Referee 1:

Comments to Authors:

In their manuscript **"Multi-decadal ozone air quality and the role of temperature in Switzerland during summertime"**, authors investigated changes in summertime ozone and its relationship with temperature from 12 national stations in Switzerland over the past two decades. Decreases in precursor levels have positively affected ozone in remote locations, while ozone is increasing close to busy roads. The ozone formation regime is becoming more NOx-sensitive, and high ozone is associated with hot days. The study is on a topic of relevance and general interest to the readers of ACP. Yet from an ozone chemistry perspective, the findings are not new. Methodologically, the exclusion of any VOC measurement, the omission of ozone production efficiency (OPE) discussion, the lack of quantitative analysis for NOx-temperature dependence discussion and titration discussion, plus correlating trends in ozone with only one key parameter (temperature) is insufficient to reveal photochemical mechanisms that control ozone levels (Line 100). Therefore, I recommend a major revision and am open to review the manuscript again if needed.

We thank Referee 1 for taking the time to review our manuscript and for their feedback. In light of the reviewer's comments, we see the need to further address the novelty of this work. Despite strong precursor reductions, ozone exceedances of healthy levels remain a matter of concern in Switzerland. The last study on ozone in Switzerland before this one addressed data up to 2014, which leaves more than a decade unaccounted for in the current literature. While most studies on ozone air quality investigate a specific city or urban area with concerning air quality levels, the excellent measurement infrastructure of the Swiss NABEL network allows the novel comparison of different site types representative of polluted conditions with large primary emissions (traffic), urban areas with reduced impact of direct emissions (suburban / urban), more pristine conditions with low local anthropogenic emissions (rural) and background conditions with negligible local pollution and some free tropospheric impact. The comparison of these different site types within the rather small geographic area of Switzerland and as part of one standardized network with consistent measurement and data analysis procedures provides a unique opportunity to characterize the dominating pathways of ozone formation, understand the underlying photochemistry and draw conclusions for required control mechanisms. Beyond that, we present evidence for decreasing O_3-temperature sensitivity over time. While this observation has been reported in the literature at various locations before, we show that the underlying mechanism is related to differences in decadal changes of O_3 in different temperature ranges (e.g. increases at traffic sites between 10 and 20°C and decreases above 30°C). Additionally, we suggest that this observation can be attributed to the decreasing impact of titration at polluted sites, which has not been reported before and could be a potential explanation for similar observations in other locations around the world. For these reasons, we believe our study provides new and valuable insights into surface ozone formation chemistry and related air quality impacts, that will be of wide interest to the ACP readership. We have revised the manuscript to clarify these aspects.

Lines 108 ff.: The NABEL network offers a unique framework for comparing O_3 formation mechanisms across a compact geographic region characterized by a high site diversity, including polluted conditions with large local anthropogenic emissions, urban conditions with less primary sources of O_3 precursors, more pristine conditions with low local emissions and background conditions with negligible local pollution and free tropospheric impact. Unlike the majority of the air quality literature focusing on a specific city or urban agglomeration, this study provides an overview of the mechanisms that control O_3 levels under these diverse conditions. Current literature on O_3 air quality in Switzerland (Boleti et al. (2018) and Boleti et al. (2019)) incorporates data through 2014. This study closes this decade-long gap and reveals unexpected increases of O_3 at polluted sites. Finally, this study provides evidence for titration as a driver of changing O_3-temperature sensitivity under polluted conditions, which has not been heretofore reported and may be an important consideration when unraveling photochemical processes in other regions.

Please find our detailed responses to the referees' remaining comments in the following.

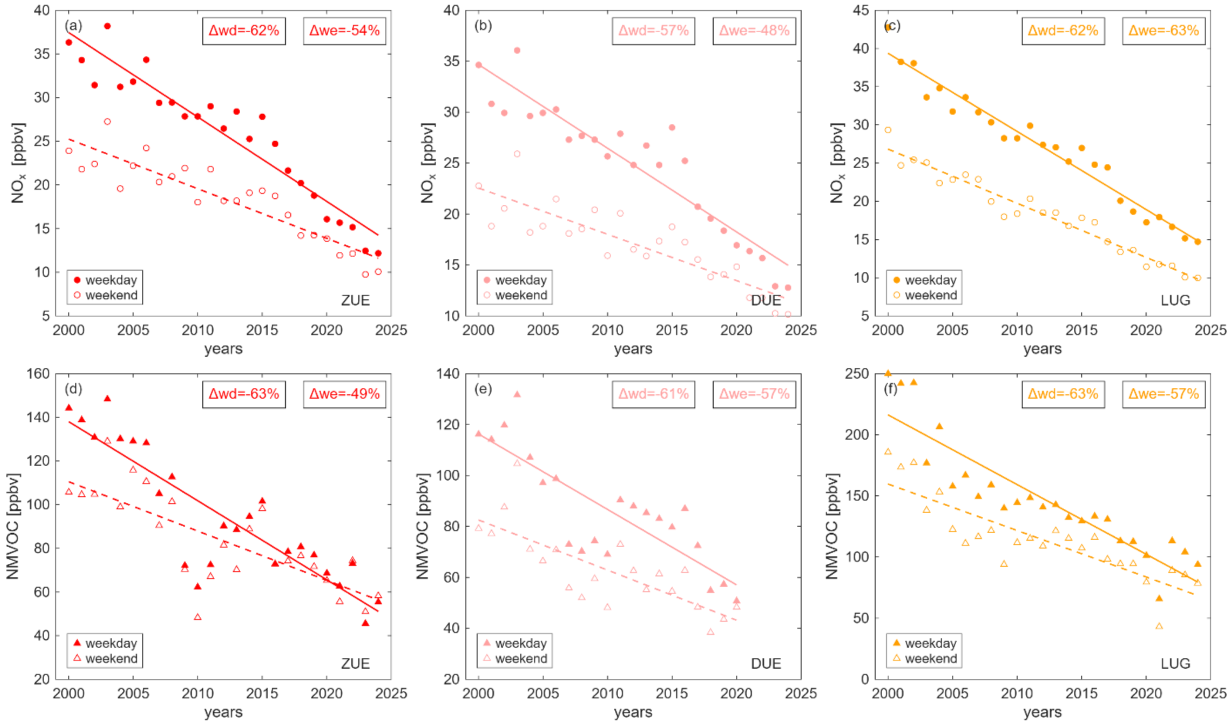
Specific comments:

1. Line 63-75, while I agree the "weekend effect" can be used to qualitatively speculate ozone formation regime, there exists varied quantitative methods to categorize the NOx-sensitive, VOC-sensitive, or transitional regimes based on direct measurement of radicals, or measurement of precursors gases + chemical modeling, or remote sensing of column HCHO/NO2. Given the NABEL network measures ozone, its precursors, and meteorology comprehensively, I am not sure why more quantitative metrics were not adopted in this study. From Line 124-125, it is understandable that VOCs are not always available for all 12 sites. But are they available in a few representative sites (at least one in each of your categories: traffic, (sub)urban, rural, and background) that could be utilized to validate your results/facilitate the discussions in Section 3.2? Diving into the mechanisms of ozone chemistry and its transitioning (Line 224-235) without the inclusion of any VOC measurement or estimation is concerning.

We thank the referee for allowing us to comment further on the ozone sensitivity and the role of VOCs.

We respectfully disagree with the referee that the presented methods are insufficient to characterize the ozone formation mechanism. The categorization of ozone formation into regimes is inherently qualitative (1. NO_x-sensitive, 2. transitional or 3. VOC-sensitive) and the weekend effect is therefore not inferior to other methods, such as the $HCHO/NO_2$ ratio. While the literature suggests qualitative cut-off values for each regime for the latter, e.g. Duncan et al. (2010): VOC-sensitivity for $HCHO/NO_2 < 1$ and NO_x-sensitivity for $HCHO/NO_2 > 2$, these are based on observational or modeling efforts which monitor the change in ozone formation with changes in NO_x or VOCs - similar to the weekend effect. The weekend effect is the only measurement-based approach to assessing the ozone formation regime across the NABEL network of sites.

We agree that the role of VOCs in O_3 formation was unclear in the first version of the manuscript. While VOC measurements are not available at traffic, rural and background sites for the full time period, continuous VOC measurements of the NABEL network are available at the urban sites in Zürich (ZUE), Dübendorf (DUE) and Lugano (LUG):



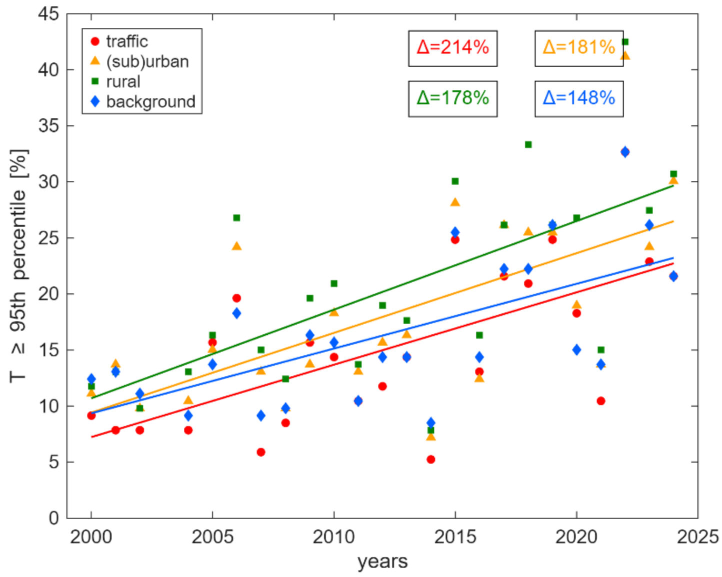
The top and bottom rows present decadal changes of NO_x and NMVOCs at these urban sites, respectively, for weekdays (filled symbols) and weekends (open symbols). These decadal trends show that the magnitude of precursor reductions has been similar for NO_x and VOCs. Therefore, we do not expect any changes in the ambient NO_x level of the transition from VOC- to NO_x-sensitive O_3 formation under urban conditions, and - assuming similar decadal VOC trends across all of Switzerland – at the remaining locations. For dominating NO_x-sensitivity, for example at background and rural sites today, changes in VOCs do not impact O_3 because the formation is limited by the availability of NO rather than peroxy radicals. For VOC-sensitive conditions, a decline in O_3 may result from VOC reductions. However, a precise quantification of the impact would require knowledge of the identity of these VOCs or the overall VOC reactivity, for which measurements are not available. We have added text to the manuscript to clarify the role of VOCs and have added the decadal trends of VOCs in Figure S5 of the Supplement.

Lines 143 ff.: Non-methane volatile organic compounds are measured via flame ionization detection, but the spatial and temporal availability of the measurements is limited. Continuous measurements are available at three urban sites (DUE, LUG and ZUE) only, which we use as an estimation for decadal VOC changes across Switzerland. Long-term speciated VOC or VOC reactivity measurements are not available at these sites.

Lines 277 ff.: Decadal changes of VOCs at ZUE, DUE and LUG (Figure S5 of the Supplement) highlight that the extent of VOC and NO_x reductions was similar over the past 20 years. Therefore, we do not expect any changes in the location of the transition point between VOC- and NO_x-sensitive O_3 formation over time. For sites characterized by NO_x-sensitive chemistry, changes in VOCs do not impact the abundance of O_3. Under VOC-sensitive conditions, a decline in O_3 may result from VOC reductions. However, a precise quantification of the impact would require knowledge of the identity of these VOCs or the overall VOC reactivity, for which additional measurements are needed at all sites.

2. Section 3.3.1 and Figure 5: I am not sure the uniform T>30C is a fair criteria for all sites. As you pointed out, the background sites are at higher elevation and therefore lower temperature and negligible exceedances. I may suggest considering using T>[a nominal percentile of the annual average T] as the more appropriate criteria to filter high temperature days for each site category. This may change your representation of Figure 5b and corresponding discussions. Currently, I am unable to retrieve much useful information from Figure 5b, because 1) the points are looking very scattered- I am not sure how robust is the r-square of that positive slope, 2) it is lumped from all sites, while all other discussions/figures throughout your manuscript are categorized into sites.

Thank you for this suggestion. We have investigated the decadal changes in peak temperatures considering daily maximum temperature exceedances of the 95th percentile of the dataset for each site type:



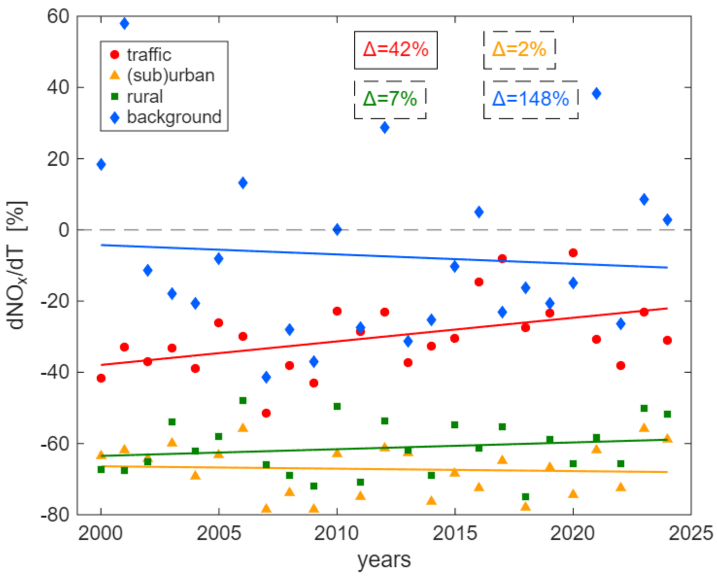
Similar to Figure 5(b) the results indicate that peak temperatures have increased by a factor of 2.5-3 at all sites. We agree with the referee that this illustration highlights the increase of peak temperatures at all sites well, which is particularly relevant when thinking about a climate penalty. However, we are discussing the impact of different temperature ranges on O_3 levels throughout the manuscript, for which fixed temperature values are beneficial: O_3 levels and exceedances are more dependent on the absolute temperature rather than the peak percentile of an individual site. We therefore keep Figure 5(b) in its current state but have added the figure showing the decadal peak temperature changes as 95th percentile exceedances to Figure S7 of the Supplement and added some additional explanation in the main text.

Lines 312 ff.: We present the share of daily maximum temperature exceedances of the 95th percentile of all measurements at individual site types in Figure S7 of the Supplement, which highlights that peak temperatures have increased similarly at all sites independent of the altitude.

While the referee is correct that Figure 5(b) shows a certain variability, highlighted by the moderate correlation of R^2=0.4, the decadal increase is statistically significant (p-value<0.05). The standard error of the calculated slope is around 25%, therefore the increase in the occurrence of peak temperatures would still be large at the lower uncertainty range. In comparison, the correlation coefficients for the linear fits of the decadal peak temperature changes as 95th percentile exceedances range between 0.40 and 0.44.

3. Section 3.3.2 and Figure 6: per Line 264-265, “Figure 6 presents the relationship between (a) NOx, (b) O3, (c) Ox and (d) the share of O3 in Ox with temperature, which all exhibit strong correlations.” Would you please clarify if the data points here are from all years? If that is the case, NOx went down (due to combustion control) and temperature went up (due to climate change) over years. They will inherently show a negative correlation, right? This correlation could be entirely physical and has nothing to do with chemistry. Therefore, I am not convinced with the interpretation from Figure 6a that higher temperatures drive a lower NOx or the temperature dependence of NOx emissions (Line 268-289). I suggest additional analysis (e.g. multivariate regression) to really distinguish the temperature impact from other confounding factors to validate the corresponding conclusion. Moreover, for the BLH discussions around Line 300, it reads speculative. Even without direct BLH measurement, your dilution theory should be validated using any gas/particle species co-measured at the NABEL that has a lifetime >> NOx.

It is correct that Figure 6 includes data from all years. We agree with the referee that NO_x and temperature could be anti-correlated over long timescales (i.e. years) given independent trends in emissions and climate. However, this does not drive the correlations at an hourly time scale (as in our analysis). To rule out a mathematical reason for the negative temperature correlation, we have investigated the change of the NO_x-temperature correlation over time. This figure shows the relative change of NO_x between 10 and 30°C:



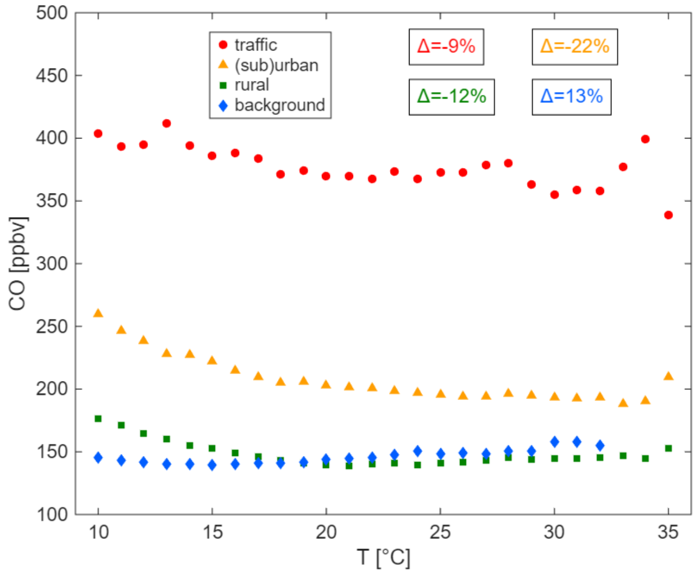
The NO_x-temperature correlation has remained constant at urban, rural and background sites. We observe a small positive change for traffic sites, but all values remain negative over the investigated time period. We can therefore exclude that simultaneous NO_x-decreases and T-increases over time affected the observed NO_x-temperature correlation. We present this finding in Figure S10 of the Supplement and have added text in the manuscript.

L. 350 ff.: The NO_x-temperature correlation (Figure S10 of the Supplement) exhibits little to no change from 2000 to 2024. This highlights that simultaneous NO_x

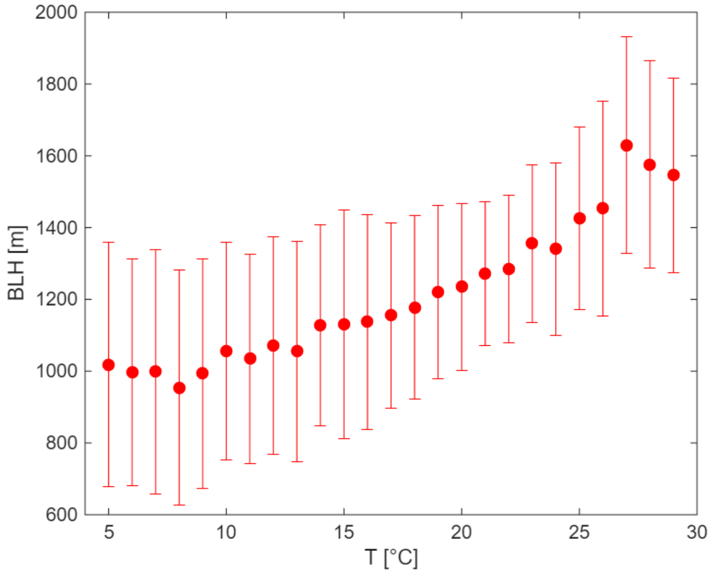
reductions and temperature increases can be ruled out as a reason for the observed NO_x-temperature correlation.

Caption Figure 6: The markers show the averages for all daytime (9-18) hourly data (2000-2024) for each temperature bin.

Carbon monoxide is co-measured at the NABEL sites and has a longer lifetime than NO_x. We also observe a negative CO-temperature correlation:



However, CO might also have temperature-dependent emission sources. An additional challenge is that due to the longer lifetime, emissions and meteorological conditions of previous days and weeks could distort the conclusions. We are therefore not confident that a longer-lived species could demonstrate the boundary layer impact convincingly. We have additionally investigated ERA5 reanalysis data across Switzerland:



This figure shows the daily boundary layer height at 2pm binned to temperature (average across Switzerland). The resolution of the dataset is 0.25°x0.25°, which cannot resolve the topography of Switzerland. However, it can provide an estimation of the BLH-temperature correlation, which is strongly positive and therefore in support of our dilution theory.

Without an extensive source apportionment of NO_x, a footprint analysis and a characterization of the temperature correlation of these sources, which is outside of the scope of this study, we are not able to draw final conclusions on the roots of the NO_x-temperature correlation. Instead, we have added the BLH-temperature correlation to Figure S11 of the Supplement in support of the dilution theory. The revised text further clarifies that while we explore potential mechanisms, a definitive explanation is not possible within the scope of this study.

Lines 358 ff.: Figure S11 presents the BLH-temperature correlation across Switzerland, based on ERA5 reanalysis data of the daily summertime BLH and the 2m-temperature at 14:00 local time. While the resolution of the ERA5 data (0.25°x0.25°) is not sufficient to resolve the topography of Switzerland, it provides an estimation of the BLH-temperature correlation. The positive correlation supports our theory that dilution effects could impact the temperature correlation of trace gases and that the day-to-day variability of the BLH is significant.

Lines 366 ff.: The hypotheses discussed above provide likely explanations for the observed NO_x-T correlation. However, the definitive driver(s) can only be identified through extensive source apportionment, footprint analysis and a precise characterization of the temperature behavior of these sources, which is outside the scope of this study.

4. Throughout the manuscript, ozone "titration" is repeatedly mentioned. However, in both the manuscript and SI, I am unable to identify any quantitative analysis that showed the actual titration effect. Given the main dataset for the analysis focused on summer daytime, I am not convinced of the importance of the titration effect on explaining many observations. From my limited experience, titration usually happens at night-time or early morning, when NO persists (no photolysis) and the boundary layer is shallow. But during daytime, especially between 9:00-18:00 local time in summer as the author stated, NO emitted to the troposphere should theoretically be rapidly converted to NO2 by ROx and HOx within minutes, orders of magnitude faster than NO + O3 titration reaction. But I am no expert on the atmospheric condition in Switzerland. Since you do have simultaneous NO, NO2, and O3 measurements, why not plot the diurnal average of O3 and NO at each site (or categories of lumped sites) to see if NO increases at traffic hours, does ozone drop? If that anti-correlation is obvious and universal across the traffic sites, then you can attribute some of your findings to titration. If O3 remains high even at rush hours, then titration is negligible. You could also try plotting the daytime vs. nighttime O3/NO ratio, as the nighttime titration should be obvious.

The referee is correct that the rate constant for NO + HOx/ROx is significantly larger than the rate constant for NO + O3:

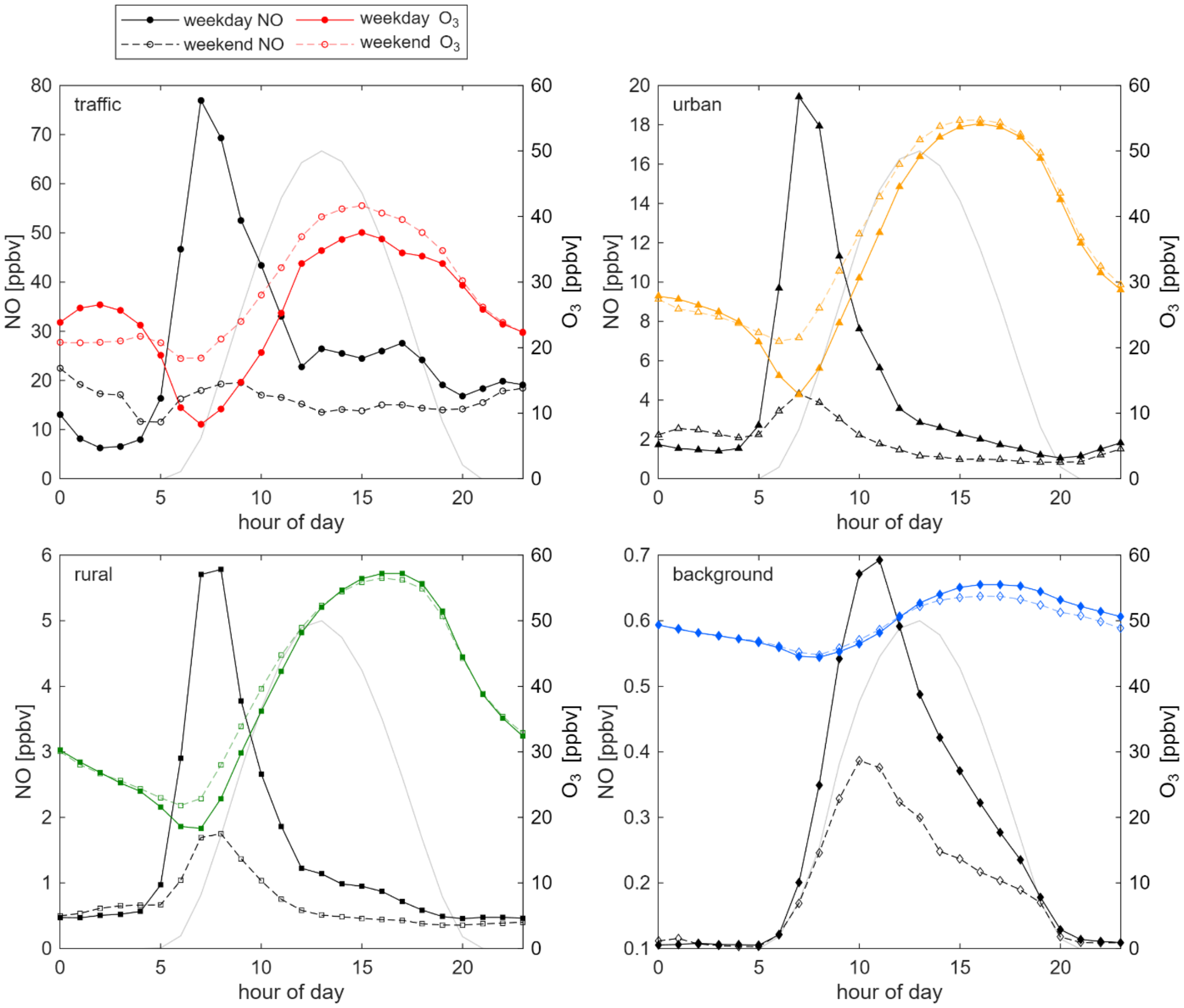
$k(NO+HO_2) = 8.5e\text{-}12\ cm^3\ molecule^{-1}\ s^{-1}$ (at 298K, IUPAC)

$k(NO+CH_3O_2) = 7.7e\text{-}12\ cm^3\ molecule^{-1}\ s^{-1}$ (at 298K, IUPAC)

$k(NO+O_3) = 1.9e\text{-}14\ cm^3\ molecule^{-1}\ s^{-1}$ (at 298K, IUPAC)

At 25°C, the reaction of NO + O_3 is around 400-500 times slower than NO + peroxy radicals, however O_3 is much more abundant than HO_2 or CH_3O_2. While we do not have any measurements of peroxy radicals, levels are typically of the order of ppt compared to ppb levels of O_3. Therefore, the amount of NO that reacts with O_3 is much larger compared to the reaction with peroxy radicals.

We thank the referee for the suggestion to investigate diurnal cycle as an additional confirmation of the role of titration:



This figure shows the diurnal cycles of NO (black lines) and O_3 (coloured lines) at traffic, urban, rural and background sites, separated into weekdays (solid lined) and weekends (dashed lines). We show data for the beginning of the record (for summer days between 2000 and 2005), when titration was particularly important at polluted sites. The gray line indicates the diurnal cycle of radiation, normalized to the right y-axis to fit in the shown frame. Traffic sites are characterized by a large morning NO peak, which can be majorly attributed to the morning rush hour as demonstrated by the large weekday-weekend difference. It is accompanied by a distinct daily O_3 minimum, which supports the conclusion that titration plays a major role under these conditions. This effect is also visible for (sub)urban and rural sites but weakens when moving away from fresh vehicle NO emissions. Further away from primary sources, O_3 diurnal cycles are dominated by other mechanisms: O_3 levels decrease throughout the night due to nighttime loss mechanisms and are increasing after sunrise due to beginning photochemistry. Additionally at low elevation sites, the rise of the boundary layer in the morning mixes the O_3-poor stable nighttime boundary layer with O_3-richer air from the residual layer. The diurnal cycle of O_3 at background sites is less pronounced, which is likely due to the elevated altitude of the sites, which could be located outside of the boundary layer during the night and potentially parts of the day. We have added the diurnal cycles to Figure S6 of the Supplement.

Lines 295 ff.: This conclusion is additionally supported by the diurnal cycle of NO and O_3 (Figure S6 of the Supplement), which shows that weekday morning NO peaks at traffic sites are associated with distinct daily O_3 minima.

We have additionally clarified the term “titration” in the introduction.

Lines 59 ff.: The term titration refers to a temporary sink of O_3 through reaction with NO, which can dominate NOx cycling at night due to the absence of NO_2 photolysis or in proximity to large primary NO sources, which rapidly convert all or a part of O_3 to NO_2.

Technical corrections:

1. Around Line 50, discussion in Pusede et al. (2015) is an estimation of PO3 as a function of NOx and VOCR in a typical U.S. city under 2015 emissions, and the EKMA figure itself is a steady-state simplification. It is classic and important, but since then, more comprehensive field observation-based modeling studies in populated areas around the world have shown that peak ozone formation did not necessarily happen during the transitional regime but rather highly localized. They can occur well within the NOx- or VOC-sensitive regime:

- Peak PO3 in VOC-sensitive regime: Los Angeles, CA, U.S.: Stockwell et al., 2025 (https://doi.org/10.5194/acp-25-1121-2025).

- Peak PO3 in NOx-sensitive regime: San Antonio, TX, U.S.: Guo et al., 2020 (https://doi.org/10.1016/j.atmosenv.2021.118624).

- Peak PO3 in VOC- and NOx-sensitive regime in the morning and afternoon respectively, but not the transitional regime in between: Houston, TX, U.S.: Mazzuca et al., 2016 (https://doi.org/10.5194/acp-16-14463-2016).

- Peak PO3 in NOx-sensitive regime: North China Plain, China: Tan et al., 2024 (https://doi.org/10.1016/j.scib.2018.07.001).

I recommend incorporating these studies in the introduction and revise the corresponding lines.

We have revised the text to highlight that peak $P(O_3)$ occurs at the transition point in an idealized scenario but that depending on the spatial resolution and the meteorological conditions peak $P(O_3)$ can also occur in air masses that are characterized as NO_x- or VOC-sensitive. We have added the suggested citations to the manuscript.

Lines 49 ff.: The crossover between NO_x- and VOC-sensitive chemistry is described as a transitional regime (Pusede et al., 2015). While in theory O_3 formation peaks in this transition (given a large local, homogeneous air mass), depending on the spatial resolution and the meteorological conditions maximum O_3 production can also occur in air masses characterized as NO_x- or VOC-sensitive. Several studies have reported this observation in the U.S. and China (Mazzuca et al., 2016; Tan et al., 2018; Guo et al., 2021; Stockwell et al., 2025).

2. Section 3.3.2, Line 265, do you mean “data points above 10 and below 35C” instead?

Thank you, we have corrected the sentence.

3. I see no where that ozone production efficiency (OPE) was mentioned, which is modulated by both precursor levels and meteorological conditions (jNO2, temperature, cloud coverage, etc.). With NOx and O3 measurement but without NOy, it won't be easy to use the regression method to calculate OPE. But it should be considered in the discussion, because when the NOx went down and T went up, the OPE could increase and lead to more rapid ozone production (more propagation cycles) as shown in:

- Kleinman et al., 2002 (https://doi.org/10.1029/2002JD002529)

- Chace et al., 2025 (https://pubs.acs.org/doi/10.1021/acs.est.5c02073)

And also in those referred literature above. It won't change the main conclusion of your study so I listed it in technical corrections. But it is important to be incorporated and might facilitate some of your discussions (e.g. around Line 365, Line 380, Line 410, and else where).

As the referee points out correctly, unfortunately we do not have any NO_y measurements needed to calculate the OPE. However, we added the suggested citations and some text referring to the potential impact of OPE changes.

Lines 54 ff.: Various parameters, including ambient NO_x levels, VOC reactivity, temperature and photolysis rates, can additionally impact the number of O_3 molecules produced per NO_x, which is referred to as the ozone production efficiency (OPE) (Kleinman et al., 2002; Chace et al., 2025).

Lines 430 ff.: Changes in the ozone production efficiency over time could additionally impact the temperature sensitivity of O_3. Local measurements of NO_y would be required to investigate OPE changes.