**RC1**: 'Comment on egusphere-2024-720', Anonymous Referee #1, 18 Apr 2024, **Citation**:

https://doi.org/10.5194/egusphere-2024-720-RC1

This is a very detailed paper using a large amount of satellite, ozonesonde and modelling data to investigate the precursor drivers to the trends in total column tropospheric ozone between 2005-2019 on regional and global scales. The use of $NO_2$, VOC, HCHO tropospheric column data is novel for this type of analysis, is within the scope of ACP and should be published subject to a slight restructure and few minor corrections.

We thank the reviewer for his comments and recommendations. Our responses are in blue following each comment.

**General comments**

It is unclear to me the relevance of the model analysis for different parts of the troposphere (Figure 5) if it isn't referred to in the later interpretation of the measurements or in the conclusion.

The simulated tropospheric ozone and its precursors in the lower, middle and higher troposphere are now mentioned in the discussion (e.g., secs. 3.3, and 3.43) and in the conclusion.

There is some clear parallel in the model analysis where the contribution and trends are separated by region (Figure 11) but can this be brought into the discussion more and perhaps section 3,3. (and Figure 5,11) be moved to after the measurements are presented (3.4.4, 3.4.5, 3.4.6, 3.4.7 ). A summary could then also include a discussion about which parts of the column are driving the trends in different regions of the globe, otherwise why include the model information?

We thank the reviewer for this comment. We have added this discussion to the conclusions as suggested. Figures 5 show the simulated mean partial column of tropospheric O3, CO, NO2, and HCHO and we believe it is suitable here in section 3.3 which addresses the model simulation. Figure 11 is located in section 3.4.3 for regional trends and likewise is suitable there since it addresses trends for several regions and latitudinal bands. We have included now a discussion in the conclusion regarding which parts of the columns are driving the trends.

Are the model trends inline with the measurements? Please include some reference to the model findings in the precursor measurement discussions and conclusions.

Comparisons to measurements are already in the text, for example, in section 3.4.3, as stated "Simulated TrC-$O_3$ trends are also quite comparable to those observed by OMI/MLS within the measurement model uncertainty (see **Error! Reference source not found.** and **Error! Reference source not found.**). Over Australia, the OMI/MLS trend of 1.05 DU/decade is higher than the model trend of about 0.2 DU/decade (see **Error! Reference source not found.**). However, since OMI/MLS trend has a calculated uncertainty (2σ) of 1.44 DU/decade, both the model and OMI/MLS for Australia are not statistically different."

We have also added related discussion to the conclusion.

The figures are a little confusing. It would make sense to use similar figures for each of the ozone precursors to allow easier interpretation. The discussion on CO trends includes more plots (including anomaly trend plots) for which the other precursor species there is a summary (also nice but maybe don't need both). Can the plots used be the same for all species in sections 3.4.4, 3.4.5, 3.4.6, 3.4.7, either anomaly time-series or summary of anomalies?

We have added new CO figures for the trend summaries, similar to NO2 and HCHO as the reviewer suggested.

As stated above Figure 5 perhaps relates more to the $O_3$ discussion and should sit with Figure 11 as they are related (contribution to each part of the column from model and actual trend). Also perhaps Figure 4 should sit later with Figure 12 (see later specific points).

As we mentioned earlier, Figure 5 presents the burdens of each precursor in while Figure 11 presents the trends for each region. We believe that Figure 5 sits in the correct place (sec. 3.3) following figure 4 that shows the burdens of all precursors globally. Figure 11 shows the simulated trends sitting in section 3.4 (tropospheric trends)

I think it is just a misunderstanding on my part but there should be a consistency with the time period that you are discussing, for the most part the time period 2005-2019 is shown but the main $O_3$ trend figure 6 is possibly until 2021. There is also some reference to COVID years and this seems a bit out of place in the paper unless related to the above point?

All figures are from 2005 to 2019 except for Figure 8b (2005-2021) which is shown only to demonstrate the effect of COVID-19. Figure 6 is also from 2005-2019 as shown on the legends on top of each panel. However, there was a typo in the caption that says 2004-2021, which is corrected now. We thank the reviewer for mentioning that typo.

**Specific comments**

Figure 2: Please include time range (2005-2019) in the figure caption.

Done!

Line 263:  Use 'peroxyl' not 'proxy'.

Done!

Line 272: Self referencing, can you choose other references for these fundamental reactions?

Done!

Lines 281-282 and Figure 4: $NO_2$ column is stated to be decreasing in North America, Europe and Australia.  Please include a reference for this relating to air pollution controls or alternatively Figure 4 should show the trend of $NO_2$ rather than the mean if you are referring to it? The trends are shown later in Figure 12 so discussion about them should be there unless you have another reference for it?

Done! A reference has been added.

Section 3.2, lines 290-295 generally needs more references when discussing sources from certain regions, not just 'e.g.' in brackets.

Done!

Figure 5: Model shows lower, middle, upper differences in precursor contribution. At this point the reader is interested in the trends within the column and whether any specific part of the troposphere has been increasing/decreasing over this time and in which regions, actually shown later in Figure 11. Can these be put together, perhaps in a later discussion?

Done!

Figure 6: What timescale are the trends over, 2005-2019 or 2005-2021?

Done! It is 2005-2019, the caption is corrected.

Figure 7: Does the right plot show the 'zonal mean trend' of column depths or should the caption say 'mean $O_3$' by latitude for different column depths for 2005-2019?

Done! The caption of the right panel has been further clarified "zonal mean of different column depths (right) from 2005-2019"

Figure 9: Can latitude of the observations be included on this plot?

Done! Table S 1 includes a list of the coordinates of ozonesonde stations used in the study. This is now mentioned in the caption as well.

Line 431: What is a partial column, is it defined?

The partial columns are labeled on Figure 11 as (lower, middle, and upper troposphere) in addition to the full troposphere. They are also defined in section 3.3: "lower (up to 700hPa), middle (700-400hPa), and upper (400hPa to tropopause) portions of the troposphere". We have further defined them in the text in section 3.4.3.

Line 547: Include reference for biomass burning activity

Done!

Figure 16: This is a nice figure showing average CO anomalies in column mean 2005-2021 but with trends only until 2019 which is good. Can we have similar plots for $NO_2$?

The trends are calculated only until 2019 so that it is consistent with other species and model simulations. As per the reviewer's earlier suggestion, we have included additional figures for Trend summaries similar to that of NO2 and HCHO.

Figure 18, Summary of trends, for HCHO, why don't we have this type of plot for CO?

As per the reviewer's earlier suggestion, we have included additional figures for Trend summaries similar to that of NO2 and HCHO. Figure 24: Monthly anomalies of HONO from soil by region, please include trend data on these.

Done. The figure is now updated with the trend values and their uncertainties.

**C2: 'Comment on egusphere-2024-720', Anonymous Referee #2, 22 Apr 2024, Citation**:

https://doi.org/10.5194/egusphere-2024-720-RC2

We thank the reviewer for his comments. Our responses are in blue following each comment.

This manuscript describes global and regional trends of tropospheric ozone and its precursors ($NO_2$, CO, and HCHO) and aims to investigate the spatio-temporal characteristics of the ozone formation regime. Satellite observations of the tropospheric column have been used as the main data source, while ozone sonde data and GEOS-GMI model simulations have also been analyzed to study the sub-columns. The topic is central to the scope of the journal, and the trend analysis from OMI/MLS seems sufficiently valid.

However, particularly for the part analyzing ozone formation regimes, I find the authors' discussion rough and even flawed: my main argument is that without considering 1) the trends of "long-range transported" ozone, 2) the seasonality, or 3) the major components from lower/middle/upper tropospheric sub-columns that drive the trends (although treated in the model for Figure 11), the assessment of the regimes is not correct. For example, in lines 652-653, it is doubtful to conclude that most regions in the southern hemisphere are VOC sensitive regions (lines 365 and 652), simply from the fact that the trends of $O_3$ and HCHO are decreasing while the trend with $NO_2$ is increasing. In the atmospheric chemistry theory, VOC-limited conditions must occur where $NO_x$ is abundant (and thus OH loss is controlled by its reaction with $NO_2$), which is unlikely for "most regions in the southern hemisphere".

Answer: We agree with the reviewer that other factors contribute to the burdens of the tropospheric ozone column such as stratosphere-troposphere exchange (STE), regional and long-range transport of ozone precursors, reactivity, and seasonality. We have now included a discussion about possible contributions from STE as it has been recently highlighted as an important contributor to tropospheric ozone column especially in the middle and upper troposphere, and particularly in midlatitudes. We also noted in section 3.4.7 that this analysis does not consider variations of the ratios and their trends with respect to season or altitude. Regarding the chemical regimes, we have clarified that the trends of the HCHO/$NO_2$ ratio indicate moving towards a VOC or NOx sensitivity regime rather than already in a VOC or NOx-sensitive regime.

Another crude statement is made in lines 343-344, that the positive trends in the 30-60degS band are mainly driven by oceanic emissions, without any supporting results. All other parts discussing regimes need to be reviewed and reconsidered.

The statement has been further clarified (… and the positive trends in this band are contributed mainly by oceanic regions (see **Error! Reference source not found.**).).

The discussion on the TrC-HCHO/TrC-NO ratio (section 3.4.7) seems to be the opposite. If the ratio decreases, the chemical status must be becoming more VOC sensitive (rather than NOx sensitive, line 675). The increasing trend should indicate more NOx sensitive conditions (rather than ROx sensitive, line 678).

As explained in section 3.4.7, there are two important aspects to differentiate between, 1) the HCHO/NO ratio, 2) the trend in HCHO/NO2. The mean HCHO/NO2 ratio is shown in Figure 19. We explain in lines 657 – 665 that higher HCHO/NO2 ratio is related to NO sensitive condition as the reviewer pointed out. There is no discrepancy here.

We also added the following sentence to clarify the different interpretations of the HCHO/NO2 trends. “For example, over the eastern US and Europe, the HCHO/NO2 ratio (Figure 19) is low but the HCHO/NO2 trend is showing a slightly increasing trend indicating a direction towards the opposite, NO sensitive conditions.

However, there is a typo mistake in lines 675 and 678 that was made in the final stage of the article and was not detected before the submission. We thank the reviewer for mentioning this typo, which we have corrected.

I also did not understand why the positive emission trends with soil HONO in the southern hemisphere lead to a decrease in O3 (line 1074).

This is a typo and the sentence has been removed.

When presenting the satellite data used in Section 2.2.1, the authors need to describe what kind of data screening was applied, in particular with respect to cloud fraction and solar zenith angle. It is also necessary to describe which emission inventory was used for the GEOS-GMI model simulations has to be described (leading to an erroneous positive CO trend over East Asia).

The Satellite data products used in this article are already published and their references are listed in Table 1 and cited as appropriate in the text. The same applies to the GEOS-GMI setup and simulation results are described. In addition, we include now in section 2.2.3. a discussion and references for the emissions used in GEOS-GMI simulations.

In section 3.2, only the first authors papers are cited. It is needed to provide a more balanced citation.

More references are now cited.

Considering the importance of understanding the chemical regimes and providing valid information for the abatement strategy (line 141), I do not recommend publication of this manuscript in its current form.

The article has been revised including the reviewer’s comments.

**Community Comments, CC1: 'Comment on egusphere-2024-720', Owen Cooper, 02 May 2024**

**Major Comments:**

1) As stated on the first line of the abstract, methane is an important ozone precursor, but this paper does not address the distribution and trends of methane. Why has methane been omitted? Methane should be addressed as studies have shown its impact on recent ozone increases (Zhang et al., 2016), and as shown in Chapter 6 of IPCC AR6 (Szopa et al., 2021), the only future scenario with an increasing tropospheric ozone burden is SSP3-7.0, which is driven by increasing methane. NOAA GML observations of methane (https://gml.noaa.gov/ccgg/trends_ch4/ ) show that methane concentrations in the atmosphere have increased sharply since 2005 (an 8% increase from 2005 to 2023).

Answer: While oxidation of methane and NMHCs was mentioned in the introductory statement in the article, it was not investigated in this study since we focused in this article more on the reactive species, NO2, CH2O, and CO. Methane is an important precursor and we also think future assessments should focus on its analysis to include methane and other precursors.

We have included the following paragraph in section 3.2 to address methane contribution to tropospheric ozone: While this paper focuses on ozone precursors with higher reactivity, we note that methane, with an assessed total atmospheric lifetime of 9.1 ± 0.9 years (Szopa et al., 2021), is also a crucial driver (Fiore et al., 2002; Isaksen et al., 2014), given its accelerated growing rate of 7.6 ± 2.7 nmol $mol^{-1}$ $yr^{-1}$ between 2010 and 2019 (Canadell et al., 2021), largely driven by anthropogenic activities (Szopa et al., 2021).

2) Lines 66-68 When summarizing global tropospheric ozone trends, the best reference is Section 2.2.5.3 in Chapter 2 of IPCC AR6 (Gulev et al., 2021). While observations in the Southern Hemisphere are limited compared to the northern hemisphere, the available in situ and satellite observations do indicate an increase of ozone since the late 20th century: "Observations in the SH are limited, but indicate average tropospheric column ozone increases of 2–12% (1–5 ppbv) per decade in the tropics (Figure 2.8c), and weak tropospheric column ozone increases (<5%, <1 ppbv per decade) at mid-latitudes (Cooper et al., 2020). Above Antarctica, mid-tropospheric ozone has increased since the late 20th century (Oltmans et al., 2013)."

Answer: We thank Owen for this comment and we have updated this sentence as follows: "…..radiative forcing of $(0.47^{+0.23}_{-0.23})$ W $m^{-2}$; Forster et al., 2021). Since the mid-1990s, free tropospheric ozone trends based on in situ measurement and satellite retrievals have increased with high confidence by 1-4 nmol $mol^{-1}$ $decade^{-1}$ across the northern mid-latitudes and 1-5 nmol $mol^{-1}$ $decade^{-1}$ within the tropics (Guleb et al., 2021). In the Southern Hemisphere, with more limited observation coverage compared with the Northern Hemisphere, the tropospheric column ozone shows an increase since the mid-1990s by less than 1 nmol $mol^{-1}$ $decade^{-1}$ with *medium confidence* at southern mid-latitudes (Gulev et al., 2021, Cooper at al., 2020). Tropospheric $O_3$ short- and long-term..".

3) As stated in Section 5 of the 'Guidance note on best statistical for TOAR analyses': "One of the most critical components of statistical analysis is to acknowledge the uncertainty. Every estimation must be accompanied by a quantification of the associated uncertainty (or error bar), which is used to assess the reliability of the (trend) estimate and is considered to be as equally important as the estimate". According to the guidance note, all trends need to be reported with the 95% confidence intervals and p-values. Basically, a trend value without an uncertainty

estimate is meaningless. For example, on lines 463-466 model trends are compared to OMI/MLS trends. But because the model trends have no uncertainty range, the trend value is meaningless and no conclusions can be drawn from this comparison.

Answer: We added error bars to the model trends in Figure 11 and clarified the model trend discussion. All trends are now shown with their corresponding error.

4) Another important piece of advice from the ‘Guidance note on best statistical for TOAR analyses’ is that all TOAR analyses should abandon the use of the phases “statistically insignificant” or “statistically significant”. Compelling arguments for this policy are provided by the highly influential paper by Wasserstein et al., 2019. The submitted paper has many instances of the phrases “statistically insignificant” or “statistically significant”. These phrases need to be removed, and they can be replaced by statements from the authors regarding their confidence in the reported trend values. Advice is given in the Guidance Note, and this advice can also be applied to figures such as Figure 13.

Answer: We appreciate the advice, and we will certainly consider in future submissions.

5) Section 3.5 I found the section on LNOx to be too long and it lacks clear statements on lightning trends. While the section cited previous work that thunderstorm days have increased in some regions (and decreased in others), no number were given, so it’s not clear by how much thunderstorm days have increased. In terms of flash rate, some regions showed increases and some showed decreases, but there was no summary statement that lets the reader know if lightning has clearly increased or decreased on the global scale. Line 714 states that lightning contributes to positive ozone radiative forcing, but it’s not clear to me that this is really the case. In the UT ozone has a strong longwave radiative effect (i.e. it absorbs outgoing longwave radiation) and of course LNOx can affect ozone in the UT and therefore affect ozone’s longwave

radiative effect. But are there any studies that have shown that LNOx impacts ozone's radiative forcing (as opposed to ozone's longwave radiative effect)? IPCC defines radiative forcing as the change in the Earth's radiative balance since 1750. If lightning is impacting radiative forcing then there must be conclusive evidence that lightning frequency has increased on the global scale. If there is no clear evidence for a global increase (or decrease) of lightning then the link to radiative forcing cannot be established.

Answer: Section 3.5 has been shortened and a table has been removed. Section 3.5.1 now has a rough estimate of the global trend in thunder days, and makes it clear that no long-term trend in global flash rates has been detected. All mentions of "radiative forcing" have been removed, and instead, the terminology, "effects by ozone on longwave radiation absorption" is now used.

6) lines 391-393 Regarding the number of ozone profiles required to accurately detect a trend, several studies over the years have shown that once-per-week sampling is often inadequate for accurate trend detection. A paper recently accepted for publication in the TOAR-II Community Special Issue (Chang et al., 2024) addresses this issue, and the paper's conclusions need to be considered when interpreting ozone trends based on sparse sampling.

Answer: We acknowledge this limitation, and we further clarified this aspect in the text including two references (Chang et al., 2020 and Chang et al., 2024). However, as mentioned by Chang et al (2024) only 3 European stations have achieved such high sampling frequency (Hohenpeissenberg, Germany; Payerne, Switzerland, and Uccle, Belgium). In the meantime, despite the lower sampling frequency at the rest of the global stations, ozonesonde observations continue to be the gold standard against which satellite data are validated. Furthermore, ozonesonde climatologies are critical to provide feedback to satellite observations for which they continue to be used with this long-term purpose. Thus, with proper acknowledgment of the frequency limitation, we believe that ozonesonde trends published in previously peer-reviewed studies are valuable information for the ozone community.

7) Line 362 Here it is claimed that the pandemic period led to increases in emissions and therefore an increase in the ozone rate of change, but no convincing references are provided to support this claim. The paper by Oleribe et al. 2021 has nothing to do with atmospheric chemistry, and the paper by Matandirotya et al., 2023 only looks at 3 cities in South Africa. This statement seems like speculation and it should be removed.

Answer: It is not mentioned in any part of the article that "the pandemic period led to increases in emissions and therefore an increase in the ozone rate of change"

We mentioned that the higher $O_3$ trends in the southern hemisphere is due to the lesser impact of the pandemic and we cited Oleribe et al. (2021) since they explained "why Sub-Saharan Africa Experienced a less severe COVID-19 Pandemic in 2020". Similarly, Matandirotya et al., 2023 assessed the $NO_2$ atmospheric air pollution over three cities in South Africa during 2020 COVID-19 pandemic, and both articles cover important regions in the southern hemisphere. However, we agree that these references do not provide concrete evidence as to why $O_3$ trends in the southern hemisphere were higher, therefore we remove this sentence as suggested.

8) Section 3.4.2 This section seems to only review ozone trends from previous studies by Wang et al., 2022 and by Christiansen et al., 2022. Does this paper actually calculate updated trends from available ozonesonde records? Section 2.2.2. in the Methods section lists ozonesondes as a data source, but I see no new data analysis.

Answer: Figure 9 was prepared by the authors for this paper, using trends from Wang et al 2022. As pointed out, this portion of the manuscript is based on a review of global ozonesonde trends calculated and published in previous studies (Wang et al., 2022 and by Christiansen et al., 2022). This is indicated in the caption of Figure 9. However, we added a sentence at the bottom of the corresponding methods section for further clarification.

**Minor Comments:**

line 66 The stated radiative forcing for ozone (0.34) is incorrect. As reported in Section 7.3.2.5 of Chapter 7 of IPCC AR6 (Forster et al., 2021), ozone has an assessed effective radiative forcing of 0.47 [0.24 to 0.70] W m–2.

Answer: The numbers we showed are correct for the global average Radiative Forcing (RF) of ($0.34^{+0.09}_{-0.06}$ W $m^{-2}$; IPCC, 2023) for clear sky conditions based on the *Ramaswamy et al., 2018 (IPCC AR6)*. Page 363 of the IPCC AR6 report states that "For total sky conditions, the range in globally and annual averaged tropospheric O3 forcing from all of these models is from 0.28 to 0.43 Wm−2,… The tropospheric O3 forcing constrained by the observational climatology is 0.32 Wm−2 for globally averaged, total sky conditions."

The numbers in the comment are for Effective Radiative Forcings (ERF), which include all tropospheric and land surface adjustments, particularly aerosol-cloud interactions to aerosol forcing, which is highly uncertain itself (Smith et al., 2020, https://doi.org/10.5194/acp-20-9591-2020). Both numbers are correct but reflect different things and are nevertheless very close (within the uncertainty range). However, since the reference Forster et al., 2021 is newer and include the latest increase of GHG as well as improved cloud parameterization for RF, we will update our number to that reference.

Line 76 More context needs to be given regarding the ozone increase of 40 ppb. Is this at the surface or in the free troposphere? Over which continent? If stating the extreme ozone increase, it would help to also provide the average ozone increase. A useful number is the approximate 45% increase in the tropospheric ozone burden. A recent paper published in ACP (Nussbaumer et al., 2023) is highly relevant to this submission and some discussion of their conclusions is warranted.

Answer: The sentence has been updated as follows: CMIP6 models simulate large increasing trends of surface concentrations of $O_3$ and $PM_{2.5}$ in East and South Asia with an annual mean increase of up to 40 ppb and 12 $\mu gm^{-3}$, respectively, over the historical periods (1850-2014; Turnock et al., 2020). The reference is useful, and we have cited it properly.

Line 350 When discussing the impact of COVID-19 on tropospheric ozone there are some key papers that should be cited: Steinbrecht et al., 2021; Chang et al., 2022; Putero et al., 2023

Answer: References are cited now.

Line 400 Very strong ozone trends above Japan since 2010 was not a major conclusion of Christiansen et al. (2022). They only show the higher ozone values after 2010 in the supplement, and they recommend that these data sets be treated with caution because the instruments changed from carbon-iodide to ECC after 2010; these time series have not been homogenized to correct for the change in instruments.

Answer: We updated the sentence to "For example, ozone in East Asia (Japan) has been increasing at a cautious rate of 3.5 to 5 ppbv/decade, particularly since 2010 (Christiansen et al., 2022)."