

## **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<sub>2</sub>CO) 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 ( $\pm 1\sigma$ ) 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 ( $\pm 1\sigma$ ) 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  $\sim 6$  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<sub>3</sub> 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 ( $\pm 1\sigma$ ).”

In the Figure 3 caption, we also add the note that “Error bars denote  $\pm 1\sigma$  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<sub>2</sub>O 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  $X_{O_3,p}$  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):**

“ $X_{O_3,p}$  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,  $X_{O_3,p}$  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.