Air Mass Transport to the Tropical West Pacific Troposphere inferred from Ozone and Relative Humidity Balloon Observations above Palau

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Abstract.

Due to the unique local air chemistry, the transport history of tropospheric air masses above the remote tropical West Pacific (TWP) is reflected by local ozone (O_3) and relative humidity (RH) characteristics. In boreal winter, the TWP is the main global entry point for air masses into the stratosphere and therefore a key region of atmospheric chemistry and dynamics. However, a long-term in situ monitoring of tropospheric O_3 to assess the variability of TWP air masses and the respective controlling processes has yet been missing. The aim of our study was to identify air masses with different origins and pathways to the TWP and their seasonality using the new Palau time series (2016-2019) of mostly fortnightly Electrochemical Concentration Cell ozone and radio soundings. Based on monthly statistics of O_3 volume mixing ratios and RH we defined a free tropospheric locally-controlled background and analyzed anomalies for both tracers in the 5-10 km altitude range. We found that anomalously high O_3 indicates a remote origin, while RH is controlled by a range of dynamical processes resulting in a bimodality in RH anomalies. The Palau time series confirms a year-round presence of low O_3 background air masses and a seasonal mid-tropospheric cycle in O_3 with a prominent anti-correlation between O_3 volume mixing ratios and RH. We assumed five different types of air masses with differing tracer characteristics and origin which we validated by analyzing backward trajectories calculated with the transport module of the Lagrangian chemistry and transport model ATLAS. The main result is a clear separation of origin and pathways for the two most contrasting types of air masses, i.e. ozone-poor and humid versus ozone-rich and dry air. Both, potential vorticity and air mass origin analyses, reveal no indication for stratospheric influence for the ozone-rich dry air masses. Rather, we found indications for O_3 production due to biomass burning or anthropogenic pollution at the origins of these air masses and drying due to clear sky subsidence during long-range transport. The seasonal occurrence is tied to the position of the Intertropical Convergence Zone which opens a pathway from potential source regions which are confirmed by the trajectory analysis.

We conclude, that dominant ozone-poor and humid air masses are of local or Pacific convective origin and occur year-round, but dominate from August until October. Anomalously dry and ozone-rich air is generated in Tropical Asia and subsequently transported to the TWP via an anticyclonic route, mostly from February to April. The areas of origin suggest different sources of ground pollution as a cause for O_3 production. We propose large-scale descent within the tropical troposphere and subsequent radiative cooling in connection with the Hadley circulation as responsible for the vertical displacement and dehydration.

1 Introduction

The Tropical West Pacific (TWP), an area extending from the Maritime Continent to the International Date Line, is considered the major air mass transport pathway from the troposphere to the stratosphere during boreal winter (e.g., Newell and Gould-Stewart, 1981; Fueglistaler et al., 2004; Krüger et al., 2008). Air masses entering the stratosphere here, also originate in the local TWP boundary layer and free troposphere (Rex et al., 2014). Thus, the local tropospheric air composition has a key impact on concentrations of various chemical species within the global stratosphere, even up to a potential impact on polar ozone depletion.

Understanding (1) the variability of composition and transport of air masses to this region as well as (2) the unique air chemistry are therefore of great relevance. The monitoring of tropospheric ozone (O_3) volume mixing ratios (VMR) sheds light on both aspects: (1) O_3 is a chemical tracer for both local convection ("low" O_3 in clean, maritime air, e.g. Kley et al. (1996); Pan et al. (2015)) and long-range transport processes to the region ("high" O_3 from polluted or stratospheric origin, e.g. Anderson et al. (2016); Randel et al. (2016); Tao et al. (2018)). (2) The hydroxyl (OH) radical essentially defines the oxidizing capacity of the local troposphere; the close coupling of O_3 and OH in the very low NO_x environment of the TWP (Levy, 1971) allows estimation of the OH abundance from O_3 and relative humidity (RH) measurements and thus assessment of chemical lifetimes (e.g., Rex et al., 2014; Nicely et al., 2016; Bozem et al., 2017).

Major research activities focusing on tropospheric air chemistry and O_3 observations have been conducted in the wider region since the late 1980s (e.g., Pan et al. (2017) and overview in Müller (2020)). The typical tropospheric composition of the TWP has been related to the local humid, marine, pollution-free environment, favouring O_3 destruction (e.g., Kley et al., 1996; Levy, 1971):

$$O_3 + h\nu(\nu < 310\,\text{nm}) \rightarrow O_2 + O(^1D) \tag{R1}$$

$$O(^1D) + H_2O \rightarrow OH + OH \tag{R2}$$

Observations in the TWP found low NO_x concentrations inhibiting O_3 production and thus facilitating an O_3 loss rate via the above reactions of 3.4% per day (Crawford et al., 1997). For boundary layer O_3 in the equatorial Pacific the efficiency of this loss mechanisms results in a lifetime of around 5 days (e.g., Liu et al., 1983; Kley et al., 1997). Lifting the clean boundary layer air up to the Tropical Tropopause Layer (TTL), deep convective outflow in conjunction with convective overturning and a lack of in situ net O_3 production creates a well-mixed, humid tropospheric profile with a uniform vertical O_3 distribution (e.g., Pan et al., 2015). These typical dynamical conditions are conducive to a respective zonal wave one pattern with a persistent tropospheric O_3 minimum in the TWP in particular (e.g., Thompson et al., 2003b; Rex et al., 2014).

Many studies highlight dry intrusions of enhanced O_3 VMR against the humid, ozone-poor background as characteristic features of the mid-troposphere for the wider tropical Pacific (e.g., Newell et al., 1999; Stoller et al., 1999; Thouret et al., 2000; Browell et al., 2001; Oltmans et al., 2001; Hayashi et al., 2008; Pan et al., 2015; Anderson et al., 2016). The importance of these distinct, anomalous layers for local air composition and climate forcing are often acknowledged (e.g., Mapes and Zuidema,

1996; Kley et al., 1997; Yoneyama and Parsons, 1999). Their genesis, source region and impact on the local radiative budget
60 and oxidizing capacity are, however, the subject of an ongoing debate (Anderson et al., 2016; Randel et al., 2016; Nicely et al.,
2016; Tao et al., 2018). Most studies agree, that they have been advected from remote regions and thus indicate a departure
from the above described dominating conditions, i.e. an absence of the local imprint on air composition (see Anderson et al.,
2016, for an overview).

A long-term monitoring of tropospheric O_3 in the TWP as a key region of stratospheric entry has yet been missing (Smit and
65 Thompson, 2021), but is essential to clarify the source regions of air masses and their annual and interannual variability. All
relevant major research campaigns in the TWP were temporarily limited to specific seasons and years (e.g. PEM Tropics/West
(Newell et al., 1996), CEPEX (Kley et al., 1996), TransBrom (Krüger and Quack, 2013; Rex et al., 2014), CONTRAST/CAST
(Pan et al., 2017)). To fill the observational gap, the Palau Atmospheric Observatory (PAO) has been established in 2015 and
has since been providing an unprecedented regular balloon sounding program for O_3 and RH. It is located in the center of
70 the warm pool on the island state Palau, 1000 km east of the Philippines (7.34° N, 134.47° E). The instrumental setup and
meteorological conditions for the time series used in this study are introduced in more detail in a companion study by Müller
et al. (2023) (c.f. Müller, 2020).

The aim of this study was to examine major air mass transport processes and pathways to the TWP troposphere by using
balloon-borne O_3 and RH measurements from the PAO. Based on our process understanding explained in Section 3.1.3, we
75 propose five major air mass pathways to Palau resulting in distinct relations between the O_3 abundance and RH in the column
of air above the TWP. The continuous 4 years ozone- and radiosondes time series (2016-2019) enables a seasonal analysis of
the source regions, reflected mainly in the O_3 variability. We distinguished between air mass categories first using a statistical,
data-based approach and performed a seasonal analysis. Lagrangian backward trajectories were then used to verify an according
differentiation in air mass origin. A potential vorticity (PV) analysis was included to investigate a possible stratospheric origin.
80 In the following, we first introduce the observational data (Sect. 2) and methods (Sect. 3) used to define different categories
of air masses, which we relate to different pathways to Palau (Sect. 3.1.1). Main results of this study are the characterization
of seasonal tropospheric air mass variability (Sect. 4.1) and the verification of our process-based understanding of air mass
transport using trajectory modelling (Sect. 4.2). After a discussion (Sect. 5), we conclude (Sect. 6) that the maximum of the
mid-tropospheric seasonal O_3 cycle can be associated with long-range transport mainly from potentially polluted areas in
85 South East Asia. We found no evidence of transport from the extra-tropical stratosphere. Additional figures with more details
on the full seasonal extent are in the Appendix.

2 Data

2.1 Sondes

Our analysis is based on Electrochemical Concentration Cell (ECC) ozonesonde and radiosonde observations from 01/2016-
90 10/2019 conducted at the PAO. Balloon-borne measurements with ECC ozonesondes (Komhyr, 1969; Smit, 2014) are the
most practical way to observe and continuously monitor O_3 in situ, especially at more remote sites (e.g., Thompson et al.,
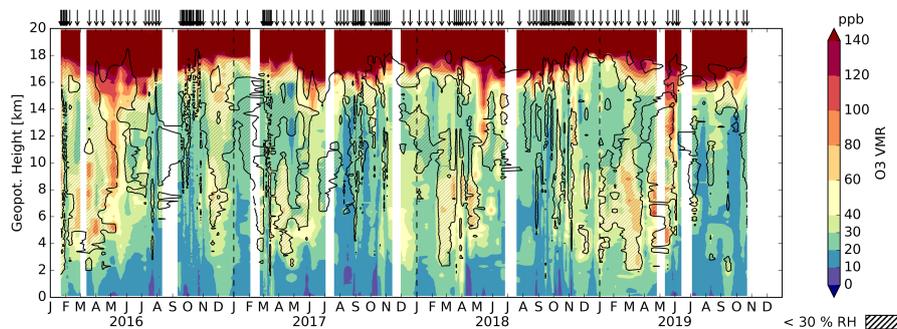
Figure 1. Tropospheric (0-20 km) time-height cross-section of O_3 VMR (in colors) and coinciding RH observations below 30 % (hatched areas enclosed in black contours) derived from PAO sounding data; arrows on top indicate individual soundings; data is linearly interpolated between soundings; measurement gaps longer than 20 days are in white, beginning 7 days after/before the last/next sounding; note the non-linear scaling; O_3 VMR are calculated using a pressure dependent background current correction, see Müller et al. (2023) for more details.

2019). The specific instrumentation (models SPC 6A and Vaisala RS92/41) and dataset are introduced and described in detail by Müller et al. (2023), who provide additional meteorological and climatological context for the Palau time series. While carefully following the Standard Operating Procedures (SOP) as recommended by Smit (2014), the O_3 VMR are calculated

95 using a pressure dependent background current correction (see Müller et al., 2023, for details). Figure 1 shows a time-height cross-section of the dataset with individual soundings marked by arrows, ozone in colors and RH observations below 30 % enclosed in hatched contours. Fortnightly measurements, mostly during mid-day, are complemented by one or two intensive campaigns per year. The onset of measurements in the beginning of 2016 coincides with a very strong El Niño event (e.g., Huang et al., 2016; Diallo et al., 2018). As a consequence and in compliance with acknowledged El Niño Southern Oscillation

100 (ENSO) indices (c.f. Müller et al., 2023), data before August 2016 was disregarded in some of the following statistical seasonal analysis and will be referred to as "excluding El Niño 2016". The 2019 El Niño episode, weaker in nature, is still included.

The sparsity of the O_3 data with a sounding frequency of zero to eleven launches per month and the resulting non-uniform distribution of the data affects the assessment of the temporal variability in our 4-year time series, which is still short for climatological studies. Details about our statistical averaging calculations can be found in the Appendix B. For the trajectory

105 analysis, the dataset was limited to 138 soundings due to missing meta data (timestamps) in some of the soundings and the vertical profile resolution was reduced by selecting every 10th sonde reading. This dataset will be referred to as the trajectory dataset, including 13627 individual observations in the 5-10 km altitude range.

2.2 Meteorological Data

Back trajectory calculations were driven by 3D meteorological fields and diabatic heating rates from the European center
110   for Medium-Range Weather Forecasts (ECMWF) Reanalysis data ERA5 in a 1.125° x 1.125° horizontal and 3 h temporal
resolution (Hersbach et al., 2020).

3   Methods and Analysis

The identification of air mass origin by local O_3 and RH profile measurements crucially depends on the definition used to
separate air masses. We chose air mass categories derived from statistical analysis of the two tracers from the PAO balloon-
115   borne time series, which reflect our process understanding in this particular location. The interplay of local and non-local
atmospheric processes in time and space governs the chemical composition of the tropospheric column above Palau. Different
air masses can be identified by chemical or dynamical properties and hence attributed to different local or non-local source
regions. The tropospheric column can consist of a variety of air masses, sometimes visible as distinct layers within particular
tracer profiles.

120   In the following, we use $O_3\pm RH\pm$ as a qualitative notation for air masses of low ("-") or high ("+") O_3 or RH respectively
(compare e.g. Stoller et al. (1999)). This leads to a qualitative grid with four categories, which we use to explain our process
understanding and for comparison with previous studies (Fig. 3). The "Δ" symbol denotes quantitative air mass categories by
anomalies ("+" or "-") from atmospheric background conditions (denoted as "○") as defined by our statistical approach. Here,
we established a quantitative grid with nine categories with boundaries derived from the distributions of O_3 and RH anomalies,
125   ΔO_3 and ΔRH (Fig. 7). With this approach, we particularly targeted the questions of local or non-local genesis of background
air masses ($\Delta O_3\circ\Delta RH\circ$), which are humid and ozone-poor, and anomalously dry O_3-rich air ($\Delta O_3+\Delta RH$-) together with
their respective seasonality.

3.1   Air Mass Definition

3.1.1   Tracers and Process Understanding

130   O_3 is a common tracer in transport studies within the TWP, with typical dynamical conditions being conducive to a tropospheric
column of low O_3 VMR attributed to local air masses (e.g., Kley et al., 1996; Pan et al., 2015). Dominant marine convection
leads to low NO_x concentrations and subsequently low O_3 production rates (e.g., Crawford et al., 1997; Rex et al., 2014). In
this environment the HO_x driven loss of O_3 is favored (see reaction R2) resulting in a lifetime of about 5 days for boundary
layer O_3 (e.g., Liu et al., 1983; Kley et al., 1997). The low NO_x environment is fostered by dominating easterly winds in the
135   annual mean and entire tropospheric column (Müller et al., 2023). Most of the air reaching Palau has crossed the Pacific and
has thus been cleaned of O_3 precursors from anthropogenic or other continental pollution. Palau has a hot, humid and wet
climate all year, resulting in a continuously high convective activity (Gettelman and Forster, 2002; Müller et al., 2023). This
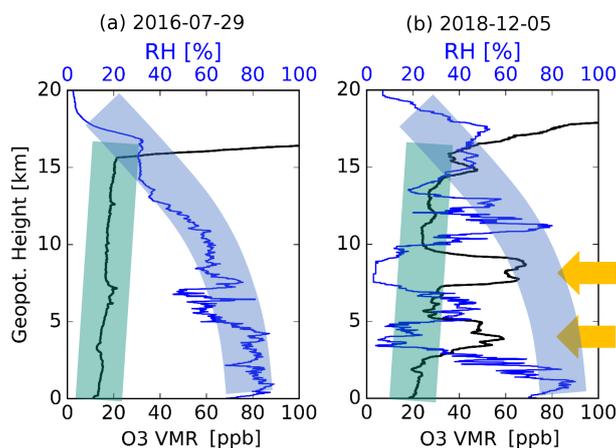
Figure 2. Example tropospheric O_3 VMR (black lines) and RH (blue lines) profiles from the PAO for the background atmosphere (a) and anomalously dry ozone-rich layers (b). The ideal shape for the background atmosphere in (a) is illustrated in green and blue shading; two layers disrupting the respective background are indicated by yellow arrows in (b).

persistent high convective activity creates a well-mixed profile of uniformly low O_3 VMR throughout the free troposphere, as illustrated in Fig. 2a. We refer to this as the clean state of the atmosphere or simply "background".

140   Layered structures of higher O_3 VMR in the mid-troposphere disturbing the uniform low O_3 profile are often observed and a signature of non-local air masses (e.g., Pan et al., 2015; Anderson et al., 2016; Randel et al., 2016). Figure 2b shows an example profile with two distinct layers of enhanced O_3 levels (>50 ppb) around 4 and 8 km, interrupting otherwise quite constant levels of low O_3 VMR ($\sim$ 25 ppb). Enhanced tropospheric O_3 levels are generated either by photo-chemical processes in high tropospheric NO_x regimes, i.e. in polluted air masses, or by photo-dissociation of O_2 in the stratosphere and subsequent

145   transport to the troposphere. In situ net O_3 production is unlikely at this altitude in the remote TWP, which is far from pollution sources and shows a lack of lightning activity (Christian, 2003; Cecil et al., 2014). Free tropospheric O_3 life times are in the order of weeks and comparable to the dynamical timescales of long-range transport within the tropics and from the subtropics (e.g., Folkins, 2002; Ploeger et al., 2011). Thus, air masses transported either from polluted areas elsewhere or the extra-tropical stratosphere can retain their high O_3 VMR until arrival in the deep tropics.

150   To complement O_3 as an indicator of air mass origin, we made use of RH as a measure of vertical displacement of air masses. The benefit of using RH is the readily available data from the combined sonde measurements. The dominant anti-correlation between O_3 and RH in the PAO dataset further suggests closer examination of RH (Figs. 1 and 2). RH allows us to distinguish between different underlying processes affecting either local or non-local air masses (e.g., Hayashi et al., 2008; Schoeberl et al., 2015). Local air masses of low O_3 VMR often show high RH values (O_3-RH+) in accordance with

155   the assumed dominance of convective activity and uplift. The example in Fig. 2a shows, that RH values characteristically decrease with altitude, but remain greater than 45% throughout the mid-troposphere (c.f. Mapes, 2001). Non-local, ozone-rich air masses often correspond to low RH compared to the air masses above and below the humid tropical column (O_3+RH-). The
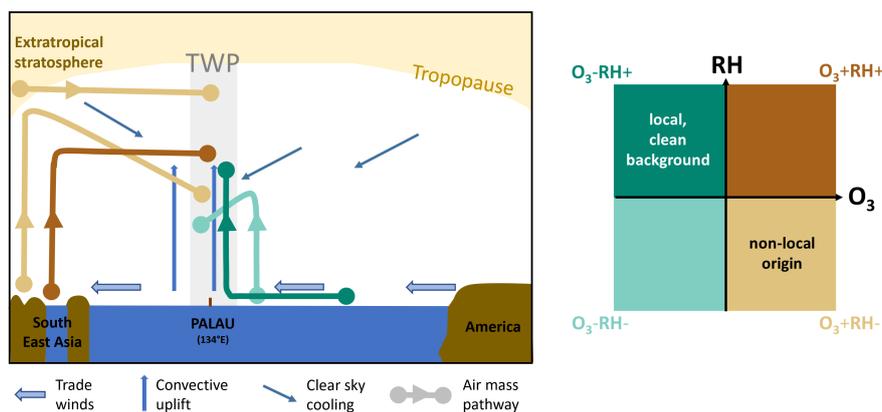
Figure 3. Schematic for transport pathways to Palau and the TWP on the zonal plane, major dynamical drivers are marked with arrows (blue colors), transport pathways are color-coded according to the air masses' O_3/RH characteristics shown in the qualitative grid (turquoise colors for O_3-, brown colors for O_3+, hue for RH±); O_3+RH- air (light brown) masses above Palau may have followed two of the five shown pathways (for details see text).

depressed RH levels can be explained by either stratospheric origin or various dynamical processes during transport, mostly involving a descent of air masses towards Palau which results in adiabatic compression and heating of the air, reducing RH at

160   constant absolute humidity (Cau et al., 2007; Dessler and Minschwaner, 2007; Anderson et al., 2016). The study of RH data thus supports our understanding of processes governing O_3 variability above Palau.

The competing hypotheses for the genesis and origin of O_3+RH- air demand the use of an additional tracer (e.g. Stoller et al., 1999). In this study, we use potential vorticity (PV) as a dynamical tracer to identify a potential stratospheric origin of air masses. We assume a significant in-mixing of extra-tropical stratospheric air for air masses with an absolute PV greater than

165   1.5 PVU for at least one day during ten days before arrival in Palau (Waugh and Polvani, 2000; Kunz et al., 2011).

In conclusion, we propose five qualitative categories of air masses with differing origin identifiable by our tracers, as illustrated in Fig. 3 for O_3±RH± in a qualitative two times two grid. Ozone-depleted air masses (O_3-, turquoise colors) are of local or Pacific, convective origin and ozone-rich air masses (O_3+, brown colors) originate from non-local pollution or the stratosphere. High RH results from a dominant convective uplift of air masses (RH+, darker hues), while low RH indicates a

170   stratospheric origin or dehydration of previously lifted air masses during transport due to clear sky cooling and descent (RH-, lighter hues).

As discussed above, the two important air mass categories are tied to the dominant anti-correlation of O_3 and RH above Palau: O_3-RH+ background air and O_3+RH- air masses occurring mostly in layers interrupting the background. Air masses with positively correlated O_3 and RH are observed less often and more difficult to assess. O_3+RH+ air masses (dark brown)

175   are potentially caused by non-local pollution convectively lifted in the source region and transported rapidly towards Palau on the same altitude, conserving the high humidity. We further suggest, that O_3-RH- air (light turquoise) consists of clean

boundary layer air convectively lifted in the Pacific vicinity of Palau, dehydrated due to clear sky cooling during transport. Other processes, like remoistening or in-mixing of mid-latitude air during transit to the TWP could also play a role (Cau et al., 2007; Sherwood et al., 2010; Schoeberl et al., 2015; Tao et al., 2018) and is difficult to assess just using the tracer data.

3.1.2 Previous Approaches

To detect and assess anomalous layers from measured balloon and aircraft profiles different methods have been applied (Stoller et al., 1999; Thouret et al., 2000; Hayashi et al., 2008; Pan et al., 2015). Stoller et al. (1999) used data from three NASA campaigns (PEM-Tropics, PEM West A and B) to calculate a free tropospheric background mode for different atmospheric constituents (O_3, H_2O, CO, CH_4) and for individual profiles. In an approach similar to a spike detection in signal processing, they produced extensive statistics for the frequent occurrences of anomalous layers, which together sampled the whole tropical Pacific region in two different seasons. The same methodology was applied to MOZAIC aircraft data by Thouret et al. (2000). Its main disadvantage lies within an arbitrary threshold used to determine the background mode. Besides the resulting uncertainty within the statistics of layer occurrences, a key conclusion of Stoller et al. (1999) is the recognition of the importance of anomalous air layers in the tropical Pacific region and the demand for their inclusion in dynamical models mapping chemical processes due to the high frequency of their occurrence.

A similar analysis of longer time series from three SHADOZ sites (Southern Hemispheric Additional Ozonesondes Network Thompson et al., 2003a, b, 2012, 2017) confirms the frequent occurrence of dry enhanced O_3 layers below 12 km (Hayashi et al., 2008). Using a statistical method for the layer detection, the study found respective layers in approximately 50 % of profiles per year at each station with differing seasonal variations. The study relies on the separation of a wet and distinct dry season at the respective stations, which is not applicable for the Palau site (c.f. Müller et al., 2023).

Pan et al. (2015) isolated the low O_3 background or "primary mode" by removing all "dry" data with RH less than 45 % for all observations during the CONTRAST campaign (Pan et al., 2017). They thus refrained from resolving the individual vertical structure of layers, but proposed the RH threshold as an overall criterion in the free troposphere to separate local and non-local air masses. Pan et al. (2015) emphasized the possible variability of air mass origin within the individual vertical column, which is obscured in seasonal or even annual profile averages, i.e. layered structures in the O_3 profile hidden within the typical so-called "S"-shape (c.f. Sect. 4.1). Their method, however, seems limited to the specific sites and season of the CONTRAST campaign, as it does not yield a robust output for the Palau data during all seasons (Müller et al., 2023).

3.1.3 Statistical Definition of Background and Anomalies

For a quantitative definition of air masses above Palau, we roughly followed the approach of Hayashi et al. (2008) and determined a statistical free-tropospheric background from the PAO O_3 and RH time series. First, we defined monthly background profiles for both tracers using the 20th quantile for O_3 VMR (Q20) and the 83.3th quantile, i.e. the upper boundary of the central 66.6 % range, for the RH values (Q83) respectively. Figure 4 shows an example of these background profiles for the month of March and the free troposphere, including the median and central 66.6 % ranges for both tracers separately, calculated

March (16 Profiles)
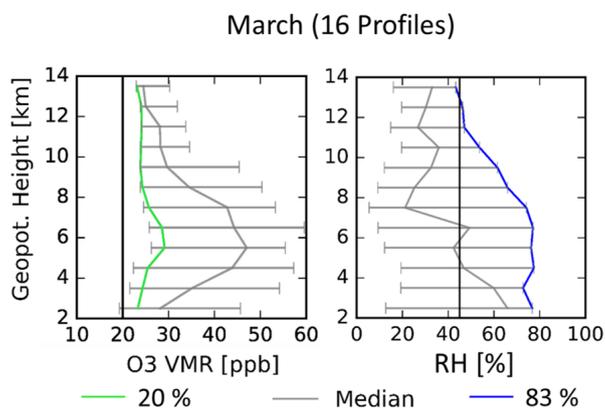
Figure 4. O_3 VMR and RH statistics for the month of March as example for Palau free tropospheric profiles per km: the 20th quantile (Q20) for O_3 is shown in green and the 83.3th quantile (Q83) for RH in blue (both vertically smoothed using exponentially weighted moving averages), the median is marked in grey and the central 66.6 % range in grey horizontal bars; number of included individual profiles in brackets, for orientation 20 ppb O_3 VMR and 45 % RH are marked in black (see also Figs. A3 and A4).

from 16 individual profiles (see Müller, 2020, for more details). The quantile profiles have been vertically smoothed using first

210 a 1-km-binning and then exponentially weighted moving averages (see also Figs. A3 and A4).

This less conservative approach in regard of O_3 compared to Hayashi et al., who defined air masses with O_3 VMR above the 83.3th quantile as O_3 enhanced layers, accounts for our physical understanding of the Palau background atmosphere as a uniform, well-mixed low O_3 profile, caused by uplift of ozone-poor boundary layer air in active convection. We chose this particular O_3 quantile to yield the most uniform, "straight-line" profile in the free troposphere for all monthly averages

215 of the given time series. This essentially smoothes out any interrupting layers occurring at varying altitudes in individual profiles. While Hayashi et al. analyzed RH in ozone-enhanced anomalous layers in contrast to the air masses above and below, we applied the statistical approach to both tracers and chose Q83 for RH to detect typical convection associated with the background. The resemblance of both the particular low O_3 and high RH quantiles with the example of an individual background profile in Fig. 2a is evident. The monthly averaging accounts for the seasonal variability of the background as the

220 uniform O_3 profile shifts towards higher base VMR from summer/fall to winter/spring (compare Figs. 2 and A3).

In a second step, we determined the anomalies against the monthly background for individual measured O_3/RH pairs within each sounding and in their respective month-altitude bin, denoted in the following by ΔO_3 and ΔRH. We now denote the background air mass category as "$\Delta O_3 \circ \Delta RH \circ$" and thus additionally consider eight different anomaly categories (c.f. Fig. 7 in Sect. 4.1.3). In our analysis, we focused on the altitude region between 5 and 10 km, where the weakest cloud-mass

225 divergence occurs, i.e. the weakest convective outflow/detrainment (Folkins and Martin, 2005) and the greatest frequency of anomalous layers. The prominent anti-correlation of the two tracers revealed dry ozone-rich air as the most opposite anomaly. We thus limited our study to the two most interesting air mass groups, $\Delta O_3 \circ \Delta RH \circ$ and $\Delta O_3 + \Delta RH -$. In contrast to Hayashi et al. we did not assess vertically concise anomalous layers in individual profiles. Hence, neither the layer thickness nor the

layer position within the profile were considered. Any measured data point of a profile was quantitatively attributed to one of
230   nine specific categories, which were then analyzed "in bulk".

3.2   Trajectory Analysis

We deployed the trajectory module of the fully Lagrangian chemistry and transport model ATLAS (Wohltmann and Rex, 2009;
Wohltmann et al., 2010) driven by ERA5 data (see Sect. 2). The model uses a hybrid vertical coordinate, which gradually
transforms from pressure at the surface to potential temperature in the stratosphere. The corresponding vertical velocities
235   change from vertical winds in pressure coordinates to diabatic heating rates, respectively.

    10-days backward trajectories with a time step of ten minutes were initialized every tenth sonde reading of a profile (approx-
imately every 50 m, i.e. 20 trajectories per km) for all profiles within the trajectory dataset. They are considered as a footprint
for transport pathways towards Palau. We assume O_3 to be a passive traver during transport, i.e. did not implement chemical
reactions. This assumption is justified for dry, mid- to upper tropospheric air because of photo-chemical lifetimes of O_3 in the
240   order of several weeks to months under these conditions. In the wet lower troposphere and marine boundary layer this approach
is only valid for a few days, because of O_3 lifetimes in the order of days (e.g., Thompson et al., 1997). Convection is not treated
explicitly in the model setup, but partly reflected in the reanalysis data.

4   Results

We first present the variability of the PAO tropospheric O_3 time series to assess air mass seasonality and the application of our
245   method to determine different groups of air masses. Then, our results from the trajectory analysis are shown, first investigating
general seasonal tracer variability, and second applying our method of air mass distinction to analyze transport pathways (Fig.
3). A physical interpretation of the results follows in the discussion (Sect. 5).

4.1   Air Mass Variability

4.1.1   Annual O_3 Variability

250   Figure 5 shows time-height cross-sections of the annual variability of tropospheric O_3 for monthly means (a) and anomalies
(b) from the annual mean profile of the overall time series (c, black solid line), excluding El Niño 2016. Panel (c) also shows
the standard deviation (SD) and the relative standard deviation (RSD) of the overall annual mean profile (dashed and dotted
lines, respectively), as well as the annual mean profiles of individual years (colored lines). As the fraction of the SD relative to
the annual mean, the RSD can be considered as a measure of variability with altitude (c.f. Ogino et al., 2013). The annual mean
255   tropospheric O_3 VMR profile (Fig. 5c) has an "S"-shape typical for tropical sounding stations (e.g., Folkins, 2002; Thompson
et al., 2003a, b; Pan et al., 2015). O_3 VMR are lowest in the boundary layer (< 20 ppb) and also low between 10 and 12 km ($<$
30 ppb). They increase in the mid-troposphere to about 35 ppb and again above 12 km towards their stratospheric maximum,
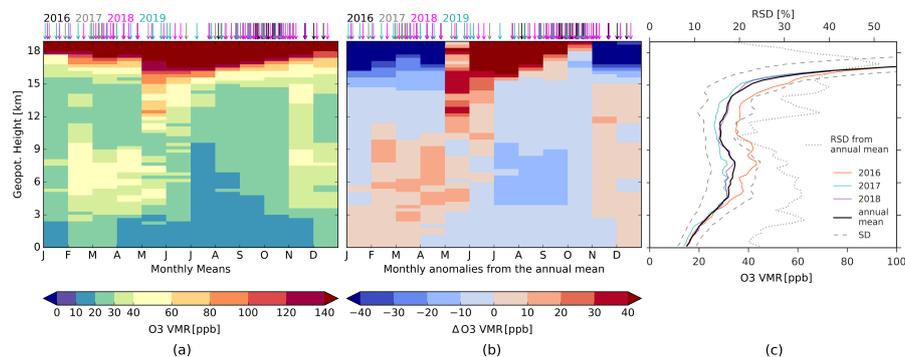
Figure 5. Monthly means (a), anomalies from the annual mean (b) and the annual mean profiles for individual years (thin colored lines) and for the whole time series excluding El Niño 2016 (thick black line) with standard deviation (grey dashed lines) and relative standard deviation (RSD) (grey dotted line); individual soundings are marked as arrows above with different colors for different years; non-linear scaling is used in (a) to match the differing orders of magnitude in the lower and upper troposphere(compare Müller et al., 2023, Fig. 6)

which is an order of magnitude higher. The interannual variability of the annual mean O_3 profile is low for all years with the exception of 2016.

260   The monthly O_3 VMR (Figs. 5a and b) reveal two dominant signals: an annual cycle in the 5-10 km altitude range with the maximum from February until April (30-60 ppb) 2-3 times greater than the minimum from July until October (10-30 ppb), and a reverse, strong cycle in the TTL with maximum anomalies (> 40 ppb) from June until September. The peak in RSD of 50 % at about 17 km reflects the strong TTL cycle. The enhanced variability in mid-tropospheric O_3 (RSD ~ 30 %) corresponds with the cycle revealed by the monthly means. Annual variations in O_3 observations are smallest between 10-12 km and especially

265   in the boundary layer (RSD ~ 20 %), thus coincidental with the O_3 minima of the annual profile. The regionally typical ozone-poor background is clearly subject to seasonal variations.

4.1.2   Seasonal O_3 Profiles

A more detailed analysis of the seasonal O_3 variability helps to identify reoccurring seasonal characteristics and differences in controlling processes like synoptical or meteorological conditions. Therefore, we divided our time series into four seasons,

270   shifted by one month compared to the temperate climate seasons: November-December-January (NDJ), February-March-April (FMA), May-June-July (MJJ) and August-September-October (ASO). These Palau seasons reflect different influences dependent on the time of the year and were chosen empirically by sorting monthly O_3 profiles (Müller et al., 2023, Fig. A1) by similar shape, considering the full free-troposphere. The resulting four most different types of profile shapes are shown in Fig. 6. The Palau seasons turned out to be centered around the equinoxes, which is reasonable for a tropical station.

275   In the 5-10 km altitude range FMA and ASO show the largest differences and represent the extremes of the mid-tropospheric cycle. The "S"-shape of the annual mean profile prevails in the winter seasons, NDJ and most pronounced in FMA. The interannual variability is particularly high during FMA from 5 to 10 km with generally enhanced O_3 VMR between 40 and
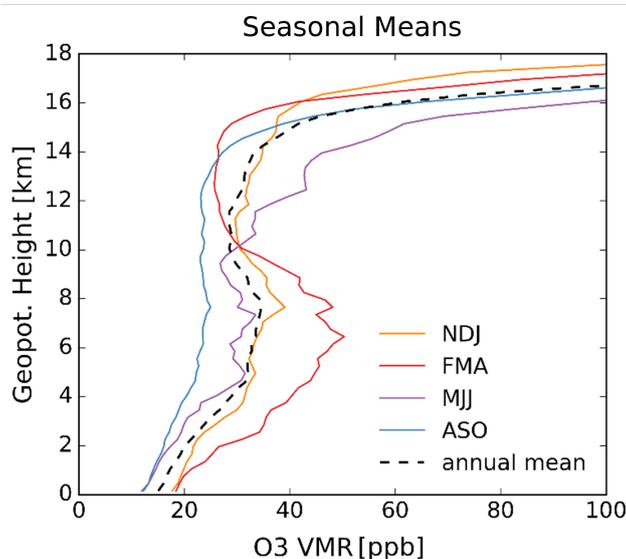
Figure 6. Seasonal mean O_3 VMR profiles (colored solid lines) in comparison to the annual mean (dashed black line), all excluding El Niño 2016, for Palau seasons November-December-January (NDJ), February-March-April (FMA), May-June-July (MJJ), August-September-October (ASO)

50 ppb (Fig. A1). The ASO profile is closest to the uniform background profile (20-25 ppb O_3 VMR) with little interannual variability, while having the highest sampling rate (59 profiles). We thus refer to ASO as the background season. In the TTL,

280 both extreme seasons, ASO and FMA, show a pronounced O_3 minimum, except during the 2016 El Niño FMA season (Fig. A1). The steeper onset of higher levels of (stratospheric) O_3 VMR in ASO occurs at lower altitudes compared to the NDJ and FMA seasons.

MJJ and NDJ can be considered as intermediate seasons with respect to the mid-tropospheric cycle. While the NDJ profile follows the annual mean profile up to about 14 km, the MJJ profile diverges towards higher values from 10 km upwards. The

285 tilted line shape during MJJ, compared to the straight line profile during ASO, implies a weak O_3 gradient in the UT and TTL (c.f. Müller et al., 2023) and a lack of a pronounced O_3 minimum in the UT. In this season high, stratospheric O_3 VMR occur at the lowest altitude of the year.

4.1.3 O_3 and RH: Background and Anomalies

The application of our method to separate air masses on the full PAO time series for the free troposphere (3-14 km) yields the

290 distribution of anomalies from the background, ΔRH and ΔO_3, given in Fig. 7 (see also Sect. 3.1.3). The 2D-histogram in Fig. 7a shows anomalies from all months and altitudes percentages of all measured free-tropospheric O_3/RH data pairs in grey-scale. Data along the zero lines indicate zero anomalies and thus an attribution to the respective background, Q20 of monthly

O_3 VMR and Q83 of monthly RH values. The marginal 1D-histograms show the distributions of both tracers individually normalized to unity.

295 Both ΔRH and ΔO_3 show heavily skewed distributions, with a long tail in the ΔO_3 distribution towards less frequent high O_3 occurrences and even a bimodal distribution for ΔRH with a secondary maximum in the tail towards dry air masses. These distributions motivate the separation of air masses into three domains for both parameters, one corresponding to the low tail, one to the bulk of the observations and one corresponding to the high tail. Overall this leads to nine air mass categories in a three times three grid referred to as the "quantitative" grid (Fig. 7b). The boundaries were chosen empirically with respect to

300 the shape of the distributions with a range of -5/+15 ppb ΔO_3VMR and -20/+5 % for ΔRH for the central group.

In particular, the correlated occurrence of air masses with high O_3 and low RH (ΔO_3+ΔRH-) stands out as a separate population of points in Fig. 7a (lower right quadrant), while the central group (ΔO_3∘ΔRH∘) represents the most frequent conditions and is referred to as background. Here, we focus on the distinct population of ΔO_3+ΔRH- air masses in contrast to this background. The background is characterized by significantly higher RH and lower O_3 and is therefore also referred to as

305 humid, ozone-poor background.

The anomalies are mostly clustered within 20 ppb along the ΔO_3 zero line indicating an overall dominance of the low O_3 background. Apart from the tail towards less frequent higher O_3, the narrow distribution is nearly Gaussian and centered around 0 ppb ΔO_3 VMR with a tendency towards positive values. The majority of ΔRH values appears between -60 and 20 %. The bimodality of the ΔRH distribution is persistent in all seasons with the exception of MJJ (Fig. A5). The primary, dominant

310 mode is centered slightly off the ΔRH zero line towards negative values, i.e. the majority of measured RH values matches the Q83 or slightly lower values of the respective month-altitude bin. The secondary mode occurs for RH values 40 % lower than their background estimates.

Figure 8 shows the ΔO_3/ΔRH distribution for the seasons FMA and ASO. As expected from the previous overview of the annual O_3 variability, ΔO_3+ΔRH- are almost missing during the ASO season. But in contrast to the seasonal FMA O_3 profile

315 (Fig. 6), the distribution reveals a still dominant background within the free troposphere. A statistical view on the seasonal occurrence of different air masses in the mid-troposphere emphasizes the year-round dominance of ΔO_3∘ΔRH∘ air, which were observed in more than 70 % of profiles within each season (Fig. A6).

4.2 Air Mass Transport and Processes

4.2.1 Trajectory Origin by Season

320 A footprint of air mass transport to Palau is given in Fig. 9 by an overview over all trajectory calculations for the study period (2016-2019), showing 10-days backward trajectories sorted by season arriving in Palau in the 5-10 km altitude range. For better visualization, a representative subset was chosen, displaying only every 20th trajectory of a day/profile (roughly 1 trajectory per km). Colored line-segments show three different time periods backwards, 3, 5 and 10 days, thus indicating the velocity of air mass transport.
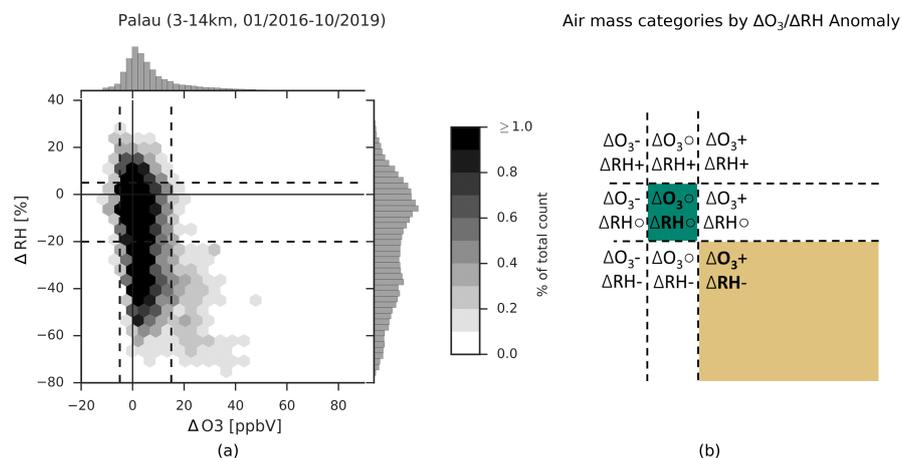
Figure 7. (a) Free-tropospheric (3-14 km) relation between tracer anomalies ΔO_3 VMR and ΔRH from the monthly background defined in Section 3.1; color shading indicates percentages of total count of measured O_3/RH data pairs per grid point; marginal plots for individual tracer anomaly distributions are normalized to unity; dashed lines refer to air mass categories in the three times three quantitative grid as illustrated in (b), with boundary values for the central grid box ($\Delta O_3 \circ \Delta RH \circ$) of -5/+15 ppb for ΔO_3 VMR and -20/+5 % for ΔRH; two target categories of the analysis are highlighted in color in (b), compare to Fig. 3.
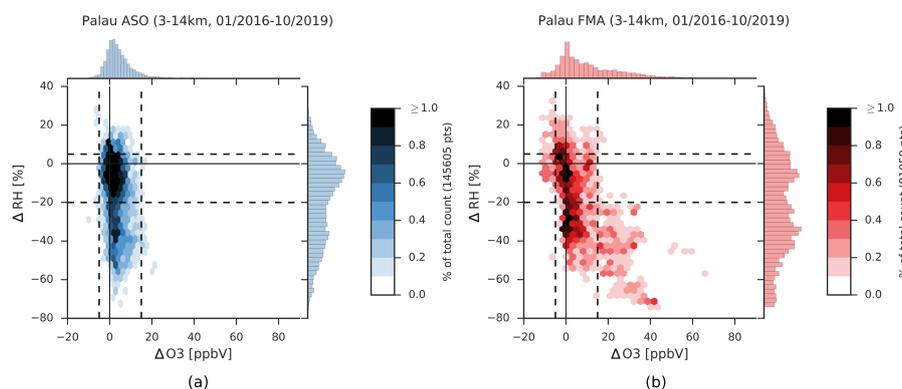
Figure 8. Seasonal free-tropospheric (3-14 km) relation between tracer anomalies ΔO_3 VMR and ΔRH, total number of datapoints in brackets, colors according to Fig. 6, more details in Fig. 7.

Most air masses reach Palau from the east, but have traveled two different paths on different timescales. The seasonal distinction of trajectories roughly separates an Eastern Pacific pathway, dominating in MJJ and ASO, from an anticyclonic route in NDJ and FMA, connecting Palau with South East Asia and some remote areas as far as the African continent. The anticyclonic route can be associated with long-range transport on shorter timescales compared to the Pacific route. As these transport patterns are most pronounced in FMA and ASO, respectively, which also exhibit the greatest tracer differences in the mid-troposphere (compare Fig. 6), we focus on these two Palau seasons in the following.

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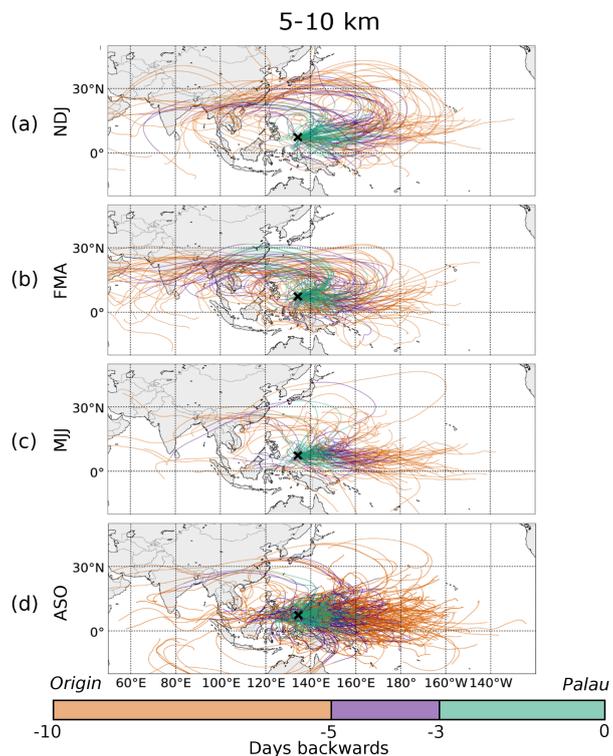
Figure 9. Geographical footprint of air masses: 10-days backward trajectories from ATLAS arriving at Palau in the 5-10 km altitude range by season (2016-2019), colored segments represent time periods of maximal 3 (green), 5 (purple) and 10 (orange) days backwards, respectively; the x marks the location of Palau; only a selection (every 20th data point of a profile, roughly one per km) from the trajectory dataset is shown.

The geo-spatial extent of the footprints differs significantly for season FMA and ASO. While all trajectories stay mostly within the tropical zone between 0° to 30° N, trajectories during FMA have a wider longitudinal extent than during ASO. Most ASO air masses never left the Pacific Ocean area within 10 days before arrival in Palau and have traveled shorter distances. Only a few trajectories on a Southern hemispheric cyclonic route show the influence of the Western Pacific monsoon, which is

335 active from July to October, but governs air mass transport mostly below 5 km altitude (Müller et al., 2023).

The origin of air masses, defined by the 5-days backwards trajectories' earliest points, is presented for the seasons FMA and ASO in Fig. 10. The geo-spatial probability density function of data points is highlighted as black contour lines in Fig. 10a. Here, the colors indicate O_3 VMR as observed upon arrival in Palau. Figures 10b and c show the same earliest points as Fig. 10a, but colored-coded by RH (b) or difference in pressure height, measured five days before measurement (c), i.e. red colors

340 indicate descent, blue colors ascent towards Palau.

The dominant source region of free-tropospheric Palauan air masses, indicated by the center of the density distribution in Fig. 10 a, is located east of Palau during both seasons and corresponds to low O_3 VMR ($\leq$ 30 ppb). During FMA, the eastern

15
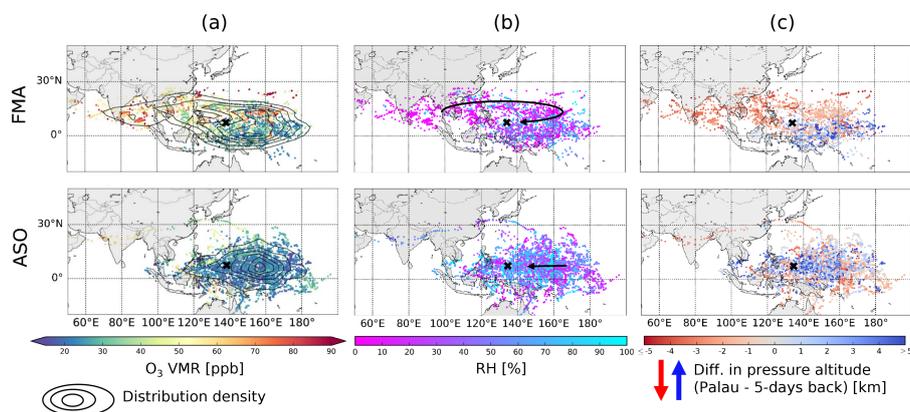
Figure 10. Origin of air masses by season: 5-days backward trajectories' earliest points arriving in Palau in the 5-10 km altitude range for Palau seasons FMA (upper row) and ASO (lower row), color-coded either by O_3 VMR (a) or RH (b), both measured at Palau, or by difference in pressure altitude, measured at Palau minus 5 days before measurement (c); in addition, black contours in (a) show distribution density and schematic arrows in (b) indicate the pathway as shown by the footprint in Fig. 9.

center of the distribution is actually split in two parts along a latitudinal axis. The dominant part is located further south on the equator, exhibiting low O_3 VMR. The northern part of the eastern center is of higher O_3 VMR. A separate cluster of

345 trajectory points showing enhanced O_3 VMR ($\geq$ 60 ppb) exists northwest of Palau during FMA, roughly extending from India to Taiwan. As revealed by the full 10-days trajectories in Fig. 9b, all air masses of higher O_3 VMR during FMA can be related to the anticyclonic route, though some took longer than 5 days to travel from South East Asia to Palau. During ASO the overall unimodal distribution is centered on Palau's latitude, 20° east, and observations of enhanced O_3 VMR originate outside the main cluster. For both seasons, air masses with O_3 VMR greater than 60 ppb rarely originate south of Palau.

350 The distinction between the two pathways is also reflected in RH (Fig. 10b) and even more clearly in the vertical displacement of air masses from origin to destination (Fig. 10c). In FMA, Fig. 10c shows descended air masses originating north and ascended air south of Palau. Here, the descent of air masses corresponds with greater O_3 VMR and lower RH, although the pairwise correlation, R, of these two parameters with the pressure height difference is not strong (R=-0.53 for O_3 VMR and R=0.44 for RH, for the latter c.f. Fig. A7). We can, however, associate these dry, descending air masses with the anticyclonic

355 route shown in the 10-days backward trajectory footprint.

For ASO air masses, the picture is not as clear, but ascent and humid air masses with low O_3 VMR are slightly dominating (Figs. 10c and A7b) and have likely followed the Pacific pathway. The pairwise correlation for pressure height difference and O_3 VMR or RH, respectively, is even lower than during FMA (R=-0.36 for O_3, R=0.35 for RH). However, there are clearly two main groups of air masses, one with RH below 40 %, descended mostly only 1 km, and one group with RH centered around

360 70 %, ascended mostly 1 km or more.
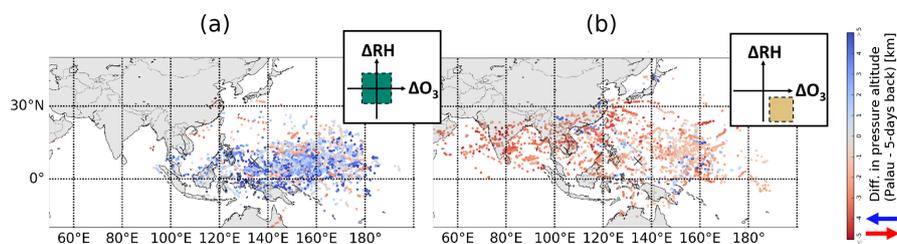
Figure 11. Origin of air masses by air mass anomalies: 5-days backward trajectory earliest points arriving in Palau in the 5-10 km altitude range for $\Delta O_3 \circ \Delta RH\circ$ and $\Delta O_3 + \Delta RH-$ air masses as indicated by the pictograms, color-coded by difference in pressure altitude, sonde - endpoint, see also Figs. 7 and 10.

The investigation of the history of PV for Palauan air masses revealed no stratospheric pathway. Below 1 % of all 13627 trajectories stayed above 1.5 PVU for more than a day during 10 days transit to Palau. Within five days before arrival only few trajectories crossed the 1.5 PVU threshold.

4.2.2 Trajectory Origin by Air Mass

365 While we have looked at the origin of the trajectories as a function of season in the previous section, we now turn to the origin as a function of air mass. The classification of trajectories by air mass category as defined in Section 3.1 yields the distribution of source regions as shown in Fig. 11. Background $\Delta O_3 \circ \Delta RH\circ$ air masses originate within a compact region in the Pacific, mostly east of Palau stretching as far as 180° E. The origin pattern for $\Delta O_3 + \Delta RH-$ air masses clearly show transport from the South East Asian region and along the anticyclonic path to Palau. In comparison to the seasonal analysis, the classification

370 of trajectories by air masses shows a clear distinction for the history of vertical displacement of the air masses. On their way towards Palau most $\Delta O_3 \circ \Delta RH\circ$ air masses have been ascending, while $\Delta O_3 + \Delta RH-$ air has descended.

A seasonal analysis of the trajectories sorted by air mass anomalies reveals some differences in the source regions of $\Delta O_3 + \Delta RH-$ air masses (Fig. A8). The origin hot spots around India and the Southeast Asian peninsula are almost exclusively observed during FMA. The Southern Philippines and the area slightly North East of Palau are equally dominant source

375 regions in this season. In ASO $\Delta O_3 + \Delta RH-$ air masses are less frequently observed and their origins are clustered around three main areas: 1. north east of Palau in the West Pacific, 2. between Borneo and the Southern Philippines and 3. in the New Guinea region, extending towards Northern Australia.

5 Discussion

The central goal of our study was to identify the air mass origin of TWP air and its seasonality by means of the observed O_3/RH

380 relation above the PAO. Our qualitative transport scheme for different types of air masses ($O_3\pm RH\pm$, Fig. 3) distinguishes between local and non-local processes. Calculated Lagrangian backward trajectories support this hypothesis. The PAO 4-year time series reveals the seasonality of air mass types and thus origin. By separating trajectories by O_3/RH anomalies from a

statistically defined background, we achieve a separation in Palauan air mass origin and transit properties for $\Delta O_3 \circ \Delta RH \circ$ and $\Delta O_3 + \Delta RH-$ air masses. Our analysis thereby confirms the quality of O_3 and RH as combined tracers for air mass origin in the

385 TWP.

5.1 Seasonality and Air Mass Definition

The PAO time series provides unprecedented insight into the seasonality of tropospheric air composition in the TWP (Müller, 2020; Müller et al., 2023). An important observation from the PAO dataset is the dominant anti-correlation between O_3 and RH (Fig. 1). The cyclic behaviour of O_3 in the mid- and upper troposphere was expected from satellite observations and earlier

390 studies, especially the zonal wave one pattern in the TTL (e.g., Thompson et al., 2003b; Randel et al., 2007), but had not been monitored thoroughly with in situ measurements before. Here, the high temporal and vertical resolution of the ozonesonde dataset revealed day-to-day variations, but also the prevalence of significant seasonal signals modulating these. Especially the increased sampling frequency during the extremes of the mid-tropospheric cycle shows the robustness of this signal for Palau and the dominance of the local low O_3 mode during late summer (Fig. 6). Currently, the shortness of the time series and

395 statistical bias due to the differences in monthly sampling frequencies have to be taken into account. A future analysis of the growing time series will be better able to assess the influence of interannual variability. The ENSO cycle will likely play the most important role in this.

The mid-tropospheric O_3 cycle is in accordance with the annual movement of the Intertropical Convergence Zone (ITCZ). The dominance of a clean convective (local) state over (non-local) atmospheric transport to the TWP is regulated by the two

400 major barriers ITCZ and Southern Pacific Convergence Zone (SPCZ). Müller et al. (2023) showed the correspondence of the ITCZ's position north of Palau with the minimum in O_3 measurements (c.f. Fig. 5). This relates to previous studies on air mass transport to the region: during the PEM-Tropics West B campaign, Browell et al. (2001) found that layers of high O_3 VMR advected to the TWP from remote polluted areas are mostly confined north of the ITCZ. Very low O_3 values were only present in the "equatorial wedge" between ITCZ and SPCZ and associated with enhanced vertical mixing in convection in the absence

405 of gross ground pollution. Palau is enclosed between these bands during ASO (Sun et al., 2023), therefore the best season to observe the clean air background. During FMA, when the ITCZ is located furthest south, transport from higher northern latitudes is possible. MJJ and NDJ can be considered as intermediate seasons with respect to both, the mid-tropospheric cycle and the similar location of the ITCZ during its annual crossing. This feature explains, why studies related to the CONTRAST campaign which took place in January/February 2014 did not see low O_3 extremes (Pan et al., 2015; Newton et al., 2016; Nicely

410 et al., 2016; Tao et al., 2018) and why background conditions of the region need to be assessed by long-term measurements. Its unique location and year-round operation makes the PAO an excellent background site to study the influence of dynamics (c.f. Thompson et al., 2021; Sun et al., 2023).

The minimum in the vertical O_3 profile in the TTL (the so called chemopause) can be attributed to deep convective outflow. Recognized as a characteristic feature of tropical profiles, low UT O_3 is often used as an indicator for deep convective detrain-

415 ment (e.g., Kley et al., 1996; Folkins, 2002; Solomon et al., 2005; Gettelman et al., 2009; Paulik and Birner, 2012). Satellite observations confirm year-round convective activity in Palau, with some variability due to the traverse of the ITCZ twice a

year (Gettelman and Forster, 2002; Müller et al., 2023). The low variability in UT O_3 (Fig. 5c) can hence be explained by the persistence of deep convection and the level of convective outflow in association with the Hadley and Walker circulation (e.g., Folkins, 2002; Solomon et al., 2005; Takashima et al., 2008). Müller et al. (2023) associate the occurrence of the strongest
420 winds at 15 km when the ITCZ is furthest south or north of Palau with the outflow of the Hadley circulation. The dry environ-ment at this altitude increases O_3 lifetimes and makes in situ O_3 destruction unlikely, although it is discussed as a consequence of convectively injected water vapor (Schoeberl et al., 2015; Anderson et al., 2016). The PAO dataset is predestined for future studies on the seasonality of deep convective outflow and stratosphere-troposphere exchange (STE) processes in this region of major entry into the stratosphere in boreal winter.

425 The specific classification of seasons used in this study corresponds to distinct dynamical conditions. In particular, the Palau seasons can be related to the movement of the ITCZ, the main driver of dynamical variability. Our interpretation of the profile shapes is supported by the separation of trajectory footprints in Fig. 9, i.e. different dominating pathways for the different seasons, and a comparison with an analysis of SHADOZ station profiles from Java and American Samoa by Stauffer et al. (2018). They used a sophisticated clustering technique to characterize ozonesonde profile variability related to different
430 controlling processes. Out of four cluster profiles, the low O_3 cluster associated with convective lifting of low O_3 VMR compares well with the Palau ASO profile. The cluster with highest average O_3 VMR exhibits a similar "tilted line" shape like Palau MJJ with a lower tropopause and weak gradient, explained by Stauffer et al. (2018) with STE. This corresponds well with the minimum annual tropopause height and a shift in wind regimes due to the crossing of the ITCZ around June (Müller et al., 2023). The horizontal wind is weakest throughout the entire tropospheric column in May, as the subtropical ridge shifts
435 south with increasing altitude, which could favor quasi-horizontal transport of extra-tropical stratospheric air into the TTL. July can be seen as a transition month, as the tropopause is comparable with May and June, but mid-tropospheric O_3 VMR are as low as observed in August and September (c.f. Fig. A1 in Müller et al., 2023). In July, the Western Pacific monsoon already reaches Palau in lower altitudes in the form of equatorial westerlies, but the tropopause is still low. While the construction of 3-month-seasons remains arbitrary in any case, it could be reconsidered especially for the summer months (MJJ, ASO) to
440 further differentiate between these processes.

Our new method to define background air masses is adequate to separate trajectories. It provides an improved criterion compared to using fixed thresholds based on absolute tracer values, as have been used in previous studies (e.g. Anderson et al., 2016; Nicely et al., 2016; Randel et al., 2016; Tao et al., 2018), who defined O_3+RH- air masses with RH < 20 % and O_3 VMR > 40 ppb. Our approach using quantiles based on a 4-year time series focuses on a physically motivated background
445 definition and shows an improved separation of processes in the trajectory analysis, namely between ascent and descent of air masses (not shown here). The main advantage of our method compared to algorithms of layer detection in individual profiles (e.g., Stoller et al., 1999) lies within its simplicity and the use of the identified bimodality in the RH anomalies. In principal, it is also applicable for sounding data time series from other tropical stations. However, it may not yield the best results as atmospheric processes and mechanisms determining air composition might be specific to this geographic region.

450 The bimodality in RH anomalies is a striking result of our study. It further justifies our separation between ΔRH○ and ΔRH-air masses in the three times three quantitative grid classification (dashed lines in Figs. 7 and 8). The differentiation of free-

tropospheric air mass anomalies by season in Fig. 8 again reproduces the known absence of $\Delta O_3+\Delta RH$- air in ASO and MJJ compared to their prominent appearance in NDJ and FMA (see marginal 1D histograms for RH in Figs. A5 and 8). During the latter seasons, both maxima in ΔRH are of similar amplitude, which emphasizes the importance of dry air masses intruding into the otherwise humid troposphere (c.f. Stoller et al., 1999). While the relevance of $\Delta O_3+\Delta RH$- filaments is undisputed, other categories of air mass anomalies are encountered less often and are thus more difficult to relate to underlying atmospheric processes.

The selection of Q83 for RH, also in context of the ΔRH bimodality, could be revisited for the analysis of a larger time series, as the maximum of the anomalies is mostly just below the background values (Figs. 7, 8 and A5). This is also reflected in the dominant occurrence of both $\Delta O_3 \circ \Delta RH \circ$ and $\Delta O_3 \circ \Delta RH$- found for the 5-10 km subset of the Palau data (Fig. A6). An adjustment of the RH quantile and corresponding center on the $\Delta O_3 \circ \Delta RH \circ$ group could still improve the air mass selection. The monthly profiles are not uniform throughout the column, which is proposed as the ideal, purely convective profile (compare Figs. 2 and A3, A4). During the months of increased occurrence of dry ozone-rich layers, i.e. FMA and NDJ, the Q20 profile still incorporates the "S"-shape, presumable caused by these layers. This could possibly be reduced by changing the temporal resolution from monthly to seasonal statistics, which has not been assessed yet. A growing time series will help to validate our approach as it reduces possible biases caused by different sampling frequencies per season.

5.2 Air Mass Transport and Processes

The trajectories reflect the dominating general circulation patterns, namely the Hadley and Walker circulation and the trade winds, with all air masses eventually reaching Palau from the East (Fig. 9). The influence of the Western Pacific Monsoon, active from July until October, becomes more apparent below 5 km altitude (c.f. Müller et al., 2023). With the anticylonic route, air masses can travel from the ascending branch of the Hadley circulation towards the descending branch along the subtropical ridge (Anderson et al., 2016). Once air parcels reach the West to Central Pacific during winter they are either diverted eastwards by the (subtropical high) anticyclone, possibly associated with the upper air mass divergence from air rising above the warm pool, or are picked up by the general trade wind circulation. In contrast, with a subtropical ridge further north during summer, transport is governed by the trade winds and monsoon circulation.

The results of the backward trajectory analysis support our assumptions on combined O_3 and RH as tracers to identify local and non-local air masses in the 5-10 km altitude range. They further allow conclusions on air mass origin, frequency of occurrence and controlling processes. Seasonal variability in O_3 VMR, RH and the vertical movement already separate between pathways to the TWP and air mass origin. The additional quantitative tracer anomaly categorization emphasizes the link between air mass origin and tracer variability directly tied to different processes.

The two categories, $\Delta O_3 \circ \Delta RH \circ$ and $\Delta O_3+\Delta RH$-, can be related to the two governing transport patterns for Palau mid-tropospheric air masses, the clean Pacific and the polluted anticyclonic pathway, respectively (Fig. 11). The anticyclonic route for $\Delta O_3+\Delta RH$- air masses occurs particularly during FMA. These air masses originate in tropical South East Asia, where biomass burning is a potent source of pollution. They subside during transport within the tropics and, with exceptions, experience absolute PV below 1.5 PVU within 10 days. That means, they do not originate in the extra-tropical stratosphere, but

have been subject to dehydration within the tropical troposphere, which can be explained by large-scale clear-sky subsidence associated with the Hadley circulation (Dessler and Minschwaner, 2007; Anderson et al., 2016). During ASO, these air masses are missing and we therefore see the undisturbed, extremely ozone-poor background (Fig. 8a). The $\Delta O_3 \circ \Delta RH \circ$ background air masses ascend towards Palau, consistent with convective uplift in the convectively active local Pacific region, which they

490 do not leave within 10 days before arrival in Palau.

Tao et al. (2018) conducted a quantitative study of the origin of O_3+RH- layers for the CONTRAST campaign using an artificial stratospheric tracer in the Lagrangian transport model CLaMS. They found a stratospheric influence in 60% of O_3+RH-air masses due to in-mixing during isentropic transport and point out the limitations of calculating pure Lagrangian trajectories without chemical transport. According to our analysis, the anticyclonic route identified for $\Delta O_3 + \Delta RH$- air masses reaching

495 Palau is indeed a pathway along the subtropical ridge, i.e. in close proximity of mid-latitude UTLS air masses. But a lack of air masses with high PV and the clustering of the trajectory ending points near centers of pollution sources on the ground are strong evidence for the tropical tropospheric origin. Other supporting arguments are the seasonality of $\Delta O_3 + \Delta RH$- layers coinciding with the annual low in convective activity in FMA. We, however, cannot fully rule out a possible contribution of in-mixing of extratropical stratospheric air along the way to Palau. The additional use of aerosol observations from the co-located

500 lidar instrument ComCAL and potentially more tracer observations during the ACCLIP campaign in late summer 2022 will contribute to the debate. Further insights will be found during the next El Niño cycle, when the Walker circulation will reverse and we expect to observe a higher frequency of O_3+RH- air masses throughout the year.

We propose biomass burning or anthropogenic pollution as a source of O_3 production in dry, ozone-rich layers at their remote origin. Their seasonal occurrence tied to the position of the Intertropical Convergence Zone indeed opens a pathway

505 from potential source regions which is confirmed by the trajectory analysis. If the attribution to tropical biomass burning holds, this might become a strong argument for policy makers. Anderson et al. (2016) pointed out, that due to the contribution of tropospheric O_3 to radiative forcing, present legislation aiming at the limitation of O_3 precursor emissions in the extra-tropics might not be enough to mitigate climate change.

6   Conclusions

510 Our study sheds light on air mass transport to the TWP as a key region of stratospheric entry and sets a valuable contribution to the discussion about anomalous layers of dry ozone-rich air. With our Lagrangian backward trajectory and seasonal analysis of the balloon-borne PAO O_3 and RH time series (2016-19) we can differentiate between air masses in the 5-10 km altitude range above Palau regarding their origin, frequency and underlying processes. We conclude, that humid, ozone-poor ($\Delta O_3 \circ \Delta RH \circ$) air masses are of local or Pacific convective origin and occur year-round, but dominate from August until Oc-

515 tober. Anomalously dry ozone-rich ($\Delta O_3 + \Delta RH$-) air is generated in Tropical Asia and subsequently transported to the TWP via an anticyclonic route, mostly from February to April. The areas of origin suggest different sources of ground pollution as a cause for O_3 production. No evidence for a potential stratospheric origin was found by investigating the 1.5 PVU threshold of 10-days backward trajectories or by analyzing the geographical distribution of their origin. Some potential contribution from

520 in-mixing of extra-tropical stratospheric air cannot be ruled out. We thus propose that large-scale descent within the tropical troposphere and subsequent radiative cooling in connection with the Hadley circulation is responsible for the vertical displacement and dehydration. In the future, an extended time series incorporating more ENSO cycles, coinciding measurements from the ACCLIP campaign and aerosol observations by the co-located lidar system ComCAL will be applied to further validate the non-stratospheric origin of anomalous layers.

525 In summary, the TWP is characterized by very clean air and generally exceptionally low O_3 concentrations in the free troposphere. However, layers of enhanced O_3 levels deviate significantly from this clean background, particularly during Northern Hemispheric spring. We present evidence that these layers are caused by anthropogenic pollution originating in South East Asia, rather than by stratospheric intrusions and the natural stratospheric O_3 production.

Appendix A

Figures A1, A2, A3 and A4 all give detailed insight into the seasonal or monthly variability of O_3 VMR and RH measured at the PAO. The following Figs. A5, A6 and A8 refer to the anomaly categories $\Delta O_3 \Delta RH$ as defined in Sect. 3.1.3. Figure A7 shows data from the trajectory dataset for the seasons FMA and ASO.
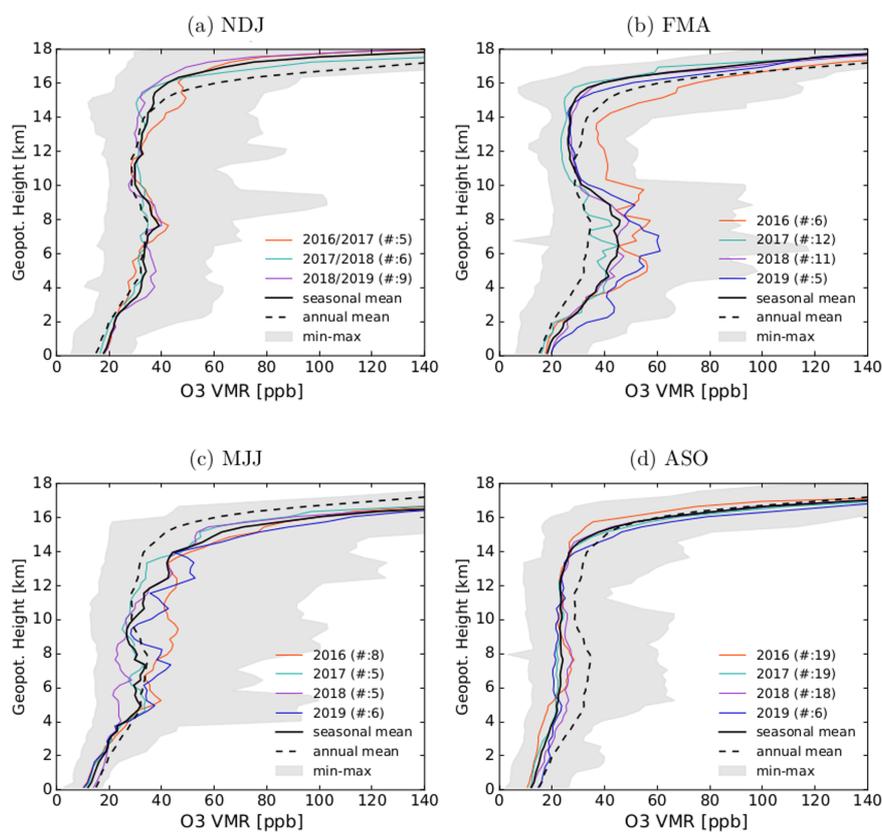
Figure A1. Variability of seasonal mean O_3 VMR profiles for Palau (black solid lines) in comparison to the long-term annual mean (dashed black line) in individual panels per season (a-d), all excluding the El Niño 2016 event, i.e. starting 08/2016; the grey shaded area encloses all observations, minimum to maximum, thin colored lines indicate seasonal means per year, number (#) of profiles included in the calculations given in brackets (compare Fig. 6).
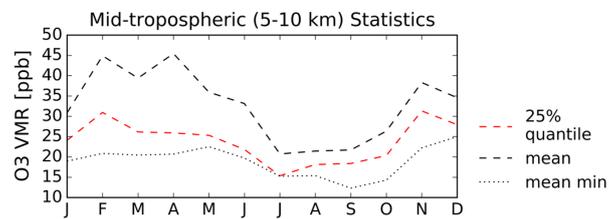
Figure A2. Statistical O_3 VMR measures for the 5-10 km altitude range highlighting the minimum O_3 season: monthly means from individual soundings' 25 % quantiles (red dashed line), mean (black dashed line) and minimum (black dotted line).
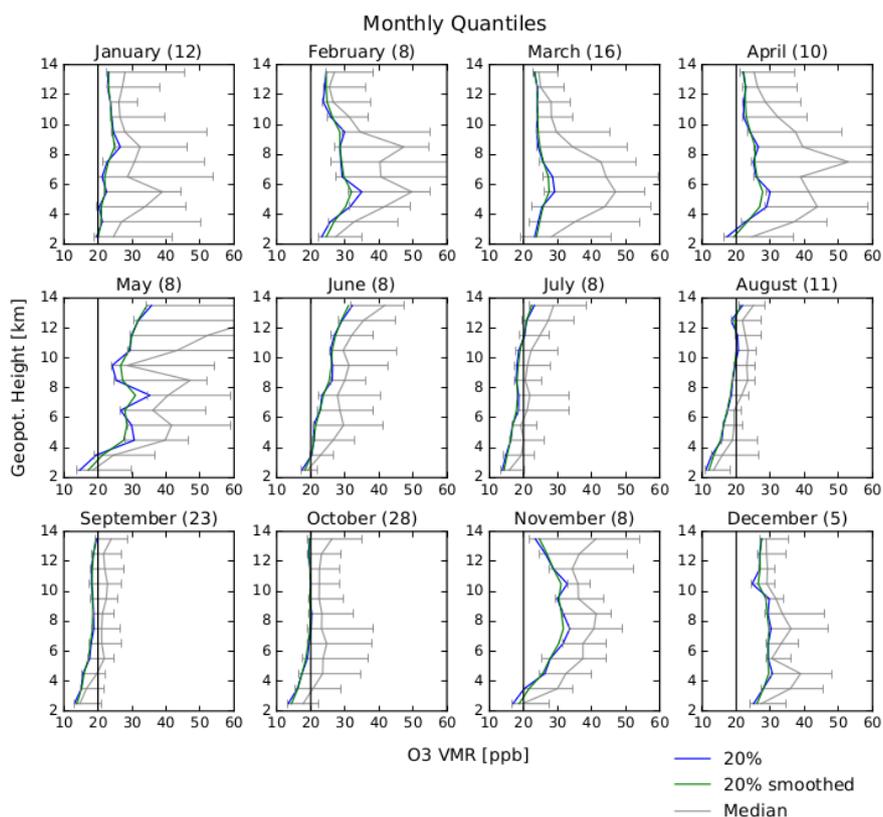
Figure A3. Monthly O_3 VMR statistics for Palau free tropospheric profiles per km: 20th quantile (Q20) in blue, vertically smoothed using exponentially weighted averages in green, median in grey and central 66.6 % range in grey horizontal bars; number of included individual profiles in brackets, for orientation 20 ppb O_3 VMR is marked as a black vertical line (compare Figs. 4 and A4).
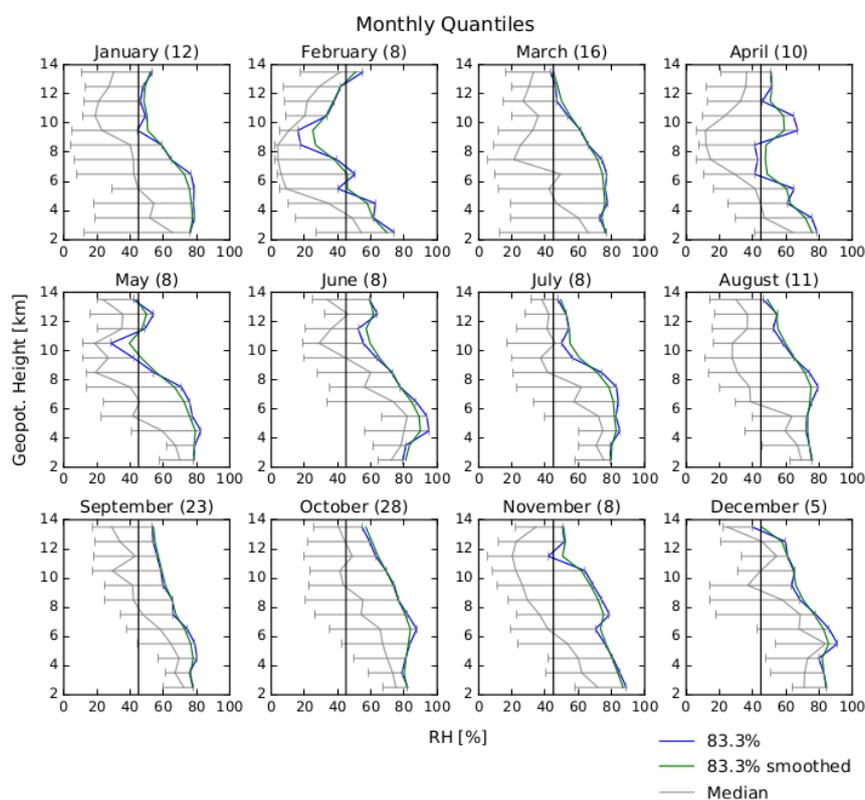
Figure A4. Monthly RH statistics for Palau free tropospheric profiles per km: 83.3th quantile (Q83) in blue, for more details see Fig. A3; 45 % RH is highlighted by a black vertical line (compare Figs. 4 and A3).
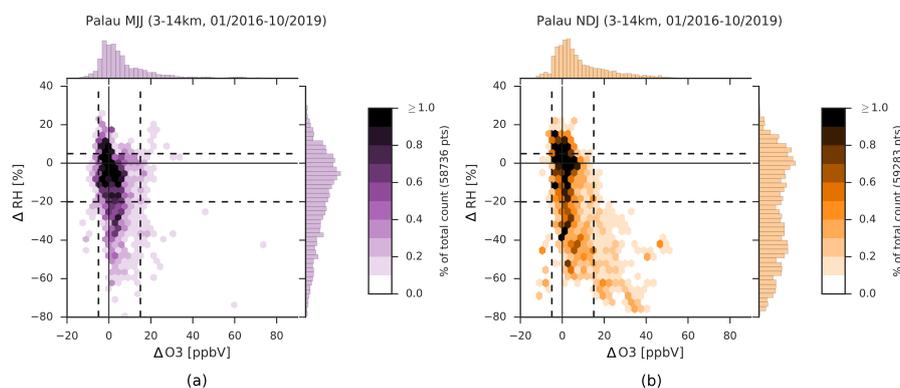
Figure A5. Seasonal free-tropospheric (3-14 km) relation between tracer anomalies ΔO_3 VMR and ΔRH for November-December-January (NDJ) (a) and May-June-July (MJJ) (b), colors according to Fig. 6, more details in Figs. 8 and 7.
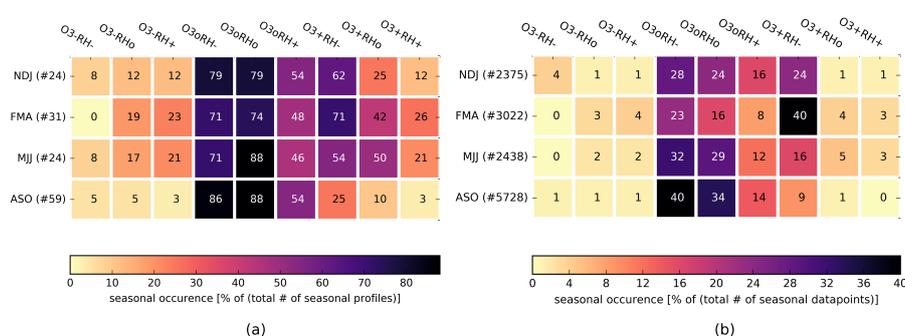
Figure A6. Heat map for the seasonal occurrence of air mass anomaly categories $\Delta O_3/\Delta RH$ regarding the definition given in Sect. 3.1.3 and presented in Fig. 7 for Palau observations in the 5-10 km altitude range (trajectory dataset, see Sect. 2); panel (a) shows the occurrence relative to the total number (#) of seasonal profiles and panel (b) relative to the total number of all data points within the season; total numbers are given in brackets per season.

For the trajectory dataset in the 5-10 km altitude range, we observed $\Delta O_3 \circ \Delta RH \circ$ air masses in 74 % of FMA profiles and 88 % of ASO profiles (Fig. A6). $\Delta O_3 + \Delta RH$- air masses occur in 71 % of all individual FMA profiles and only 25 % of ASO profiles. In relation to the total number of seasonal data points, this contrast is even stronger: 40 % of all observed FMA data points and only 9 % of all ASO data points are identified as $\Delta O_3 + \Delta RH$- air.
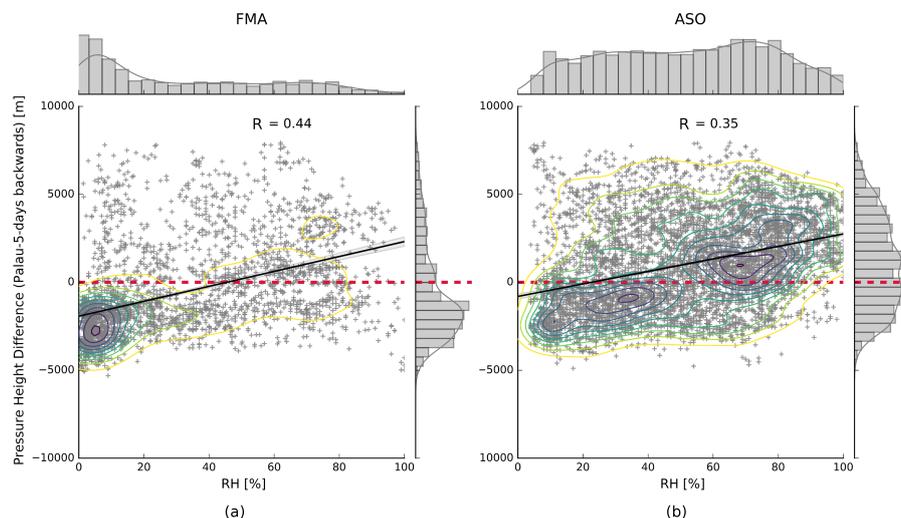
Figure A7. Measured relative humidity (RH) in relation to difference in pressure altitude (measured - 5 days before measurement) derived from the backward trajectory analysis for the seasons FMA (a) and ASO (b); grey "+" indicate individual measurements from the trajectory dataset, colored contours show the distribution density, the black line indicates a fit by linear regression with a grey shaded 95 % confidence interval, the red dashed line highlights the zero line for the altitude difference with positive values indicating ascent and negative values descent towards Palau, correlation coefficient R is shown in the plot; the marginal plots show univariate histograms and kernel-density estimated curves.

540   Figure A7 visualizes the correlation between RH and ascent/descent in a 2D histogram with a linear regression line. For FMA (Fig. A7a), the distribution emphasized by the marginal histogram plots for both parameters reveals a cluster of very dry (<20 % RH) air masses that descended towards Palau ($\approx$ 3 km). This cluster at the lower end of the physically possible scale dampens the correlation between the two parameters, which is surprisingly low despite the clear geographical separation visible in Fig. 10c.
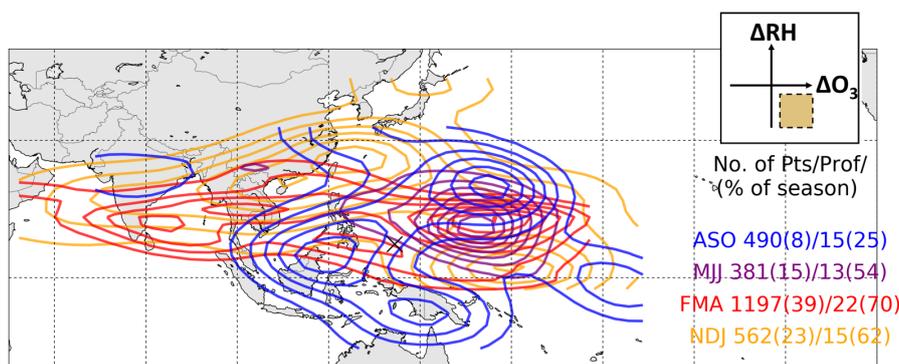
Figure A8. Seasonal distributions of $\Delta O_3 + \Delta RH-$ air masses according to the definition shown in Fig. 7 from 5-days backward trajectory earliest points arriving in Palau within 5-10 km; number of individual air masses (points) and profiles per season given in absolute values and as seasonal fraction in brackets.

Appendix B: Statistical Averages

There are different ways to derive a climatological season average and choosing the best-suited definition is not trivial with our given data set. Data from an individual sounding are first averaged within 300 m height bins using an arithmetic mean (hereafter referred to as "mean"), which essentially complies with the vertical measurement resolution, introducing only a slightly further smoothing (c.f. Müller et al., 2023). In the following temporal binning, the order of required steps must be considered as they lead to different values in our time series. There are four different possible sequences for (i) monthly, (ii) seasonal and (iii) annual averaging (Müller, 2020). In our case, we chose to first directly average individual profiles $x_i(m,y)$ of month m of all years y to a climatological month mean, climmonmean(m), then to a climatological season mean over all years, climseasmean(s):

$$\text{climmonmean}(m) = \frac{1}{\sum\limits_{y=1}^{Y} N(m,y)} * \sum_{y=1}^{Y} \sum_{i=1}^{N(m,y)} x_i(m,y) \tag{B1}$$

$$\text{climseasmean}(s) = \frac{1}{M(s)} * \sum_{i=1}^{M(s)} \text{climmonmean}(i), \tag{B2}$$

with $M(s)$ as the months in season s, $N(m,y)$ as the number of profiles in month m of year y and Y as the number of years. climseasmean(s) will not overestimate single months with very few and/or outlying profiles, assuming the interannual variability of the months is small compared to variations between different months.

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