Response to reviewer 1 (https://doi.org/10.5194/egusphere-2025-5643-RC1).

First, we greatly appreciate the detailed and very constructive review provided. Please find below a response (normal text in black) to each comment (text in cursive and blue).

This manuscript investigates the ozone trends and drivers at a Southern Hemisphere background site in Chile. It is well structured and written and illustrates original and interesting results. I suggest accepting the manuscript for publication after taking into consideration the following comments.

Thanks for your overall statement.

Comments

Page 2, lines 18-19: The sentence needs elaboration. The changes of the net stratospheric influx in STE are linked to changes of the stratospheric Brewer–Dobson Circulation and the amount of ozone in the lowermost stratosphere, which are strongly influenced in a changing climate by the emissions of ODSs and GHGs (Butchart 2014, Banerjee et al 2016, Morgenstern et al 2018, Meul et al 2018, Akritidis et al 2019).

This is certainly correct! The text has been expanded considering your suggestion.

Page 6, line 16: Please clarify within the text the meteorological reasons for this decision.

As stated in line 14 on page 6, we did not use the observed data because there were significant data gaps, particularly regarding humidity. Thus, to have consistent time series we used bias corrected reanalysis data.

Page 7, line 29: Please describe at first place what were the meteorological fields to drive the simulations of TM4-ECPL.

The CTM was driven by year-specific assimilated meteorology (ECMWF ERA-Interim for the years 1980–2014). This has been added to the text.

Page 8, lines 16-18: The criterion for the identification of SI is arbitrary and I suggest to comment the limitations. It could be possible that subsidence/transport of upper tropospheric air could possible have a similar result and can be accounted as SI. Another important issue for the identification is the lifetime of the filamentary structures of stratospheric origin in the troposphere which can persist for several days in the troposphere before cascading down to smaller scales and getting mixed with the surrounding air. Due to this dissipation process of stretched filamentary structures and the irreversible mixing associated with deep stratospheric intrusions, the characteristic signs of stratospheric air with high O3 content, high values of potential vorticity (PV) and low humidity dilute and disappear over the period of a few days. This complicates the observation of stratospheric intrusions in the lower troposphere and especially within the atmospheric boundary layer and near surface unless in cases of direct and *intense deep intrusion events that can result to distinct spikes in measured stratospheric tracer concentrations (e.g. see Stohl et al., 2003).*

We do agree that it is difficult to identify ozone of stratospheric origin, and that any threshold in ozone or humidity (or potential vorticity) is somewhat arbitrary due to the complexity of the processes involved. We would need measurements of ^{7}Be or ^{10}Be to better ascertain the occurrence of STE, and/or a detailed modeling of such episodes, including high-resolution back trajectories. But now we have neither (We only provide a few examples of back trajectories, crossing the PV=-2 units). Instead, we decided to identify the events of high ozone and low humidity of possible stratospheric and upper tropospheric origin occurring upwind or over Tololo. Furthermore, we put more strict thresholds on ozone and humidity aiming at more intense events and carried out a clustering that identifies several synoptic configurations, many of which are consistent with the possibility of stratospheric ozone intrusions. The text has been changed accordingly.

Page 9, lines 24-25: Maybe you also mention here that the explanatory variables used are indicated in Table 2. This will help the reader while reading this paragraph.

We added a few examples. The information is clearly stated later when applying the method.

Page 14, lines 20-23: Since TM4-ECPL has a dedicated stratospheric ozone tracer, you may look also O3s at Tololo for El Nino and La Nina years.

As stated in the text, while the seasonality in stratospheric ozone intrusions is adequate, we deem it to be overestimated due to the way the ozone upper boundary condition is treated. This was the reason not to analyze its changes between El Niño and La Niña years, nevertheless we have added a supplementary figure in the Supplementary Material. The differences in the seasonality in the model outputs using the stratospheric tracer for El Niño and La Niña years very is consistent with the one derived from the observations.

Page 15, lines 10-11: I am rather confused with the plots of anomalies (Figures 6 and 7) with respect to the 12-day period mean. I think that if you want to clearly illustrate more thoroughly the passage of the trough, I would rather suggest plotting the actual fields of geopotential height and vertical velocity at 500 hPa.

What we show in figures 6 and 7 corresponds in essence to averages of many synoptic conditions which are similar but not identical, and particularly not always occurring in the same spot. Therefore, we opted to show the anomalies, an approach that is rather conventional. Showing the actual composites (averages) and not the anomalies result in a blurry picture. In any case, as we have added a clustering of these events, the corresponding synoptic situations become more defined. All in all, we prefer to keep the anomalies.

Page 18, lines 1-4: There is a misunderstanding here. Stratospheric air penetrating into the troposphere is characterized by high PV- values (not negative as discussed here). I would rather *suggest plotting the actual PV values rather than the anomalies to see the evolution of the filament. Potential vorticity generally provides a good indication of air of recent stratospheric origin. Threshold values for dynamical tropopause reported in the literature range from 1.0 or 1.6 pvu (Stohl et al. 2000) to 3.5 pvu (Hoerling et al. 1991) with a value of 2 pvu used most often (Hoskins and Berrisford 1988; Stohl et al. 2003; Akritidis et al. 2019). Partly, this value depends on the vertical resolution of the meteorological data, and partly it depends on the synoptic situation and the geographical location (Hoinka 1997).*

Indeed, there is confusion because we are discussing potential vorticity (PV) over the subtropics of the Southern Hemisphere, where the Coriolis parameter (f) is negative, and we are typically under very stable conditions ($g\frac{\partial\Theta}{\partial p} < 0$). Thus, over an isentropic surface and considering cyclonic circulation (ζ<0), the following expression is strictly negative.

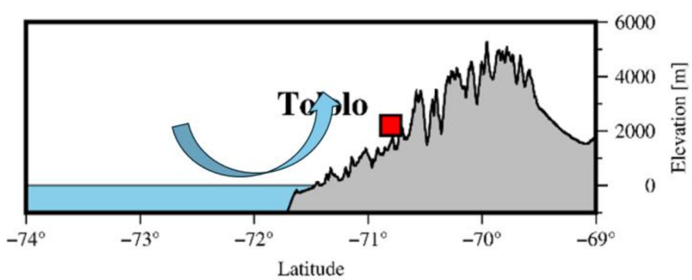
$$PV = -g(f + \xi)\frac{\partial\Theta}{\partial p}$$

Furthermore, in the Southern Hemisphere air, PV is characterized by large and negative values.

Again, we chose to show anomalies and not composite potential vorticity because the location of intrusions varies in space, which when averaged over many cases (places) is diluted. The reviewer can see analysis for individual intrusions showing the absolute fields in (Rondanelli, 2025; Rondanelli et al., 2002).

Page 22, line 25: The way is written here sounds more like a chemical effect (e.g. ozone chemical loss because of more water vapour in unpolluted environment). But later on you attribute it to dynamical effect from more efficient mixing upwards of boundary layer air rich in water vapour and low in ozone. Please clarify.

The first part refers to the role of water vapor as a chemical sink of ozone. The second part refers to the source of water vapor, which in the case of Tololo is the marine boundary layer (See illustration).



Water vapor entrainment to Tololo in connection with the vertical development of the marine boundary layer in summer, or when deep troughs and sometimes cutoff lows reach the subtropics vigorously mixing up wet air.

Response to reviewer 2 (https://doi.org/10.5194/egusphere-2025-5643-RC2)

First, we greatly appreciate the detailed and very constructive review provided. Please find below a response (normal text in black) to each comment (text in cursive and blue).

This manuscript provides a thorough analysis of the long-term surface ozone trend at Tololo, Chile. Tololo is a very important and unique monitoring site, the topic is within the scope of the journal, and the findings are of value to the research community. In general, the findings of the study are supported by the data and the analysis, but there are three issues that need to be addressed before the paper is published, as described below.

Thank you for your appreciation. The issues are addressed below.

Major Comments:

1) The authors conclude that rising methane is the most likely explanation for the increase in ozone, but they don't evaluate this conclusion in terms of studies that have quantified the impact of rising methane on the long-term tropospheric ozone trend. For example, model assessments suggest that a 100 ppbv enhancement in methane mixing ratios could lead to an increase of 2.57-3.86 Tg/yr in the tropospheric ozone burden (West et al., 2007; Fiore et al., 2008; Zhang et al., 2016). Is your observed increase of ozone from 2006 to 2023 consistent with these model estimates?

Points are well taken. We have expanded somewhat the discussion on the impact of increasing methane on ozone. Over the period 2006-2023, ozone (median) shows a trend of about 2.1 ppbv/decade. Thus, over 17 years, the corresponding change in ozone is ca. 3.6 ppbv. Assuming this is well mixed, the corresponding change in ozone mass burden is 30 TgO_3 or a yearly average of 1.8 TgO_3. Over the same period (2006-2023), methane volume mixing ratios have changed by 145 ppbv, which corresponds to a change in mass burden of 408 $TgCH_4$ and a yearly average of 24 $TgCH_4$. In sum, the mass burden ratio is ≈0.08 TgO_3/ $TgCH_4$. According to Fiore et al (2008), who summarize multiple model estimates, this rate ranges between 0.12 and 0.16 (See Figure 1 and text in said paper). West et al (2007) report a range from 0.09 to 0.19. So, our estimate is at the lower end but of the same order of magnitude. Part of this analysis has been added to the main text.

Fiore, A. M., et al. (2008), Characterizing the tropospheric ozone response to methane emission controls and the benefits to climate and air quality, J. Geophys. Res., 113, D08307, doi:10.1029/2007JD009162.

West, J.J., et al., 2007. Ozone air quality and radiative forcing consequences of changes in ozone precursor emissions. Geophysical Research Letters, 34(6).

Zhang, Y., et al. (2016), Tropospheric ozone change from 1980 to 2010 dominated by equatorward redistribution of emissions, Nature Geoscience, 9(12), p.875, doi: 10.1038/NGEO2827.

2) Figure 3 indicates that specific humidity has decreased since 1996. Given that drier air has greater ozone concentrations than moist air, could the ozone increase simply be explained by a shift in circulation that is bringing drier air to the site? I recommend selecting a specific humidity threshold value to filter out moist air (perhaps throw out the wettest 25% of data). You will have to use the same threshold for each year, which will result in more data being thrown out in the early part of the record, but this is necessary in order to be certain that you are looking at similarly dry air masses in each year. Then calculate the ozone trend for the dry air masses. If the ozone trend diminishes then one can conclude that the increased frequency of dry air masses was contributing to the trend. But if the trend stays the same then you have clear evidence that ozone is increasing in the dry air masses, consistent with increasing methane concentrations.

We checked and the resulting trend cannot be attributed to changes in humidity. In fact, when suppressing the upper 25% of the humidity values (considering the seasonal variability, i.e., removing the highest 25% values of each season), we obtain a trend of 2.0± 0.6 ppbv/decade that is rather similar to the one obtained considering all data (2.1± 0.8 ppbv/decade). As stated elsewhere, there is little impact of marine boundary layer upon Tololo, so what we observe there is mostly free tropospheric air.

Also, the observed trends in ozone and humidity do not affect our identification of air of stratospheric and upper tropospheric origin (SUTO). The identification considers the running average of 10 days so any trends in ozone or humidity are irrelevant.

3) Regarding the identification of stratospheric intrusions, I have no doubt that aged stratospheric air reaches Tololo, however, I am very skeptical that the simple method of flagging events with high ozone and low water vapor can distinguish between a stratospheric intrusion and aged air from the mid- or upper troposphere. None of the ozone values observed at Tololo are very high (do any values exceed 60 ppbv?) so we can conclude that fresh intrusions do not reach the site. Rather, any intrusion that reaches the site would be heavily diluted with tropospheric air. I think that all the authors can say is that they have selected data that are likely to be indicative of the mid- and upper troposphere, and that these air masses contain an indeterminant quantify of stratospheric ozone.

Considering your comment we have expanded the discussion and redefined the events as “air of stratospheric or upper tropospheric origin (SUTO)”. In addition to this, we have established a stricter criterium to identify said events, avoiding fast passing synoptic disturbances (Now they must last for at least 18 hours). This resulted in the reduction of the number of cases from 336 to 252. The resulting composite of cases using the stricter criteria is nevertheless quite similar to the previous one, showing that most of the time, increases in ozone and decreases in humidity occur in connection with troughs that reach the subtropics at different locations, and said configurations are largely consistent with the potential occurrence of stratospheric intrusions. Of course, that is the average result. So, to learn more about the underlying configurations we carried out a clustering analysis. Three out of four of them show, again, troughs occurring in different locations. One of them lead to strengthening of subsidence over Tololo. The fourth group shows a different picture in which a westerly flow brings upper tropospheric air, and possibly turbulence associated with it mixes down dry and ozone rich air. Furthermore, we calculated back trajectories for representative cases (maximum ozone anomalies of each group) from the four cluster groups. Interestingly, three of those cases show air of stratospheric origin, i.e., at some point the trajectory crosses the PV=-2 units. So, the reviewer is right when saying that the identification of passing troughs does not assure air of stratospheric origin. Nonetheless, stratospheric air seems to be a recurring feature in connection with said configuration.

Regarding the magnitude of the ozone anomalies, we see much lower values here compared to those in the Northern Hemisphere at similar latitudes. This must be linked to the generally stronger STE observed in the Northern Hemisphere compared to the Southern Hemisphere (e.g., Holton, 1990).

Holton, J. R.: On the Global Exchange of Mass between the Stratosphere and Troposphere. J. Atmos Sci, 392–395, https://doi.org/https://doi.org/10.1175/1520-0469(1990)047%3C0392:OTGEOM%3E2.0.CO;2, 1990.

Several of these authors are also authors on a recent ACP paper that investigates hemispheric differences in ozone across the stratosphere–troposphere exchange region (Seguel et al., 2025, https://doi.org/10.5194/acp-25-8553-2025). Seguel et al. show observed ozone vs. H2O in the southern hemisphere UTLS region, and it's clear that for ozone mixing ratios between 100 and 200 ppbv (indicative of the lowermost stratosphere) there is a very wide range of H2O mixing ratio values (see their Figure 2b). How do your values of ozone vs H2O (within intrusion events) compare to the range of values reported by Seguel et al.? Are your values indicative of the lowermost stratosphere? Or do they simply resemble the typical range of values encountered in the mid- and upper troposphere?

The ozone mixing ratios measured at Tololo are relatively lower than those observed in the lower stratosphere and upper troposphere as reported by Seguel et al (2025). Even during the intrusion events identified in the manuscript, ozone mixing ratios remain well below this range. As the reviewer correctly notes, this difference is expected because the air masses reaching Tololo are diluted and mixed with tropospheric air and undergo photochemical processing during transport. Therefore, the ozone–H_2O values presented in this study are not representative of the lowermost stratosphere, but rather of diluted air masses influenced by stratospheric intrusions. However, despite the difficulty of distinguishing the impact of intrusions at the surface level using in situ measurements, the composite of SUTO events consistently shows that from the onset of the intrusion events (hour 0), ozone increases while water decreases. While this evidence alone is not sufficient to unambiguously attribute a stratospheric origin, it is consistent with a stratospheric influence when interpreted in the broader context provided in the manuscript.

Minor Comments:

The paper states that the site is affected by upslope winds during the day, and downslope winds at night. Previous studies (e.g. Gaudel et al., 2018) have used nighttime data at mountaintop sites in order to focus on the free troposphere and to limit the impact of local air masses. Have you filtered your data so that you only focus on nighttime observations?

We decided not to work with nighttime values only. The reason being that the semi-permanent presence of the subtropical high is rather efficient in limiting the upward mixing of marine boundary layer air. The ozone diurnal cycle is lightly impacted, even during summer, by the mesoscale radiatively driven circulation in discussion.

The title gives no indication if this paper focuses on the troposphere or stratosphere. I recommend changing the title to "Tropospheric ozone trends and drivers…"

Point well taken! We have changed the title as recommended.

page 2, line 11

Innes et al. 2015 is missing from the list of references

The reference has been added to the list of references

page 2, line 14

Please specify if you are just talking about ozone trends in the free troposphere, because if we look at Figure 2.8 of IPCC AR6 WG1 we see that ozone trends in the lower troposphere have a range of positive and negative values at northern midlatitudes.

Thank you for noticing the ambiguity, this has been clarified in the text.

page 2, line 17

This statement "particularly variations in stratosphere-troposphere exchange" gives the impression that STE is a major driver of ozone trends, but it's most likely only a minor component. STE only contributes 10% to the global tropospheric ozone budget, so if STE changed by an unrealistically large amount of 10%, it would only have a 1% impact on the tropospheric ozone budget. The paper by Skerlak et al. only looks at the changes in STE flux from 1979 to 2011. While their calculation shows an increase in net STT for 2001-2011, we have no way of knowing if this is a short-lived anomaly, as their analysis ended 15 years ago. The paper by Li et al. 2024 focuses on wintertime when ozone production is limited, so any ozone trend driven by STE is not representative of the full year.

Yes, we do agree that the evidence is incomplete. We have changed the text accordingly.

page 2, line 20

An important paper that explores the impact of climate variability on STE is Neu et al., 2014.

Neu et al., 2014, Tropospheric ozone variations governed by changes in stratospheric circulation, Nature Geoscience, DOI: 10.1038/NGEO2138

Thank you. This reference has been revised and added.

Page 2, line 23

When discussing ozone increases since the 20th century the key TOAR paper to cite is Tarasick et al. 2019, with further consolidation of evidence assessed by IPCC AR6, WGI, Chapter 2 (Gulev et al., 2021).

Absolutely, revisited and added to the list.

Page 3, line 6

The key study that demonstrated the impact on ozone of emissions shifting from mid-latitudes toward the equator is Zhang et al., 2016.

Zhang, Y., et al. (2016), Tropospheric ozone change from 1980 to 2010 dominated by equatorward redistribution of emissions, Nature Geoscience, 9(12), p.875, doi: 10.1038/NGEO2827.

We agree. Added.

Page 3, line 21

A key study on ozone production over the South Pacific is Schultz et al., 1999, On the origin of tropospheric ozone and NOx over the tropical South Pacific, JGR, 104(D5)

We do agree but the list of references is already long as it is.

Figure S3

The figure legend says Tololo data are in orange, but the figure caption says the Tololo data are colored blue. Which is it?

Thank you for noticing, it is now corrected.

Page 7, line 2

In the statement, "This index is elaborated by NOAA Physical Sciences Laboratory", the word elaborated is not used correctly, and I'm not sure what you are trying to say. Can you just say "This index is provided by the NOAA Physical Sciences Laboratory"?

Corrected.

page 26, line 13

"growing median trend" implies that the trend is changing over time and becoming stronger, for both the 1996-2006 period and the 2006-2023 period. I don't think this is what you are trying to say. If the trend value is not changing just say "positive ozone trend".

Corrected.