights of 3–6 km or even < 3 km near the southern border.
of the TP, and then entering the TP mainly from the west or south (Fig. 9a1–3). Aside from that, trajectories from the NW mostly traveling within 0–6 km (above ground level) were also associated with high springtime O$_3$. High springtime PAN, however, was only associated with trajectories crossing over South Asia and entering the TP from the southeastern border. In addition, air masses from the Indian Ocean that traveled within 0–3 km and crossed over Bangladesh and Bhutan were also associated with high PAN but not with high O$_3$ (Figs. 8b and 9b1–3).

During summer, the PSCF of O$_3$ revealed a largely different distribution from that in spring. High-altitude westerly air masses that entered the TP from the west in spring have not been seen in summer, while air masses sweeping along the southern border of the TP (Nepal and northern India) at altitudes below 6 km and approaching NMC from its south were still partly associated with high O$_3$ during summer (Figs. 8c and 9c1–3). Southerly low-altitude (0–3 km) maritime air masses that traveled over Bangladesh and Bhutan before entering the TP were also sometimes linked to high O$_3$ at NMC. However, the major summertime O$_3$ source regions were located to the north of NMC, including southern Xinjiang province, northern Tibet and western Qinghai province (Fig. 8c). High O$_3$ was mostly associated with low-altitude air masses from the NW and N directions (Fig. 9c1). Summertime PAN was only rarely associated with northerly air masses, but mostly linked to westerly trajectories that travel along the southern TP border (mostly within 0–3 km, small parts within 3–6 km altitude, Fig. 9d1–2) and southerly trajectories traveling over Bangladesh and Bhutan within 3 km altitude (Fig. 9d1).

Thus, O$_3$ and PAN revealed distinct source regions in both spring and summer, while they also shared some common source regions. This explains why despite highly similar diel variation patterns, the day-to-day variation was often different between the two photochemical pollutants. Overall, springtime synoptic conditions resulted in a relatively monotone origin of air masses at NMC, mostly favoring the subsidence of high-altitude air masses under westerly airflow, which were rich in both O$_3$ and PAN. With the onset of the South and East Asian monsoon during summer, circulations drastically changed and resulted in influences of various distinct air-mass origins at NMC. These vastly different air-mass origins also exhibited completely different O$_3$ levels, with those originating in the north exhibiting even higher O$_3$ levels than those observed during springtime and southerly air masses revealing much lower O$_3$ levels than during springtime. PAN, however, was more linked to westerly and southerly air masses during summer.

Aside from changes in air mass origins at NMC, seasonal variations in large-scale synoptic conditions were also deterministic of STE and the overall spatial distribution of O$_3$. Since the ERA5 reanalysis data have only considered simplified stratospheric O$_3$ chemistry and the physical transport of O$_3$, the O$_3$ mixing ratio in the ERA5 dataset is a good indicator for the investigation of stratospheric influences. During the spring period, the averaged ERA5 500 hPa O$_3$ revealed relatively lower mixing ratios in the TP region (especially in southeast TP) and higher mixing ratios outside the TP in the latitude band between 15 and 25$^\circ$ N. As was shown in previous studies, the downward transport of stratospheric O$_3$ and its distribution is closely linked to the location of the subtropical jet stream (W. Xu et al., 2018), which is typically located above the TP during the spring period (Fig. 10c1). Due to large-scale circulations, lower-stratospheric O$_3$ is typically high in polar regions, decreasing with latitude and reaching its lowest level in the equatorial belt (Fig. 10c1). Deep stratospheric intrusion and O$_3$ subsidence often occur along the lower edge of the subtropical jet stream, which is a slope extending from the lower stratosphere (150 hPa) between 38 and 42$^\circ$ N down to the middle or upper troposphere below 28$^\circ$ N. STE processes are especially promoted by fronts, which are accompanied by large-scale subsidence of cold air from above (Stohl et al., 2003). STE mostly increased the O$_3$ levels in Southeast Asia to the west and south of the TP, which in turn could enhance O$_3$ at NMC through the westerly air-mass transport passage (Fig. S6). Direct STE influence was also frequently observed during the spring period (on 5–8, 13, 23, 31 May and 3, 5 and 9 June, Figs. S7–S13), with NMC frequently located near low-pressure troughs behind cold fronts. These STE events were typically associated with high O$_3$ and low PAN concentrations, except for 13 May, when stratospheric O$_3$ was transported to lower lati-

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**Figure 8.** Potential source contribution function (PSCF) of O$_3$ (a, c) and PAN (b, d) during spring (a, b) and summer (c, d) periods.
Figure 9. Residence time of trajectories associated with \( \text{O}_3 \) (a, c) and PAN (b, d) above their respective 67th percentiles during spring (a, b) and summer (c, d) periods within height ranges (above ground level) of (1) 0–3 km, (2) 3–6 km and (3) > 6 km.

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Statistically, \( \text{O}_3 \) only explained 0.1 % of the observed daytime \( \text{O}_3 \) day-to-day variability during spring \( (r = 0.033) \); however, it explained 22 % of the summertime \( \text{O}_3 \) variability \( (r = 0.47) \), contributing on average 10 % during the entire observation period (Fig. S16), which was overall in accordance with previous results reported in Yin et al. (2017). It is also worth noting that observed \( \text{O}_3 \) at NMC was typically higher than the 550 hPa ERA5 \( \text{O}_3 \) mixing ratio, especially during spring and early summer (Fig. 10d). During the entire observation, stratospheric \( \text{O}_3 \) transport explained 83 % of the observed daytime \( \text{O}_3 \) concentration \( (\text{O}_3, \text{ERAS}/\text{O}_3, \text{NMC}) \), with a lower contribution during spring (77 %) and a higher one during summer (88 %). This suggests that despite the small contributions of STE to the day-to-day variability of observed \( \text{O}_3 \), the overall daytime \( \text{O}_3 \) concentration was mainly maintained by the long-range transport of stratospheric \( \text{O}_3 \) (as opposed to direct strike of stratospheric \( \text{O}_3 \) during deep STE intrusions into the PBL). Additionally, the unexplained \( \text{O}_3 \) concentration might indicate photochemical \( \text{O}_3 \) formation aside from pure physical transport. However, whether it was caused by local photochemical production or the long-range transport of photochemically produced \( \text{O}_3 \) still requires further investigation.

3.4 Impact of local photochemistry

As was already manifested, \( \text{O}_3 \) has its natural sources and is more affected by STE processes at high-altitude locations such as NMC. \( \text{O}_3 \) is highly reactive and can be easily depleted in regions with high \( \text{NO}_x \) and VOC emissions; how-
ever it has a relatively longer lifetime in pristine background areas and can by directly or indirectly transported (transport of its precursors) over large distances, affecting O$_3$ levels at remote locations (W. Xu et al., 2018). The impact of local photochemistry on the budget of O$_3$, however, was often under debate in previous studies conducted in background areas of the TP. Under such pristine atmospheric conditions, it was manifested that O$_3$ production was strongly NO$_x$-limited, with NO$_x$ concentrations being the key factor determining whether O$_3$ was net produced or destructed in local photochemistry (Ma et al., 2002). However, the lower detection limit and precision of commercial instruments can hardly meet the needs for NO$_x$ measurements in such clean environments, which made it difficult to determine whether there has been net O$_3$ formation. At higher altitudes, PAN has a long lifetime and can be transported over long distances. PAN measurements have been previously conducted at Mt. Waliguan (northeastern TP) in 2006 (Xue et al., 2011) and at NMC station in the springs and summers of 2011 and 2012 (X. Xu et al., 2018). At both sites, PAN contributed substantially to reactive nitrogen and acted as a good indicator for regional and long-range transport of polluted air plumes. The photochemical formation of PAN requires the presence of peroxy acetyl radical and NO$_2$. The former is only formed in photochemical reactions of its precursor OVOCs, which are predominantly emitted within the boundary layer, while the latter is also mostly emitted near the surface, with the exception of lightning processes. Overall, the formation of PAN in comparison with O$_3$ is more likely to occur near the surface and has no natural sources. Nevertheless, the impact of local PAN formation versus those of transport to observed concentration levels was not discussed before due to the lack of its precursor measurements.
To evaluate the contribution of local photochemistry to observed $O_3$ and PAN, simulations were performed using an MCM-based box model for the period of 1 to 21 May, when VOC measurements were available. Observed $O_3$ revealed much larger fluctuations than those obtained from all three simulation scenarios, which respectively used measurement constraints on OVOCs, NO$_2$ or both of them (Fig. 11a). With constraints on NO$_2$, modeling results revealed significant daytime increases, indicating positive local net photochemical formation of $O_3$ (Fig. 12a). However, when NO$_2$ was unconstrained, modeled $O_3$ concentrations were significantly lower and displayed very small variability, with very small positive net $O_3$ production during the morning and mostly negative ones during the day (Fig. 12a). Nevertheless, none of the simulations could account for the large variability and steep morning increases within observed $O_3$. With OVOCs and NO$_2$ both constrained by measurements, modeling results could only explain $28\pm19\%$ ($5\%$–$66\%$) of the observed daytime increases (Fig. 11b), while even less could be explained when only OVOCs or NO$_2$ was constrained ($3\%\pm6\%$ and $21\%\pm14\%$, respectively). Days with relatively stronger local photochemical $O_3$ formation were not necessary days with high observed $O_3$. In turn, days with high $O_3$ were also often associated with weak photochemical net $O_3$ formation. This indicates that physical transport and mixing processes were determinative of $O_3$ diel cycle as well as the day-to-day $O_3$ variability, while local photochemistry further added to the daytime $O_3$ burden. Additionally, intercomparison among simulations also confirmed the high sensitivity of

Figure 11. (a) Observed (black) and modeled $O_3$ using constraints on OVOCs (green), NO$_2$ (blue) and both (red), (b) percentage of observed daytime $O_3$ concentration increment ($\Delta O_3$$_{,obs}$) that can be explained by those modeled under different constraints ($\Delta O_3$$_{,mod}$), (c) observed (black) and modeled PAN under OVOCs (green), NO$_2$ (blue) and both constraints (red), (d) percentage of observed daytime PAN concentration increment ($\Delta$PAN$_{,obs}$) that can be explained by those modeled under different constraints ($\Delta$PAN$_{,mod}$).
O$_3$ formation towards NO$_x$ and the relatively weaker sensitivity to VOCs in such a pristine environment.

Simulated PAN levels under NO$_2$ constraints were, however, significantly higher than observed PAN concentrations, especially when OVOCs and NO$_2$ were both constrained. However, when NO$_2$ was unconstrained, PAN concentrations were mostly underestimated by simulations. Thermal decomposition of PAN was very weak under low springtime temperatures, and net photochemical PAN formation rates were positive under all simulation scenarios. However, only NO$_2$-constrained cases revealed strong formation throughout daytime hours (08:00–20:00 LT), while unconstrained NO$_2$ simulations only displayed a very weak morning time (07:00–09:00 LT) photochemical formation. Only NO$_2$-constrained simulations overestimated PAN concentrations by a factor of 1.8 on average; however, they could reproduce observed daytime PAN increments by 94 ± 84 %. Additionally, days with high simulated PAN photochemical production (4–6 and 13–17 May) corresponded to episodes with elevated observed PAN concentrations, which indicates that photochemical formation of PAN was determinative of its day-to-day variability. Compared to O$_3$, PAN was sensitive to concentrations of both OVOCs and NO$_2$, since some of the OVOCs are direct precursors of PA radicals, which combine with NO$_2$ in PAN formation. According to modeling results in Fig. S17, acetaldehyde oxidation contributed majorly to PA radical formation at Nam Co (71.8 %), followed by methylglyoxal (9.0 %) and biacetyl (5.1 %). Still, NO$_2$ was more decisive of the overall O$_3$ and PAN production, since without its constraint, O$_3$ net loss and negligible PAN net formation would be yielded.

It should also be noted that both observed O$_3$ and PAN were not necessarily formed within the local boundary layer, since springtime winds in the TP were very strong, especially during daytime. Due to its relatively long lifetime, PAN might have been formed on the transport pathway to NMC, while O$_3$ might undergo both destruction and production during air-mass transport. This might partly explain why PAN formation was overestimated by simulations representing surface conditions. But, overall, it could be concluded that O$_3$ was mainly determined by physical transport, particularly STE processes, while PAN was largely determined by local photochemistry and that along the transport passageway. Fresh STE plumes reaching NMC from the north that are low in PAN concentrations result in depleted surface PAN, while relatively aged STE air masses crossing over polluted regions of the Indo-Gigantic Plain led to simultaneous enrichment in surface O$_3$ and PAN. The high sensitivity of O$_3$ and PAN formation towards NO$_x$ indicates that increased natural emission of NO$_x$ under global warming, enhanced anthropogenic emissions of NO$_x$ within the TP region due to the development of highways and transportation, and increased transport input from South Asia might greatly enhance O$_3$ and PAN formation in background regions, while increased VOC emissions and regional transport promote PAN formation more than that of O$_3$.

4 Conclusions and implications

In this study, continuous measurements of O$_3$ and PAN as well as their precursors were conducted during the spring and summer season at a very pristine high-altitude site in the southern TP (NMC station) to investigate the factors determining their variations. Due to the local topography, surface observations at NMC reflect free-tropospheric air conditions during daytime and nocturnal boundary layer conditions during nighttime. Both O$_3$ and PAN revealed steep increases after sunrise and reached a flat plateau during daytime. While average diurnal variations of O$_3$ and PAN highly resembled each other, their day-to-day variations were often different, suggesting that they might have been influenced by distinct physicochemical processes.

Backward trajectory modeling and PSCF analysis revealed distinct source regions connected to high O$_3$ and PAN. During spring, air masses rich in O$_3$ were mainly associated with high-altitude westerly air masses that either entered the TP from the west or from the south, while PAN was only rich in westerly air masses that transported along the polluted regions in northern India and Nepal before entering the TP from the south or in southerly air masses of maritime origin that crossed over polluted South Asian regions before entering the TP. During the summer monsoon season, air masses from the north were associated with the highest O$_3$ levels, while westerly and southerly air masses revealed lower O$_3$ levels. Elevated PAN concentrations, however, were still linked to westerly and southerly air masses crossing over polluted South Asian regions. O$_3$ at NMC was strongly influenced by STE, which brought down high stratospheric O$_3$ concentrations from the southwest route during spring and from the northwest during summer, explaining 77 % and 88 % of the observed O$_3$ level in spring and summer, respectively. PAN concentrations were, however, typically lower in air masses with strong stratospheric influence, except if they transported over polluted regions south of the TP.

Photochemistry resulted in positive net formation of both O$_3$ and PAN. While only 28 ± 19 % of the observed daytime growth in O$_3$ could be explained by photochemical simulations, the daytime growth of PAN was highly overestimated by the model if OVOCs and NO$_2$ were both constrained. Photochemistry was not the factor determining the day-to-day variability of O$_3$; however, it explained observed PAN variabilities well. While both O$_3$ and PAN formation were highly sensitive to NO$_x$ levels, PAN was also quite sensitive to VOC concentrations. Therefore, future concentrations of O$_3$ and PAN over the TP may be significantly impacted by increases in the concentrations of NO$_x$, VOCs, and other precursors (Cui et al., 2016), which either originate from the surrounding regions (in particular South Asia) or from anthropogenic
and natural sources within the TP. Special attention should be paid to PAN, which is mostly determined by photochemical processes sensitive to both NO$_x$ and VOCs and can be transported over very long distances.

Data availability. The data used in this study are available on the @Tibet ftp server (http://at-tibet.quickconnect.cn/, Ye, 2023) and can be made available upon request to the corresponding authors (zhanggen@cma.gov.cn and c.ye@pku.edu.cn).

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