Response 1

In “Tropospheric Low Ozone and Its Diurnal Cycle over the Western Pacific Warm Pool from Solar Absorption FTIR observation”, Sun et al. present FTIR-based tropospheric ozone column measurements over the Palau Atmospheric Observatory in the Pacific Warm Pool between September and October 2022. Low ozone is observed and attributed to the low precursor availability, including low lightning activity, and the transport of clean marine air. The authors find a pronounced diurnal cycle of ozone, which cannot be reproduced by GEOS-Chem model simulations.

The paper is well-written and presents interesting observations in a part of the globe that is currently still understudied, but highly important to atmospheric chemistry processes with global implications. I have a few questions and comments. Once these are addressed, the paper will be a valuable addition to the current literature.

Specific comments:

L. 31 f.: An important removal process for O_3, that’s missing here, is photolysis and subsequent reaction with H_2O, particularly in the marine boundary layer.

Response: Yes, we agree with you and thank you for this helpful comment. The photolysis-driven ozone loss pathway was previously implicit in our discussion of HOx chemistry. To make this more explicit, we have revised the text to clearly state that ozone photolysis followed by reaction with water vapor constitutes a major primary removal pathway in the sunlit marine boundary layer. This process acts as a principal source of OH radicals, thereby initiating and sustaining subsequent HOx-mediated ozone loss cycles. In the revised manuscript, this process has been moved to the beginning of the ozone removal discussion to better reflect its importance under clean marine background conditions, relative to processes such as dry deposition.

We added in L31:

“In the sunlit marine boundary layer, a major chemical sink of ozone is photolysis, followed by reaction of excited oxygen atoms with water vapor, producing OH radicals (Levy, 1971). Additionally ...”

L. 33 f.: The reaction of NO with O_3 is not really a sink of O_3 because NO_2 can be photolyzed back to O_3 and the interconversion occurs on a short timescale.

Response: We agree that, in sunlit, low-NO_x marine environments, ozone loss is dominated by photolysis followed by reaction with water vapor and subsequent HOx chemistry, whereas other processes play a more limited role in controlling ozone concentrations. To avoid overemphasizing non-dominant pathways, we have removed dry deposition from this paragraph and revised the text to focus on the chemically relevant ozone loss processes under marine boundary layer conditions.

L. 250 / Figure 2: Which area does the model represent? Is it the grid extracted at the observatory? How do the error bars look like?

Response: The model results shown in Fig. 2 represent the GEOS-Chem grid cell containing the Palau Atmospheric Observatory (PAO), corresponding to the 2° × 2.5°

grid box spanning 132.5°–135° E and 6°–8° N. No additional spatial averaging was applied.

The error bars indicate the temporal standard deviation (1σ) of the model output over the averaging period. Because model-simulated ozone over the tropical marine region exhibits relatively weak temporal variability, the resulting error bars are small.

L. 267 / Figure 3: Are these hourly averages including all observation days? I recommend adding error bars to the plot or showing them in the Supplement.

Response: Yes, the hourly averages include all available observation days during the campaign. We have added error bars to quantify the variability within each hourly bin.

L. 270: Is there really any significant variation in the model throughout the day? Please add error bars.

Response: We agree that the modeled diurnal variation is weak. To address this, error bars have been added to the hourly mean model results in the revised manuscript (Fig. 3). These error bars represent the temporal standard deviation (1σ) of the model output within each hourly bin.

The small magnitude of the error bars reflects the smooth temporal behavior of simulated ozone over the tropical marine region, indicating that the model exhibits little intrinsic diurnal variability. The modeled ozone diurnal cycle is now provided in the Appendix.

L. 276: What about the diurnal cycle of other trace gases? And it would be interesting to look at the diurnal cycle of ozone production and loss, since you have the GEOS Chem outputs.

Response: We thank the reviewer for this suggestion. Following this comment, we have analyzed the modeled diurnal cycles of NO, NO_2, and OH, and added the results to Appendix B (Fig. B1).

The model results show that while these radicals exhibit significant relative diurnal variability (e.g., OH increases by midday), their absolute concentrations remain extremely low (peak OH < 0.5 ppt; NO < 20 ppt; NO_2 < 40 ppt). Under these pristine conditions, the absolute magnitude of net ozone photochemical production and loss is too small to drive a discernible diurnal amplitude in the O_3 column. This analysis explains why the model's O_3 cycle appears muted despite active diurnal chemistry in the model. We have updated the manuscript (Lines 278-282) to include this discussion.

L. 291 f.: Is the pattern significant given the large variability in the data points? Please add error bars.

Response: We agree that the variability of individual data points needs to be quantified. In the revised manuscript, we clarify that the diurnal pattern is assessed based on hourly mean values rather than individual measurements. We add error bars representing the uncertainty of the hourly mean (standard deviation).

In addition, we include supplementary figures showing the hourly mean concentrations from ozonesonde with their variability in Appendix A, Fig. A1.

L. 319: HCHO is not only a precursor, but also an important by-product of O_3 formation from VOCs.

Response: We agree that HCHO is not solely an ozone precursor, but also an important intermediate and by-product of VOC oxidation associated with ozone formation. We have revised the text to distinguish between ozone precursors and photochemical tracers, and no longer refer to HCHO as a precursor. The revised sentence is this:

“Satellite retrievals support this interpretation. A broad ozone minimum is evident over the western Pacific warm pool (Fig. 4c), coinciding with low column densities of major ozone precursors and photochemical tracers, including CO (Fig. 4d), HCHO (Fig. 4e), and NO_2 (Fig. 4f).”

L. 325: NO_x itself is not removed by precipitation; it can only be removed indirectly after formation of HNO_3.

Response: We agree that NO_x itself is not directly removed by precipitation. We have revised the text to clarify that precipitation removes nitrogen reservoir species formed from NO_x oxidation (e.g., HNO_3), thereby indirectly reducing NO_x availability for ozone production. The revised sentence is like:

“Enhanced humidity in the tropical troposphere promotes ozone loss via OH chemistry. At the same time, precipitation efficiently removes soluble species such as HCHO and nitrogen reservoir species produced from NOx oxidation (e.g., HNO_3), indirectly reducing NOx availability and suppressing ozone production.”

L. 325: Is Rex et al., 2014, really the correct citation here regarding the washout of soluble species?

Response: Thanks, we agree. To avoid an imprecise citation, we have revised the text and removed this reference. The statement is now presented as a general description of well-established processes in the tropical troposphere.

L. 328 f.: HCHO might not be transported over long distances, but it can be formed locally from longer-lived VOCs, including CH_4.

Response: We agree that HCHO can be produced locally from the oxidation of longer-lived VOCs, including methane, and is therefore not solely controlled by transport. We have revised the text to clarify that the low HCHO columns over Palau reflect weak VOC oxidation and overall photochemical activity under pristine marine conditions, rather than inefficient transport alone. The interpretation for NO_2 remains based on its short lifetime and limited transport. The sentence has been revised like:

“HCHO, while also short-lived, is primarily produced locally through VOC oxidation; its low abundance therefore indicates weak photochemical activity under pristine marine conditions (Fig. 4e), further limiting in situ ozone formation.”

L. 368 / Figure 6: Could the authors also show a panel for NOx to highlight the changes introduced by the sensitivity run?

Response: We agree that changes in NO_x are relevant for interpreting the sensitivity experiments. We have added the plots for NOx (Fig. C1) in the appendix and the difference between the base and the sensitivity simulations for NOx (Fig. 6).

L. 371: Is the difference really only 7 pptv? If so, that would show that lightning has basically no impact on O_3 (< 0.1%). Or is 7 ppbv meant here? However, that would be a surprisingly large impact.

Response: We thank the reviewer for pointing this out. The unit in Fig.6 was incorrectly labeled as pptv and has been corrected to ppbv. The simulated ozone differences associated with the lightning NOx sensitivity experiments are on the order of several ppb, reaching approximately 5–10 ppb over the tropical western Pacific.

While this magnitude may appear large, it reflects the strong chemical sensitivity of free-tropospheric ozone to NOx under low-background conditions, where lightning constitutes a major NOx source. These sensitivity experiments are intended to illustrate the chemical response under idealized conditions rather than to represent realistic variability.

L. 373: I recommend adding a sensitivity study with enhanced lightning, e.g. doubled or tripled lightning NO_x emissions. The Warm Pool experiences very low lightning activity and therefore it would be interesting to show the impact of lightning enhancements on O_3 and OH as well.

Response: Yes, thank you for this suggestion. We add the simulation with 2xLnox and put the results in the Fig. 6.

Technical comments:

L. 226 f.: Please double-check the sentence: double use of “available”.

Response: Checked and deleted the words “available”.

L. 406: Do you mean day-to-day variation here? “Daily” implies “Diurnal” to me.

Response: Yes, thanks. We changed the word to “day-to-day”.

L. 440: Same here; day-to-day would be better than daily.

Response: Yes, thanks. We also changed the word to “day-to-day”.

Response 2

Tropospheric low ozone and its diurnal cycle over the Western Pacific warm pool from solar absorption FTIR observations.

General comment

This manuscript investigates the diurnal cycle of tropospheric ozone above Palau (7.3°N, 134.5°E), using primarily observations performed with a FTIR spectrometer during a campaign-type effort. More specifically, two months of observations collected in September-October 2022 are analyzed and interpreted, taking advantage of supporting data sets consisting in ozone soundings performed from the same place, GEOS-Chem dedicated simulations, 10-days HYSPLIT back-trajectories and satellite observations of precursors (e.g., CO, H_2CO) as well as other relevant parameters (cloud effective radius, dust aerosol information). The scientific motivation lies in the exceptionally low tropospheric ozone levels which are characterizing the Tropical Western Pacific (TWP) and the Western Pacific Ocean warm pool, and this manuscript intends to advance our understanding of the factors at play.

After a nice overview of previous works, the authors carefully characterize and exploit the tropospheric ozone measurements at hand. An uncertainty budget is established, and the sensitivity of the FTIR measurements in the troposphere is evaluated, notably accounting for the effect of the viewing geometry (solar elevation). These are compared with sondes measurements and GEOS-Chem simulations, allowing the authors to determine typical abundance of tropospheric ozone for the available time period and to derive its diurnal variation, showing maximum concentrations around noontime. A reasonable agreement is found with the soundings data. GEOS-Chem is shown to reproduce day-to-day variations fairly well but fails to capture the diurnal cycle.

Overall, this is an interesting manuscript, logically organized. The figures have been prepared with care and they are readable. This study conveys useful information to the scientific community. At places, I found that the English could have been improved or polished, but this will likely be handled by the journal at a later stage.

I would recommend publication after consideration of the suggestions provided below.

Major comments

Figure 3 is really central in this study, as it presents the diurnal variation of tropospheric ozone over September-October 2022 derived from the FTIR observations, with a comparison to other data sets. However, we only have partial information on how the measurements have been combined, and we also lack information on the measurement statistics, leaving the reader unsure about the relative weight of each circle/mean in the panel a of Figure 3. I would recommend providing such information: how many days, how many measurements were retained to compute these averages? Furthermore, my view is that some uncertainty information should be added to each means, e.g., the standard deviation around each of them. This way, we would have a better feeling on the possible maximum or minimum magnitude of the tropospheric ozone diurnal cycle. At present, the authors somewhat speculate (line 299) that the amplitude of the variation could be larger than as indicated by the FTIR, but the low-end value of 6 ppb does not account for any uncertainty other than the possible “damping effect”.

Response: Thank you for your constructive suggestion. We have revised Fig. 3 and the accompanying text to clarify how the diurnal means are constructed and to better quantify their statistical robustness.

Specifically, we now explicitly report the number of days and individual FTIR measurements contributing to each hourly bin. In addition, error bars (±1σ) from FTIR and model have been added to Fig. 3a, representing the standard deviation of the FTIR-derived and model simulations of the tropospheric ozone column within each hourly bin and thus reflecting hour-to-hour in Fig.3 and day-to-day variability in Fig. 2. The error bars (±1σ) from ozonesonde have been added to Fig. A1 in the Appendix.

We emphasize that these error bars characterize statistical variability rather than retrieval systematic uncertainties, which are discussed separately in Sect. 2 and Appendix A. With this clarification, the observed peak-to-peak diurnal amplitude of ~6 ppb should be interpreted as a lower bound on the near-surface variability, while the statistically robust afternoon decrease remains well supported by the FTIR observations.

These sentences have been added in the method section “Solar absorption FTIR spectrometry and O_3 measurement campaign”:

“The number of FTIR measurements contributing to each hourly bin ranges from 10 to 55, with the highest sampling between 11:00 and 14:00 local time. Each hourly bin includes measurements from multiple independent days (typically 3–10 days per hour, see appendix).”

These sentences has been added in the result section “Tropospheric Ozone Measurement by FTIR and Comparison with Ozonesondes.”

“The error bars in Fig.3a indicate an hourly variability of approximately 2–6~ppb (±1σ).”

In the Figure 3 caption, we also add the note that “Error bars denote ±1σ variability within each hourly bin.”

Minor comments

[line 30] are we missing some parentheses around Müller et al. and Anderson et al.?

Response: Thank you. We added the parentheses.

[line 65] in case of reduced oxidative capacity, I would expect a lengthening of the reactive trace gas lifetimes as one of the sink is of less importance?

Response: Yes, we change “shortening” to “lengthening”.

[Table 1] Is water vapor the only fitted interference in such a busy spectral region? Is the adopted retrieval strategy commonly used in your community? If yes, this should be mentioned and at least one relevant reference should be added.

Response: We thank the reviewer for raising this point. We clarify that water vapor is not the only interfering species considered in the retrieval. In the revised Table 1, we now explicitly list all interfering gases included in the retrieval window.

In the adopted retrieval strategy, H_2O is the only interfering species whose profile is actively fitted, as it exhibits strong variability and has a dominant impact on the FTIR profile retrieval in this humid tropical environment. Other interfering species are included with fixed a priori profiles, as their variability is expected to be small at this remote marine site and their influence on the retrieved ozone profile is limited.

This retrieval approach is commonly used in the FTIR community for remote sites and tropical conditions, and has been applied in previous studies (e.g., Vigouroux et al., 2015). We have clarified this point in the text and updated Table 1 accordingly.

[line 109] What is typically the tropopause height above Palau in September-October?

Response: The height of the cold point tropopause is around 16-18 km. We added one note for this here for clarity:

“The vertical range we use in this study represents the low troposphere in the tropical region.”

[Equation 1] There is a bit of confusion resulting from the use of the “column” wording [e.g., line 116] and the adoption of the “TOC” acronym (expressed in ppb), while in fact it is a mole fraction, as correctly stated on [line 113].

Response: We thank the reviewer for this insightful comment. We agree that the term "Total Ozone Column (TOC)" is conventionally associated with the integrated total abundance expressed in Dobson Units (DU), and using it to represent a mole fraction in ppb could lead to confusion.

To resolve this and ensure physical consistency, we have revised the manuscript as follows:

1. Refined the Definition: We have clarified that $X_{O3,p}$ is a column-averaged mole fraction, derived by dividing the ozone partial column by the dry-air partial column.
2. Clarified the Units: We have added an explicit note stating that this quantity represents a normalized concentration (ppb), which is equivalent to a column-weighted mean mixing ratio (ppb) calculated by dividing the ozone partial column by that of the dry air. This is to facilitate direct comparison with ozonesonde profiles and model outputs.

Revised text (Lines 113–120):

"$X_{O3,p}$ represents the dry-air partial column-averaged mole fraction of ozone, which is equivalent to a column-weighted mean mixing ratio (ppb) calculated by dividing the ozone partial column by that of the dry air. This approach is adopted to facilitate direct comparison with ozonesonde profiles and model outputs. For simplicity, $X_{O3,p}$ is hereafter referred to as the tropospheric ozone column-averaged mole fraction (TOC), noting that its unit (ppb) distinguishes it from the total column abundance expressed in Dobson Units (DU)."

[line 124] …and this inevitably…

Response: Corrected.

[line 137] Please rephrase this sentence.

Response: We rephrased it:

“When interpreting the diurnal cycle from FTIR-derived TOC, the SZA dependence of the measurements should also be considered.”

[Table 2] Why is the day-to-day variability lacking a relative uncertainty (in %)?

Response: We added a relative uncertainty.

[line 209] It is stated that the soundings are released at varying times, but the morning time period does not seem to be covered (based on Fig. 3). Why is this the case?

Response: We thank the reviewer for this question. During the September–October 2022 campaign, ozonesonde launches at Palau were not conducted in the morning, as the launch times were determined by operational and logistical constraints of the routine sounding program. Consequently, no morning ozonesonde data are available for this period.

As a result, the morning increase in ozone cannot be evaluated using ozonesonde observations. This time window is instead covered by the FTIR measurements, which provide continuous daytime observations from early morning to afternoon and therefore capture the full diurnal evolution. We added the following sentence:

“However, no launches were performed in the morning due to operational constraints. As a result, ozonesonde observations do not cover the morning period, which is instead captured by the FTIR measurements.”

[line 210] I feel like the end of the sentence, after the semicolon, should be rephrased?

Response: Yes, this sentence has been rephrased.

[line 257] Is the TOC on the 16 October 2022 really that low? I don’t see it standing as an outlier in Figure 2(a).

Response: We thank the reviewer for this comment. Upon re-examination, we agree that the value on 16 October 2022 does not stand out as a clear outlier in Fig. 2(a) when considering the overall variability during the campaign. We have therefore removed the sentence suggesting an anomalous event on that day to avoid over-interpretation of day-to-day variability.

[line 257] a space is missing (after “Figure 3b).

Response: Corrected.

[line 306] indicating that transport

Response: Corrected.

[line 312] boundary layer and increasing with…

Response: Corrected.

[lines 337 and 340] they appear redundant/repetitive, please check.

Response: Corrected. We deleted the redundant sentence.