

# Observations of ozone-poor air in the Tropical Tropopause Layer

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**Abstract.** Ozonesondes reaching the tropical tropopause layer (TTL) over the West Pacific have occasionally measured layers of very low ozone concentrations—less than 15 ppbv—raising the question of how prevalent such layers are and how they are formed. In this paper we examine aircraft measurements from the ATTREX, CAST and CONTRAST campaigns based in Guam in January–March 2014 for evidence of very low ozone concentrations and their relation to deep convection. The study builds on results from the ozonesonde campaign conducted from Manus Island, Papua New Guinea, as part of CAST, where ozone concentrations as low as 12 ppbv were observed between 100 and 150 hPa downwind of a deep convective complex.

TTL measurements from the Global Hawk unmanned aircraft show a marked contrast between the hemispheres, with mean ozone concentrations in profiles in the Southern Hemisphere between 100 hPa and 150 hPa of [between 10.7 ppbv and 15.2 ppbv](#). By contrast, the mean ozone concentrations in profiles in the Northern Hemisphere were always above [15.4 ppbv](#) and normally above 20 ppbv at these altitudes. The CAST and CONTRAST aircraft sampled the atmosphere between the surface and 120 hPa, finding very low ozone concentrations only between the surface and 700 hPa; mixing ratios as low as 7 ppbv were regularly measured in the boundary layer, whereas in the free troposphere above 200 hPa concentrations were generally well in excess of 15 ppbv. These results are consistent with uplift of almost-unmixed boundary layer air to the TTL in deep convection. An interhemispheric difference was found in the TTL ozone concentrations, with values <15 ppbv measured extensively in

the Southern Hemisphere but seldom in the Northern Hemisphere. This is consistent with a similar contrast in the low-level ozone between the two hemispheres found by previous measurement campaigns. Further evidence of a boundary layer origin for the uplifted air is provided by the anticorrelation between ozone and halogenated hydrocarbons of marine origin observed by the three aircraft.

## 1 Introduction

### 1.1 Background

Air entering the stratosphere in the Brewer–Dobson circulation originates in the Tropical Tropopause layer (TTL), a region between around 13 and 17 km altitude with characteristics intermediate between the highly convective troposphere below and the stratified stratosphere above (Holton et al., 1995; Highwood & Hoskins, 1998; Folkins et al., 1999; Gettelman & Forster, 2002; Fueglistaler et al., 2009). The TTL lies above the main convective outflow (10–13 km) and although deep convection can reach, and even overshoot the tropopause (e.g. Frey et al., 2015), the region is not well-mixed and both radiative and large-scale dynamical processes influence its structure and composition (Fueglistaler et al., 2009). A key question about the TTL is whether deep convection is nevertheless capable of lifting very short-lived halogenated species near enough to the tropopause that their breakdown products reach the stratosphere and contribute to ozone destruction. In this paper we use ozone measurements

from a unique aircraft campaign to investigate the uplift of air from near the Earth's surface to the TTL.

The oceanic Tropical Warm Pool in the Western Pacific and Maritime Continent is marked by very warm surface temperatures ( $>27^{\circ}\text{C}$ ) and is therefore able to sustain widespread deep convection. Above the Warm Pool a number of ozonesonde observations have shown very low ozone concentrations near the tropopause (Kley et al., 1996; Heyes et al., 2009; Rex et al., 2014; Newton et al., 2016), possibly indicative of uplift of near-surface air by deep convection. Unfortunately, accurate ozonesonde measurements in this part of the atmosphere are very difficult as the sondes produce a poorly-characterized background current which can be half the measured signal in the TTL (Vömel & Diaz, 2010; Newton et al., 2016). Nevertheless, even after taking this into account, there is evidence of ozone mixing ratios  $< 15$  ppbv occurring just below the tropopause. These are found in localized regions, or bubbles, generally associated with deep convection.

The first evidence of localized low-ozone bubbles in the TTL in the West Pacific region was provided by the CEPEX campaign (Kley et al., 1996), where near-zero ozone concentrations were reported between the Solomon Islands and Christmas Island. These ozonesondes were affected by the background current problem, and after Vömel & Diaz (2010) reanalyzed the data with a more representative background current correction, the minimum measured ozone concentration was  $\sim 8$  ppbv. Ozone concentrations  $< 15$  ppbv were found by Heyes et al. (2009) in Darwin, Australia in the ACTIVE campaign in 2005–6, and on the TransBrom cruise of 2009 in the West Pacific (Rex et al., 2014). More recently, Newton et al. (2016) presented TTL ozone measurements as low as 12 ppbv from Manus Island, Papua New Guinea ( $2.07^{\circ}\text{S}$ ,  $147.4^{\circ}\text{E}$ ); we discuss these measurements in more detail in section 3.

Bubbles of relatively low ozone have also been observed in other parts of the world. During the TC4 campaign, anomalously low ozone concentrations of  $\sim 60$  ppbv were found at 14–16 km altitude in the TTL off the coast of Ecuador—typical values of ozone at this altitude in this region were measured to be  $\geq 100$  ppbv. These low-ozone bubbles were also shown to be a result of non-local convection followed by advection to where it was measured by the NASA DC-8 aircraft (Petropavlovskikh et al., 2010).

The mechanism for producing low-ozone bubbles in the TTL are not fully understood. Clearly, uplift in deep convection is the underlying cause, but deep convection is a turbulent process and air entering at the surface would be expected to mix with its surroundings during ascent. Noting that the minimum ozone concentrations observed in the TTL above Darwin were too low to originate in the boundary layer locally, Heyes et al. (2009) proposed long-range transport in the TTL from a 'hot-spot' region north-east of New Guinea. Newton et al. (2016) found that the minimum concentrations measured over Manus were only consistent with ozone mea-

surements in the lowest 300 m over the island, suggesting uplift of air from near the surface to the TTL with little or no mixing (see below). Clearly, there is a need to corroborate these sporadic ozonesonde observations with other measurements and to determine how widespread these bubbles of low-ozone air are over the Warm Pool. This is the purpose of the present paper.

During January–March 2014, a coordinated aircraft campaign was conducted from Guam ( $13.44^{\circ}\text{N}$ ,  $144.80^{\circ}\text{E}$ ) to measure the atmosphere over the Tropical Warm Pool in unprecedented detail. Three aircraft were involved:

- the NASA Global Hawk unmanned aircraft, as part of the Airborne Tropical Tropopause Experiment, AT-TREX (Jensen et al., 2017)
- the NCAR Gulfstream V research aircraft, as part of the Convective Transport of Active Species in the Tropics Experiment, CONTRAST (Pan et al., 2017)
- the UK Facility for Airborne Atmospheric Measurement (FAAM) BAe 146 aircraft, as part of the Coordinated Airborne Studies in the Tropics (CAST) experiment, (Harris et al., 2017)

Together these three aircraft were able to sample the tropical atmosphere from the surface to the lower stratosphere, enabling detailed measurements of the inflow and outflow of deep convection and the environment in which it formed. Of particular interest to this paper is the Global Hawk, which extensively sampled the TTL. With a typical flight range of 16,000 km and duration of up to 24 hr, the aircraft continuously executed profiles between 45,000 ft (13.7 km) and 53,000–60,000 ft (16.2–18.3 km) (Jensen et al., 2017). Thus it was able to gather a wealth of profiles of ozone and other gases through the TTL both in the Northern and Southern Hemisphere. The NCAR Gulfstream V aircraft sampled mainly in the Northern Hemisphere, between sea level and 15 km altitude (Pan et al., 2017) although some measurements were also made in the Southern Hemisphere, most notably on a flight to  $20^{\circ}\text{S}$  on 22 February 2014. The FAAM aircraft sampled the lower atmosphere, from the ground to 10 km altitude but with most of the measurements in the boundary layer. These measurements were almost all in the Northern Hemisphere.

## 1.2 Article overview

In section 2 we describe the instruments that were used on board the three aircraft to collect the measurements described in this article. Section 3 provides a brief overview of the CAST ozonesonde measurements from Manus, which were described in detail in Newton et al. (2016), that provided the first evidence of the occurrence of localized low ozone concentrations during the campaign.

We then introduce the Global Hawk ozone profiles in section 4, concentrating on one flight that sampled well into the Southern Hemisphere from Guam in section 4.3—this flight produced further evidence of low-ozone concentrations, especially in the Southern Hemisphere portion of the flight. Within this section, we also discuss the uncertainties, and implications thereof, of the UCATS ozone instrument on board the Global Hawk, and how we approached the issue of noise in the UCATS dataset. This is followed by a brief discussion of the other ATTREX flights in section 4.4.

Section 5 discusses the lower troposphere measurements that were made by the CAST and CONTRAST aircraft, providing information on boundary layer ozone concentrations that can be used to infer the origin of low ozone in the TTL. Section 6 shows a subset of the very short lived substances (VSLs) that were measured using Whole Air Samplers (WAS) on board all three aircraft, showing the composition differences between the VSLs in low-ozone and high-ozone cases to infer that recently convected ozone-deficient air has a distinct chemical composition compared to high-ozone cases. (A supplementary section contains the full dataset of WAS VSLs chemical data.) Finally section 7 summarizes the findings of this article.

## 2 Instrumentation

Ozone was measured in situ by all three aircraft in the CAST, CONTRAST and ATTREX campaigns. The FAAM BAe 146 carried a Thermo Fischer Model 49C UV absorption photometer, which had an uncertainty of 2% and a precision of 1 ppbv for 4 s measurements (Harris et al., 2017). Ozone on the Gulfstream V aircraft was measured using the NCAR Chemiluminescence instrument, which uses the chemiluminescent reaction between nitric oxide and ozone. The detection limit was below 0.1 ppbv, and its accuracy within 5% for the entire range of ozone measurements made during CONTRAST (Ridley et al., 1992; Pan et al., 2015, 2017).

On the Global Hawk, the UCATS instrument (UAS (Unmanned Aerial System) Chromatograph for Atmospheric Trace Species) provided measurements of ozone, plus nitrous oxide ( $\text{N}_2\text{O}$ ), sulphur hexafluoride ( $\text{SF}_6$ ), hydrogen ( $\text{H}_2$ ), carbon monoxide ( $\text{CO}$ ) and methane ( $\text{CH}_4$ ) (Jensen et al., 2017). Ozone in the UCATS unit is measured by two Model 205 UV photometers from 2B Technologies (Boulder, Colorado) modified for high altitude operation. The first was mounted inside the UCATS package, whilst a second, newer Model 205 photometer was added to the front panel of the UCATS. Both instruments were modified to include stronger pumps (KNF model UNMP-830), scrubbers with magnesium oxide ( $\text{MgO}$ ) coated screens, and pressure sensors with a range from 0 hPa to >1000 hPa (Honeywell ADSX series). The model 205 is a 2-channel photometer, with the flow continuously split between the unscrubbed (ambient) air into one cell and scrubbed (ozone-free) air into the other for measurement by the Beer-Lambert law absorption of 253.7 nm radiation from a Hg lamp. Flow is switched every two seconds

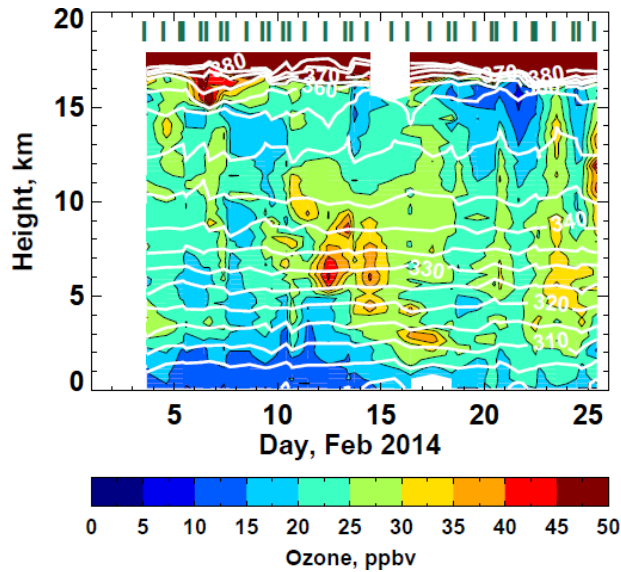
and data recorded at this rate for the newer instrument but averaged to 10 s in the older model. The instruments were calibrated on the ground against a NIST-certified calibration system (Thermo Electron, Inc.) before and after the mission. In both cases, the slope of the regression line between the instrument and calibrator data was within 1% of unity and the offset less than 2 ppbv (usually <1 ppbv) at ambient pressure and room temperature. However, in-flight comparisons on earlier ATTREX missions between the 2B instruments and the NOAA ozone photometer (Gao et al., 2012) revealed a possible negative bias of up to 5 ppbv at low ozone concentrations.

In addition to ozone data, selected whole air sampler (WAS) data are used to identify convective influence. Whole air samplers were on board all three aircraft, measuring a large array of compounds. All three aircraft measured dimethyl sulphide ( $(\text{CH}_3)_2\text{S}$ ), iodomethane ( $\text{CH}_3\text{I}$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), bromochloromethane ( $\text{CH}_2\text{BrCl}$ ), trichloromethane ( $\text{CHCl}_3$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ) and tribromomethane ( $\text{CHBr}_3$ ). The WAS samples collected on board the BAe 146 were analyzed typically within 72 hours of collection, with gas chromatography-mass spectrometry (GC-MS; Agilent 7890 GC, 5977 Xtr MSD) (Andrews et al., 2016; Harris et al., 2017). The CONTRAST and ATTREX whole air samples were analyzed for a much larger array of compounds, and were also analyzed by the GC-MS. The samples were split between an Agilent HP-AL/S PLOT (porous layer open tubular) column with a flame ionization detector, and the remaining sample was split again between an electron capture detector and an Agilent 5975 GC-MSD (gas chromatograph—mass selective detector) (Schaufler et al., 1999; Apel et al., 2003; Andrews et al., 2016).

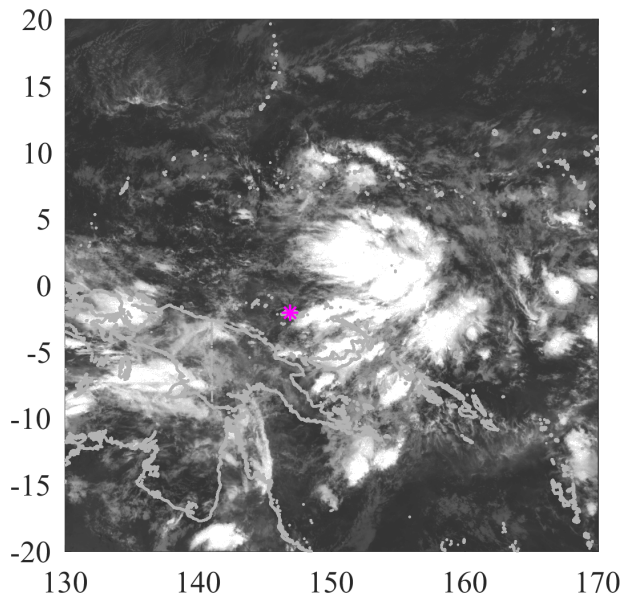
## 3 Manus ozonesondes

Thirty-three ozonesondes were launched from Manus Island during February 2014 as part of CAST. A salient result of the campaign was further insight into the background current: where this quantity was  $\lesssim 50$  nA, a constant offset was subtracted from the measured current, but when the background current was larger, a hybrid correction was applied which decreased with height (Newton et al., 2016). These procedures gave good agreement with nearby ozone measurements on the Gulfstream V on 5 and 22 February, verifying the use of ozonesondes to measure very low ozone concentrations near the tropical tropopause.

Another salient result from the ozonesonde measurements was the low-ozone event in the TTL between 18 and 23 February, visible in figure 1, where measured ozone was as low as 12 ppbv. As Folkins et al. (2002) argued, the only region of the tropical troposphere able to generate ozone concentrations  $\leq 20$  ppbv is near the surface, so this air mass is likely to be of recent boundary layer origin. Ozone concen-



**Figure 1.** Contour plot of ozone concentrations from the Manus ozonesondes. The white lines are potential temperature isolines. Note the very low concentrations in the upper troposphere around 21–22 February. Green bars along the top denote launch times of ozonesondes. For further details see Newton et al. (2016).



**Figure 2.** MTSAT infrared satellite image from 19 February 2014 at 18:00 UTC, showing the convection to the east of Manus Island (pink star) that was determined to be the origin of the low-ozone air in the TTL above Manus.

trations through most of the boundary layer over Manus in this period were higher than in the TTL; only in the bottom 300 m of the profiles did the ozonesondes measure  $< 20$  ppbv, with concentrations at the ground around 8–15 ppbv (Newton et al., 2016). This suggests either that the ozone-poor air was lifted from near the surface, or that bound-

ary layer ozone concentrations in the uplift region were lower than over Manus. A back-trajectory analysis of the low-ozone bubble with the on-line HYSPLIT model (Stein et al., 2015) indicated that the origin of the low concentrations of ozone was a mesoscale convective system to the east of Manus Island that uplifted air from the lower troposphere into the tropopause layer (see figure 2), combined with a strong easterly jet that advected the air towards Manus Island. Unfortunately, ozone measurements were not available in this area at this time so the altitude from which the ozone-poor air was lifted remains an open question. To examine whether further examples of ozone-poor layers were encountered during the CAST/CONTRAST/ATTREX campaign, we now examine the Global Hawk observations in the TTL during February and March 2014.

## 4 Global Hawk measurements

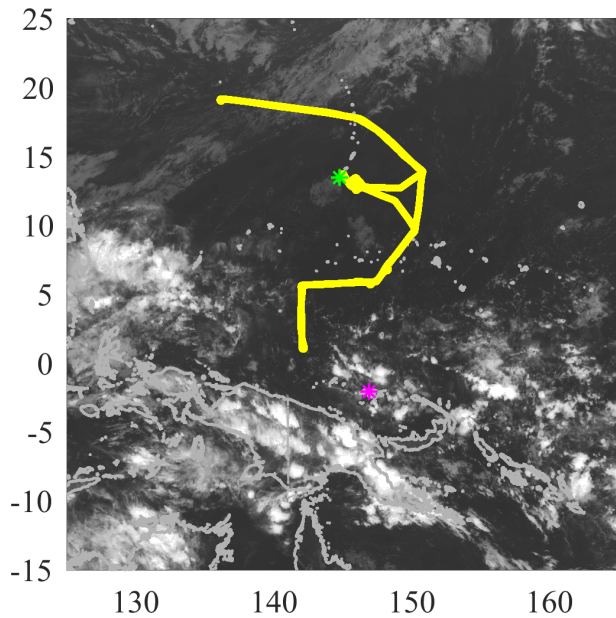
### 4.1 ATTREX flights

The Global Hawk measured in the same altitude range as the layer of ozone-poor air above Manus Island: the aircraft performed ascents and descents between 150 hPa (13.6 km) and 100 hPa–75 hPa (16.1 km–18.0 km), depending on fuel load. The ascent rate was slow, of the order of 45 minutes to complete at an average vertical velocity of  $\sim 0.5 \text{ m}\cdot\text{s}^{-1}$ , but the descent rate was much quicker, of the order of 5–10 minutes to complete at  $\sim 4 \text{ m}\cdot\text{s}^{-1}$ . Only the ascent data are used in this study as the descent was found to be too quick for reliable ozone measurements.

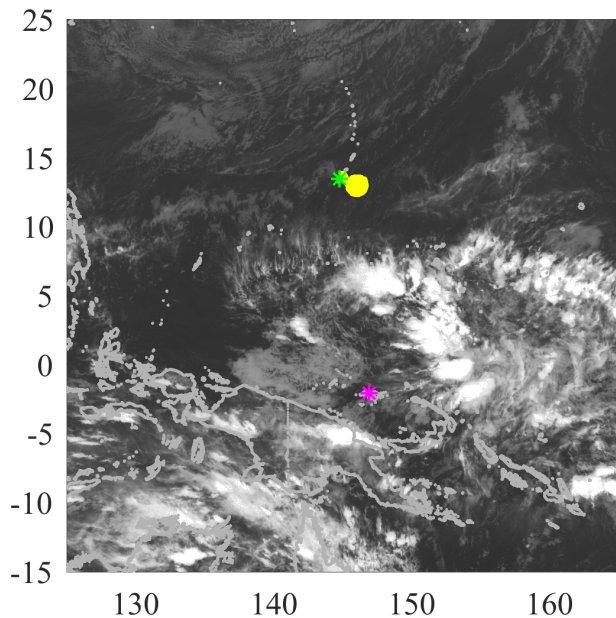
In total, six research flights were flown by the Global Hawk from Guam during the ATTREX campaign. The first two, RF01 and RF02, were on 12 and 16 February when the CAST and CONTRAST campaigns were active, but there was a gap of fifteen days between the second and third flights as the aircraft developed a problem; the final four flights, RF03, RF04, RF05 and RF06 were on 4, 6, 9 and 11 March respectively—after CAST and CONTRAST had finished. [The transfer flight from Armstrong Flight Research Center in California to Andersen Air Force Base in Guam on 16 January and the return flight on 13 March made few measurements in the West Pacific region and are not considered here.](#)

Flight RF01 on 12–13 February focused on the composition, humidity, clouds and thermal structure of the Northern Hemisphere part of the Warm Pool region. Convection was situated mostly around the Maritime Continent on this day (figure 3), with no notable convection around Guam. The second flight, RF02 occurred on 16–17 February with similar scientific objectives to RF01. As a result of a satellite communications problem, the aircraft was required to stay in line-of-sight contact with the airbase in Guam, and consequently the aircraft flew in a small area of airspace close to





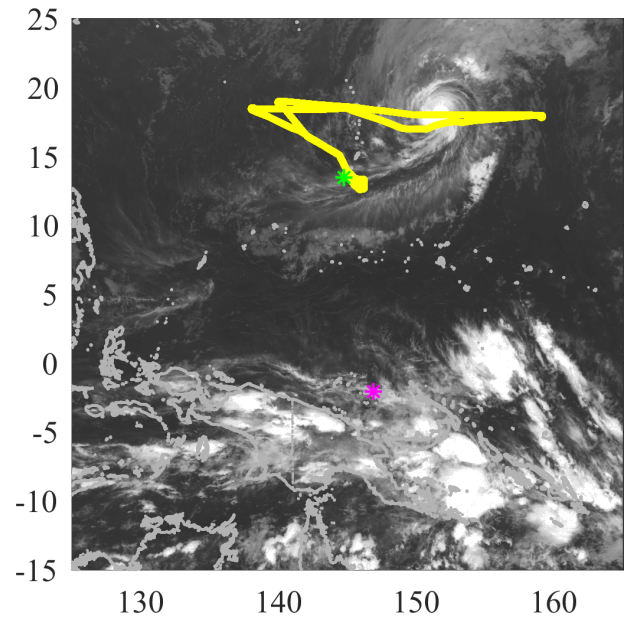
**Figure 3.** MTSAT infrared satellite image from 12 February at 12:00 UTC, coincident with flight RF01 (yellow track). Green asterisk denotes location of Guam; magenta asterisk that of Manus Island. Convection is centred mostly around the Maritime Continent on this day.



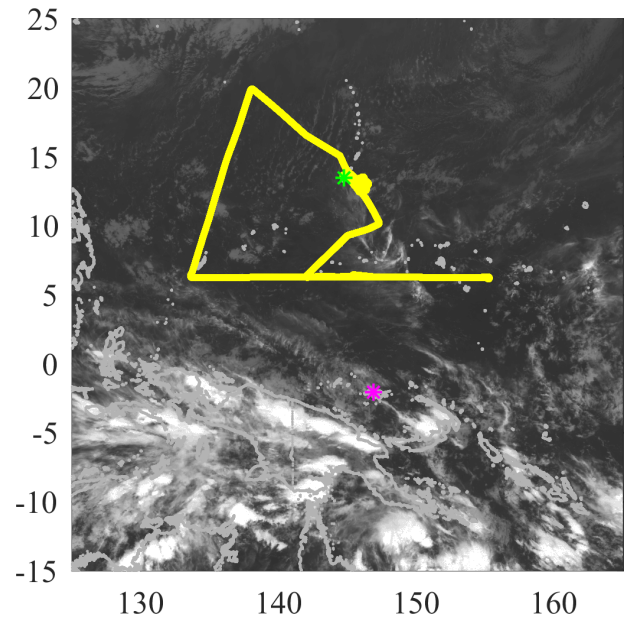
**Figure 4.** As figure 3 but for 16 February at 12:00 UTC coincident with flight RF02. A band of convective activity is visible to the southeast of Guam.

the island. On this day, convection was visible to the southeast of Guam in the MTSAT satellite imagery (figure 4).

The third flight took place after a two-week hiatus on 4–5 March. Its objectives were to sample the outflow of tropical cyclone Faxai, which developed in the region in the pre-



**Figure 5.** Satellite image of March 4 at 12:00 UTC, coincident with flight RF03. Cyclone Faxai is visible to the northeast of Guam.



**Figure 6.** Satellite image of March 6 at 12:00 UTC, coincident with flight RF04. Convection is minimal in the Northern Hemisphere, and is concentrated mostly in the Southern Hemisphere.

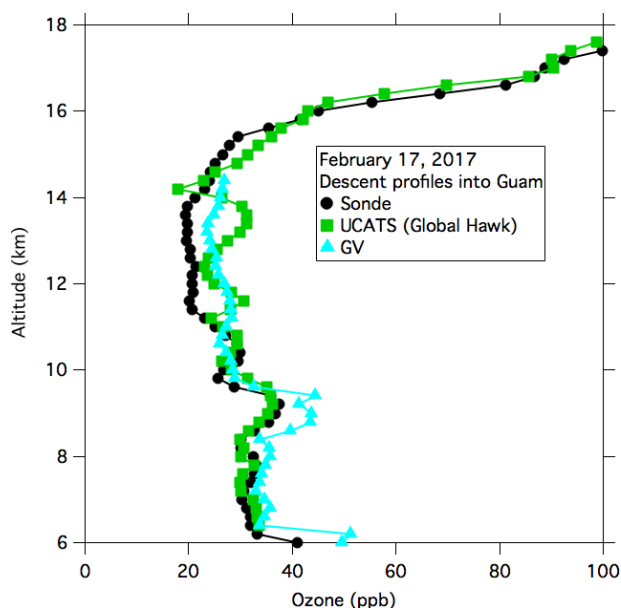
vious few days, with vertical profiles performed to observe the outflow cirrus cloud from the cyclone. Apart from tropical cyclone Faxai, the majority of the convection was in the Southern Hemisphere around Papua New Guinea (figure 5).

Flight RF04 took place on 6–7 March. Tropical cyclone Faxai had dissipated by this time, leaving a dearth of convection in the Northern Hemisphere; the most convectively ac-

tive region was around Papua New Guinea (figure 6). RF05 surveyed the Southern Hemisphere on 9–10 March, measuring the lowest ozone concentrations observed by the Global Hawk during the ATTREX campaign. This flight is discussed in detail in the next section. The final research flight, RF06, took place on 11–12 March, surveying latitudes north of 10°N either side of the subtropical jet, and is outside the scope of this paper. A full description of the ATTREX flights and meteorological conditions encountered can be found in Jensen et al. (2017).

## 4.2 Systematic errors in ATTREX ozone data

As discussed in section 2, previous studies have suggested there may be a low bias in UCATS ozone measurements. Fortunately, flight RF02 on 16/17 February offered an opportunity to examine data from this campaign for any evidence of such a bias. As shown in figure 4 (and later, figure 16), the entire flight took place just south-east of Guam, within an area spanning 1° in latitude and longitude.



**Figure 7.** Intercomparison of UCATS descent ozone profile on RF02 with nearby profiles from the Gulfstream V and an ozonesonde. The Global Hawk profile was measured between 09:20 and 10:45 UTC, the sonde between 08:46 and 10:44 UTC and the Gulfstream V between 05:02 and 05:23 UTC.

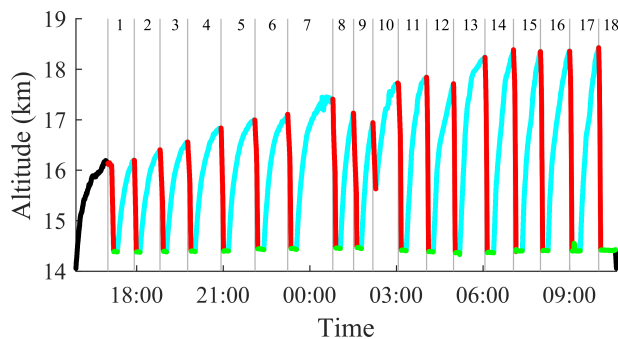
Figure 7 shows a comparison between UCATS data measured on the descent to Guam, the descent profile from the Gulfstream V (around 5 hours earlier), and the descent profile from an ozonesonde coincident in time with the Global Hawk descent. (The ozonesondes were flown with a valved balloon, allowing both ascent and descent rates to remain below 6 m s<sup>-1</sup>, thus enabling ozone measurements on descent). The UCATS ozone follows the descent sonde profile closely

below 10 km, but in the region of lowest ozone concentration, between 12 and 14 km, it tends to be more consistent with the Gulfstream V, although showing rather more structure than the other two profiles.

Given the obvious variability in tropospheric ozone shown by figure 7, a quantitative validation of the UCATS ozone would require many more comparisons. We can conclude however that there is no evidence from this example of a low bias in the UCATS measurements at low concentrations. This allows measurements across the Tropical Warm Pool by the Global Hawk to be used to explore regions of very low ozone concentration.

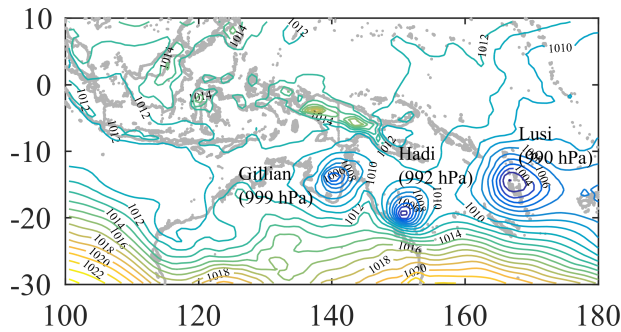
## 4.3 ATTREX flight RF05

ATTREX RF05 surveyed into the Southern Hemisphere on 9–10 March, sampling the outflow of strong convection along the South Pacific Convergence Zone (SPCZ). The aircraft took off at 15:30 UTC on 9 March and flew a straight path southeast, reaching its furthest point away from Guam at 00:30 UTC on 10 March before returning on a path closer to the Solomon Islands and Papua New Guinea. The aircraft returned to the vicinity of Guam at around 08:00 UTC and flew around the island before landing at 11:00 UTC. Figure 8 shows the altitude of the aircraft during RF05: after the initial ascent there were basically 18 repeats of a relatively rapid descent, a short level section near 14.5 km, and relatively slow ascent (with the exceptions that there was no level section in set 10 and the aircraft descended to Guam after the final level section).



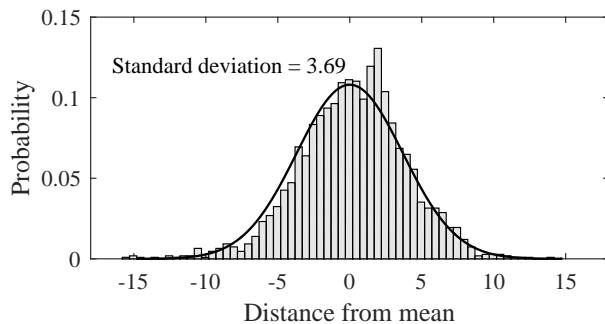
**Figure 8.** Altitude of Global Hawk on RF05 as a function of time. The flight has been divided into sections, numbered at the top of the plot; these numbers correspond to the section or profile numbers in figures 11, 12 and 14.

Large amounts of convection were present in the Southern Hemispheric portion of the Warm Pool region around the time of ATTREX RF05. A series of tropical cyclones are shown in the synoptic analysis chart in figure 9: tropical cyclone Gillian in the Gulf of Carpentaria, tropical cyclone Hadi near the east coast of Queensland, and Tropical Storm Lusi which was intensifying to become a tropical cyclone near the Solomon Islands on 10 March.



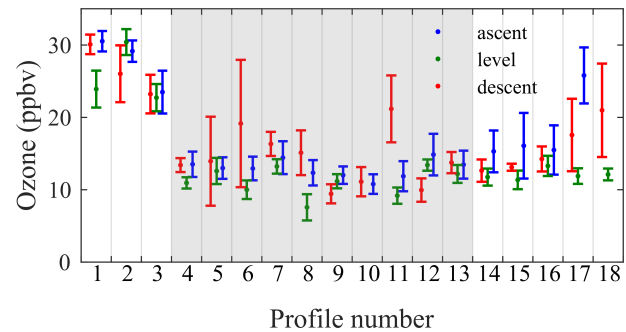
**Figure 9.** Synoptic chart from ECMWF ERA-Interim data from 10 March at 00:00 UTC. The three tropical cyclones are labelled, along with their central minimum pressure.

Before examining the Global Hawk ozone measurements in a meteorological context, account needs to be taken of noise in the UCATS data. Ozone measurements from the level sections (figure 8) were first examined to determine the random measurement error. The combined histogram of the departures from the mean along each level section is shown in figure 10; this approximates well to a Gaussian distribution with standard deviation 3.69 ppbv, suggesting that instrumental random errors in UCATS may be reduced by averaging the data.



**Figure 10.** Histogram of departures of UCATS ozone measurements from the mean along each level section of flight.

As the standard deviation is so large compared with the background ozone values in low-ozone bubbles (< 15 ppbv), there is little to be gained from trying to identify individual structures in the ascent and descent profiles. Instead, the approach used here is to average all the data in the troposphere above 14 km along an individual ascent or descent. This requires a definition of the tropopause, taken to be the lowest altitude above which ozone increases by 20 ppbv within a 5 hPa span, and continues to increase thereafter to >50 ppbv. The result of averaging the data along each flight section in this way is shown in figure 11. To calculate the error bars, consideration needs to be given to real variations of ozone along the profiles, which affect the statistical independence of the measurement points. The method described by Wilks



**Figure 11.** Means and  $1\sigma$  standard errors of UCATS ozone along the different sections of RF05. Shading denotes profiles in the Southern Hemisphere.

(1995, p.127) was used to calculate the effective number of independent points  $N'$ :

$$N' = \frac{N(1 - \rho_1)}{(1 + \rho_1)}$$

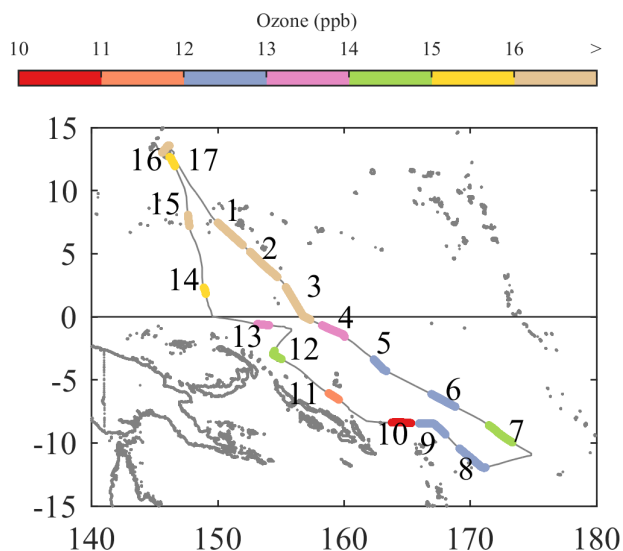
where  $N$  is the number of data points along a section and  $\rho_1$  is the lag-1 autocorrelation of the data along that section. The standard error in the mean was then calculated as  $\sigma/\sqrt{N'}$ , where  $\sigma$  was the standard deviation for that section.

The three sets of points shown in figure 11 are independent of one another, and show a consistent pattern. For the first three sets, all the means were above 20 ppbv, with a sharp fall to < 15 ppbv in set 4. The means along the level sections remained below 15 ppbv thereafter, but the ascent and descent averages show an increase towards the end of the flight. As expected given the slower ascents and faster descents, error bars for the descents tend to be larger than for the ascents for most of the profiles. Averages along the ascent profiles therefore provide the most precise and representative measures of the mean TTL ozone concentration along the flight path, with a typical standard error of 2 ppbv. We now examine these means in a meteorological context.

Mean concentrations derived from the ascent profiles during RF05 are shown in figure 12, where it can be seen that the mean tropospheric ozone concentrations are lowest in the Southern Hemisphere, typically between 10 and 13 ppbv. These values are very similar to those measured in the TTL over Manus between 18 and 23 February. In the Northern Hemisphere, ozone concentrations on the return leg (between 06:00 UTC and 08:30 UTC on 10 March) were ~15–16 ppbv on average, compared to the outbound leg (between 15:45 UTC and 19:45 UTC on 9 March), which were above 30 ppbv.

The relationship between the appearance of the low concentrations of ozone and areas of deep convection was investigated using the Met Office's Numerical Atmospheric-dispersion Modelling Environment (NAME) (Jones et al., 2007). NAME is a Lagrangian model in which particles are released into 3-D wind fields from the operational output of



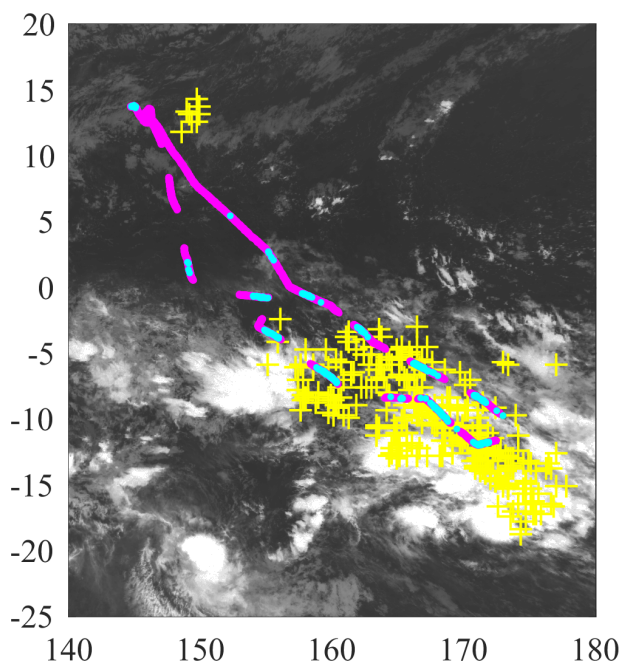


**Figure 12.** Flight track of RF05, with each ascent profile performed by the Global Hawk chronologically numbered, and coloured by mean tropospheric ozone in each profile. The length of each coloured profile corresponds to the time the aircraft was below the tropopause on that section.

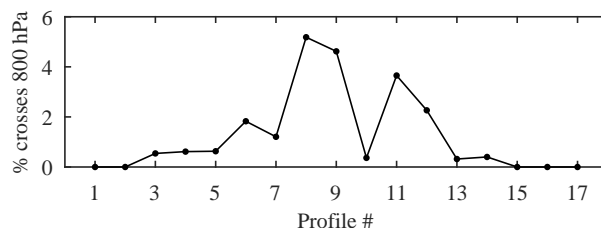
the UK Met Office Unified Model meteorology data (Davies et al., 2005). These winds have a horizontal resolution of 17 km and 70 vertical levels, which reach  $\sim 80$  km. In addition, a random walk technique was used to model the effects of turbulence on the trajectories (Ryall et al., 2001). The NAME model was used in single-particle mode, initializing one trajectory at each point along the RF05 flight track where an ozone measurement was made. Back-trajectories were run for one day, with output at six-hour intervals.

NAME suggests that the Southern Hemisphere air originated from the southeast, in the area where tropical cyclone Lusi was situated. Figure 13 shows the start-points of the back-trajectories initialized in the troposphere (below 100 hPa) along the flight track of RF05: sections of track from which back-trajectories crossed the 800 hPa isobaric surface are shown in cyan; sections where they did not are in magenta. The yellow markers denote the final position, after 24 hours, of the back-trajectories that crossed the 800 hPa isobaric surface, indicative of rapid convection. The majority of these trajectories are in the Southern Hemispheric portion of the flight, and are projected by NAME to originate from tropical cyclone Lusi. It should be noted that the NAME model cannot capture the effect of individual convective cells because of the low horizontal resolution of the meteorological data, but its convection parameterization is capable of reproducing net vertical transport over relatively large areas (Ashfold et al., 2012; Meneguz & Thomson, 2014).

The back-trajectories initialized in the Northern Hemisphere also came from the southeast, but in the twenty-four hour period of the NAME model run, the trajectories had



**Figure 13.** MTSAT infrared satellite image at 18:00 UTC on 8 March 2014, around 24 hours before the mid-point of flight RF05 to coincide with the endpoints of the 24 hour back-trajectories. Tropical storm Lusi is visible as the cluster of convection centred around ( $170^{\circ}\text{E}$   $20^{\circ}\text{S}$ ). The tropospheric ( $>100$  hPa) portion of the flight track of RF05 is shown in magenta, and, in the case where trajectories crossed the 800 hPa isobaric surface, in cyan. The positions after 24 hours of the trajectories that crossed the 800 hPa isobaric surface at some point in the model are marked as yellow crosses.

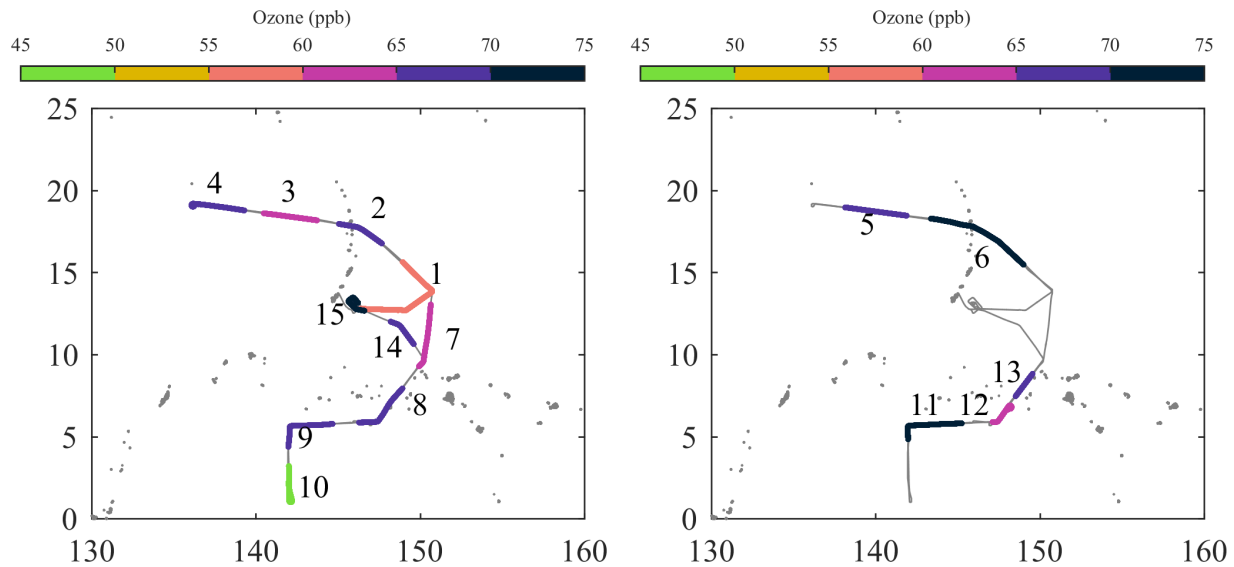


**Figure 14.** Percentage of back-trajectories crossing the 800 hPa surface within one day from the different ascent profiles on RF05.

only reached the edge of the tropical storm, so the sampled air mass passed through this region whilst the storm was developing, rather than when it was mature.

Figure 14 shows the number of back-trajectories that crossed the 800 hPa isobaric surface. None of those initialized from the Northern Hemisphere profiles 1, 2, 15, 16 and 17 crossed 800 hPa, and fewer than 1% from profiles 3, 4, 5, 13 and 14 did so. However, up to 5% of back-trajectories initialized along profiles 6–12 in the Southern Hemisphere cross the 800 hPa isobaric surface, with exception of profile 10. These are also the sections with the lowest ozone





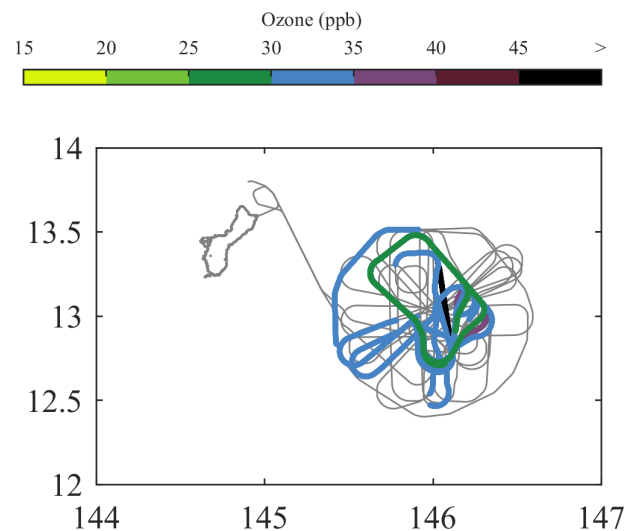
**Figure 15.** Flight track of RF01 with each profile coloured by mean tropospheric ozone as in figure 12. The profiles that would otherwise be obscured by other profiles are shown on the right-hand plot.

concentrations, with values similar to those observed by the ozonesondes over Manus. Again, the low concentrations are consistent with recent uplift in deep convection.

#### 4.4 Other ATTREX flights

The other research flights observed no notably low ozone concentrations in the tropical tropopause layer, hinting that the lowest ozone concentrations were confined to the Southern Hemisphere during the ATTREX campaign. RF01 flew in an arc, approximately following the streamlines of the monsoon anticyclone, which, along with most of the convection that day was situated a long way to the west of Guam. Ozone concentrations on this flight were high, and none of the profiles had mean tropospheric concentrations below 45 ppbv (figure 15). Likewise, RF02, which flew within a small circle of airspace for the duration of its  $17\frac{1}{2}$  hour flight providing repeated measurements of the same airmass, observed mean ozone concentrations of 25–40 ppbv (figure 16).

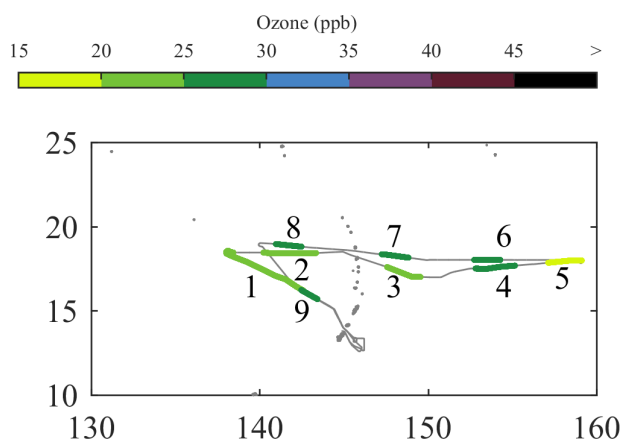
RF03 flew eastwards to intercept the outflow of cyclone Faxai, before returning on a similar flight track back to Guam. Mean ozone concentrations decreased below 20 ppbv on one occasion (19.5 ppbv in profile 5—figure 17), but no other examples of low ozone concentrations were observed, even in the vicinity of Faxai. RF04 flew in similar meteorological conditions as RF03, except for the dissipation of Faxai between the two flights. The flight track took the aircraft from Guam south to  $6^\circ\text{N}$ , where it performed a constant altitude flight along this line of latitude from  $155^\circ\text{E}$  to  $135^\circ\text{E}$  before travelling northwards and back to Guam. Similar to RF03, only one profile—16.1 ppbv in profile 1—had mean tropospheric ozone concentrations below 20 ppbv.



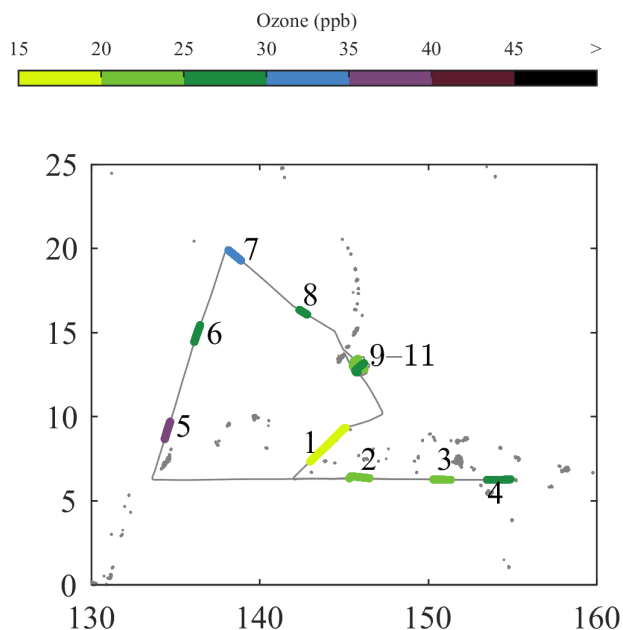
**Figure 16.** Flight track of RF02 with each profile coloured by mean tropospheric ozone as in figure 12. Of the twelve profiles taken, two profiles have mean ozone concentrations of 25–30 ppbv, seven have 30–35 ppbv, and two have 35–40 ppbv.

RF06 flew north into the extra-tropics where ozone concentrations are significantly higher, and is therefore not reproduced here.

In summary, an examination of the ATTREX flight data found mean upper tropospheric ozone concentrations as low as 10 ppbv in the outflow of cyclone Lusi in the Southern Hemisphere during flight RF05, but a corresponding flight in the Northern Hemisphere in the outflow of cyclone Faxai found the lowest mean ozone concentration to be 17.5 ppbv. Meanwhile, the FAAM aircraft measured boundary layer



**Figure 17.** Flight track of RF03 with each profile coloured by mean tropospheric ozone as in figure 12. Cyclone Faxai was situated at  $\sim(20^{\circ}\text{N}, 150^{\circ}\text{E})$  during this flight (see figure 5).



**Figure 18.** Flight track of RF04 with each profile coloured by mean tropospheric ozone as in figure 12.

concentrations around 10–12 ppbv between  $1^{\circ}\text{S}$  and  $3^{\circ}\text{N}$  on 4 February in a flight south from Chuuk along  $152^{\circ}\text{E}$ , values which are consistent with the Manus boundary layer measurements at that time (figure 1). Previous campaigns that measured boundary layer ozone in this region include PEM-West A of October 1991, which observed average ozone concentrations of 8–9 ppbv between the equator and  $20^{\circ}\text{N}$  (Singh et al., 1996), and PEM-tropics B in March 1999 which measured low-level ozone concentrations  $< 15$  ppbv in the Southern Hemisphere (Browell et al., 2001; Oltmans et al., 2001), consistent with the CAST measurements. In addition, BIBLE A and B of August–October 1998 and 1999 (Kondo

et al., 2002a), measured ozone concentrations of  $\sim 10$  ppbv below 2 km between  $2^{\circ}\text{S}$  and  $20^{\circ}\text{N}$  (Kondo et al., 2002b).

Evidence of an interhemispheric difference in boundary-layer ozone at the time of year of the CAST/CONTRAST/ATTREX campaign may be found in measurements made by the HIPPO (HIAPER Pole-to-Pole Observations) programme (Wofsy, 2011), which measured latitudinal transects of a range of trace gases along the Date Line and over the Warm Pool (see <http://hippo.ucar.edu/instruments/chemistry.html>). For HIPPO-1, in January 2009, and HIPPO-3, in March–April 2010 (the two missions closest in time of year to the ATTREX campaign) boundary-layer ozone concentrations below 15 ppbv were found between  $5^{\circ}\text{N}$  and  $20^{\circ}\text{S}$ . In addition, profiles near  $15^{\circ}\text{S}$  in January and  $2^{\circ}\text{S}$  in March–April showed values  $< 15$  ppbv extending up to 5 km. By contrast, ozone concentrations in January were  $> 15$  ppbv north of  $5^{\circ}\text{N}$  in the boundary layer and  $> 20$  ppbv north of  $5^{\circ}\text{S}$  above 2 km, while in March–April they exceeded 20 ppbv at all altitudes north of  $1^{\circ}\text{N}$ . It is therefore likely that the differences measured in the TTL in ATTREX originated from the inter-hemispheric differences in boundary layer ozone concentrations.

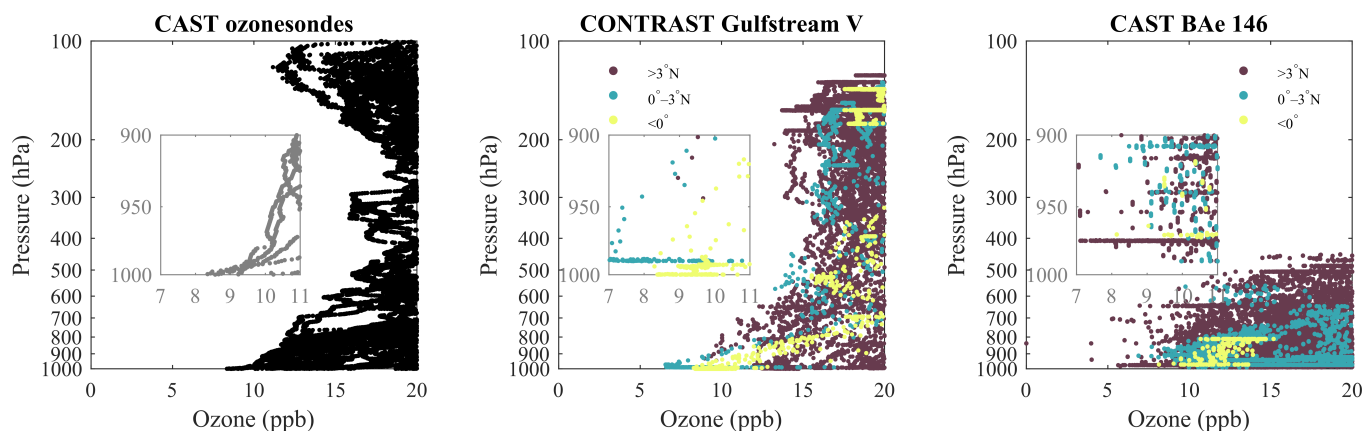
## 5 CAST and CONTRAST ozone measurements

The ozonesonde and Global Hawk measurements found TTL concentrations below 15 ppbv only in the Southern Hemisphere, but the sparse sampling means that similar layers in the Northern Hemisphere may just have been missed. Many more flights of the CAST and CONTRAST aircraft were made during February 2014, extending from sea level to 120 hPa. We now examine the measurements from these aircraft for evidence of very low ozone concentrations.

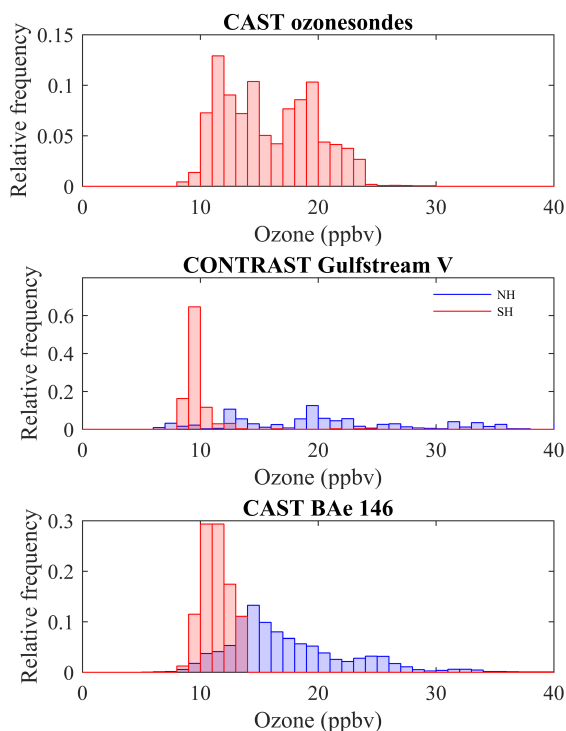
The FAAM BAe 146 aircraft focused on measuring close to the surface and within the boundary layer, making twenty-five flights between 18 January and 18 February (Harris et al., 2017). The NCAR Gulfstream V mostly measured in the upper troposphere in the region of main convective outflow, although many measurements were also made in the boundary layer (Pan et al., 2017); it conducted thirteen research flights and three transit flights between 11 January and 28 February.

Other than the brief excursion to  $1^{\circ}\text{S}$  on 4 February, the FAAM aircraft flew exclusively in the Northern Hemisphere, as its range was insufficient to reach the Southern Hemisphere from Guam. The NCAR Gulfstream V crossed into the Southern Hemisphere on only two occasions, thus its measurements also are predominantly in the Northern Hemisphere.

The ozone data from the two aircraft and the CAST ozonesondes from Manus Island (see section 3) are summarized in figure 19. In all three panels, ozone concentrations below 15 ppbv are frequently found below 700 hPa. The ozonesondes show a second region of ozone-poor air in the



**Figure 19.** Complete dataset of ozone measurements from the CAST ozonesondes (left), the CONTRAST Gulfstream V aircraft (centre) and the CAST FAAM BAe 146 aircraft (right), with the aircraft data split into the Southern Hemisphere measurements (yellow), equator–3°N (blue) and higher Northern Hemisphere latitudes (purple). In all cases, minimum ozone near the surface was lower than minimum ozone in the mid-troposphere. The insets show the low ozone concentrations measured in the lowest 100 hPa of the atmosphere in each case.



**Figure 20.** Histograms of ozone concentrations in the lowest 100 hPa from CAST ozonesondes, CONTRAST Gulfstream V and the CAST FAAM BAe 146 aircraft, split into Northern Hemisphere data (blue) and Southern Hemisphere data (red).

TTL, corresponding to the event discussed in Section 3, but the CONTRAST data do not—there are isolated examples around 15 ppbv up to  $\sim 180$  hPa but not above. The FAAM aircraft’s ceiling is around 300 hPa so it did not measure in the TTL, but again there are only a few ozone values lower than 15 ppbv above 700 hPa. The histograms of the bound-

ary layer measurements by the CAST ozonesondes and the CAST and CONTRAST aircraft (figure 20) show the majority of the measurements in the Southern Hemisphere were below 15 ppbv, whereas the Northern Hemisphere measurements were broadly distributed with a large proportion of measurements above 20 ppbv.

These results are consistent with a hemispheric difference in the ozone distribution in the boundary layer over the Warm Pool, which resulted in the layers of very low ozone concentrations being lifted to the TTL around the equator and further south, but not in the Northern Hemisphere.

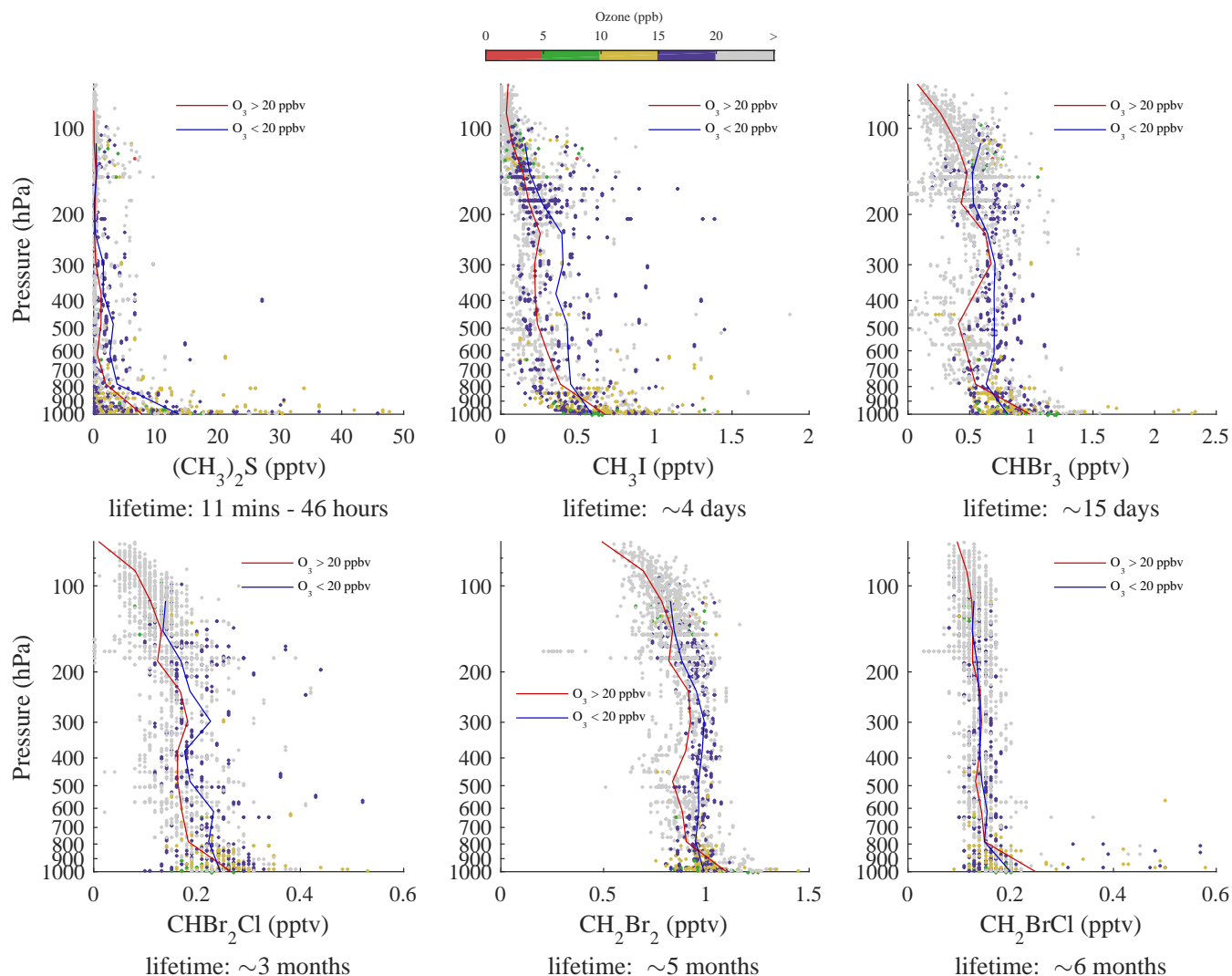
## 6 Very short lived substances

Whole air samplers (WAS) on board the CAST, CONTRAST and ATTREX aircraft provided measurements of very short lived substances (VSLs), of which eight were measured by all three aircraft: dimethyl sulfide ( $(\text{CH}_3)_2\text{S}$ ), iodomethane ( $\text{CH}_3\text{I}$ ), tribromomethane ( $\text{CHBr}_3$ ), dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), bromochloromethane ( $\text{CH}_2\text{BrCl}$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and trichloromethane ( $\text{CHCl}_3$ ).

We present six of these molecules here—dichloromethane and trichloromethane, as well as the species measured by the CONTRAST and ATTREX aircraft but not the CAST aircraft are plotted in the supplementary material. Dichloromethane is a predominantly industrially produced chemical with a strong anthropogenic signal and relatively long lifetime ( $\sim 6$  months), while trichloromethane has mostly natural, but some anthropogenic, sources (McCulloch, 2002), and has a long lifetime of  $\sim 6$  months.

Of the six remaining molecules, the atmospheric lifetimes range from a few minutes to a few months:  $(\text{CH}_3)_2\text{S}$  has a lifetime between 11 minutes and 46 hours (Marandino et al., 2013);  $\text{CH}_3\text{I}$  a lifetime of  $\sim 4$  days and  $\text{CHBr}_3$  a lifetime of





**Figure 21.** Panel plot of six compounds measured by the whole air samplers on board the three aircraft. The red line indicates the average profile of measurements taken where ozone was above 20 ppbv, and the blue line is the average profile for ozone below 20 ppbv.

~15 days (Carpenter et al., 2014); that of  $\text{CHBr}_2\text{Cl}$  is about three months, while  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_2\text{BrCl}$  have lifetimes of the order of six months (Montzka et al., 2010; Mellouki et al., 1992; Leedham Elvidge et al., 2015; Khalil & Rasmussen, 1999).

All six compounds have significant marine sources.  $(\text{CH}_3)_2\text{S}$ ,  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  are produced by phytoplankton (Dacey & Wakeham, 1986; Quack et al., 2007; Stemmler et al., 2015).  $\text{CH}_3\text{I}$  is produced by cyanobacteria and picoplankton (Smythe-Wright et al., 2006) and large concentrations of  $\text{CH}_3\text{I}$  are present in the marine boundary layer (Maloney et al., 2001).  $\text{CHBr}_2\text{Cl}$  is produced naturally by various marine macroalgae (Gschwend et al., 1985), and  $\text{CH}_2\text{BrCl}$  is emitted by tropical seaweed (Mithoo-Singh et al., 2017).

The vertical profiles obtained from combining all of the whole air sampler data from the entire CAST, CONTRAST

and ATTREX campaigns yield the plots in figure 21. (The supplementary material contains similar plots split into the individual aircraft.) Necessarily the vast majority of these points are from the Northern Hemisphere, away from the very low ozone concentrations described in section 4.3. Each data point is coloured by the ozone concentration measured at the time the WAS bottles were being filled, and average profiles for each compound were obtained for WAS samples with ozone concentrations less than 20 ppbv (in blue), and for WAS samples with ozone concentrations greater than 20 ppbv (in red). The average profiles were generated by binning the data into twenty equally sized bins in logarithmic pressure-space between 1000 hPa and 10 hPa, and averaging the data within that bin.

In the cases of  $(\text{CH}_3)_2\text{S}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CHBr}_3$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CH}_2\text{Br}_2$ , all show higher concentrations of the molecule in question when ozone concentrations were less than 20 ppbv

(low-ozone regime) compared to when ozone concentrations were greater than 20 ppbv (high-ozone regime), which suggests that the more ozone-deficient air has encountered the marine boundary layer—where these molecules were produced—more recently than the more ozone-rich air. Meanwhile,  $\text{CH}_2\text{BrCl}$  shows no difference between the low-ozone regime and the high-ozone regime because of its longer lifetime than the other VSLs measured.

The 33 species that were measured by just the CON-TRAST and ATTREX aircraft are plotted in the supplementary material. The species that were of a marine origin show the expected enhancements in the low-ozone regime compared to the high-ozone regime, while the species that were of industrial origin, show the reverse: enhancements were found in the high-ozone regime instead.

Very few WAS samples were taken in the Southern Hemisphere—only eight were taken by the FAAM BAe 146, 60 by the Global Hawk, and 134 by the Gulfstream V, compared to the Northern Hemisphere where 456 FAAM samples, 1373 Gulfstream V samples and 608 Global Hawk samples were taken. As a result, very few WAS samples were taken in areas where ozone concentrations were at their lowest during the campaign, and further investigation of these halomethanes during very low ozone events would be beneficial in future campaigns.

## 7 Conclusions

We have presented an extensive dataset of ozone observations from three research aircraft and ozonesondes over the West Pacific Warm Pool in February–March 2014, with a particular focus on the TTL. The results point to the generation of layers with very low ozone concentration ( $< 15$  ppbv) just below the tropopause due to uplift by deep convection, confirming the conclusion of Newton et al. (2016) based on the ozonesonde data. The lowest values measured in the TTL, around 10–12 ppbv, are very similar to those measured in the boundary layer in the region, consistent with uplift of boundary-layer air up to the tropopause region. This places boundary-layer air above the level of net radiative heating in the TTL and therefore in a position to ascend into the stratosphere in the Brewer–Dobson circulation. Consequently, it provides a route for very short-lived halocarbon species to reach the stratosphere. Evidence from the extensive whole air samplers carried by the three aircraft shows a negative correlation between ozone and species of marine origin, consistent with uplift in convection.

Despite the far more extensive sampling of the Northern Hemisphere than the Southern during the aircraft campaign, very low ozone concentrations in the TTL were only found in the Southern Hemisphere; even in the outflow of Cyclone Faxai the Global Hawk measured 15 ppbv of ozone, similar to measurements in convective anvils by the Gulfstream V in the Northern Hemisphere. This suggests a hemispheric

difference in the TTL ozone distribution, either because of lower boundary-layer ozone concentrations in the Southern Hemisphere or because of differences in the convective uplift. Previous measurement campaigns in this region point to an interhemispheric difference in boundary-layer ozone concentration as being responsible for the corresponding feature in the TTL.

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## 1 Principal WAS chemicals split by aircraft

The following three plots show panels of the six chemicals shown in figure 21 of the accompanying article, split into the three individual aircraft. Figure S1 shows the same panel as figure 21 for just the ATTREX data only, figure S2 shows the panel for just the CONTRAST data only, and figure S3 shows the panel for the CAST aircraft data only. In each figure, the average profile for the high-ozone case ( $>20$  ppbv) is shown in red and for the low-ozone case ( $<20$  ppbv) is shown in blue; the solid lines show the averages for just that aircraft, while the dashed lines show the averages for all the aircraft combined. The amount of CAST aircraft data is small in comparison to CONTRAST and ATTREX and so the effect on the overall averages in figure 21 is negligible. There is some overlap between ATTREX and CONTRAST: the highest altitude that the CONTRAST WAS samples were taken at was  $\sim 150$  hPa, and the lowest altitude that the ATTREX WAS samples were taken at was  $\sim 180$  hPa.

The ozone measurements taken on board the Gulfstream V aircraft in the CONTRAST campaign were of higher confidence than those taken on board the Global Hawk aircraft in the ATTREX campaign (see section 4.2 of the accompanying article for details on the uncertainties associated with the UCATS ozone measurements from the Global Hawk). However, the differences between the low-ozone cases and the high-ozone cases exist in both the CONTRAST and ATTREX data.

## 2 More WAS sample chemicals

The following plots are of chemical species measured by the whole air samplers (WAS) that were not plotted in the accompanying article. Firstly, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and trichloromethane ( $\text{CHCl}_3$ ) were measured by all three aircraft, but unlike the other six chemical species measured by all three aircraft, they both have a strong anthropogenic industrial source with relatively long lifetimes of around five months and six months respectively [Montzka et al., 2010; Carpenter et al., 2014; Khalil and Rasmussen, 1999]. Figure S4 shows the vertical profile of dichloromethane coloured by ozone concentration, with average profiles for WAS samples with ozone concentrations greater than 20 ppbv as a red line, and for WAS samples with ozone concentrations less than 20 ppbv as a blue line, in the same way as the panel plot in figure 21 of the accompanying article. Likewise the profile for trichloromethane is found in figure S5.

The remaining plots show chemical species that were not measured by the FAAM BAe 146 of CAST, but were measured by the CONTRAST and ATTREX aircraft, and categorized by their characteristics. Atmospheric lifetime information comes from González Abad et al. [2011]; Rosado-Reyes and Francisco [2007]; Rudolph [2003]; Pike and Young [2009]; Carpenter et al. [2014]; Prinn et al. [1987]; Wallington et al. [1996]; Olaguer [2002]; Rasmussen and Khalil [1983]; Atkinson et al. [1985]; and Brühl et al. [2012].

### 2.1 Aliphatic hydrocarbons

The aliphatic hydrocarbons measured by the CONTRAST and ATTREX WAS were as follows:

- ethane ( $\text{CH}_3\text{CH}_3$ ):  
lifetime =  $\sim 2$  months (figure S6),
- ethyne ( $\text{CH}\equiv\text{CH}$ ):  
lifetime =  $\sim 2$ –4 weeks (figure S7),
- propane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ):  
lifetime =  $\sim 2$  weeks (figure S8),
- methylpropane ( $\text{CH}_3\text{CH}(\text{CH}_3)_2$ ):  
lifetime =  $\sim 1$  week (figure S9),
- butane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ ):  
lifetime =  $\sim 5$  days (figure S10),
- 2-methylbutane ( $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$ ):  
lifetime = 4 days (figure S11),
- pentane ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ):  
lifetime =  $\sim 3$  days (figure S12)
- isoprene ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$ ):  
lifetime =  $\sim$ minutes–hours (figure S13)

All the hydrocarbons, with the exception of isoprene, follow a similar pattern with enhanced levels of each in the boundary layer when ozone concentrations were high. The difference diminishes with altitude, and at high altitudes, the difference between the low-ozone régime and the high-ozone régime becomes negligible.

Isoprene, however is a naturally occurring chemical emitted in large quantities by vegetation rather than as a result of the petroleum industry, which accounts for the difference between the other hydrocarbons and isoprene.

### 2.2 Haloaliphatic compounds

The haloaliphatic compounds, including chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs) and halons, measured by the CONTRAST and ATTREX WAS were as follows:

#### 2.2.1 CFCs

- CFC-12 ( $\text{CCl}_2\text{F}_2$ ):  
[dichlorodifluoromethane]  
lifetime =  $\sim 100$  years (figure S14)
- CFC-11 ( $\text{CCl}_3\text{F}$ ):  
[trichlorofluoromethane]  
lifetime =  $\sim 50$  years (figure S15)
- CFC-112 ( $\text{CCl}_2\text{FCCl}_2\text{F}$ ):  
[tetrachloro-1,2-difluoroethane]  
lifetime =  $\sim 60$  years (figure S16)
- CFC-112a ( $\text{CCl}_3\text{CClF}_2$ ):  
[tetrachloro-1,1-difluoroethane]  
lifetime =  $\sim 50$  years (figure S17)

- CFC-113 ( $\text{CCl}_2\text{FCClF}_2$ )  
[1,1,2-trichloro-1,2,2-trifluoroethane]  
lifetime =  $\sim 90$  years (figure S18)
- CFC-114 ( $\text{CClF}_2\text{CClF}_2$ )  
[1,2-dichlorotetrafluoroethane]  
lifetime =  $\sim 190$  years (figure S19)

### 2.2.2 HCFCs

- HCFC-22 ( $\text{CHClF}_2$ )  
[chlorodifluoromethane]  
lifetime =  $\sim 12$  years (figure S20)
- HCFC-141b ( $\text{CH}_3\text{CCl}_2\text{F}$ )  
[1,1-dichloro-1-fluoroethane]  
lifetime =  $\sim 10$  years (figure S21)
- HCFC-142b ( $\text{CH}_3\text{CClF}_2$ )  
[1-chloro-1,1-difluoroethane]  
lifetime =  $\sim 18$  years (figure S22)

### 2.2.3 HFCs

- HFC-134a ( $\text{CH}_2\text{FCF}_3$ )  
[1,1,1,2-tetrafluoroethane]  
lifetime =  $\sim 14$  years (figure S23)
- HFC-365mfc ( $\text{CH}_3\text{CF}_2\text{CH}_2\text{CF}_3$ )  
[1,1,1,3,3-pentafluorobutane]  
lifetime =  $\sim 9$  years (figure S24)

### 2.2.4 Halons

- Halon-1211 ( $\text{CBrClF}_2$ )  
[bromochlorodifluoromethane]  
lifetime =  $\sim 16$  years (figure S25),
- Halon-2402 ( $\text{CBrF}_2\text{CBrF}_2$ )  
[1,2-dibromotetrafluoroethane]  
lifetime =  $\sim 30$  years (figure S26)

In all of the cases of CFCs, HCFCs, HFCs and halons, very little variation can be seen, and there is no difference between the low-ozone régime and the high-ozone régime. The background values of the majority of them are non-zero, with little variation from the background values observed. All the CFCs, HCFCs, HFCs and halons are industrial chemicals with often extremely long atmospheric lifetimes. It is likely that these chemicals have reached homogeneity in the atmosphere such that there is little difference between the clean low-ozone régime and the polluted high-ozone régime.

### 2.2.5 Others

- chloromethane ( $\text{CH}_3\text{Cl}$ )  
lifetime =  $\sim 12$  months (figure S27),
- bromomethane ( $\text{CH}_3\text{Br}$ )  
lifetime =  $\sim 9$  months (figure S28),
- 1,1,1-trichloroethane ( $\text{CH}_3\text{CCl}_3$ )  
lifetime =  $\sim 6$  years (figure S29),
- tetrachloromethane ( $\text{CCl}_4$ )  
lifetime =  $\sim 26$  years (figure S30),

- 1,2-dichloroethane ( $\text{CH}_2\text{ClCH}_2\text{Cl}$ )  
lifetime =  $\sim 3$  months (figure S31),
- trichloroethene ( $\text{CHCl}=\text{CCl}_2$ )  
lifetime =  $\sim 5$  days (figure S32),
- tetrachloroethene ( $\text{CCl}_2=\text{CCl}_2$ )  
lifetime =  $\sim 5$  months (figure S33)

All of these chemicals are produced industrially. Chloromethane, bromomethane and 1,2-dichloroethane have the expected profiles for anthropogenic chemicals—the polluted, high-ozone régime is enhanced compared to the clean, low-ozone régime. However, 1,1,1-trichloroethane and tetrachloromethane are the opposite way round; their lifetimes are particularly long, similar to the lifetimes of the CFC, HFC, HCFC and halon groups. Both trichloromethane and tetrachloroethene show large enhancements in the high-ozone régime in the boundary layer, but in the mid-troposphere there is an unexpected enhancement of each in the low-ozone régime.

## 2.3 Aromatic compounds

- benzene ( $\text{C}_6\text{H}_6$ )  
lifetime =  $\sim$ months (figure S34)
- chlorobenzene ( $\text{C}_6\text{H}_5\text{Cl}$ )  
lifetime =  $\sim 2$  weeks (figure S35)

Benzene and chlorobenzene are industrial solvents, and both show enhancements in the high ozone régime compared to the low ozone régime, which is what is expected. However, in the mid-troposphere, chlorobenzene shows the opposite.

## 2.4 Sulfides

- carbonyl sulfide ( $\text{OCS}$ )  
lifetime =  $\sim 35$  years (figure S36)

Like dimethyl sulfide, shown in figure 15 of the accompanying article, carbonyl sulfide, shows a slight enhancement in the low-ozone, clean régime.



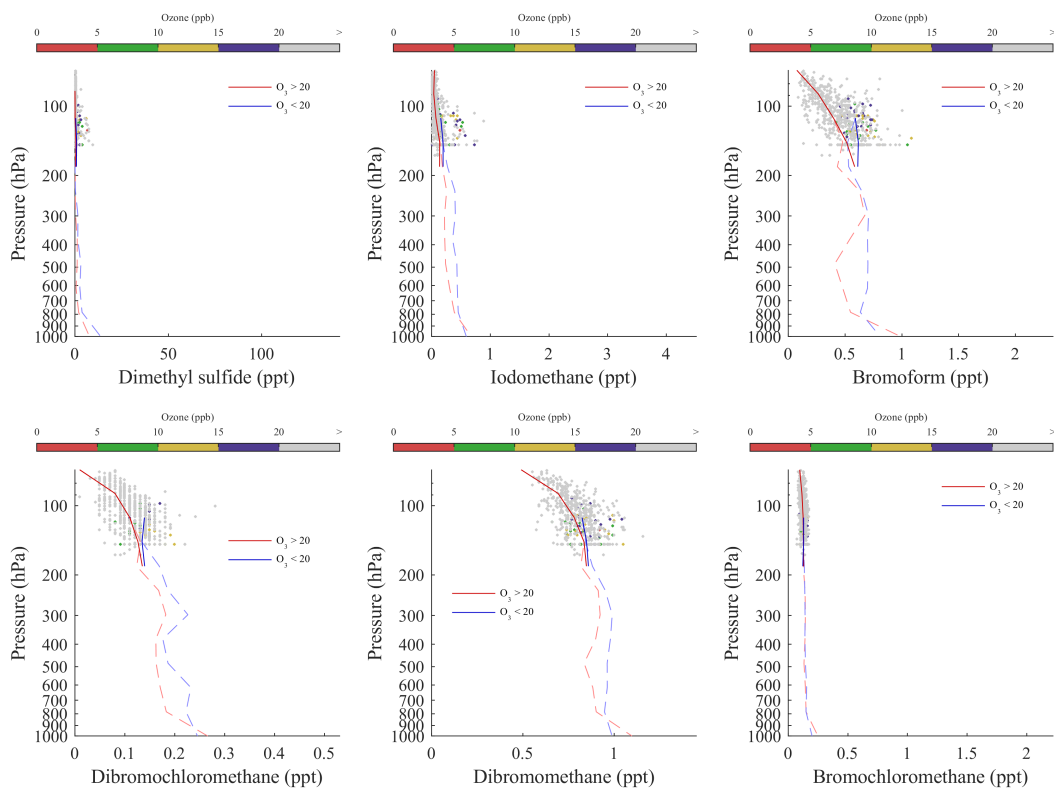


Figure S1: Panel of the six principal WAS chemicals using the ATTREX WAS sample data only.

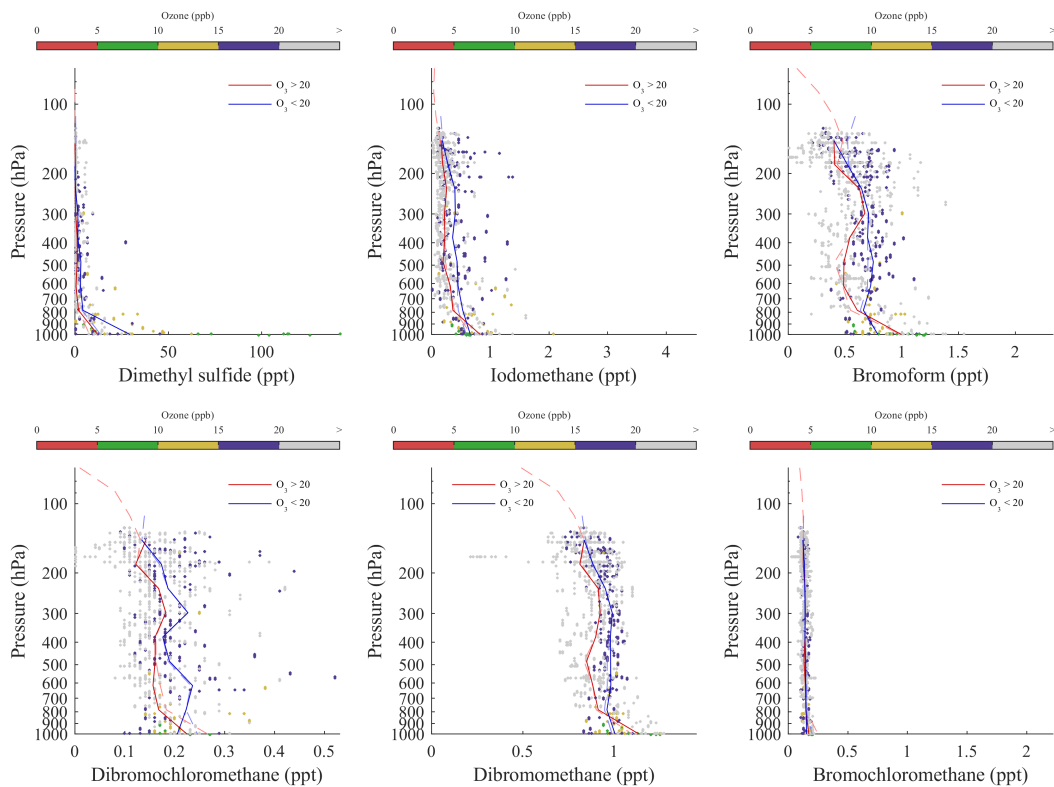


Figure S2: Panel of the six principal WAS chemicals using the CONTRAST WAS sample data only.

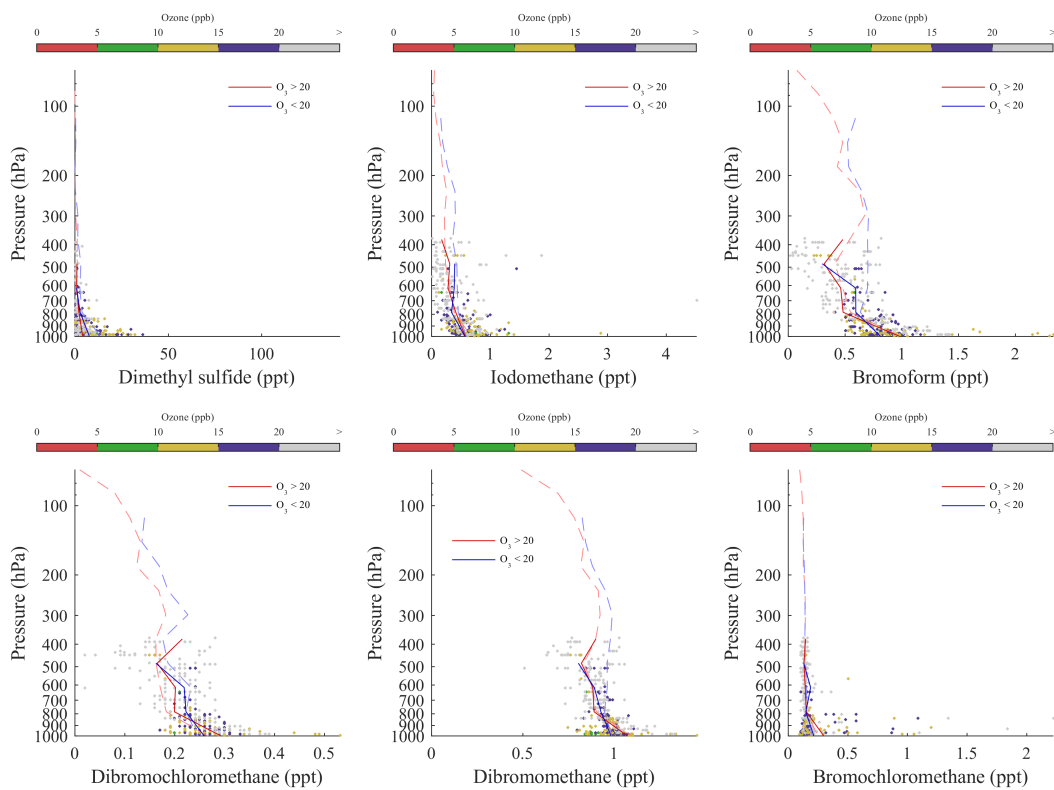


Figure S3: Panel of the six principal WAS chemicals using the CAST aircraft WAS sample data only.

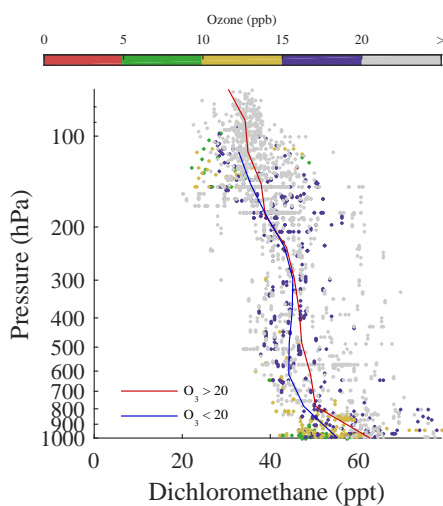


Figure S4: Dichloromethane

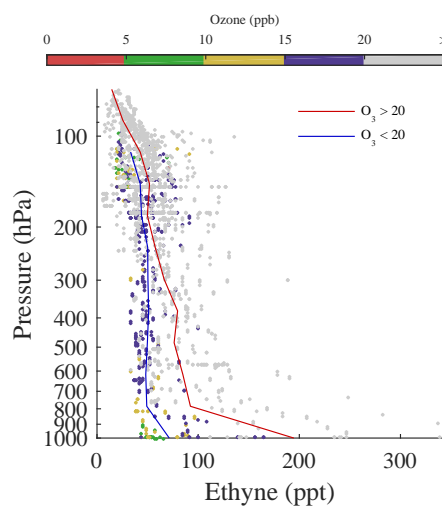


Figure S7: Ethyne

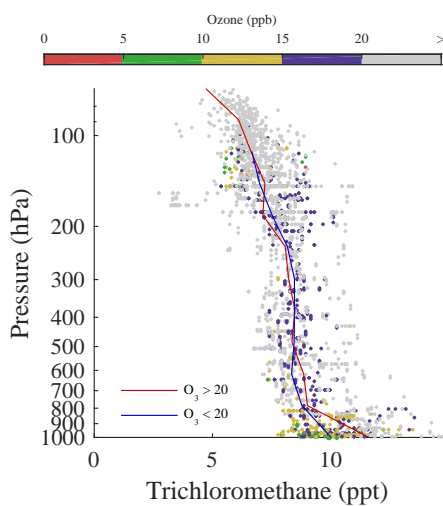


Figure S5: Trichloromethane

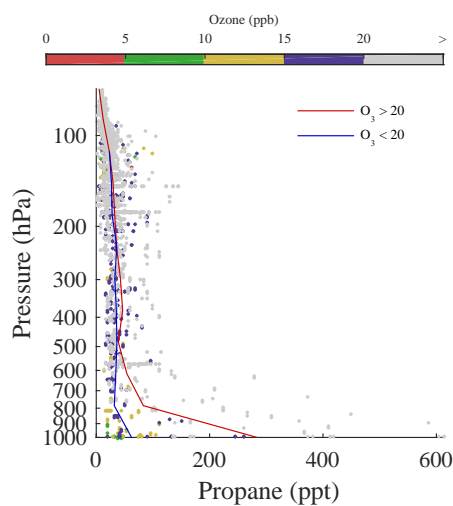


Figure S8: Propane

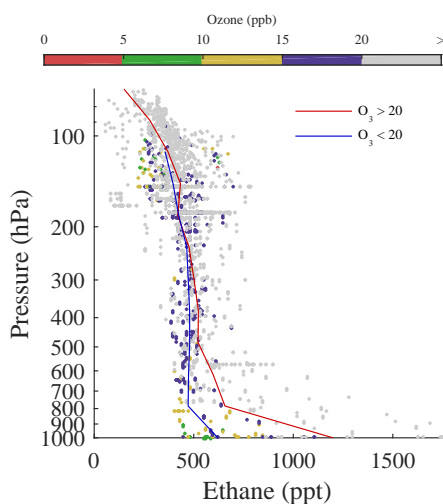


Figure S6: Ethane

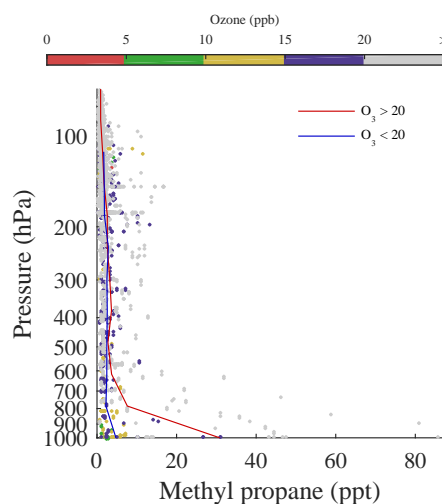


Figure S9: Methylpropane

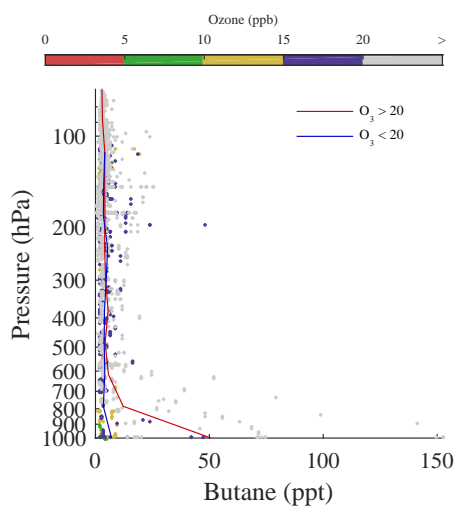


Figure S10: Butane

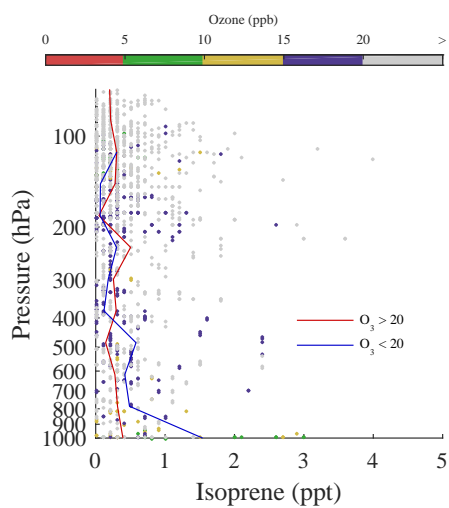


Figure S13: Isoprene

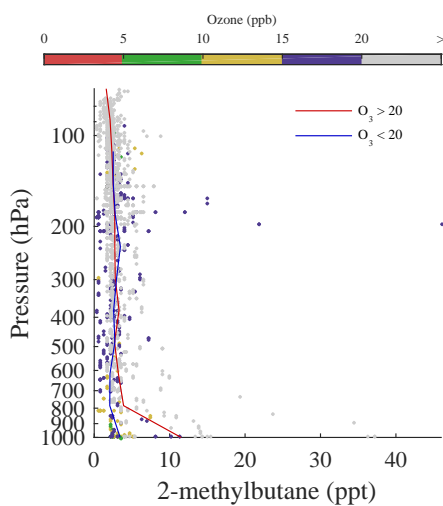


Figure S11: 2-Methylbutane

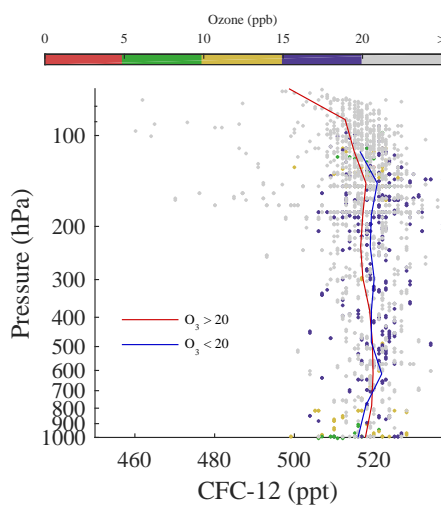


Figure S14: CFC-12

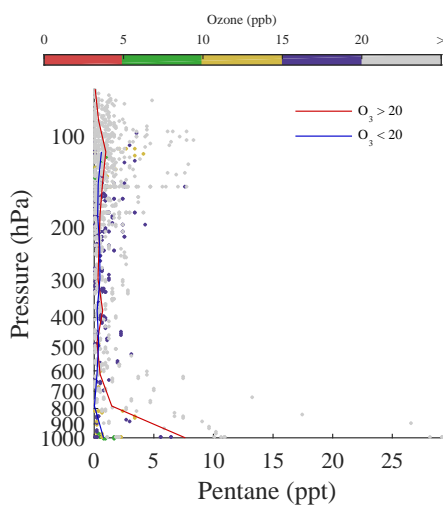


Figure S12: Pentane

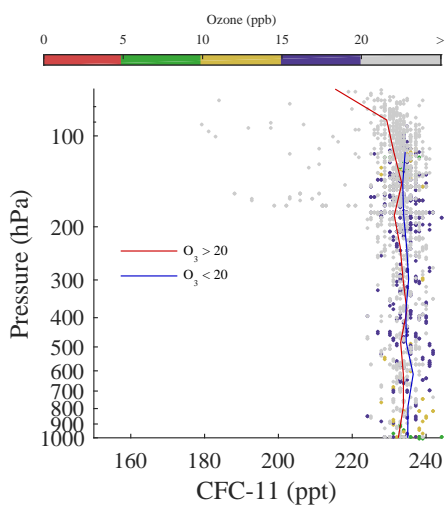


Figure S15: CFC-11



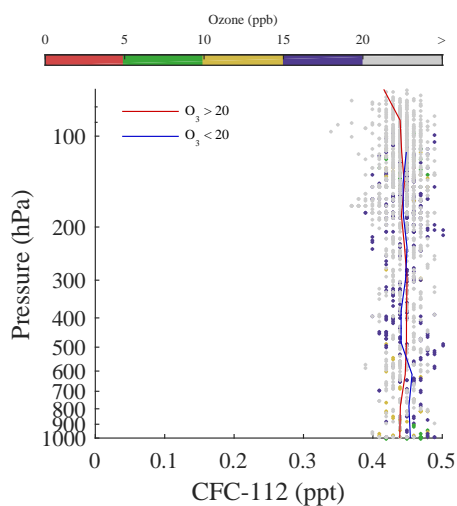


Figure S16: CFC-112

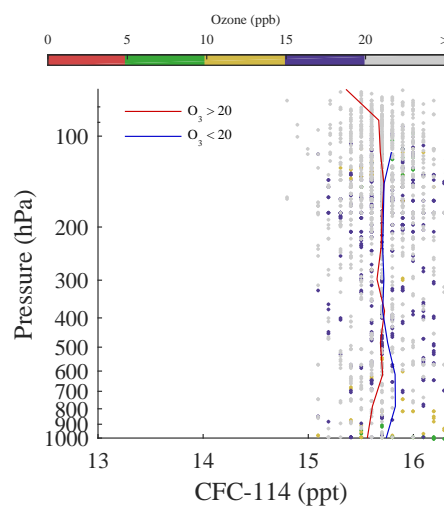


Figure S19: CFC-114

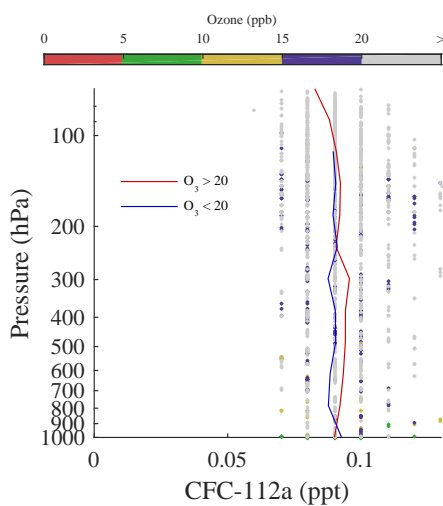


Figure S17: CFC-112a

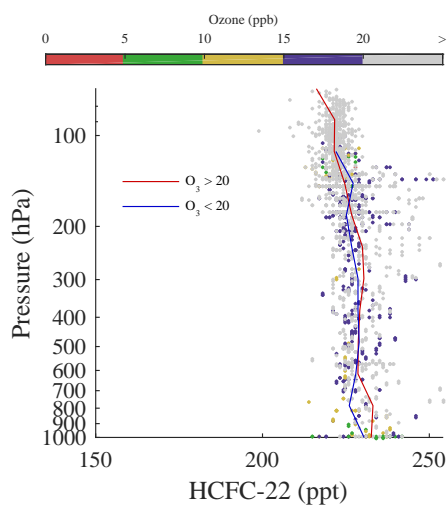


Figure S20: HCFC-22

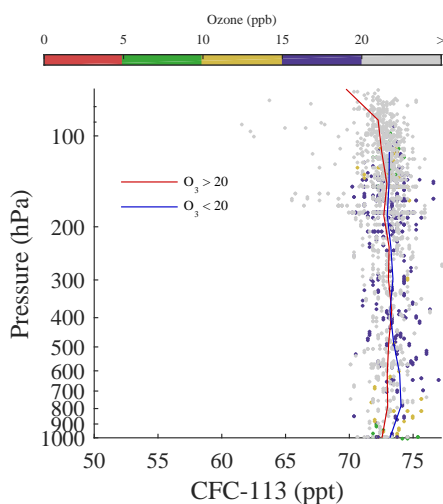


Figure S18: CFC-113

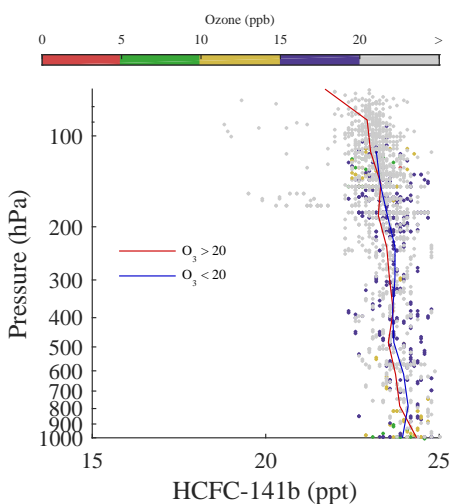


Figure S21: HCFC-141b

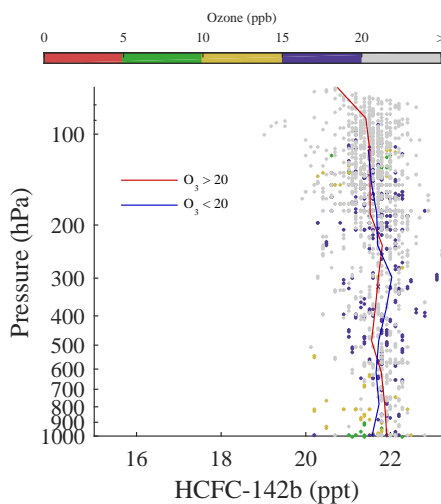


Figure S22: HCFC-142b

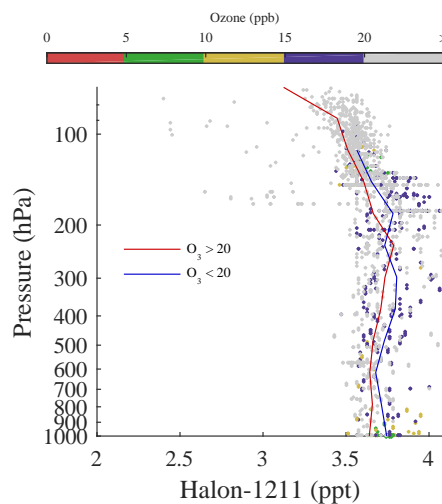


Figure S25: Halon 1211

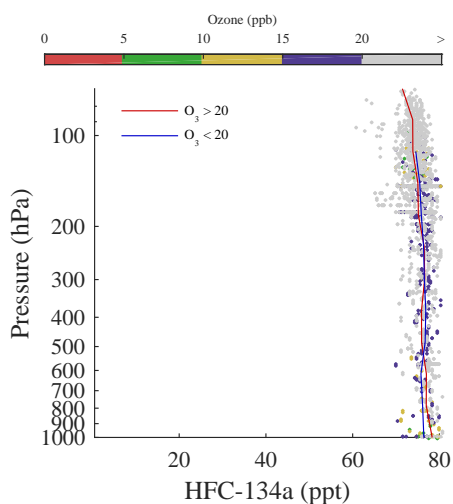


Figure S23: HFC-134a

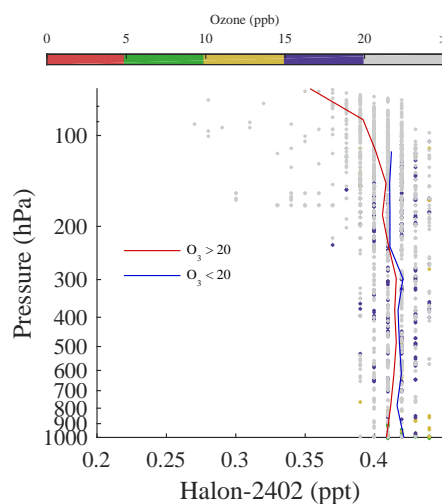


Figure S26: Halon 2402

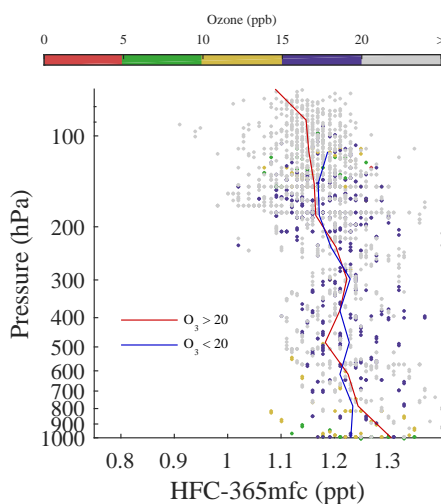


Figure S24: HFC-365mfc

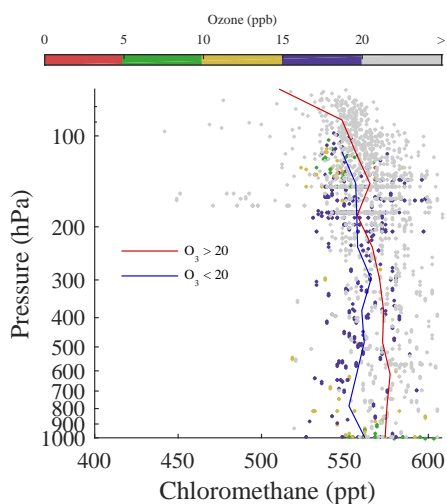


Figure S27: Chloromethane

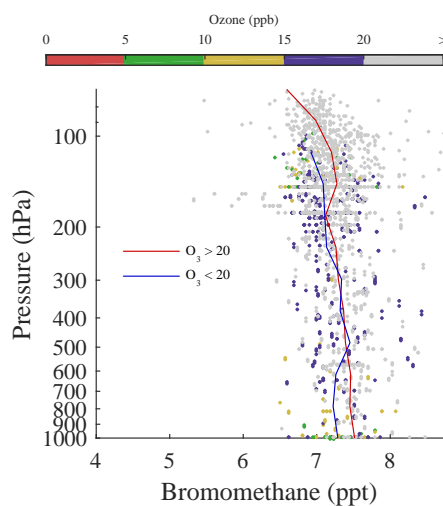


Figure S28: Bromomethane

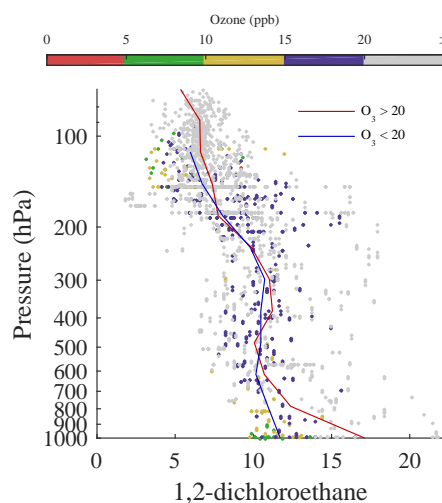


Figure S31: 1,2-dichloroethane

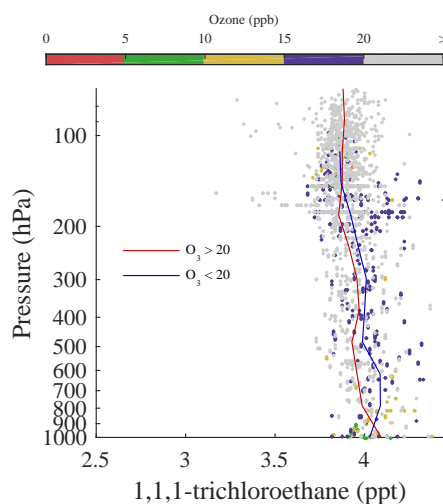


Figure S29: 1,1,1-trichloroethane

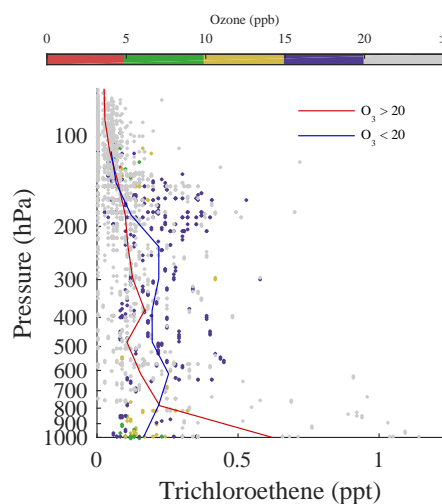


Figure S32: Trichloroethene

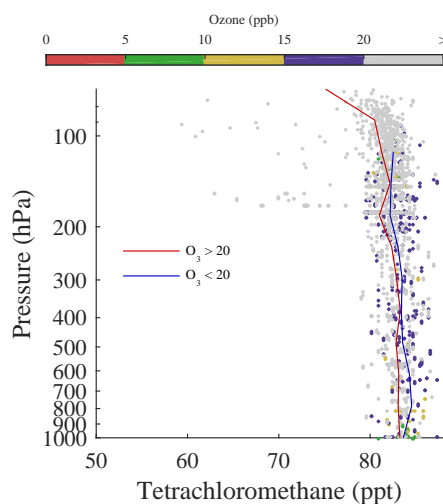


Figure S30: Tetrachloromethane

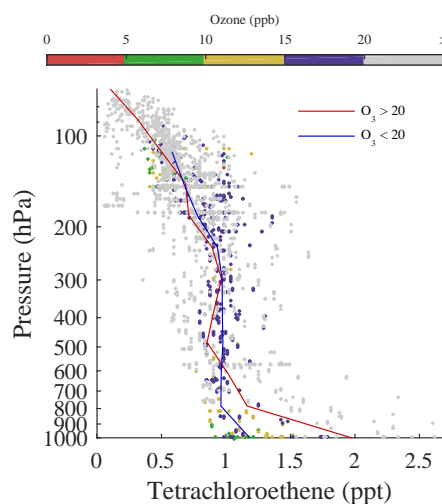


Figure S33: Tetrachloroethene

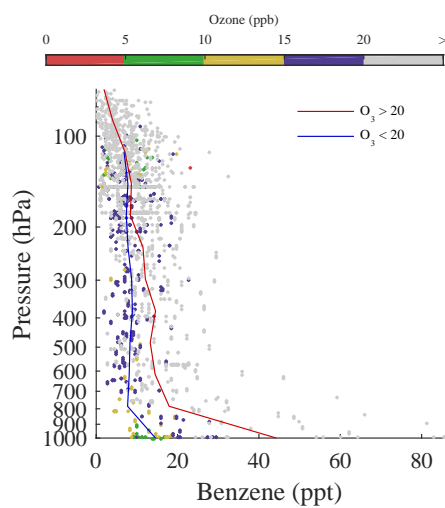


Figure S34: Benzene

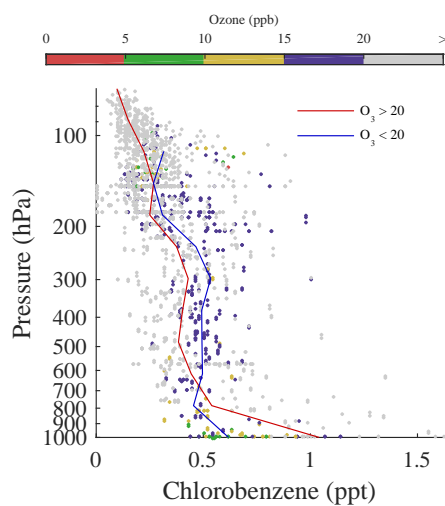


Figure S35: Chlorobenzene

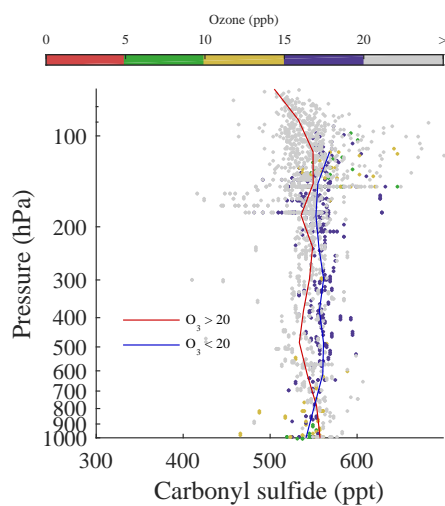


Figure S36: Carbonyl sulfide



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## Response to Anonymous Referee #1

We thank the reviewer for their comments on the paper. We respond below to the specific comments made.

1. *[The authors] should acknowledge a number of other papers that describe NH-SH ozone gradients (from surface and aircraft) and/or very low ozone in the upper troposphere and TTL throughout the tropical Pacific. The latter includes PEM-Tropics (1990s) and TC4 (2007).*

The introduction has been expanded to include discussion of TC4. The PEM series of flights only measured up to 12 km [Hoell et al., 1999; Raper et al., 2001] and are not relevant to a discussion of the TTL. We refer to PEM-West and PEM-tropics in section 4.4 of the paper where we discuss boundary-layer ozone. The following passage has been added to the introduction:

Bubbles of relatively low ozone have also been observed in other parts of the world. During the TC4 campaign, anomalously low ozone concentrations of ~60 ppbv were found at 14–16 km altitude in the TTL off the coast of Ecuador—typical values of ozone at this altitude in this region were measured to be  $\geq 100$  ppbv. These low-ozone bubbles were also shown to be a result of non-local convection followed by advection to where it was measured by the NASA DC-8 aircraft [Petropavlovskikh et al., 2010].

2. *The very important motivating question posed on page 2, namely, “do enough reactive species penetrate the lower stratosphere to perturb the composition?” is not really answered. It is recommended that the authors conclude the paper with summarizing how their findings address this issue.*

The focus of this paper, and the objective described on page 2, was to “corroborate the ozonesonde measurements with other measurements and to determine how widespread these bubbles of low-ozone air over the Warm Pool,” rather than whether reactive species penetrate into the lower stratosphere. The key question posed in the introduction was “whether deep convection is nevertheless capable of lifting very short-lived halogenated species near enough to the tropopause that their breakdown products reach the stratosphere” rather than direct penetration of the lower stratosphere. We don’t think that the reviewer has read this part of the paper correctly and therefore do not make any changes to the paper.

## Response to Anonymous Referee #2

We thank the reviewer for their careful and considered comments. We respond below to the specific comments made.

1. *The paper provides a somewhat limited review of the scientific literature of the TTL low-ozone problem.*

A similar comment was provided by Anonymous Referee #1, and is addressed in the Response to Anonymous Referee #1.

2. *The paper would benefit from a more focussed detailing of what they are looking for in the various analyses they lay out and what the train of the argument will be. While this becomes clearer as you go along in the text, it would have been better if the reasoning had been presented at the outset.*

A new section in the introduction, labelled “Article overview” has been created to do this. The following text has been added to this section:

In section 2 we describe the instruments that were used on board the three aircraft to collect the measurements described in this article. Section 3 provides a brief overview of the CAST ozonesonde measurements from Manus, which were described in detail in Newton et al. [2016], that provided the first evidence of the occurrence of localized low ozone concentrations during the campaign.

We then introduce the Global Hawk ozone profiles in section 4, concentrating on one flight that sampled well into the Southern Hemisphere from Guam in section 4.2—this flight produced further evidence of low-ozone concentrations, especially in the Southern Hemisphere portion of the flight. Within this section, we also discuss the uncertainties, and implications thereof, of the UCATS ozone instrument on board the Global Hawk, and how we approached the issue of noisiness in the UCATS dataset. This is followed by a brief discussion of the other ATTREX flights in section 4.3.

Section 5 discusses the lower troposphere measurements that were made by the CAST and CONTRAST aircraft, providing information on boundary layer ozone concentrations that can be used to infer the origin of low ozone in the TTL. Section 6 shows a subset of the very short lived substances (VSLs) that were measured using Whole Air Samplers (WAS) on board all three aircraft, showing the composition differences between the VSLs in low-ozone and high-ozone cases to infer that recently convected ozone-deficient air has a distinct chemical composition compared to high-ozone cases. (A supplementary section contains the full dataset of WAS VSLs chemical data.) Finally section 7 summarizes the findings of this article.

3. *Left unexplained is why the ascent segments appear in the figure to be coterminous. (Are the descents nearly instantaneous?)*

Changes made to section 4 clarify this diagram, which has been modified to show exactly where the aircraft was below the tropopause. The following text has been added to the caption of figure 7 to ensure this confusion is not encountered by other readers.

The grey line shows the flight path between profiles.

4. *Given that the UCATS ozone data are so central to the analysis in this section, indeed the whole paper, the rather severe shortcomings of UCATS ozone measurement mentioned in passing in Section 4 ought to have been discussed fully in Section 2 on instrumentation. Particularly concerning is the possible negative bias of up to 5 ppbv at low ozone concentrations. Given the possibility of such a substantial bias, the reader might fairly ask how much confidence can be placed in the hemispheric difference suggested in Fig. 7. I would suggest that the authors show at least an extended section of the ozone data in time series format to give the reader a better sense of the uncertainty in the averaged values.*

We thank the referee for this comment which did indeed identify a serious omission in the original paper. We hope this is now rectified, in the form of a new section 4.2 discussing systematic errors in the UCATS data and an enlarged section 4.3 (old 4.2) discussing the random errors and why we choose the ascent sections of the flights rather than both ascent and descent in the colour line plots. Fig. 11 shows a time series of (averaged) data with error bars along RF05.

5. *Section 6 shows in Figure 17 some separation between profiles of Very Short-lived Substances originating in the marine boundary layer on the basis of ozone. Here again, though, the noisiness of the UCATS ozone data cloud the picture in the critical TTL altitudes. By lumping all the WAS data together, the differences in the quality of the ozone data between aircraft are essentially blurred. Would, for example, we see the same strong difference in methyl iodide at 300 hPa if each aircraft were plotted separately? Indeed, where do the Global Hawk data leave off? Are Global Hawk descent profiles at Guam used at all in Figure 17? Here again then, as in Section 5, questions about the quality of the UCATS ozone data limit the confidence in the authors' conclusions.*

A new section in the supplementary material has been created to address this entitled “Principal WAS chemicals split by aircraft”, which shows three panel plots similar to figure 17 (figures S1–S3) but with the data from just one aircraft plotted on each. The conclusion from these plots was that there was little data from the CAST aircraft compared to CONTRAST and ATTREX, so this dataset would not have much of an effect on the overall averages, and the overlap between the CONTRAST and ATTREX data occurs only between 150 hPa and 180 hPa. The overall trends in the six principal WAS chemicals hold true when plotting only the CONTRAST data and when plotting only the ATTREX data.

## Changes made following discussions with co-authors

After discussions between co-authors, the following issues have been resolved.

1. Section 6: *Very Short lived substances* has been amended with trichloromethane ( $\text{CHCl}_3$ ) described in paragraph 2 as having “mostly natural, but some anthropogenic, sources” rather than “industrially produced with a strong anthropogenic signal”. Section 6 has been redrafted for better clarity, and mention of  $\text{CH}_2\text{Cl}_2$  has been removed as this was not one of the six chemicals plotted in figure 21. Paragraph 2 of section 6 now reads:

We present six of these molecules here—dichloromethane and trichloromethane, as well as the species measured by the CONTRAST and ATTREX aircraft but not the CAST aircraft are plotted in the supplementary material. Dichloromethane is a predominantly industrially produced chemical with a strong anthropogenic signal and relatively long lifetime (~6 months), while trichloromethane has mostly natural, but some anthropogenic, sources [?], and has a long lifetime of ~6 months.

and paragraphs 6 and 7 of section 6 now read:

In the cases of  $(\text{CH}_3)_2\text{S}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CHBr}_3$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CH}_2\text{Br}_2$ , all show higher concentrations of the molecule in question when ozone concentrations were less than 20 ppbv (low-ozone regime) compared to when ozone concentrations were greater than 20 ppbv (high-ozone regime), which suggests that the more ozone-deficient air has encountered the marine boundary layer—where these molecules were produced—more recently than the more ozone-rich air. Meanwhile,  $\text{CH}_2\text{BrCl}$  shows no difference between the low-ozone regime and the high-ozone regime because of its longer lifetime than the other VSLs measured.

The 33 species that were measured by just the CONTRAST and ATTREX aircraft are plotted in the supplementary material. The species that were of a marine origin show the expected enhancements in the low-ozone regime compared to the high-ozone regime, while the species that were of industrial origin, show the reverse: enhancements were found in the high-ozone regime instead.

2. A coding issue was discovered, which erroneously removed much of the ozone data from the FAAM aircraft. The affected figures were figure 19, the bottom plot of figure 20, and figure 21, and have now been plotted with the correct data-set.
3. p. 3, l. 40 “The [ATTREX] instruments were calibrated on the ground against a NIST-certified calibration system before and after [the mission](#)” rather than before and after every flight.

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