VERTICAL PROFILING IN THE WEST PACIFIC WARM POOL

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Abstract

The University of Manchester

Richard Newton

Degree of Doctor of Philosophy

Vertical Profiling in the West Pacific Warm Pool

Friday 15th December, 2017

This thesis consists of three distinct parts of CAST, CONTRAST and ATTREX, which were aircraft and field campaigns in the West Pacific in January–March 2014.

The first section comprises of ozonesonde measurements from Manus Island, Papua New Guinea. A contamination issue affected the first 14 ozonesondes, and so particular care was required to characterize the background current, and as a result, a ‘hybrid’ background current correction was developed, which combines a constant correction with a pressure-dependent correction. Collocated measurements with the CONTRAST aircraft—the NCAR Gulfstream V—suggests the new hybrid correction produces better ozonesonde profiles than the other corrections that are found in the literature. The results of the ozonesonde measurements revealed a low-ozone event, with minimum ozone concentrations of ~12 ppbv, which was coincident with an easterly jet, and traced back to an area of deep convection: clean marine boundary layer air was uplifted into the tropical tropopause layer (TTL) and then advected in the easterly jet across to Manus Island.

The second section attempted to find more examples of low-ozone conditions in the TTL from the aircraft data. The ATTREX aircraft—the NASA Northrop Grumman Global Hawk—observed ozone concentrations of ~10 ppbv in the Southern Hemisphere in proximity of tropical storm Lusi. Whole air samples from all three aircraft suggests the low-ozone air had recently encountered the boundary layer, with enhanced concentrations of surface-generated very short lived substances (VSLSs) compared to air with higher ozone concentrations. No low-ozone events were found in the Northern Hemisphere, even in the vicinity of tropical cyclone Faxai.

The third section explores the low-ozone events in the WRF-Chem (Weather Research and Forecasting—with chemistry) in order to see whether the model was capable of recreating the low-ozone event measured by the ozonesondes on 21–23 February as a case study. The WRF-Chem simulation did correctly reproduce the large convective storm in a similar area to that observed by satellites, and surface tracers were uplifted in large quantities as hypothesized. However, no evidence of injection of air into the stratosphere was found in the simulation, and, rather than uplift directly from the surface, mixing of air in the boundary layer followed by uplift into the TTL was the main mechanism for producing the low-ozone event.
Declaration

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

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Chapter 1

Introduction

1.1 The West Pacific Warm Pool

The West Pacific Warm Pool is a region to the east of the archipelagos of Indonesia, Borneo, New Guinea, the Philippines and Malaysia—known collectively as the Maritime Continent—which has significant climate implications to the planet as a whole. The sea surface temperatures are higher than anywhere else on Earth (figure 1.1), and large areas of the West Pacific Warm Pool are above 27°C (300 K), which is the threshold for deep convection to occur [Wang and Mehta, 2008], and as a result, deep convection is prevalent in this region. The role of ocean-atmospheric coupling in the West Pacific Warm Pool is important in maintaining the high sea surface temperatures, and is also a major driver of the El-Niño–Southern Oscillation (ENSO) phenomenon [Webster and Lukas, 1992], which produces global changes in precipitation rates, temperatures and marine life. Also in this region, the South Pacific Convergence Zone (SPCZ) is present, especially during Austral summer (November–April), which is a band of convection that stretches from New Guinea east-southeastwards to about 30°S, 120°W [Vincent, 1994; Haffke and Magnusdottir, 2013]. The SPCZ merges with, and is sometimes considered a part of, the Intertropical Convergence Zone (ITCZ) [Board et al., 1999; Linsley et al., 2006].

As a result, the West Pacific Warm Pool is a significant region for air entering the stratosphere [Newell and Gould-Stewart, 1981], and the composition of the troposphere in this region can have profound implications on the composition of the stratosphere. The slow moving Brewer-Dobson circulation transports stratospheric air from equatorial latitudes towards the poles [Brewer, 1949], therefore trace gases that are found in the troposphere in the West Pacific Warm Pool can be propagated around the planet.

Troposphere-to-stratosphere transport can occur in multiple ways in the tropics. Firstly, because of the step change in tropopause altitude at the subtropical jets, lateral mixing between the tropical upper troposphere and extratropical lower stratosphere
Figure 1.1: Average global sea surface temperatures in the month of February 2014. The green colours are sea surface temperatures greater than 27°C, where deep convection is more likely to occur (note the colour scale is not linear to emphasize the warm temperatures). Data from NOAA OI SST V2 High Resolution Dataset.

can occur [Fueglistaler et al., 2009]. This occurs at ∼30°N and ∼30°S, which is outside the West Pacific Warm Pool region and is not discussed here further.

The second method is injecting air from the troposphere above the cold point tropopause directly into the stratosphere. Such transport occurs only in the largest, long-lived deep convective storms [Rossow and Pearl, 2007], and it is estimated that only 0.5–2% of storms penetrate directly into the stratosphere. When it does occur, however, boundary layer air can be transported into the stratosphere in approximately 30 minutes or less [Thompson et al., 1997], which means very short lived substances (VSLSs) can persist when they are directly injected into the stratosphere and will therefore be able to contribute more to global warming [Rex et al., 2014].

The third method is the most common mechanism for troposphere-to-stratosphere transport, which involves convective uplift of tropospheric air into the tropical tropopause layer, above the level of zero net radiative heating but below the cold point tropopause. Air in this layer is subject to positive net radiative heating and slowly rises into the stratosphere over the course of 1–2 months [Sherwood and Dessler, 2001]; air below the level of zero net radiative heating sinks back into the troposphere.
The West Pacific Warm Pool is also notable for having low concentrations of ozone in the troposphere compared to the rest of the world. Ozone in the tropical troposphere is naturally lower in concentration than in the extra-tropical troposphere, and within the tropical troposphere is a zonal wave-one structure where its maximum is in Africa and its minimum is in the West Pacific [Thompson et al., 2003b]. However, increasing industrialization in the Maritime Continent and Asia is contributing to changes in the composition of the troposphere in the remote Pacific [Zhang et al., 2003].

The inaccessibility of the West Pacific due to the remoteness of the land in the area and the lack of infrastructure means that making measurements is difficult, and as a result very few measurements have been made *in situ* in the West Pacific [e.g Board et al., 1999]. Several intensive field campaigns have been performed, but very few long term measurement records exist for this region. Table 1.1 shows the field campaigns that have been done in the West Pacific Warm Pool region since 1987.

### 1.2 Previous field campaigns

Many of the field campaigns have reported observations of low concentrations of ozone in the tropical tropopause layer. Such observations are indicative of deep convection transporting ozone-deficient air from the lower troposphere into the tropical tropopause layer.

The first measurements of low ozone concentrations in the West Pacific were found with ozonesondes launched as part of the CEPEX (Central Pacific Experiment) campaign. CEPEX was a ship cruise that took place aboard the Research Vessel (RV) *Vickers* from 7 March to 7 April 1993 on a constant-latitude journey along 2°S from 150°E to 160°W [Kley et al., 1996]. In many of the profiles (reproduced in figure 1.2), ozone concentrations in the TTL were lower than those in the lower troposphere, creating the impression that ozone was being destroyed in the TTL [Kley et al., 1996]. However, reprocessing the data with a more representative background current correction (see section 1.4.2 for further details) made the near-zero measurements disappear, and the ozone profiles were nearly constant throughout the troposphere, with minimum ozone concentrations of around 10 ppbv both in the TTL and lower troposphere [Vömel and Diaz, 2010]. The reprocessed CEPEX profiles are shown in figure 1.3.

The Pacific Exploratory Mission—Tropics A and B (PEM-T A, PEM-T B) involved the NASA Douglas DC-8 airborne research laboratory and Lockheed P-3B Orion aircraft, taking place between August and September 1996 [Hoell et al., 1999] and September–October 1999 [Raper et al., 2001] respectively. Board et al. [1999] and Maloney et al. [2001] looked at back trajectories to determine the origin of air...
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<td>ACTIVE/SCOUT-O3/TWP-ICE</td>
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Table 1.1: Field campaigns that surveyed within the West Pacific Warm Pool region, and references from that campaign that are discussed in this thesis are listed.

measured on the NASA Ames Research Center (ARC) Douglas DC-8 for PEM-T A and PEM-T B respectively. Figures 1.4 and 1.5 show the findings from Board et al. [1999] and Maloney et al. [2001]. In both PEM-T A and PEM-T B, the air masses that were of aged marine origin, and those of convective, and SPCZ and ITCZ origins had considerably lower ozone than the air masses of continental origin, which is as expected since pollution and biomass burning enhances ozone concentrations in continental air, whereas clean marine air and recently convected air is naturally ozone-deficient. Furthermore, ozone from aged marine and convective sources were lower in ozone concentration in PEM-T B than PEM-T A, regularly
Figure 1.2: The original ozonesonde profiles from the CEPEX campaign, reproduced from Kley et al. [1996]. The solid lines represent the ozone mixing ratio from 0 to 100 nmol/mol (upper x-axis scale), the dotted lines represent the relative humidity from 0 to 100% (upper x-axis scale), and the dashed lines represent the temperature from 180 to 300 K (lower x-axis scale).

below 15 ppbv, suggesting March–April is a more preferable time of year for low-ozone than August–September. Maloney et al. [2001] splits the aged marine sources
into Northern Hemisphere and Southern Hemisphere sources, and the air masses originating in the Southern Hemisphere had less ozone than those originating in the Northern Hemisphere. A similar finding was described by Hamilton et al. [2008] who hypothesized from the ACTIVE campaign that Southern Hemisphere measurements of ozone were higher in concentration than those in the Northern Hemisphere.

PEM-West A and B (PEM-W A and PEM-W B), in September–October 1991 and February–March 1994 respectively [Talbot et al., 1996, 1997], also used the NASA ARC Douglas DC-8 platform to do flights mainly in the sub-tropical and extra-tropical West Pacific where ozone is generally much higher, but did observe ozone concentrations near the surface at tropical latitudes of ~10 ppbv, and outflow
from extra-tropical typhoons to have diminished ozone below 25 ppbv, indicative of uplift of near-surface air to the upper tropopause [Browell et al., 1996]. TRACE-P (Transport and Chemical Evolution over the Pacific) also used the NASA ARC DC-8 in the same region between February and April 2001, and so is directly comparable to PEM-W B. It was found that ozone in TRACE-P was higher than ozone in PEM-W B due to increased photochemical production of ozone from southeast Asian biomass burning and Asian outflow of pollution [Browell et al., 2003].

ACTIVE was a multi-platform campaign based in Darwin from 10 November to 10 December 2005 (first part) [Vaughan et al., 2008] and 20 January to 14 February

Alongside ACTIVE was SCOUT-O3 during the SCOUT-O3 (Stratospheric–Climate Links with Emphasis on the Upper Troposphere and Lower Stratosphere) campaign during the first part, which used the Myasishchev M-55 Geophysica aircraft and the DLR Falcon. During the second part, ACTIVE was alongside TWP-ICE (Tropical Warm Pool—International Cloud Experiment), which used the ARA (Airborne Research Australia) Diamond Dimona, a de Havilland Twin Otter and the ARM (Atmospheric Radiation Measurement) Scaled Composites Proteus UAV (Unmanned Aerial Vehicle). Therefore four aircraft performed flights in the first part and five performed flights in the second leg.

During ACTIVE/SCOUT-O3/TWP-ICE, ozone concentrations as low as 4 ppbv were observed by the ozonesondes, which were traced back to the West Pacific during monsoon conditions, whereas higher ozone concentrations were traced back to the Maritime Continent during a biomass burning period (figure 1.6) [Heyes et al., 2009]. They hypothesized that the composition of the TTL in the Darwin area is determined by certain “hot-spot” regions of deep convection, and air is then advected from these hot-spot regions, which dominate the TTL composition elsewhere in the region.

ACTIVE also surveyed the Hector thunderstorm, which is a large deep-convective storm that occurs almost daily over the Tiwi Islands near Darwin, Australia, during the pre-monsoon season between November and February [Allen et al., 2008; de Reus et al., 2009]. The M-55 Geophysica observed large ice crystals in the stratosphere, above the cold point tropopause, which is indicative of troposphere-to-stratosphere transport [de Reus et al., 2009]. Modelling studies have been done to quantify the amount of cross-tropopause transport in the Hector storm, which are discussed in section 1.5.

Ozonesondes from the TransBrom ship cruise also observed low concentrations of ozone. Ozone sondes were launched daily during TransBrom aboard the Research Vessel (RV) Sonne, which travelled approximately meridionally from Tomakomai, Japan (42°N, 142°E) to Townsville, Australia (19°S, 147°E) on a non-stop transit through the tropical West Pacific [Krüger and Quack, 2013]. Ozone concentrations below 15 ppbv were observed in all six ozonesondes between 14·9°N and 7·2°S, which were coincident with extremely low concentrations of the hydroxyl radical (OH*), whereas the ozonesondes launched north of 14·9° and south of 7·2°S were greater than 15 ppbv (figure 1.7) [Rex et al., 2014]. The hydroxyl radical is known as the “detergent of the atmosphere” [Riedel and Lassey, 2008], which removes pollutants from the atmosphere. The hydroxyl radical is formed through the photolysis of ozone.
Figure 1.6: Ozone and back-trajectory information from the ACTIVE ozonesondes that underwent rapid uplift. The locations of the circles shows where the back trajectories crossed the 500 hPa surface, the values correspond to the ozone concentrations measured by the ozonesondes, and the colours denote the meteorological phase the ozonesondes were launched in. Figure reproduced from [Heyes et al., 2009].

(equation (1.1)) followed by a reaction with water vapour (equation (1.2)).

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O} \]  

\[ \text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH}^* \]  

where \( h\nu \) is solar radiation at wavelengths less than about 325 nm [Lawrence et al., 1999]. Therefore the low-ozone events that coincide with low concentrations of the hydroxyl radical increases the atmospheric lifetimes of pollutant species such as hydrochlorofluorocarbons (HCFCs) that would otherwise be broken down by the hydroxyl radical, and therefore increase the global warming potential of those species [Rex et al., 2014].

Finally, SHADOZ (Southern Hemisphere Additional Ozonesondes) provides insight into the long-term trends of low-ozone events across the world. SHADOZ is a network of long-term ozonesonde stations that commenced in 1998, which comprises of thirteen current ozonesondes stations throughout the tropics, and four defunct
stations. Within the West Pacific, Suva (Fiji), Pago Pago (American Samoa) and Kuala Lumpur (Malaysia) are still launching ozonesondes on a regular basis, approximately fortnightly, and one former station in Watukosek (Indonesia) launched ozonesondes monthly from 1998 to 2013 [Thompson et al., 2003a,b, 2007]. These constitute the only long-term ozonesonde measurements in the tropical West Pacific and Maritime Continent. The long term ozonesonde measurements at Pago Pago, Hawaii and Natal (Brazil) all indicate that the frequency of low-ozone events (defined as those with ozone concentrations < 20 ppbv) have increases between the later 1970s and 2005, which means that the amount of deep convection has increased over that thirty-year period.

Other field campaigns focused on measurements other than ozone. The STEP (Stratosphere-Troposphere Exchange Project) Tropical campaign was concerned with investigating stratosphere-troposphere exchange in the West Pacific Warm Pool using the NASA ER-2 high-altitude aircraft [Russell et al., 1993]. Kritz et al. [1993] used radon-222 as a tracer for investigating stratosphere-troposphere exchange because of its source in the continental crust, its short, 3.8 day radioactive half-life, and its inability to be washed out by precipitation or water vapour. Kritz et al. [1993] concluded that the higher radon activities in the upper troposphere/lower stratosphere (UTLS) were always associated with convective activity with evidence of a reduction of water mixing ratios; consistent with rapid localized convection being responsible for troposphere-to-stratosphere transport and dehydration, rather than slow radiative ascent being responsible. However, more contemporary measurements suggest that

![Figure 1.7: Ozone profiles from TransBrom, reproduced from Rex et al. [2014]. The grey shading denotes ozonesondes that measured ozone concentrations of less than 15 ppbv.](image)

091011: 33.5°N
091012: 26.2°N
091013: 23.1°N
091014: 18.8°N
091015: 14.9°N
091016: 10.5°N
091017: 6.2°N
091018: 1.1°N
091019: 3.1°S
091020: 7.2°S
091021: 11.8°S
091022: 14.4°S
such rapid localized convection that results in convective overshooting directly into
the stratosphere only occurs in $\sim$0.5–1% of storms globally [Gettelman and Forster,
2002; Liu and Zipser, 2005; Hosking et al., 2010], and only the larger, longer-lived
tropical storms contribute to stratosphere-troposphere exchange [Rossow and Pearl,
2007]. Therefore uplift into the TTL followed by slow radiative uplift into the
stratosphere is thought to contribute more globally to troposphere-to-stratosphere
transport than convective overshooting. Further insights into the question of whether
slow radiative uplift contributes more to troposphere-stratosphere exchange than
convective overshooting have been found through modelling work, discussed further
in section 1.5.

TOGA COARE (Tropical Ocean–Global Atmosphere, Coupled Ocean–Atmosphere
Response Experiment) investigated the ocean-atmosphere coupling on time scales of
months to years, which is of importance to the maintenance of the high sea surface
temperatures (SST) in the West Pacific, and also the El Niño–Southern Oscillation
[Webster and Lukas, 1992], as part of the wider TOGA program that lasted for ten
years. TOGA-COARE addressed the lack of long-term detailed measurements in
the West Pacific Warm Pool, which was identified as an issue for modelling studies
attempting to simulate the sea surface temperatures, which were often too warm when
the climatological heat flux forcings were used, and also ENSO, which underestimate
the wind anomalies [Webster and Lukas, 1992].

BIBLE (Biomass Burning and Lightning Experiment), conducted in 24 September–
10 October 1998 (BIBLE A) and 30 August-14 September 1999 (BIBLE B) using
a Gulfstream II aircraft [Kondo et al., 2002a], investigated the effects of biomass
burning and lightning on ozone and its precursors, and also aerosols, and concluded
that lightning elevated the levels of NO$_y$ such that photochemical production of
ozone in the presence of such high NO$_y$ elevated ozone concentrations by $\sim$15 ppbv
[Kondo et al., 2002b].

1.3 CAST, CONTRAST and ATTREX campaigns

Coordinated Airborne Studies in the Tropics (CAST), Convective Transport of Ac-
tive Species in the Tropics (CONTRAST) and the Airborne Tropical Tropopause
Experiment (ATTREX) were multi-platform field campaigns, which took place in
January–March 2014, adding to the dataset in the West Pacific. Aircraft were based
in Guam, namely the FAAM (Facility for Airborne Atmospheric Measurements) BAe
146-301 large Atmospheric Research Aircraft (ARA), which conducted flights for
CAST, the NCAR (National Center for Atmospheric Research) Gulfstream V, which
conducted flights for CONTRAST, and the NASA (National Aeronautics and Space
Agency) Northrop Grumman Global Hawk, which conducted flights for ATTREX.
Each aircraft operated in different parts of the atmosphere: the FAAM BAe 146 flew mostly in the lower troposphere and in the boundary layer, the Gulfstream V sampled primarily at the level of convective outflow (~12–14 km) [Pan et al., 2017], whereas ATTREX sampled in the tropical tropopause layer (TTL) and lower stratosphere.

In addition, a field site was set up at Momote Airport, Manus Island alongside the Atmospheric Radiation Measurement (ARM) field site. A μDirac set up at the site measured halocarbons, viz. iodomethane (CH$_3$I), trichloromethane (CHCl$_3$), 1,1,1-trichloroethane (CH$_3$CCL$_3$), tetrachloromethane (CCl$_4$), dibromomethane (CH$_2$Br$_2$), tetrachloroethene (C$_2$Cl$_4$) and tribromomethane (CHBr$_3$) [Gostlow et al., 2010], a Picarro Cavity Ring-Down Spectrometer G2401 measured methane, carbon dioxide and water vapour [Crosson, 2008], and surface ozone was measured at the site using a TECO-49 UV absorption ozone analyzer. Finally, thirty-nine ozonesondes were launched from the ARM field site between 2 February and 25 February 2014. The ozonesonde measurements are described in detail in chapter 2.

Each campaign worked towards different mission objectives, and flights were designed around meeting these objectives: the CAST flights were designed to characterize the inflow to convection in the lower troposphere and boundary layer in the West Pacific [Harris et al., 2017], CONTRAST was designed to characterize the influence of deep convection on ozone, organic bromine and iodine at the level of convective outflow and the TTL [Pan et al., 2017], and the ATTREX campaign focused primarily on TTL composition, cross-tropopause transport and cloud processes affecting water vapour and short-lived trace gases [Jensen et al., 2017]. However several opportunities were taken for collocated measurements between the different campaigns, and indeed different platforms.

### 1.3.1 Salient results from CAST/CONTRAST/ATTREX

Folkins et al. [2002] describes the mean tropical ozone profile as being ‘S-shaped’, with the lowest values at the surface, a maximum at ~6·5 km, a minimum at ~11·2 km, and then an increase towards stratospheric values. Pan et al. [2015] used the CONTRAST ozone data to argue that the ‘S-shape’ results from the averaging of two separate air masses—the ‘primary mode’ of ~20 ppbv that is typical of tropical air, and the ‘secondary mode’ broadly distributed around ~60 ppbv occurs in the mid-troposphere between 5 km and 8 km, which has extra-tropical characteristics of high ozone and low relative humidity (RH<45%). Therefore the maximum in the mid-troposphere at ~6·5 km is a result of horizontal advection from the extra-tropics, rather than large scale descent and chemistry as Folkins et al. [2002] describes.
The ozonesonde measurement technique was first developed and described by Komhyr [1972]. The majority of ozonesondes used presently are electrochemical concentration cell (ECC) ozonesondes [De Backer et al., 1998], which use the electrochemical reaction between ozone (O$_3$) and potassium iodide (KI) to create a current proportional to the amount of ozone reacting with the potassium iodide. The cell comprises of two chambers, the cathode and the anode, which contain halide salt solutions of slightly different composition, connected by a salt bridge. Several recipes have been used for the cathode and anode solutions [Smit and Sträter, 2000], but the recipe used in the CAST ozonesondes is the 1% KI full buffer solution and is as follows: the cathode contains 2.5 ml of a solution consisting of:

- 10.000 g l$^{-1}$ potassium iodide (KI)
- 25.000 g l$^{-1}$ potassium bromide (KBr)
- 5.000 g l$^{-1}$ sodium hydrogen phosphate (Na$_2$HPO$_4$·12H$_2$O)
- 1.414 g l$^{-1}$ sodium dihydrogen phosphate (NaH$_2$PO$_4$·2H$_2$O)

The anode solution contains 1.5 ml of an identical solution to the cathode solution but with potassium iodide added until saturation. The sodium hydrogen phosphate and sodium dihydrogen phosphate act as a buffer, which prevent changes in pH of the solution.

Figure 1.8 shows an annotated diagram of an ozonesonde. The ozonesonde is placed inside a polystyrene box to insulate it against the cold temperatures that would otherwise freeze the solutions and stop the ozonesonde working. A radiosonde is attached to the polystyrene box and connected to the ozonesonde, which provides telemetry of the meteorological conditions (temperature, pressure, relative humidity, wind speed and direction) and also transmits the ozonesonde data.

Air is pumped into the cathode container, and the cathode reacts with ozone in the air according to the following formula: 2KI+O$_3$+H$_2$O $\rightarrow$ 2KOH+I$_2$+O$_2$. This liberates iodine (I$_2$), which then allows the following half-cell reactions to take place: at the anode 3I$^{-} \rightarrow$ I$_3^-$ + 2e$^{-}$ takes place, whilst at the cathode I$_2$ + 2e$^{-} \rightarrow$ 2I$^-$ occurs. This gives an overall reaction of 3I$^{-}$ + I$_2$ $\rightarrow$ I$_3^-$ + 2I$^-$ [Komhyr, 1972].

The reaction causes a flow of electrons, directly proportional to the rate of conversion of iodine (I$_2$) to iodide (I$^-$). The partial pressure of ozone is determined from the ozonesonde current according to the following formula (1.3) [Vömel and Diaz, 2010]:

$$p_{O_3} = \frac{R}{\chi F} \gamma T_{\text{box}} f_{100} I_{\text{corr}}$$

(1.3)
Figure 1.8: Annotated diagram of an ozonesonde.

where $R = 8 \cdot 31432 \text{J mol}^{-1} \text{kg}^{-1}$ is the universal gas constant, $\chi = 2$ is the yield ratio of two electrons per molecule of iodine, and $F = 9.6485 \times 10^4 \text{s A mol}^{-1}$ is the Faraday constant. Substitution of constants leads to the following equation (1.4):

$$p_{O_3} = 4 \cdot 309 \times 10^{-4} \gamma T_{\text{box}} f_{100} I_{\text{corr}}$$  (1.4)

where $\gamma$ is the pump flow rate correction factor (dimensionless), $T_{\text{box}}$ is the temperature inside the ozonesonde box (in K), as measured by a temperature sensor attached to the inlet pipe, $f_{100}$ is the flow rate (in s·(100 ml)$^{-1}$), and $I_{\text{corr}}$ is the background-corrected ozonesonde current (in $\mu$A) [Johnson et al., 2002; Vömel and Diaz, 2010]. Further discussion of the background-corrected ozonesonde current is found in section 1.4.2.

The ozone partial pressure (in mPa) is then converted to ozone concentration (in ppbv) by the following equation (1.5):

$$C_{O_3} = \frac{p_{O_3}}{p_{\text{atm}}} \times 10^{-4}$$  (1.5)

where $C_{O_3}$ is the concentration of ozone (in ppbv), $p_{O_3}$ is the ozone partial pressure (in mPa), and $p_{\text{atm}}$ is the total atmospheric pressure (in hPa).

In the CAST campaign, the ozonesondes used were EnSci model Z ozonesondes supplied by Droplet Measurement Technologies (DMT), connected to Väisälä RS-92 radiosondes.
1.4.1 Standard operating procedures

The standard operating procedures (SOP) for ozonesondes require the ozonesonde to be prepared twice, the first time normally 3–7 days before the flight, and the second time just before the ozonesonde is launched. Using the current standard operating procedures leads to the best precision and accuracy, of $< \pm 5\%$ Smit et al. [2013].

The method involved in the first preparation for EnSci ozonesondes is reproduced below, from Smit et al. [2013] (the asterisks denote places where the CAST ozonesondes deviated from the Standard Operating Procedures):

1. Run ozonesonde on purified air free of ozone for 10 minutes*
   
   (a) Check pump motor current is $< 100 \text{ mA}$
   
   (b) Check pump pump pressure is $> 66.6 \text{ kPa}$
   
   (c) Check pump vacuum is $< -66.6 \text{ kPa}$ at atmospheric pressure of 1000 hPa, or $< -53.3 \text{ kPa}$ at 780 hPa

2. Condition tubing, pump and cathode chamber with very high ozone ($> 10 \text{ ppmv}$) for 30 minutes

3. Run on purified air free of ozone for at least 5 minutes

4. Add 3 ml of 0.5% buffered cathode solution*

5. Wait 2 minutes and add 1.5 ml anode solution*

6. Run on purified air free of ozone for 10 minutes

7. Run on moderate ozone ($5 \mu \text{A}$) for 10 minutes*

8. Run on purified air free of ozone
   
   (a) Record current after 1 minute running on purified air free of ozone
   
   (b) Continue running on purified air free of ozone for 10 minutes and record the background

9. Add 2 ml more of cathode solution, then electrically short the cell leads*

10. Store in a cool, dark place until the day of flight

The CAST ozonesonde preparation deviated from the standard operating procedures in the following ways, all of which are not expected to affect the functioning of the ozonesonde in any way:

1. This step was skipped, and (a) to (c) were done as part of step 2 instead
4. 2.5 ml of cathode solution was used

5. The anode solution was added immediately after the cathode solution, as it was considered unnecessary to wait 2 minutes

7. This step was skipped: exposing the ozonesonde to any ozone concentrations during preparation was found to be detrimental, and the method of producing moderate ozone was the source of a contamination issue discussed in section 2.1.

9. No more solution was added to the cathode chamber

The method involved in the day-of-flight preparation for EnSci ozonesondes is reproduced below, again from Smit et al. [2013], with asterisks showing where CAST ozonesondes deviated from the SOPs:

1. Remove cell caps and discard anode and cathode solutions
2. Rinse cathode chamber by adding 5 ml fresh cathode solution and remove
3. Add 3 ml fresh cathode solution*
4. Add 1.5 ml fresh anode solution
5. Remove electrical short on cell leads and connect leads to test unit
6. Run on purified air free of ozone for 10 minutes
7. Record background current $i_{bg,0}$, which must be <50 nA
8. Run on moderate ozone (5 μA) for 5 minutes*
9. Record the ozonesonde current*
10. Switch to run on purified air free of ozone*
   (a) Record current after 0, 0.5, 1, 3, 5 and 10 minutes on purified air*
   (b) Check that current decay decreases at least 80% in the first minute*
   (c) Record background current $i_{bg,1}$ after 10 minutes of running on ozone free air*
11. Continue running ozonesonde on purified air. Connect flowmeter to exhaust port of cathode cell.
12. Measure 5 flow rates of pump and take average value
13. Record air temperature, pressure and relative humidity in preparation room
14. Calculate the humidity correction based on room temperature and relative humidity of the gas used during flowrate measurement

15. Turn off ozonesonde pump and prepare ozonesonde box for launch

16. Turn on radiosonde telemetry system and run on purified air free of ozone for 10 minutes and record background current $i_{bg,2}$

17. Remove the ozonesonde from the filtered air and measure surface air until values stabilize, usually 3–5 minutes just prior to launch. However, in cases of strong air pollution or extreme weather situations the launch should be done as fast as possible

18. Ozonesonde ready for launch

The CAST ozonesondes deviated from the day-of-flight preparation in the following ways:

3. 2·5 ml of cathode solution was used

8–10. Moderate ozone steps were omitted, as the final background current ($i_{bg,2}$) was found to be higher if these steps were included, and the method of producing moderate ozone was the source of a contamination issue discussed in section 2.1.

1.4.2 Background current

The background current is the current that is generated in an ozonesonde by any other means than the reaction with ozone. The background current, and the best way to correct for it, is the largest source of uncertainty in ozonesonde measurements [Vömel and Diaz, 2010]. In the tropics, where ozone concentrations are very low, the background current comprises the majority of the overall signal: Kley et al. [1996] attributed up to 90% of the overall signal to the background current [Vömel and Diaz, 2010]. As a result, a good understanding of the background current is required in order to produce a quantitative ozone profile in the tropical troposphere using ozonesondes. In the stratosphere and the extra-tropical troposphere, ozone concentrations are higher and the background current is less significant.

The cause of the background current is not fully understood and therefore the variability with time, altitude, pressure etc. is a matter of conjecture. The background current was thought to be oxygen-dependent, and therefore decreased as a function of altitude [Vömel and Diaz, 2010, and references therein]. This was refuted by Thornton and Niazy [1982], who instead attributed the background current to the reduction of triiodide, and therefore the background current is a function
of the mass transfer rate. The mass transfer rate is roughly constant at pressures between 1000 hPa and 100 hPa, and it reduces logarithmically between 100 hPa and 10 hPa (because the solution is ‘stirred’ less at these lower pressures where the pump efficiency decreases) [Thornton and Niazy, 1983]. The background current is also known to decay with time, even whilst sat in the laboratory [Vömel and Diaz, 2010], and the time at which the background current should be measured is disputed: three background currents, \( i_{bg,0}, i_{bg,1} \) and \( i_{bg,2} \) are measured throughout the day-of-flight preparation (see section 1.4.1). Thornton and Niazy [1982] notes that the background current diminishes continuously over a period of several hours up to a value of \( \sim 5–10 \) nA, and so measuring the background too early in the preparation would give rise to an overestimation of the background current. Meanwhile, Reid et al. [1996] suggests using the pre-exposure background current value \( (i_{bg,0} \) from section 1.4.1) for processing tropospheric data, with the caveat that the background current becomes too large in the stratosphere leading to an underestimation of stratospheric ozone by 2–6%.

As a result of the lack of consensus over the causes of the background current, several different methods of correcting the background current have been proposed, which produce significantly different ozone concentration values, especially in the tropical upper troposphere. These corrections include subtracting a constant background current (equation (1.6)) [Allen et al., 2009],

\[
I_{corr} = I - I_{bg}
\]

(1.6)

a correction dependent on the mass transport within the sonde (equation (1.7)) [Thornton and Niazy, 1983],

\[
I_{corr} = \begin{cases} 
I - I_{bg} & \text{for } p > 100\text{ hPa} \\
I - I_{bg}\left(\alpha \ln p\right) & \text{for } p < 100\text{ hPa}
\end{cases}
\]

(1.7)

an empirical correction formulated by Vömel and Diaz [2010] from measurements using known ozone concentrations (equation (1.8)),

\[
I_{corr} = (1 - \beta)I - \gamma
\]

(1.8)

and a pressure dependent correction (equation (1.9)) [Smit et al., 2007].

\[
I_{corr} = I - I_{bg}\left(\frac{\delta}{p}\right)
\]

(1.9)

In equations (1.6) to (1.9), \( I_{corr} \) is the background-corrected ozonesonde current (in \( \mu A \)), \( I \) is the measured current, \( I_{bg} \) is the background current that is recorded during
preparation of the ozonesondes (in μA—see section 1.4.1), and \( p \) is pressure (in hPa). In equation (1.7), \( \alpha \), \( \beta \), \( \gamma \) and \( \delta \) are all constants. For the 1% full buffer solution used in the CAST campaign, the coefficients in equation (1.8) are \( \beta = 0.090 \pm 0.005 \) and \( \gamma = 0.007 \pm 0.004 \) μA.

1.5 Models

The lack of long-term, high resolution measurements in the West Pacific increases the importance of modelling studies in the region. One of the most difficult phenomena to model is convection, which is the main meteorological régime in the tropics. Convective systems are highly localized, but contribute to a large proportion of the precipitation in the tropics. Fine-resolution, regional models are capable of resolving the small scale convective systems, but in coarser resolution, global models, such convective systems are smaller than the grid spacing and so cannot be resolved in the model. Sub-grid scale convective processes are instead parameterized in these models to imitate the effect of convection, and as a result, convection is one of the major sources of uncertainty in global climate models (GCMs) [Arteta et al., 2009a].

Many of the modelling studies conducted in the West Pacific region have looked at reproducing the measurements made in the field campaigns discussed in section 1.2. Lawrence et al. [1999] used MATCH-MPIC (Model of Atmospheric Transport and Chemistry—Max Planck Institute for Chemistry version) to attempt to reproduce the ozone profiles from CEPEX. MATCH-MPIC is a global model, which was run at a resolution of \( \sim 1.9^\circ \) with a convection parameterization scheme turned on. The conclusions given by Lawrence et al. [1999] was that the model was able to capture some of the key features such as the presence of the upper troposphere ozone minimum and lower troposphere ozone maximum, and also the low ozone concentrations in the West Pacific associated with convection, but was not able to quantitatively reproduce the extreme upper troposphere ozone minima seen in the CEPEX ozonesondes, which were often <5 ppbv [Kley et al., 1996]; instead the modelled minima in MATCH-MPIC was \( \sim 10 \) ppbv. Figure 1.9 shows a comparison for two CEPEX profiles with MATCH-MPIC. However, the finding of Vömel and Diaz [2010] that the ozonesondes were biased low because of the background current means that the upper troposphere ozone minima were closer to \( \sim 10 \) ppbv, reconciling the ozonesonde measurements with the model data. Unfortunately, the comparison with the MATCH-MPIC model results and the reprocessed CEPEX data has not been made, so it is unclear by how much the reprocessed ozonesonde data would improve the fit to the model data. In addition, the model was unable to reproduce the fine vertical structure of the ozone profiles because of the coarse vertical resolution (28 levels between the surface and 2 hPa).
Zhang et al. [2003] modelled the period of the TRACE-P campaign in the CMAQ model (Models-3 Community Multiscale Air Quality modelling system) coupled with RAMS (Regional Atmospheric Modelling System). They found that elevated concentrations of carbon monoxide (CO), ozone (O$_3$) and sulfate (SO$_4^{2-}$) from the pollution and biomass burning from southeast Asia typically remain north of 25°N, leaving the West Pacific Warm Pool area largely unaffected. Zhang et al. [2003] also notes that the area with the lowest model skill was at high altitudes and low latitudes where ozone concentrations were measured to be ~20 ppbv and the model prediction was ~80 ppbv due to overestimation of stratospheric contributions, reinforcing the case that convection in the tropics is more difficult to model than the more synoptic-scale meteorology that dominate in the extratropics.

Several modelling studies have been done of Hector, the outflow of which was measured during the ACTIVE/SCOUT-O3/TWP-ICE campaigns. Its predictability in time and space means that it can be easily modelled in high resolution, and is therefore used as an archetypal convective storm to draw conclusions about the characteristics and development of convective storms in general. Chemel et al. [2009] and Frey et al. [2015] both used the WRF (Weather Research and Forecasting) model, ARW (Advanced Research WRF) core to simulate the development of Hector on
30 February 2006. Frey et al. [2015] argues that the composition of the tropical tropopause layer in the Hector storm is determined not only by updraft from the boundary layer, which diminish ozone concentrations, but also downdrafts from the stratosphere, which enhance ozone concentrations. Chemel et al. [2009] also looked at the stratosphere-troposphere exchange associated with Hector; they note that the relative importance of direct stratospheric injection versus gradual radiative uplift from the TTL is a problem that requires further research, but found evidence of overshooting convection both in the ACTIVE radar measurements and in the WRF ARW model simulation. One consequence of stratosphere-troposphere exchange is the moistening of the stratosphere [Dessler et al., 2013], which Chemel et al. [2009] found in the model, though Frey et al. [2015] found both hydration and dehydration in different parts of the same Hector system. Stratospheric water vapour acts as a greenhouse gas, contributing to the warming of the planet [Dessler et al., 2013], so knowledge on the moistening/dehydration effects of the stratosphere through convective stratosphere-troposphere exchange is important in quantifying global warming effects. Evan et al. [2013] found that the cold-point tropopause is colder in their WRF model simulations than in the ERA-Interim (European Reanalysis—Interim) and MERRA (Modern-Era Retrospective Analysis for Research and Applications) reanalyses by \( \sim 1.2 \) K, and a colder minimum temperature increases the dehydration effect on the air passing through the tropopause. Furthermore, the largest temperature discrepancy between model and reanalyses is within the 100 hPa–70 hPa range—where the most important part of the temperature profile is for troposphere-to-stratosphere transport.

Some of the modelling studies focused on the uncertainties that are ubiquitous in models, such as those derived from the convection parameterization scheme and model resolution.

Many different convective parameterization options exist in models, which are used to reproduce convective processes that may be on a scale smaller than the grid resolution of the model, and each convective parameterization scheme produces a different solution to the simulation. Arteta et al. [2009a] simulated the location and time of the ACTIVE/SCOUT-O3/TWP-ICE campaigns, testing the sensitivity of the CATT-BRAMS (Coupled Aerosol Tracer Transport model—Brazilian Regional Atmospheric Model System) model to the choice of convective parameterization scheme. The most significant difference between schemes tested by Arteta et al. [2009a] was the precipitation rates: the best performing convection schemes (viz. Arakawa-Schubert and Kain-Fritsch) reproduced 75–77% of the measured rainfall from TRMM (Tropical Rainfall Measuring Mission), whereas the worst performers (viz. Low omega, Grell 3-d and the Moisture Convergence scheme) only reproduced 37–47% of measured rainfall, highlighting the sensitivity of the model to the parameterization.
Arteta et al. [2009b] considered the same model domain as Arteta et al. [2009a], but investigated the sensitivity of the model to horizontal and vertical resolutions. Arteta et al. [2009b] showed that a coarser resolution in the horizontal of $60\,\text{km}\times 60\,\text{km}$ compared to $20\,\text{km}\times 20\,\text{km}$, and also in the vertical—43 layers at $850\,\text{m}$ resolution compared to 56 layers at a resolution of $300\,\text{m}$—led to underestimations in the occurrence and intensity of convection in their models. However, for very fine-resolution models, the resolution does not appear to be consequential: Chemel et al. [2009] modelled Hector at resolutions of $1\,\text{km}$ and $250\,\text{m}$, producing similar outputs in each, except for the emergence of horizontal convective rolls at $250\,\text{m}$ resolution.

1.6 Radiation budget and radiative forcing

The Earth’s radiation budget is the balance between the incoming shortwave solar irradiance and the outgoing radiation components comprising of reflected shortwave radiation and longwave radiation emitted by the surface of the Earth. Numerous factors determine the radiation budget, including the amount of solar energy reaching the top of the Earth’s atmosphere, the Earth’s albedo—including the reflectance of the Earth’s surface, the reflectance of clouds, and amount of cloud cover, and atmospheric composition.

The radiative forcing of a particular forcing agent is the change in the Earth’s radiation budget as a result of a change in that forcing agent, for example the change that results from the increase in carbon dioxide concentrations in the atmosphere. The IPCC (Intergovernmental Panel on Climate Change) defines radiative forcing more specifically as “the change in net irradiance at the tropopause after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values” [Ramaswamy et al., 2001]. Figure 1.10 shows a bar chart of the radiative forcing of the main forcing agents between 1980 and 2011; carbon dioxide and other well mixed greenhouse gases have the largest positive radiative forcing, while the total effective radiative forcing of aerosols is the strongest negative contribution [Myhre et al., 2013].

The radiative forcing of ozone is negative in the stratosphere, due to the depletion of polar stratospheric ozone as a result of anthropogenic ozone-depleting halocarbon emissions reducing the amount of absorbed solar ultraviolet radiation and subsequently reducing radiative heating. However, the radiative forcing of ozone is positive in the troposphere, especially in the northern hemisphere, due to the increase in anthropogenic emissions of methane and other volatile organic compounds, nitrogen oxides and carbon monoxide, which photochemically react to form ozone [Myhre
Figure 1.10: Reproduced from Myhre et al. [2013].

The radiative forcing effect, and resultant surface temperature change, due to changes in ozone concentrations is largest in the upper troposphere/lower stratosphere (UTLS), as shown in figure 1.11 [Forster and Shine, 1997].

Within the tropical upper troposphere/lower stratosphere (UTLS), there is a secondary radiative forcing effect of ozone. An increase in tropical UTLS ozone concentrations induce a warming of the tropical tropopause temperature [Hardiman et al., 2015], which in turn results in an increase in water vapour entering the...
1.7 Convection

Convection is the upward vertical motion of an air mass, which occurs when an air parcel is less dense, and therefore more buoyant, than the surrounding air. In order for this to occur, the air parcel must be warmer than its environment, which will allow the air parcel to rise. In doing so, the air parcel undergo adiabatic cooling, and so—for dry air—the gradient of the potential temperature determines the ability of the air parcel to rise, and the level to which the air parcel will rise: if $\frac{d\theta}{dz} < 0$, then the air is unstable and is able to rise, if $\frac{d\theta}{dz} = 0$ then the air is neutrally buoyant, and if $\frac{d\theta}{dz} > 0$ then the air is stable and will sink [Laing and Evans, 2016].

The adiabatic lapse rate for dry air is $\Gamma \equiv -\frac{dT}{dz} = g c_p = 9.8$ K·km$^{-1}$, however, when air is moist the adiabatic lapse rate is less than 9.8 K·km$^{-1}$ due to the release of latent heat of vaporization, which counteracts the cooling process—the saturated adiabatic lapse rate varies with temperature, and can be between $\sim 4$ K·km$^{-1}$ at 20°C and $\sim 9$ K·km$^{-1}$. Consequently, the ability for moist air to undergo convection is greater than that of dry air.

In the tropics, intense insolation during the day heats the surface, which becomes unstable on a near-daily basis. Marine convection also occurs in the tropics, especially in warm pools where sea surface temperatures (SSTs) are $>27^\circ$C, where the sea temperatures are greater than the air above, creating instability. The moisture
content of air in the tropics is high, with relative humidity often above 80%, further enhancing the potential for convection to occur [Romps, 2014]. Much of the weather in the tropics is therefore driven by convective activity, with two-thirds of global precipitation occurring in the tropics [Costantino and Heinrich, 2014], and about half of the rainfall in the tropics comes from mesoscale convective systems (MCSs) [Nesbitt et al., 2006].

In deep convective systems where air is uplifted from near the surface all the way up to near the tropopause, a further release of energy due to the release of latent heat of fusion as water vapour in clouds transitions to the ice phase. As this occurs close to the tropopause, there is a possibility that this phase change can give the air parcel the energy required to penetrate into the stratosphere.

Deep convection is the main method of transporting energy, moisture and trace chemical species in the tropical troposphere [Laing and Evans, 2016], and is therefore a highly important part of the global atmospheric circulation, especially if air penetrates the tropopause into the stratosphere, which can then be transported globally via the Brewer-Dobson circulation.

1.8 Thesis outline and outstanding questions

The dataset that was generated by the CAST, CONTRAST and ATTREX field campaigns enabled us to answer some of the outstanding scientific questions that have been highlighted in the literature.

Firstly, attention has been drawn to the ozonesonde measurement technique, and the background current correction, which has been a large source of bias and uncertainty in ozone profiles, especially in the tropical tropopause layer where low ozone concentrations and low atmospheric pressure magnifies the uncertainties [e.g Thornton and Niazy, 1982, 1983; Reid et al., 1996; Johnson et al., 2002; Vömel and Diaz, 2010]. This problem is considered in chapter 2, addressed in part by unprecedented collocated measurements between ozonesonde and aircraft in the tropical tropopause layer. Furthermore, the ozonesonde dataset adds to the measurements record in the West Pacific Warm Pool, which is particularly limited.

Secondly, multiple measurements of low ozone concentrations exist within the literature, including those measured by the ozonesondes during CAST; most of which have been observed with ozonesondes. It is therefore unclear how low ozone concentrations can reach in the upper troposphere and TTL, how frequent these low-ozone events occur, how widespread each low-ozone event is, and whether there is any preferred location for these low-ozone events. To answer these questions, the CAST, CONTRAST and ATTREX aircraft data were analyzed, and the Weather Research and Forecasting (WRF) model was used to simulate a low-ozone event.
The aircraft data was analyzed for further instances of low-ozone events during the CAST/CONTRAST/ATTREX period, which provided measurements of many chemical species including ozone, so insights in the chemical composition of these low-ozone events could be inferred, and more about the spatial extent of low-ozone events and their preferred location could be determined: the aircraft surveyed vast areas of the West Pacific during the campaign. Chapter 3 described the findings from the aircraft data.

The WRF model was used to simulate a low-ozone event that was discovered by the CAST ozonesondes in order to answer the questions of whether WRF is able to accurately reproduce the low-ozone event, and if it is, then the spatial extent of the low-ozone event can be inferred from the WRF output. Although the objective of the modelling study was to model a single low-ozone event, the concept can be applied to answer questions about the frequency of the low-ozone events and if there is a preferred location for them to occur. The findings of the WRF modelling study are described in chapter 4.

Finally, chapter 5 summarizes the conclusions drawn from the three studies in this thesis, and suggestions of future studies that could be done in light of these conclusions to further enhance understanding of the dynamics and chemistry of the West Pacific Warm Pool region, while chapter 6 contains supplementary information and data from the campaigns.
Chapter 2

Measurements

2.1 Introduction

The following article, entitled “Ozonesondes in the West Pacific Warm Pool: Measurements and validation” was submitted to Atmospheric Chemistry and Physics Discussions in June 2015, reviewed and edited, and published to Atmospheric Chemistry and Physics in January 2016. The article introduces the results of the Manus ozonesondes launched as a part of the CAST campaign.

The ozonesondes were impaired by a contamination issue that affected the first fourteen ozonesondes, and a laboratory investigation was required on returning to Manchester in order to attempt to identify the cause of the issue and determine how best to correct for the uncertainties introduced by the contaminants. The CONTRAST Gulfstream V aircraft provided two invaluable overpasses of Manus Island during the campaign; the first of which occurred within the period in which the contamination affected the ozonesondes and the second overpass occurred when the problem was rectified and the ozonesondes were being prepared clean.

A new approach to the background current correction problem was devised from the results of the laboratory investigations, and the CONTRAST Gulfstream V provided validation that the background current correction is appropriate to characterize the issues that were encountered.

The identity of the source of the contamination was not established, although an anonymous reviewer theorized that it could be hydrogen peroxide ($\text{H}_2\text{O}_2$) — reproduced below — which was consistent with the behaviour of the particular contaminant in our preparation system, and thus a likely candidate:

“Air conditioned laboratories with much colder temperatures than the outside ambient air as in the Tropics can be a source of problems of condensation of water vapor when moving instruments (e.g. gas filters or TSC01) between laboratory and ambient air (much warmer and wetter) conditions. Or particularly when sucking ambient (moist) air through
a tube into the relative colder TSC01-preparatory instrument in the laboratory. For example: when once traces of liquid (condensed) water “stick” in the TSC01-quartz glass cuvette and being irradiated with UV-light this can produce not only O₃ but also significant amounts of H₂O₂ (resolved in the liquid water). Evaporated gaseous H₂O₂, even present when UV is turned off and flushed with zero air, will react also with KI in cathode cell but its response time in ECC-sonde is very slow and typical of the order of 20-30 minutes. This might be the origin of the contamination that occur at the beginning of the campaign and explain the large background currents and the pressure dependence but which is actually a time dependent declining of contaminent(s) eg. H₂O₂ in the ECC-cathode sensing solution.”

Using the new background current correction formula, a bubble of low ozone concentrations was discovered in the tropical tropopause layer (TTL) between 21 and 23 February with a minimum ozone concentration of 9.7 ppb, which was less than the concentrations found lower in the troposphere in the ozonesonde profiles at this time, suggesting that such ozone-deficient air could not have come from locally uplifted air from nearby convection. Analysis of this low ozone bubble confirmed that the bubble coincided with a strong easterly jet and back-trajectories indicate that a mesoscale convective system (MCS) to the east of Manus over the ocean, where such ozone-deficient air is abundant.

The following section is the transcript of the article “Ozonesondes in the West Pacific Warm Pool: Measurements and validation” [Newton et al., 2016]. The co-authors on this article were Geraint Vaughan, Hugo M. A. Ricketts, Laura L. Pan, Andrew J. Weinheimer and Charles Chemel.

Geraint Vaughan, Hugo Ricketts Charles Chemel, and I were directly responsible for the ozonesonde measurements taken on Manus Island, which I primarily analyzed. Hugo Ricketts and I were responsible for the ozonesonde laboratory experiments. Laura Pan and Andrew Weinheimer were responsible for the CONTRAST aircraft data, which were used to compare with collocated ozonesonde measurements.

2.2 Journal Article: Ozonesondes in the West Pacific Warm Pool: Measurements and validation

2.2.1 Abstract

We present a series of ozonesonde profiles measured from Manus Island, Papua New Guinea, during February 2014, with new insights on the calibration of ozonesondes for measurements in the tropical troposphere. The experiment formed a part of a
wider airborne campaign involving three aircraft based in Guam, to characterise the atmospheric composition above the tropical West Pacific in unprecedented detail. Thirty-nine ozonesondes were launched between 2 and 25 February of which 34 gave good ozone profiles. Particular attention was paid to evaluating the background current of the ozonesondes, as this can amount to half the measured signal in the tropical tropopause layer (TTL). An unexpected contamination event affected the measurements and required a departure from standard operating procedures for the ozonesondes. The most significant departure was not exposing the sondes to ozone during preparation, which meant that the background current remained stable before launch. Comparison with aircraft measurements allows validation of the measured ozone profiles and confirms that for well-characterized sondes (background current $\sim 50$ nA) a constant background current could be assumed throughout the profile, equal to the minimum value measured during preparation just before launch. From this set of 34 ozonesondes, the minimum reproducible ozone concentration measured in the TTL was 12–13 ppbv; no examples of ozone concentrations $< 5$ ppbv, as reported by other recent papers, were measured. The lowest ozone concentrations coincided with outflow from extensive deep convection to the east of Manus, consistent with uplift of ozone-poor air from the boundary layer. However, these minima were lower than the ozone concentration measured through most of the boundary layer, and were matched only by measurements at the surface in Manus.

2.2.2 Introduction

The Tropical Tropopause Layer (TTL) is the region of the tropical atmosphere between the top of the main convective outflow and the base of the stratosphere (approximately 13–17 km altitude) [Holton et al., 1995; Highwood and Hoskins, 1998; Folkins et al., 1999; Gettelman and Forster, 2002; Fueglistaler et al., 2009; Ploeger et al., 2011; Pan et al., 2015]. It is a transition layer between the convectively dominated mid-troposphere beneath and the statically stable (and convection-free) stratosphere above, with composition dependent both on convective uplift and large-scale transport. Since the TTL is the main source region for air entering the stratosphere in the Brewer–Dobson circulation, the concentrations of source gases within it determine the stratospheric burden of ozone-destroying radicals such as Cl$_x$ and Br$_x$. Furthermore, the temperature of the cold point determines the concentration of water vapour in the stratosphere, while clouds in the TTL, especially near the cold point, affect the radiation budget. The TTL is therefore a region of considerable importance both for global stratospheric chemistry and for climate.

The region of the tropics from the Maritime Continent to the International Date Line is known as the Tropical Warm Pool, where very warm sea surface temperatures ($> 28$ °C) support widespread deep convection [Wang and Mehta, 2008]. The
tropopause is higher and colder here than in other regions of the tropics, especially in Northern Hemisphere winter, making this region of particular importance for the dehydration of air as it enters the stratosphere [Fueglistaler et al., 2009]. The West Pacific region is also noted for very low ozone concentrations. Satellite measurements of total ozone show a zonal wave-one structure in the tropics with a maximum over the Atlantic sector and minimum over the West Pacific [Thompson et al., 2003a; Takashima and Shiotani, 2007]. This pattern is not restricted to the stratosphere: tropospheric ozone concentrations are also a minimum in the same region, generally attributed to photochemical destruction of ozone in the very clean marine boundary layer followed by rapid vertical mixing by deep convection [Thompson et al., 2003a].

Folkins et al. [2002] noted that tropical ozone profiles typically exhibit an “S” shape with height, with a minimum concentration in the boundary layer (where ozone is destroyed photochemically), a maximum in the mid-troposphere due to long-range transport, and a further minimum at around 11 km before increasing into the stratosphere. They argued that this is consistent with the effect of deep convection lifting air from the boundary layer to the outflow region. Closer examination of this process however suggests a more complex explanation. Heyes et al. [2009] analysed a series of ozonesondes launched from Darwin, Australia as part of the ACTIVE campaign [Vaughan et al., 2008] and concluded that the lowest TTL concentrations of ozone occurred above the level of convective outflow. Back-trajectories suggested that the origin of this air lay to the north-east of Darwin, to the east and north-east of New Guinea. Uplift of air in large convective complexes over the warm ocean in this region was proposed as the source region for the lowest ozone concentrations measured over Darwin. This suggests that there may be preferred locations or “hot spots” for lifting material to the TTL.

A controversial question regarding ozone measurements in the TTL is whether the concentrations can fall to near-zero values (<10 ppbv) in the outflow of deep convection. Ozonesonde observations during the CEPEX cruise over the central Pacific frequently measured ozone concentrations less than 10 ppbv, and occasionally close to zero in the TTL [Kley et al., 1996]. The authors suggested that lifting of near-surface air (where ozone is often strongly depleted in the tropics) essentially unmodified to the outflow of the convection could explain these observations, but they also pointed out that near-zero ozone in the TTL was encountered more frequently than near the surface during the cruise, and postulated that there may be a hitherto-unknown mechanism to destroy ozone in clouds. Model simulations by Lawrence et al. [1999] showed that minima in ozone concentration in the TTL over the West Pacific result from convective uplift, but could not replicate the very low ozone concentrations found by Kley et al. Such near-zero ozone values in ozonesonde profiles were also reported by Solomon et al. [2005] and Rex et al. [2014], again in
the West Pacific region.

Doubts about the validity of these very low ozone concentrations were raised by Vömel and Diaz [2010], who examined in detail how the ozonesonde measurement is made. In particular they examined the background current – an interfering signal that must be allowed for when deriving ozone concentrations from the raw data. Vömel and Diaz [2010] pointed out that the ozonesondes in Kley et al. [1996] and Solomon et al. [2005] measuring the lowest TTL ozone concentrations also had the highest background current. A re-examination of the ozonesonde profiles of Heyes et al. [2009] shows that the same issue may have arisen there with the minimum value of 4 ppbv occurring in a sonde with a higher background current than the others in that series (Sect. 2.2.4). We discuss the issue of the background current in detail in Sect. 2.2.3, but there is clearly uncertainty in the literature on the best way to account for it when calculating ozone profiles from the raw ozonesonde data. One of the aims of this paper is to shed light on this uncertainty.

We present a series of ozonesonde profiles measured from Manus Island, Papua New Guinea (2.07° S, 147.4° E) during February 2014 as part of the CAST/CONTRAST/ATTREX (Coordinated Airborne Studies in the Tropics/Convective Transport of Active Species in the Tropics/Airborne Tropical Tropopause Experiment) campaign to investigate the composition of the atmosphere above the West Pacific Warm Pool. The campaign featured three aircraft based in Guam (13.5° N, 144.8° E), to the north of the Warm Pool: the NASA Global Hawk, the NCAR Gulfstream V and the UK Natural Environment Research Council’s BAe146 (Fig. 2.1). The ground campaign took place at the Atmospheric Radiation Measurement (ARM) site next to the airport on Manus, and comprised an ozonesonde campaign with supporting ground-level observations from a TECO-49C UV photometric ozone monitor, a Picarro G-2401 cavity ring-down spectrometer to measure CO₂, CH₄ and CO, and a home-built gas chromatograph to measure halogenated compounds [Gostlow et al., 2010]. Support with both logistics and meteorological data were provided by ARM and the Papua New Guinea Meteorological Service. The ground-based data set was collected between 1 and 25 February 2014, with 39 ozonesonde ascents (34 of which gave good data) between 2 and 25 February. As we show in this paper, overflights of the NCAR Gulfstream V provided an opportunity to validate ozonesonde measurements in the TTL during conditions of low ozone concentration.

A key result of the CONTRAST campaign, reported by Pan et al. [2015], is the bimodal distribution of free tropospheric ozone concentration measured over the tropical Western Pacific. Gulfstream V in situ measurements indicate that vertical mixing and uplift of near-surface air maintains a primary mode, narrowly distributed around 20 ppbv, from the surface to 15 km. A secondary mode below 10 km, broadly distributed around 60 ppbv, was identified as incursions of midlatitude air based
on the low humidity and layered structure. The minimum ozone concentration measured during CONTRAST between 12 and 15 km was 13 ppbv, consistent with Vömel and Diaz [2010]’s contention that ozonesonde measurements of much lower concentrations are not reliable.

![Figure 2.1: Map of the experimental area, with Manus and Guam labelled.](image)

In Sect. 2.2.3, experimental details of the ozonesonde campaign are presented, including the procedure to correct for the background current. Section 2.2.4 presents the aircraft measurements used to validate the ozonesonde profiles. Section 2.2.5 presents a summary of the ozonesonde and ground-level ozone measurements, and the conclusions are in Sect. 2.2.6.

### 2.2.3 Experimental details

#### 2.2.3.1 The ozonesonde measurement technique

The ozonesonde technique relies on an electrochemical reaction between ozone and potassium iodide (Eq. 2.1), followed by half-cell reactions in the anode (Eq. 2.2) and cathode (Eq. 2.3) [Komhyr, 1972].

\[
2\text{KI} + \text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{KOH} + \text{I}_2 + \text{O}_2 \\
3\text{I}^- \rightarrow \text{I}_3^- + 2\text{e}^- \\
\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-
\]

The anode half-cell contains a saturated potassium iodide solution and the cathode an unsaturated KI solution; as the ozonesonde ascends, a teflon pump bubbles air through the cathode cell. The current produced is proportional to the flow of ozone.
through the cathode cell, with each ozone molecule assumed to generate two electrons [Komhyr, 1972]. However, this is not the only reaction that produces a current within the ozonesonde: other reactants produce a residual background current [Thornton and Niazy, 1982], which increases the measured signal and which must be accounted for when calculating the ozone concentration.

The background current is of particular importance in the TTL where it can be a substantial fraction of the total current measured by the sonde. The best way to correct for the background current is the subject of much debate [e.g. Komhyr and Harris, 1971; Thornton and Niazy, 1982, 1983; Reid et al., 1996; Smit and Sträter, 2000; Smit et al., 2007], and the two main manufacturers of ozonesondes, Droplet Measurement Technologies and Science Pump Corporation, recommend two different methods: either a constant value measured before launch or a value that scales linearly with ambient pressure. The practice of using a pressure-dependent correction arises from early suggestions that the ozonesonde reacts with oxygen [Komhyr and Harris, 1971], but later studies ruled out this mechanism and suggested that the background current should be taken as constant with altitude, at least in the troposphere [Thornton and Niazy, 1982; Reid et al., 1996]. However, Johnson et al. [2002] found that a background reaction with the phosphate buffers of a standard electrolyte solution did lead to a time dependence.

This confusion led Vömel and Diaz [2010] to examine in detail the issue of background current. In the normal preparation of an ozonesonde, the sonde is exposed to stratospheric concentrations of ozone to check that it is responding correctly. The background current is measured as the sonde is drawing in ozone-free air before and after exposure to ozone. Reid et al. [1996] recommended that the first of these measurements be adopted as the background current and removed (as a constant value) from current measurements in flight. However the standard procedure for ozonesonde preparation [Smit et al., 2007] uses a value measured 10 min after exposure to ozone. Vömel and Diaz [2010] found that the background current continues to decrease after exposure to ozone, even for periods of hours—suggesting that a value measured 10 min after exposure to ozone will be an overestimate by the time a sonde reaches the TTL, leading to an underestimate of the ambient ozone concentration when subtracted from the measured current. This decrease in background current is strongly dependent on the strength of the phosphate buffer concentration in the cell solution. Vömel and Diaz [2010] recommended the use of a background current \( I_{bg} = 0.09I + 0.014 \mu A \) for the 1% KI, full-buffer cathode cell solutions used in this paper, regardless of the measurements made during sonde preparation; the dependence of \( I_{bg} \) on the current \( I \) suggesting that the assumption of two electrons per ozone molecule passing through the cathode cell is not correct. Reprocessing past soundings with this formula for background current was shown to
remove all the cases of near-zero ozone—not surprising as the background current of \( \sim 0.025 \mu A \) that this gives in the TTL is well below the 0.065 \( \mu A \) used for example in the original analysis of the CEPEX data. Independent verification of Vömel and Diaz [2010] has however not been performed to date, and we examine below the application of this recommendation to the Manus data set and the comparison with aircraft data.

It is clear from previous work that the background current is not a well-defined quantity, and that there is uncertainty on the best way to measure it and its possible variation during flight. This is acknowledged by the Global Atmospheric Watch (GAW) report on ozonesondes [Smit et al., 2013] which calls for more fundamental research on this topic. We now describe in detail the ozonesonde preparation method in Manus, which departed from GAW-standard procedures in a number of ways.

### 2.2.3.2 Ozonesonde preparation

The ozonesondes used here were EnSci Model Z sondes supplied by Droplet Measurement Technologies, coupled to Väisälä RS92G radiosondes which provided pressure, temperature, humidity and wind profiles. All were from the same batch of sondes supplied just before the campaign. The cathode solution comprised 1% KI with 25 g L\(^{-1}\) of KBr, 5 g L\(^{-1}\) \( \text{Na}_{2}\text{HPO}_4 \cdot 12 \text{H}_2\text{O} \) and 1.25 g L\(^{-1}\) \( \text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O} \) as buffers. Standard procedures for preparing ozonesondes follow a two-stage process aimed at reducing the background current to less than 50 nA at the time of launch and measuring the sonde’s pump flow rate. In this work the background current was obtained by drawing air into the sonde through a charcoal filter in an air-conditioned cabin where RH < 50% at all times. The current was measured with a Keithley 6485 picoammeter, and the pump flow rate \( F \) (in mL min\(^{-1}\)) with a Sensodyne Gilibrator unit. Repeated measurements of pump flow rate generally agree to 1–2%. The ozone partial pressure \( p_{O_3} \) (in mPa) was derived from the measured sonde current as

\[
p_{O_3} = 4.307 \times 10^{-4} \left( I - I_{bg} \right) T_{box} \left( \frac{6000}{F} \right),
\]

where \( T_{box} \) was measured by taping a thermistor to the inlet tube as it entered the ozonesonde pump. In this equation \( I \) and \( I_{bg} \) are both measured in \( \mu A \) and \( T_{box} \) in K. A pump correction following Komhyr et al. [1995] was also applied to the data but this is negligible for the altitude range considered in this paper.

The ozonesonde preparation procedures normally involve, at different stages, purging the electrochemical cell and/or the pump with high concentrations of ozone, characterising the cell response to expected atmospheric concentrations of ozone and drawing ozone-free air through the cell. For this a Science Pump TSC01 ozone calibration unit was available. Normally, each ozonesonde would be first prepared
3–5 days before flight, in a four-step process: (i) passing high ozone through a new cell to remove organic traces; (ii) filling the anode and cathode cells and waiting for the current to fall to 0.5 μA while drawing in ozone-free air; (iii) exposing the cell to atmospheric concentrations of ozone to verify its response; (iv) again drawing ozone-free air, measuring the time response of the cell and the background current after ~10 min. Then, on the day of flight, a second preparation would follow basically the same steps except that high ozone was only passed through the pump rather than the cathode cell. Standard ozonesonde procedures specify a change of solution once, at the beginning of the second preparation. We found in Manus, however, that repeated changes of solution were needed to reduce the background current to an acceptable value (the number of changes varied from sonde to sonde according to its requirements). The background current was measured both at the beginning of the second preparation and as the minimum value recorded by the Väisälä software after the sonde package was finally assembled (but before taking it out of the air-conditioned environment – in the humid tropical atmosphere outside the cabin the charcoal destruction filter does not work correctly).

The procedures used in Manus departed, as already mentioned, from the GAW recommendations. The most important deviation (a consequence of the malfunctioning calibration unit, see below) was that the majority of sondes were not exposed to ozone during preparation. This turns out to have been advantageous, as it avoided the decay in $I_{bg}$ reported by Vömel and Diaz [2010]. Smit et al. [2007] report that the background current measured 10 min after exposure to ozone in the final preparation exceeded that measured before exposure to ozone by 34 nA on average for a sample of five EnSci sondes. By contrast, for the uncontaminated sondes in Manus the average difference in $I_{bg}$ measured at the beginning and end of the final preparation was only 6 nA (Fig. 2.2). Together with changes in solution to ensure that $I_{bg}$ fell to around 50 nA, not exposing the cell to ozone resulted in a stable $I_{bg}$ during preparation, lending confidence to the subsequent assumption that it remained constant during flight. We examine this assumption further in the next section.

Other departures from GAW recommendations were the following:

- The use of a 1% solution rather than the 0.5% which leads to an oversensitivity to ozone and a bias of ~ +5% in ozone concentration [Smit and Panel for the Assessment of Standard Operating Procedures for Ozonesondes (ASOPOS), 2013].

- Measurement of $T_{box}$ rather than the pump temperature, leading to an underestimate of ozone by ~3% since the pump temperature is higher by around 10 °C [Smit et al., 2013].

- Use of a charcoal filter to provide ozone-free air rather than an ozone-free gas
supply. The effect of this is difficult to quantify, but will be most serious in a laboratory with humid air and measurable concentrations of ozone. In this case the relative humidity of cabin air was around 50 %, within the expected operational range of the filter. On occasion a sonde was allowed to sample laboratory air without the filter attached, but this made no difference to the measured current. This means either that the laboratory was essentially ozone-free or that the filter was not working. When the sonde was taken outside and the filter removed, an increase in signal was measured, so we conclude that the filter was working correctly and that laboratory air was essentially ozone-free.

- correction to pump flow rate measurement for humidification of air. For a laboratory at 20 °C and 50 % RH this correction reduces \( F \) in Eq. (2.4) by around 1.5 % [Smit et al., 2013], increasing ozone by the same amount – in other words equation 2.4 underestimates ozone by \( \sim 1.5 \% \).

The overall effect of departures from the GAW recommendations is therefore small – much smaller than the error due to the background current uncertainty for tropical tropospheric ozone concentrations.

### 2.2.3.3 Contamination

A complication encountered during this experiment was the sudden appearance of a contamination source inside the TSC01 which produced a large signal from the ozonesonde. This badly affected the first two sondes, rendering their data
unusable. These sondes were extensively exposed to air drawn through the TSC01 during their second preparation (the first having been completed normally before the contamination appeared). Contamination also rendered the calibration cell on the TSC01 unusable. Sondes 3 and 4 were again clean on first preparation but were briefly exposed to the TSC01 on second preparation, after an initial measurement of the background current. The remaining sondes were not exposed to the TSC01 at all during the second preparation – the sonde’s response to ozone was assumed to be normal and the background current was measured by drawing air through an external charcoal filter. Sondes 5–14 were briefly exposed to the TSC01 on first preparation and were subsequently found to have elevated background currents. Sondes 15 onwards were not exposed at all to the TSC01 and the background currents from these sondes were around 50 nA before launch.

Figure 2.2 shows how the background currents measured for each sonde varied during the campaign, compared to the minimum current measured by the cell in the TTL (taken from the Väisälä raw data telemetry). During the latter part of the campaign the background current was around half the minimum measured in the TTL, but during the early part the minimum current was close to or even lower than the background – implying an impossible negative ozone. Clearly the contamination did not remain constant during a flight.

On return from Manus a series of laboratory experiments were conducted to ascertain the properties of the contamination. These are summarised in the Appendix, but the salient result is that for lightly contaminated sondes (such as 3–15) the effects of the contamination tended to disappear over a similar timescale—\(\sim 1 \text{~h} \) —to that taken by a sonde to reach the TTL. Based on this, and the evidence in Fig. 2.2 that the minimum ozonesonde current in the TTL was remarkably stable over the campaign, we assume that in-flight the contamination disappeared and the background current returned to a value of 50 nA, consistent with the uncontaminated sondes. A hybrid background current correction was thus devised:

\[
I_{bg} = 50 \text{nA} + \left( I_{bg}^{\text{meas}} - 50 \text{nA} \right) \frac{p}{p_0}, \tag{2.5}
\]

where \(I_{bg}^{\text{meas}}\) was the measured background current before launch, \(p\) the pressure and \(p_0\) the surface pressure.

The spread in measured background current for the uncontaminated sondes was around 10 nA (0.01 \(\mu\)A, Fig. 2.2, sondes 15 onwards), with a similar difference between the values measured at the beginning and the end of the preparation, so it is reasonable to estimate an uncertainty in \(I_{bg}\) measured before flight of \(\pm 10 \text{nA}\). If \(I_{bg}\) were constant during flight this would correspond to an uncertainty of \(\pm 3.4 \text{ ppbv}\) in the TTL. According to Thornton and Niazy [1983], \(I_{bg}\) should remain constant up
to 100 mb, then decline logarithmically with pressure. Our laboratory investigations on an uncontaminated sonde (Fig. 2.17) suggest a small decrease of around 5 nA in going from lab pressure to 100 mb, consistent with Thornton and Niazy’s result within error limits. Taking this as an uncertainty (rather than a bias) in the variation of $I_{bg}$ we estimate the uncertainty in TTL ozone below 100 mb to be ±5 ppbv. The cold-point tropopause during the campaign at Manus was always between 90 and 110 mb, with the ozone concentration increasing rapidly in this range: the minimum concentration was always found below 110 mb. Above 100 mb the use of a constant $I_{bg}$ will tend to lead to an underestimate of ozone, but as ozone was generally >50 ppbv above 100 mb, and increasing rapidly with height, this effect is only manifested in the stratosphere.

The error in TTL ozone for the contaminated sondes cannot be assessed quantitatively but will certainly be greater than that for the uncontaminated sondes. We can only get an estimate of this error from a comparison with another technique, so we now turn to a comparison of ozonesonde profiles with aircraft measurements.

### 2.2.4 Validation

One of the aims of the CAST and CONTRAST campaigns was to investigate the accuracy of ozonesonde measurements in the TTL by comparing them with near-
Figure 2.4: Ozone concentrations from CAST ozonesonde 6 on 5 February (black), and the segment of Gulfstream V flight RF09 that was close to Manus Island (red). The aircraft measurements most closely resemble the ozonesonde when the hybrid background correction is used (solid line), compared to the constant (black dotted line), pressure-dependent (red dotted line) and Vömel and Diaz (green dotted line) corrections. The asterisk is the ozone concentration measured by the TECO-49 on the ground on Manus Island. The peak in the aircraft data near the surface is caused by biomass burning.

Ozonesonde 6 was affected by contamination with a high background current (143 nA). In Fig. 2.4, four ozonesonde profiles are shown—one using a constant background current correction (black dashed line), one using a pressure-dependent correction (blue dashed line), one using the recommendation of Vömel and Diaz [2010] (green...
Figure 2.5: As Fig. 2.4 for CAST ozonesonde 34 and outbound leg of Gulfstream V flight RF14 on 22 February.

dashed line) and the fourth using the hybrid correction (solid black line). It is clear that the hybrid correction fits the Gulfstream V measurements (red solid line) very well, while the constant correction gives artificially low (and in this case negative) ozone in the TTL similar to the profiles reported by Kley et al. [1996] and Rex et al. [2014]. We conclude that the hybrid correction provides a satisfactory estimate of $I_{bg}$ but reiterate the point made in the previous section that a quantitative error estimate in TTL ozone for the contaminated sondes is not possible.

Gulfstream V flight RF14, on 22 February, passed just to the west of Manus on two occasions – on an outbound journey towards Australia and then on the return journey back to Guam. On both occasions, an ozonesonde was launched so as to reach aircraft altitude as the aircraft made closest approach to Manus. Ozonesonde 34, coincident with the outbound leg, was launched at 01:31 UTC (11:31 LT) and reached the Gulfstream V cruising altitude of 13.5 km at 02:11 UTC. In the flight-path map in Fig. 2.3, the red line is the outbound leg of RF14. Figure 2.5 shows the ozone profiles from ozonesonde 34 and the co-located measurements of RF14. Likewise ozonesonde 35, launched at 04:49 UTC (14:49 LT) coincided with the return leg of RF14, reaching the Gulfstream V cruising altitude of 180 hPa (13.5 km) at 05:29 UTC. On this leg the aircraft executed a profile between 13.1 and 14.7 km as it passed by Manus. Figure 2.3 shows the flight-path of the return leg in green. Figure 2.6 shows the profiles from ozonesonde 35 and the co-located measurements from RF14.
Figure 2.6: As Fig. 2.4 for CAST ozonesonde 35 and inbound leg of Gulfstream V flight RF14 on 22 February.

Ozonesondes 34 and 35 were uncontaminated, so constant background currents of 61 and 54 nA respectively were used in the data analysis. In both cases, the agreement between the ozonesonde and the aircraft data is within 3 ppbv - consistent with the uncertainty in the background currents. By contrast, the pressure-dependent correction and that recommended by Vömel and Diaz [2010] clearly overestimate the ozone concentration. We therefore conclude that for a well-conditioned ozonesonde not exposed to ozone at all in the pre-flight preparation, where the background current at the end of the preparation is around 50 nA or less, subtraction of this constant background produces an ozone measurement in the TTL within a few ppbv of the correct value. We also conclude that our method of applying a hybrid correction produces sensible results for the contaminated sondes.

What we cannot be sure of is whether the hybrid method applies only to this particular batch of sondes, or whether it can be applied more generally to sondes where the background current in the preparation is substantially larger than 50 nA. To check this, we reanalysed an ozonesonde profile from the ACTIVE campaign in Darwin, launched on 22 January 2006. This had a background current of 85 nA which, when subtracted from the measured currents, resulted in an ozone concentration minimum of 4 ppbv in the TTL. A sonde the following day with a very similar ozone profile but a background current of 55 nA measured a minimum ozone mixing ratio of 12 ppbv. Applying the hybrid correction to the sonde on
Figure 2.7: Time series of precipitation rate (in mm hr$^{-1}$) measured by an optical rain gauge at the Manus Island ARM site. Data courtesy of ARM archive.

22 January increased the minimum value in the TTL to 12 ppbv, in line with the other sonde. This suggests that the hybrid method may have wider validity than the Manus data set and may be worth investigating further. (We should emphasise that not all ozonesonde measurements $<10$ ppbv in the TTL are artifacts of elevated background currents: the lowest measured in Darwin was 8 ppbv on 15 February 2006 with a background current of 37 nA.)

We have therefore applied the following background current correction to the Manus data set, after discarding the first two profiles:

- For sondes 3 and 4, a hybrid correction was applied using $I_{bg}$ measured at the beginning of the second preparation, before exposure to the TSC01 ozoniser. This value was considerably smaller that measured after exposure.

Figure 2.8: MTSAT channel 2 (near-infrared) image from 19 February 2014, 18:00 UTC. The convection to the east of Manus Island (red arrow) is visible as the brightest clouds in the image.
Figure 2.9: Variation of cold point tropopause temperature (red curve, right axis) and cold point potential temperature (blue curve, left axis) measured by the CAST sondes. Where double tropopauses were observed (between 9 and 16 Feb), the local temperature minimum corresponding to a steep increase in ozone concentration was taken as the tropopause. In these cases the coldest point lay around 1–2 km higher.

Note that for sondes 15 onwards $I_{bg}$ measured at the beginning and end of the second preparation were very similar (Fig. 2.2).

2.2.5 Results

We present here an overview of the measurements made at Manus during CAST. The campaign experienced two distinct weather regimes – a dry period from around 1–10 February with little precipitation (Fig. 2.7) when deep convection was well to the south of Manus, and a wetter period from 11 February on, with two particularly wet periods around 13–15 February and 20–23 February. During the latter period in particular, widespread deep convection occurred around and to the east of Manus (Fig. 2.8), providing the conditions needed to examine the ozone concentration in fresh convective outflow.

The two meteorological regimes are reflected in the time series of tropopause (cold point) temperature and potential temperature from the ozonesondes (Fig. 2.9), with $\theta$ generally around 370 K from 1–12 February and rather lower, around 364 K,
from 13 February onwards. Tropopause heights and pressures for the whole campaign (not shown) ranged from 15.7 to 17.2 km, and 89 to 115 hPa respectively. Double tropopauses were found from 9 to 16 February; the tropopause shown in Fig. 2.9 corresponds to the first steep increase in ozone concentration as the balloon ascended. (The cold point during this period was around \(-86\, ^\circ\text{C}\).) Following the period of double tropopauses, on 18 February, the tropopause was at 370 K (17 km), but as the very wet conditions became more established it descended to reach 354 K (15.7 km) on 22 February. At the same time a distinctive feature became established in the wind field (Fig. 2.10): from 16 February onwards, and especially from 20–23 February, an easterly jet with wind speed up to 40 m s\(^{-1}\) was found in the TTL, just below the tropopause. This jet was confined to the troposphere – by 1.5 km above the tropopause the wind had backed round to westerly, and remained westerly between 18 and 26 km. A corresponding minimum in wind speed (of \(\leq 2\, \text{m s}^{-1}\) in most cases) was measured 700–1200 m above the tropopause from 16 February onwards. This easterly jet is consistent with convective outflow from the large convective complexes to the east of Manus (Fig. 2.8) reaching up to the tropopause during this period but not extending into the stratosphere.

The corresponding contour plot of ozone concentration is shown in Fig. 2.11. This clearly shows the “S” shape expected of tropical ozone soundings, with low values near the surface and in the TTL, and a maximum in the mid-troposphere.
Figure 2.11: Ozone concentration (ppbv) measured by the CAST ozonesondes between 0 and 18 km during February 2014, overlaid with potential temperature (K, white contours). Green bars at the top denote the launch times of individual ozonesondes.

Minimum values of $<20$ ppbv are frequently shown in the TTL, around 14 km during the first meteorological period and then up to 16.5 km during the second period. The periods of precipitation in Manus (Fig. 2.7) both correspond to ozone concentrations $<20$ ppbv reaching the tropopause, and indeed in the very wet period between 20 and 22 February, when the TTL easterly jet was at its most intense, ozone minimum concentrations fell to $<15$ ppbv. The lowest measured value was 8.2 ppbv on 21 February – a similar minimum to that measured in Darwin during ACTIVE. This may have been an outlier (its background current was 60 nA), but five sondes reached between 12 and 13 ppbv (e.g. sonde 34 on 22 February, Fig. 2.5) and a further four between 13 and 15 ppbv. These values are entirely consistent with the minimum ozone concentration of 13 ppbv measured by the Gulfstream V during CONTRAST [Pan et al., 2015].

To confirm that the very low ozone measured in the TTL is consistent with uplift from the deep convection to the east of Manus, back-trajectory calculations were performed using the HYSPLIT on-line model. As an example, Figs. 2.12 and 2.13 show 4-day HYSPLIT back-trajectories initiated over Manus at 02:00 UTC on 22 February (corresponding to sonde 34), between 13 km (180 hPa) and 15 km (130 hPa). The trajectories clearly indicate extensive uplift from the lower troposphere in the 48 h before the measurement, indicating that the source of the low ozone in the TTL is indeed the lower troposphere north of the Solomon Islands. Of course, the HYSPLIT trajectories cannot represent ascent in individual cloud systems, and so cannot determine whether the air is really of boundary-layer origin, but they do confirm
that the meteorological conditions at this time were consistent with widespread deep uplifting of air.

Figure 2.11 shows that the low-level ozone over Manus also showed two distinct periods, consistent with the meteorology. Ozone concentrations <15 ppbv extended up to 2 km in the dry period and persisted below 1 km up to 14 February, but in the very wet period the lowest values were in the range 15–20 ppbv, more than the minima measured in the TTL. However, the ground-level measurements from the TECO-49 ozone monitor (Fig. 2.14) tell a rather different story. The dry early period of the CAST campaign, from 1 to 12 February, was characterized by a strong diurnal variation in ozone, with maxima of ~8–10 ppbv during the day and minima ~2–3 ppbv at night. Winds were very light and variable, allowing the boundary layer to stabilise overnight, so we deduce that the night-time minima during this period were a local phenomenon. Wetter conditions set in by 13 February, with the diurnal ozone variation largely disappearing in the steady north-westerly breeze. Ozone concentrations in the range 9–13 ppbv predominated up to 19 February, with 12–14 ppbv thereafter. These values are in fact consistent with the minimum values measured in the TTL (save for the very low value on 21 February)—and with the sondes, which generally measured a steep increase in ozone in the bottom 200 m of the profile (the altitude scale in Fig. 2.11 obscures this point). If the lower tropospheric ozone in the uplift region to the east of Manus was similar to that over the island,
Figure 2.13: Pressure plot of the HYSPLIT back-trajectories. Zero time is defined as the initialization time of the back trajectories, at 02:00 UTC on 22 February 2014.

this would suggest that the air reaching the very top of the TTL in the wet period originated very near to the surface and was lifted to the tropopause without significant mixing with surrounding air, consistent with the suggestion of Kley et al. [1996].

2.2.6 Conclusions

One of the aims of this paper was to determine the best way to correct ozonesonde profiles from a tropical station for the effect of the background current. We were very fortunate that the Gulfstream V flight RF14 was able to fly by Manus during the period when very low ozone concentrations were observed in the TTL by the sondes. Ozonesondes 34 and 35 were free of contamination, and when using a constant background current measured just before launch their measurements agreed with the Gulfstream V to within 3 ppbv (the realistic limit on the accuracy of the ozonesonde at 100 mb is ±5 ppbv due to background current uncertainty). We conclude that for a well-prepared sonde—i.e., (for the batch used here) one where $I_{bg} \sim 50$ nA—a constant background current correction is the best choice.

In preparing these sondes we found it necessary to change solutions in the cells up to three times during a day-of-flight preparation in order to ensure a sufficiently low background current. Other than for sondes 3 and 4, we also did not expose the sondes to ozone during the day-of-flight preparation, which removes the problem of the slow decay in $I_{bg}$ after such exposure [Vömel and Diaz, 2010]. Both these changes
Figure 2.14: Time series plot of ozone concentration (in ppbv) measured on the ground by the TECO-49 ozone monitor. The black line is the 15 min median ozone concentration, and the grey lines are the 10th and 90th percentiles. A strong diurnal cycle is established between 3 and 12 February, which disappears on 13 February, replaced by a higher, more constant ozone concentration of ~12 ppbv.

... in standard procedures are recommendations from this work. For the sondes exposed to contamination during first preparation a hybrid background current correction was adopted after the laboratory investigation. Using this, the profile for sonde 6 was found to agree remarkably well with the aircraft profile from RF09 (Fig. 2.4), lending confidence to this somewhat arbitrary correction. Care must be taken not to generalise this result too far, but we can conclude (both from the CAST sondes from Manus and the ACTIVE sondes from Darwin) that a background current in excess of 70 nA is too high for a constant $I_{bg}$ correction – as shown by Vömel and Diaz [2010] this leads to a substantial underestimate of the TTL ozone and even to negative ozone in some cases [e.g. Rex et al., 2014].

The minimum reproducible ozone concentration measured in the TTL during CAST was 12 ppbv, consistent with the minimum of 13 ppbv measured between 12 and 15 km by the Gulfstream V during CONTRAST [Pan et al., 2015]. This is also consistent with the minimum measured in Darwin with well-prepared sondes (12 and 11 ppbv on 23 January and 14 February 2006, respectively) in air whose origin, according to back-trajectory calculations, lay in deep convective uplift east and north-east of New Guinea. In both campaigns an isolated example of a lower concentration, around 8–9 ppbv, was also measured. The CAST measurements confirm Vömel and Diaz [2010]’s conclusions that ozonesonde measurements <5 ppbv in the TTL are artifacts of the background current correction.

The lowest ozone concentrations measured in the TTL above Manus occurred around 16 km during a period when widespread deep convection was occurring near and to the east of the island. This is consistent with the ‘hot spot’ idea proposed by Heyes et al. [2009] for uplift of air to the upper TTL. The lowest ozone concentrations coincided with an easterly jet, consistent with outflow from the deep convective complexes. At this time, the ozone concentration in the lowest 2 km over
Manus exceeded 15 ppbv—only at the ground and in the bottom 200 m of the profile could values as low as 12 ppbv be found. This suggests that the widespread deep convection was able to lift air from the lower boundary layer into the upper TTL without significant mixing—a hypothesis we cannot pursue further here but which will be the subject of future investigations.

2.2.A Appendix

2.2.A.1 Laboratory experiments

When the pattern found in Fig. 2.2 was discovered, the records of the CAST field campaign were examined (Sect. 2.2.A.2) and a series of laboratory experiments devised to ascertain the reasons why the background current generally decreased between sondes 5 and 14 yet the minimum measured current in the TTL remained reasonably constant. It was observed that when an ozonesonde drew air from the TSCO1 ozoniser unit, a high current was registered. This was identified in the laboratory experiments as being contamination, rather than high concentrations of ozone, as explained in Sect. 2.2.A.3.

Neither the source nor the identity of the contamination was known, and so an experiment was devised to determine the response of an ozonesonde to pressure with various degrees of contamination, by placing it into a bell jar and varying the pressure. The results of this experiment are described in Sect. 2.2.A.4. The contamination gradually disappeared over time, so the bell jar experiments were neither reproducible nor did they replicate exactly the conditions that were experienced on Manus, but they serve as a check on the validity of the hybrid background current correction.

2.2.A.2 Examination of records

The first five ozonesondes were normal on first preparation. Between the fifth ozonesonde being prepared for the first time and the following day when the first ozonesonde was being prepared for flight, the ozoniser was found to be causing the cell current to increase dramatically even when it was supplying “no-ozone” air. This affected the first two ozonesondes’ day-of-flight preparations, and their background current remained well above that of a normal working ozonesonde. Thenceforth, an external ozone destruction filter was used instead of the ozoniser to produce no-ozone air and the sonde was not exposed to the ozoniser during the day-of-flight preparation. However, ozonesondes 6 to 14 were briefly exposed to the ozoniser during their first preparation to check the response of the sonde to ozone. Since exposure to the ozoniser was resulting in elevated background currents, the ozonesonde sample tube was only connected to it for a few seconds before being removed. However, this turned out to be long enough to allow the contaminant to
get into the ozonesonde where it remained throughout the preparations.

Ozonesondes 15 onwards were not exposed to the ozoniser at all, and were therefore the most reliable ozonesondes launched during CAST.

2.2.A.3 Source of contamination

In order to investigate the cause of the high background currents in the first 14 ozonesondes, laboratory investigations were conducted after the equipment was returned from Manus to Manchester, some 2 months after the campaign ended.

First, the response of an ozonesonde was compared with that of the TECO-49 ultraviolet photometric ozone monitor. When sampling laboratory air, both TECO-49 and the ozonesonde measured comparable concentrations (~22 ppbv), and when drawing air through the external charcoal filter the sonde measured 2 ppbv while the TECO-49 measured 12 ppbv. However, when sampling supposedly ozone-free air from the ozoniser (air drawn through an internal charcoal filter) the sonde measured 189 ppbv while the TECO-49 again measured 12 ppbv. Clearly, therefore, the ozoniser was acting as a source of some contaminant which produced a positive signal in the ozonesonde but not in the photometric ozone monitor – i.e., this substance was not ozone. (The 12 ppbv signal measured by the TECO through the filters is understandable as the flow rate of the TECO-49 is much higher than the ozonesonde and exceeds the capacity of the filters). Further investigation, dismantling the ozoniser and examining different parts, identified the source of the contamination as the tube which is illuminated by a mercury lamp to generate ozone. However, contamination was found even on the PTFE manifold at the outlet of the ozoniser.

A plausible explanation for the contamination, pointed out by one of the reviewers, is that condensation of water occurred inside the tube at some point, which, when irradiated by ultraviolet light, led to the production of hydrogen peroxide. H$_2$O$_2$ is known to react with KI in the cathode cell with a very slow response time [Cohen et al., 1967], consistent with the behaviour of the contaminant, and to stick to surfaces for a long time. The contaminant appeared first thing in the morning when the equipment had been enclosed in the air-conditioned laboratory overnight.

2.2.A.4 Ozonesonde behaviour at different pressures

The effect of lowering the ambient pressure on the contamination was then investigated by placing the ozonesonde in a bell jar and lowering the pressure as the sonde continually sampled the air inside the bell jar. The bell jar was too small to admit the ozone destruction filter but ozone measurements inside the jar at ambient pressure were the same as in the laboratory with the filter attached; thus air in the bell jar was ozone-free. Three ozonesondes were exposed to different amounts of contaminant by drawing air through the TSC01 unit for different times: the first was heavily
contaminated, the second slightly contaminated, and the third not contaminated at all. The ozonesonde was placed in the bell jar and left to settle to a constant background current for about 5 min. The bell jar was then pumped down to a target pressure using a rotary pump, and then the rotary pump was switched off. The ozonesonde was left for 5 min to settle and reach a constant background current, and then a new target pressure was chosen.

The first, heavily contaminated ozonesonde emulated the first two ozonesondes launched in CAST, which were prepared just after the contamination episode, but before the contamination was recognised. The slightly contaminated ozonesonde emulated ozonesondes 3 to 14, which were only contaminated on first preparation. Ozonesondes 15 onwards were not contaminated, like the third test ozonesonde in this experiment.

The heavily contaminated ozonesonde was contaminated on both first preparation and the day-of-flight preparation and had a background current of 132 nA, which is comparable to the early ozonesondes in CAST. Figure 2.15 shows the result of the bell jar experiment. The current was erratic, which was observed with the contaminated ozonesondes during CAST: the current occasionally spiked by $\sim 20 \text{ nA}$, possibly due to the cell picking up more contamination. The most likely behaviour of the ozonesonde was a decay of the background current from 135 nA at surface pressure to 115 nA at 20 hPa, still well above the expected value for a well-functioning sonde.

**Figure 2.15**: Current measured at each pressure for the contaminated ozonesonde. The dashed line shows the order in which the measurements were taken, starting from (1000 hPa, 160 nA) (the • data point).
This confirms that a reliable background current estimate could not be made for the first two CAST sondes. The ozonesonde used in this experiment was subjected to a further preparation cycle (without exposure to contaminant) to investigate whether it could be cleaned. Its background current reached 40 nA after 15 min of no-ozone-air treatment, indicating that the contamination was changing its character over time: changing solutions in the Manus sondes did not remove the contamination.

The second ozonesonde was initially contaminated in first preparation, and then prepared cleanly in the day-of-flight preparation, similar to ozonesondes 3–14 in Manus. However, as with the first test sonde, the contamination was found to disappear so that the “day-of-flight” background current was 55 nA – consistent with a clean ozonesonde. It appears than that the contaminant changed its nature and became less adhesive over the 3-month period since the contamination event. More contaminant was therefore added at the end of the second preparation, bringing the background current to 80 nA. The bell jar experiment showed little consistency in the background current as a function of pressure, but a clear decay over time (Fig. 2.16). Since in a normal ozonesonde launch pressure decreases as a function of time, this gives weight to the idea that a decaying background current correction with pressure is appropriate for the slightly contaminated ozonesondes.

The uncontaminated ozonesonde was prepared cleanly both times, and had a background current of 45 nA. Figure 2.17 shows the result of the bell jar experiment.
The experiment was split into two sections, one in which the ozonesonde remained above 200 hPa at all times, followed by another in which the pressure was pumped down to 70 hPa. The current decreased slightly between 1000 and 100 hPa (45–40 nA), before decreasing to 27 nA at 70 hPa. This is similar to the result found by Thornton and Niazy [1983], which was attributed to a change in the mass transfer inside the ozonesonde. Within experimental accuracy of ±10 nA, therefore, a constant background current is appropriate to the uncontaminated ozonesondes up to 100 hPa, with a possible decrease above this level. As the tropopause pressure encountered in Manus was >90 hPa, with the ozone concentration increasing rapidly into the stratosphere, we have used a constant background current throughout the profile for uncontaminated sondes. (Note that the ozonesonde in this test exhibited hysteresis when exposed to pressures lower than 100 hPa.)

2.2.A.5 Conclusions from laboratory experimentation

The laboratory experiments could not reproduce the exact conditions experienced in Manus because the contamination was gradually disappearing and becoming less adhesive over time. This is consistent with the general decrease of background current between sondes 5 and 14 in Manus, despite their identical preparation procedure.
Nevertheless, the behaviour is sufficiently similar to the CAST sondes as to provide support for the method used in Eq. (2.5) to calculate the background current.

The bell-jar experiments show that the background current in this batch of ozonesondes was largely constant in the absence of contamination, while that in a slightly contaminated ozonesonde reduced with time to a “clean” value over a period of \( \sim 30 \) min. This decay in \( I_{bg} \) is consistent with the slow timescale for the reaction of KI with peroxide identified by Cohen et al. [1967]. The heavily contaminated ozonesonde did not reduce to an acceptable background current, confirming that data from the heavily contaminated ozonesondes launched in CAST should be discarded.

### 2.2.8 Acknowledgements

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**END**

### 2.3 Improvements to the ozonesonde technique

#### 2.3.1 Recommendations for changes to SOPs

As a result of the study on the background current of ozonesondes, we recommend that the standard operating procedures (SOPs) be modified in light of the consistently reduced background currents that were achieved during the latter half of the CAST campaign when the ozonesonde was not exposed to high concentrations of ozone during preparation. Exposure to high ozone, even for a short amount of time, causes a large increase in current, which diminishes over time but was found not to return to the background current measured before exposing the ozonesonde to high ozone. The recommendations for modifying the SOPs described fully in section 1.4.1 are listed below.
The steps involving exposing the ozonesonde to moderate ozone should be omitted:

- First preparation step 7: Run on moderate ozone (5 μA) for 10 minutes
- Day-of-flight preparation step 8: Run on moderate ozone (5 μA) for 5 minutes
- Day-of-flight preparation step 9: Record the ozonesonde current
- Day-of-flight preparation step 10: Switch to run on purified air free of ozone; (a) Record current after 0, 0.5, 1, 3, 5 and 10 minutes on purified air; (b) Check that current decay decreases at least 80% in the first minute; (c) Record background current $i_{bg,1}$ after 10 minutes of running on ozone free air

As a result of not running step 10, the sensitivity to ozone must be assumed, which for a correctly prepared ozonesonde with correctly prepared ozonesonde cathode and anode solutions, this is a reasonable assumption. If necessary, the day-of-flight preparation steps 8–10 should be done on a practice ozonesonde to ensure the cathode and anode solutions are functioning correctly.

If the measured background current ($i_{bg,0}$ in step 7 of the day-of-flight preparation) is above 50 nA, then procedure should be that the cathode and anode solutions are changed and re-run step 6 (run on purified air for 10 minutes) before re-measuring the background current. In the case that after multiple changes of solution a background current of <50 nA is still not achieved, then the preparation should continue as normal and the ozonesonde launched, but the new hybrid background current correction (equation 2.5) should be used when post-processing the ozone data.

### 2.3.2 Improved limit-of-detection estimate

Rex et al. [2014] argues that a limit-of-detection of 15 ppbv should be placed on ozonesondes defined by the unknown evolution of the background current during flight, and measurements in which the ozonesonde current falls below the background current measured before launch are compatible with zero ozone concentrations. One of the conclusions of this study was that a reasonable estimate for the uncertainty due to the background current in the tropopause—where ozone concentrations are lowest and therefore background current uncertainty is highest—is ±5 ppbv, which was reinforced by the collocated ozonesonde and Gulfstream V measurements that were within 3 ppbv of each other. Therefore a more reasonable limit-of-detection estimate for a well-prepared ozonesonde with a background current of ~50 nA is ~5 ppbv, and only measurements below 5 ppbv can be considered to be compatible with a total absence of ozone.
2.4 Closing remarks

The findings from this article lead to further investigation of the low ozone bubbles in the following two articles. The CAST, CONTRAST and ATTREX aircraft campaigns gathered ozone data over a large area of the West Pacific Warm Pool, and were analyzed for any low ozone bubbles that could be found. This constitutes the article in chapter 3. The Weather Research and Forecasting (WRF) model was also used to investigate whether it could recreate the low-ozone bubble described in this article, and more generally investigate the characteristics of low-ozone bubbles throughout the West Pacific Warm Pool region. This constitutes the article in chapter 4.

The remaining ozonesonde profiles that were not plotted in the journal article can be found in the supplementary materials chapter of this thesis, in section 6.1.

2.5 Corrigendum

- The wind plot—figure 2.10—colourbar label erroneously reads “m/s” instead of “knots” in Newton et al. [2016]. The caption and colourbar label have been updated in the thesis.

- The HYSPLIT back-trajectory plot—figure 2.12—was replotted to include the coastline south of 10°S, including the majority of the outline of Australia, which was missing in the plot in the journal article.
Chapter 3

Low ozone concentrations observed in aircraft data

Alongside the ozonesonde campaign on Manus Island, an aircraft campaign took place on the island of Guam. During the period between January and March 2014, three aircraft were based out of Guam: the FAAM BAe 146, which was part of the CAST campaign [Harris et al., 2017], the NCAR Gulfstream V, which was part of the CONTRAST campaign [Pan et al., 2017], and the NASA Northrop-Grumman Global Hawk unmanned aerial vehicle, which was part of the ATTREX campaign [Jensen et al., 2017]. Table 3.1 summarizes the CAST flights and their routes, table 3.2 summarizes the CONTRAST flights and their objectives, and table 3.3 summarizes the ATTREX flights and objectives. In each table, the number of low ozone measurements (concentrations of <20 ppbv) compared to the total number of ozone measurements made in each flight are shown, and the percentage of low ozone to total ozone measurements.

The following section is the transcript of the article “Observations of ozone-poor air in the Tropical Tropopause Layer” [Newton et al., 2017] that was published in Atmospheric Chemistry and Physics Discussions in October 2017, and as of writing, under review. The article explores the low-ozone phenomenon, first introduced in the previous chapter, to investigate whether the aircraft observed any complementary measurements that also correspond to low-ozone events. Because the aircraft measured a wide range of chemical species beyond ozone, a more complete picture of the atmospheric composition during low-ozone conditions can be built up. The aircraft sampled large areas of the West Pacific, both in the Northern Hemisphere and the Southern Hemisphere, and the differences between the conditions in each hemisphere are explored. The co-authors on the article are Geraint Vaughan, Eric Hintsa, Michał T. Filus, Laura L. Pan, Shawn Honomichl, Elliot Atlas, Stephen J. Andrews and Lucy J. Carpenter.

Geraint Vaughan and I were responsible for analyzing the data. Eric Hintsa and
Laura Pan were responsible for the data from the ATTREX ozone instrument and the CONTRAST ozone instrument respectively. Elliot Atlas was responsible for the whole air sample data for both CONTRAST and ATTREX. Stephen Andrews and Lucy Carpenter were responsible for the CAST whole air sample data. Michal Filus was responsible for the NAME back-trajectory modelling, used to determine the origin of air masses measured by the ATTREX Global Hawk aircraft.

<table>
<thead>
<tr>
<th>Flight #</th>
<th>Date</th>
<th>low ozone / total</th>
<th>%</th>
<th>Route</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF1 B823</td>
<td>18 Jan</td>
<td>11800 / 26915</td>
<td>43-84%</td>
<td>Kota Kinabalu (Malaysia)→Palau→Guam</td>
</tr>
<tr>
<td>RF2 B824</td>
<td>22 Jan</td>
<td>17816 / 17828</td>
<td>99-93%</td>
<td>Guam→Guam</td>
</tr>
<tr>
<td>RF3 B825</td>
<td>24 Jan</td>
<td>11664 / 11448</td>
<td>97-51%</td>
<td>Guam→Chuuk</td>
</tr>
<tr>
<td>RF4 B826</td>
<td>25 Jan</td>
<td>8267 / 10058</td>
<td>82-19%</td>
<td>Chuuk→Chuuk</td>
</tr>
<tr>
<td>RF5 B827</td>
<td>26 Jan</td>
<td>10892 / 14580</td>
<td>74-71%</td>
<td>Chuuk→Chuuk</td>
</tr>
<tr>
<td>RF6 B828</td>
<td>26 Jan</td>
<td>11984 / 12411</td>
<td>96-56%</td>
<td>Chuuk→Guam</td>
</tr>
<tr>
<td>RF7 B829</td>
<td>29 Jan</td>
<td>15202 / 18671</td>
<td>81-42%</td>
<td>Guam→Palau</td>
</tr>
<tr>
<td>RF8 B830</td>
<td>29 Jan</td>
<td>7837 / 20055</td>
<td>39-08%</td>
<td>Palau→Palau</td>
</tr>
<tr>
<td>RF9 B831</td>
<td>30 Jan</td>
<td>2443 / 16040</td>
<td>15-23%</td>
<td>Palau→Palau</td>
</tr>
<tr>
<td>RF10 B832</td>
<td>30 Jan</td>
<td>11960 / 17272</td>
<td>69-25%</td>
<td>Palau→Guam</td>
</tr>
<tr>
<td>RF11 B833</td>
<td>1 Feb</td>
<td>17247 / 19091</td>
<td>90-34%</td>
<td>Guam→Guam</td>
</tr>
<tr>
<td>RF12 B834</td>
<td>1 Feb</td>
<td>19629 / 21871</td>
<td>89-75%</td>
<td>Guam→Guam</td>
</tr>
<tr>
<td>RF13 B835</td>
<td>4 Feb</td>
<td>9460 / 13198</td>
<td>71-68%</td>
<td>Guam→Chuuk</td>
</tr>
<tr>
<td>RF14 B836</td>
<td>4 Feb</td>
<td>15770 / 17175</td>
<td>91-82%</td>
<td>Chuuk→Chuuk</td>
</tr>
<tr>
<td>RF15 B837</td>
<td>5 Feb</td>
<td>22759 / 27678</td>
<td>82-23%</td>
<td>Chuuk→Chuuk</td>
</tr>
<tr>
<td>RF16 B838</td>
<td>6 Feb</td>
<td>23213 / 23213</td>
<td>100-00%</td>
<td>Chuuk→Chuuk</td>
</tr>
<tr>
<td>RF17 B839</td>
<td>12 Feb</td>
<td>3852 / 13826</td>
<td>27-86%</td>
<td>Chuuk→Guam</td>
</tr>
<tr>
<td>RF18 B840</td>
<td>13 Feb</td>
<td>12401 / 24282</td>
<td>51-07%</td>
<td>Guam→Palau</td>
</tr>
<tr>
<td>RF19 B841</td>
<td>14 Feb</td>
<td>12272 / 17626</td>
<td>69-62%</td>
<td>Palau→Palau</td>
</tr>
<tr>
<td>RF20 B842</td>
<td>14 Feb</td>
<td>9537 / 17897</td>
<td>53-29%</td>
<td>Palau→Guam</td>
</tr>
<tr>
<td>RF21 B843</td>
<td>16 Feb</td>
<td>16304 / 29337</td>
<td>55-57%</td>
<td>Guam→Guam</td>
</tr>
<tr>
<td>RF22 B844</td>
<td>17 Feb</td>
<td>15671 / 28798</td>
<td>54-41%</td>
<td>Guam→Guam</td>
</tr>
<tr>
<td>RF23 B845</td>
<td>17 Feb</td>
<td>6574 / 14512</td>
<td>45-30%</td>
<td>Guam→Guam</td>
</tr>
<tr>
<td>RF24 B846</td>
<td>18 Feb</td>
<td>11225 / 26567</td>
<td>42-25%</td>
<td>Guam→Palau</td>
</tr>
<tr>
<td>RF25 B847</td>
<td>18 Feb</td>
<td>1586 / 6355</td>
<td>24-96%</td>
<td>Palau→Kota Kinabalu</td>
</tr>
</tbody>
</table>

| total    | 306865 / 466704 | 65-75% |

_table 3.1: Table of the CAST flights. Objectives from Harris et al. [2017]._
<table>
<thead>
<tr>
<th>Flight #</th>
<th>Date</th>
<th>low ozone / total</th>
<th>%</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF01</td>
<td>11 Jan</td>
<td>7 / 2707</td>
<td>0.26%</td>
<td>Transit</td>
</tr>
<tr>
<td>RF02</td>
<td>13 Jan</td>
<td>0 / 1703</td>
<td>0.00%</td>
<td>Transit</td>
</tr>
<tr>
<td>RF03</td>
<td>17 Jan</td>
<td>890 / 2260</td>
<td>39.38%</td>
<td>Domain survey</td>
</tr>
<tr>
<td>RF04</td>
<td>19 Jan</td>
<td>1150 / 2259</td>
<td>50.91%</td>
<td>Domain survey</td>
</tr>
<tr>
<td>RF05</td>
<td>22 Jan</td>
<td>2181 / 2486</td>
<td>87.73%</td>
<td>Convective outflow</td>
</tr>
<tr>
<td>RF06</td>
<td>24 Jan</td>
<td>303 / 2369</td>
<td>12.79%</td>
<td>Jet crossing/pre-post frontal contrast</td>
</tr>
<tr>
<td>RF07</td>
<td>29 Jan</td>
<td>707 / 2080</td>
<td>33.99%</td>
<td>SH convective outflow survey</td>
</tr>
<tr>
<td>RF08</td>
<td>1 Feb</td>
<td>1317 / 2576</td>
<td>51.13%</td>
<td>Photochemical evolution - sunset</td>
</tr>
<tr>
<td>RF09</td>
<td>4 Feb</td>
<td>780 / 2488</td>
<td>31.35%</td>
<td>Equatorial crossing, Manus O3 sonde</td>
</tr>
<tr>
<td>RF10</td>
<td>8 Feb</td>
<td>333 / 2274</td>
<td>14.64%</td>
<td>STJ pollution and ITCZ survey</td>
</tr>
<tr>
<td>RF11</td>
<td>12 Feb</td>
<td>100 / 2130</td>
<td>4.69%</td>
<td>Convective outflow, coord’ed flight</td>
</tr>
<tr>
<td>RF12</td>
<td>17 Feb</td>
<td>194 / 1827</td>
<td>10.62%</td>
<td>Convective outflow, coord’ed flight</td>
</tr>
<tr>
<td>RF13</td>
<td>19 Feb</td>
<td>1124 / 2412</td>
<td>46.60%</td>
<td>Photochemical evolution - sunrise</td>
</tr>
<tr>
<td>RF14</td>
<td>22 Feb</td>
<td>766 / 3163</td>
<td>24.22%</td>
<td>Eq. crossing, SH TTL, Manus O3 sonde</td>
</tr>
<tr>
<td>RF15</td>
<td>24 Feb</td>
<td>54 / 2785</td>
<td>1.94%</td>
<td>Jet crossing, lower strat. survey</td>
</tr>
<tr>
<td>RF16</td>
<td>28 Feb</td>
<td>1016 / 2384</td>
<td>42.62%</td>
<td>Transit</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>10922 / 37903</td>
<td>28.82%</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.2:** Table of the CONTRAST flights, with the number and percentage of low ozone data points displayed. Also shown is the objective of each flight from table 2 of Pan et al. [2017].

<table>
<thead>
<tr>
<th>Flight #</th>
<th>Date</th>
<th>low ozone / total</th>
<th>%</th>
<th>Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>transfer</td>
<td>16-17 Jan</td>
<td>5 / 12475</td>
<td>0.04%</td>
<td>Transit</td>
</tr>
<tr>
<td>RF01</td>
<td>12-13 Feb</td>
<td>57 / 10841</td>
<td>0.53%</td>
<td>TTL survey, cirrus</td>
</tr>
<tr>
<td>RF02</td>
<td>16-17 Feb</td>
<td>751 / 11186</td>
<td>6.71%</td>
<td>TTL survey, cirrus</td>
</tr>
<tr>
<td>RF03</td>
<td>4-5 Mar</td>
<td>1490 / 7616</td>
<td>19.56%</td>
<td>cyclone Faxai, cirrus</td>
</tr>
<tr>
<td>RF04</td>
<td>6-7 Mar</td>
<td>1417 / 11299</td>
<td>12.54%</td>
<td>TTL survey, wave meas.</td>
</tr>
<tr>
<td>RF05</td>
<td>9-10 Mar</td>
<td>5769 / 12515</td>
<td>46.10%</td>
<td>south survey, conv. outflow</td>
</tr>
<tr>
<td>RF06</td>
<td>11-12 Mar</td>
<td>1117 / 9510</td>
<td>11.75%</td>
<td>northern/midlat survey</td>
</tr>
<tr>
<td>transfer</td>
<td>13-14 Mar</td>
<td>492 / 12121</td>
<td>4.06%</td>
<td>Transit</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>11098 / 87563</td>
<td>12.67%</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.3:** Table of the ATTREX flights, with the number and percentage of low ozone data points displayed. Also shown is the objective of each flight from Jensen et al. [2017].
3.1 Journal Article: Observations of ozone-poor air in the Tropical Tropopause Layer

3.1.1 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 10·5 ppbv and 14·2 ppbv. By contrast, the mean ozone concentrations in profiles in the Northern Hemisphere were always above 15 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 anti-correlation between ozone and halogenated hydrocarbons of marine origin observed by the three aircraft.

3.1.2 Introduction

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 and Hoskins, 1998; Folkins et al., 1999; Gettelman and 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°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 and 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 low-ozone bubbles in the TTL 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 and Diaz [2010] reanalyzed the data with a more representative background current correction, the minimum measured ozone concentration was ∼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’S, 147°4’E); we discuss these measurements in more detail in section 3.1.4.

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 measurements
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′N, 144°80′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, ATTREX [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°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.

After describing key aircraft instrumentation, this paper first presents the salient results from the CAST ozonesonde campaign, which were described in detail by Newton et al. [2016]. We then introduce the Global Hawk ozone profiles, concentrating on one flight that sampled well into the Southern Hemisphere from Guam. After a brief consideration of the other Global Hawk flights, we examine some of the other chemical species measured by the three aircraft before ending with discussions and conclusions.
3.1.3 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 (N$_2$O), sulphur hexafluoride (SF$_6$), hydrogen (H$_2$), carbon monoxide (CO) and methane (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 (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 are calibrated on the ground against a NIST-certified calibration system (Thermo Electron, Inc.) before and after every flight. In all 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 ((CH$_3$)$_2$S), iodomethane (CH$_3$I), dichloromethane (CH$_2$Cl$_2$), bromochloromethane (CH$_2$BrCl), trichloromethane (CHCl$_3$), dibromochloromethane (CHBr$_2$Cl) and tribromomethane (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 samplers 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) [Schauffler et al., 1999; Apel et al., 2003; Andrews et al., 2016].

3.1.4 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.

![Figure 3.1: 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].](image)

Another salient result from the ozonesonde measurements was the low-ozone event in the TTL between 18 and 23 February, visible in figure 3.1, 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 concentrations 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 boundary 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 3.2), 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.

Figure 3.2: 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.
Figure 3.3: 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.

3.1.5 Global Hawk measurements

3.1.5.1 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 $\sim0.5\text{ m s}^{-1}$, but the descent rate was much quicker, of the order of 5–10 minutes to complete at $\sim4\text{ m s}^{-1}$. 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 two transfer flights to and from Anderson Flight Research Center on 16 January and 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...
Figure 3.4: As figure 3.3 but for 16 February at 12:00 UTC coincident with flight RF02. A band of convective activity is visible to the southeast of Guam.

Figure 3.5: Satellite image of March 4 at 12:00 UTC, coincident with flight RF03. Cyclone Faxai is visible to the northeast of Guam.

3.3), 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 the island. On this day, convection was visible to the southeast of Guam in the MTSAT satellite imagery (figure 3.4).

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 previous 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 3.5).

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 active region was around Papua New Guinea (figure 3.6). 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].

3.1.5.2 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 flight track is shown in figure 3.7—the aircraft took off from Guam 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 to Guam 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 Guam before landing at 11:00 UTC.

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 were active at this time: tropical cyclone Gillian was in the Gulf of Carpentaria, tropical cyclone Hadi was near the east coast of Queensland, and Lusi was intensifying to become a tropical cyclone on 10 March, shown in the synoptic analysis chart in figure 3.8, and the MTSAT satellite imagery in figure 3.9.

Because the ATTREX ozone measurements are noisy, we present here average measurements taken between ∼150 hPa and the tropopause along each ascent of the aircraft. For this purpose the tropopause is defined as the point at which ozone concentrations start increasing sharply from tropospheric levels towards the stratosphere. Mean tropospheric ozone concentrations were determined for each profile by splitting the altitude range into eight equal parts in logarithmic pressure space, finding the mean tropospheric ozone concentrations in each part, then averaging these values (omitting parts of the profile with no data from the averaging calculation). Mean concentrations so obtained from each of the profiles measured during RF05 are shown in figure 3.7, 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 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 ∼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,
Figure 3.7: Flight track of RF05, with each profile performed by the Global Hawk chronologically numbered, and coloured by mean tropospheric ozone in each profile.

in the area where tropical cyclone Lusi was situated. Figure 3.9 shows 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

Figure 3.8: 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.
Figure 3.9: 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°E 20°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.

et al., 2012; Meneguz and 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 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 3.10: Percentage of back-trajectories crossing the 800 hPa surface within one day from the different ascent profiles on RF05.
Figure 3.11: Flight track of RF01. The profiles that would otherwise be obscured by other profiles are shown on the right-hand plot.

Figure 3.10 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 concentrations, with values similar to those observed by the ozonesondes over Manus. Again, the low concentrations are consistent with recent uplift in deep convection.

3.1.5.3 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 30 ppbv (figure 3.11). 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 3.12).

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 (17.5 ppbv in profile 5—figure 3.13), 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°N, where it performed a constant altitude flight along this line of latitude from 155°E to 135°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.

RF06 flew north into the extra-tropics where ozone concentration 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

**Figure 3.12**: Flight track of RF02. 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.

**Figure 3.13**: Flight track of RF03. Cyclone Faxai was situated at ∼(20°N, 150°E) during this flight (see figure 3.5).
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 concentrations around 10–12 ppbv between 1°S and 3°N on 4 February in a flight south from Chuuk along 152°E, values which are consistent with the Manus boundary layer measurements at that time (figure 3.1). 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°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 ~10 ppbv below 2 km between 2°S and 20°N [Kondo et al., 2002b].

Further evidence of an interhemispheric difference in boundary-layer ozone may be found in measurements made by the HIPPO (HIAPER Pole-to-Pole Observations) programme [Wofsy et al., 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°N and 20°S. In addition, profiles near 15°S in January and 2°S in
Figure 3.15: 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.

March-April showed values < 15 ppbv extending up to 5 km. By contrast, ozone concentrations in January were >15 ppbv north of 5°N in the boundary layer and >20 ppbv north of 5°S above 2 km, while in March-April they exceeded 20 ppbv at all altitudes north of 1°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.

3.1.6 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°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 3.1.4) are summarized in figure 3.15. 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 TTL, corresponding to the event discussed in Section 3.1.4, but the CONTRAST data do not—there are isolated examples around 15 ppbv up to ~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 boundary layer measurements by the CAST ozonesondes and the CAST and CONTRAST aircraft (figure 3.16) 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.

Figure 3.17: 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.

3.1.7 Very short lived substances

Whole air samplers (WAS) on board the CAST, CONTRAST and ATTREX aircraft provided measurements of very short lived substances (VSLSs), of which eight were measured by all three aircraft: dimethyl sulfide ((CH$_3$)$_2$S), iodomethane (CH$_3$I), tribromomethane (CHBr$_3$), dibromochloromethane (CHBr$_2$Cl), bromochloromethane (CH$_2$BrCl), dichloromethane (CH$_2$Cl$_2$), dibromomethane (CH$_2$Br$_2$) and trichloromethane (CHCl$_3$). Dichloromethane and trichloromethane are industrially produced chemicals with a strong anthropogenic signal, and are thus not plotted here; these, along with the other species measured by the CONTRAST and ATTREX aircraft but not by CAST are plotted in the supplementary material.

The atmospheric lifetimes of these molecules range from a few minutes to a few months: (CH$_3$)$_2$S has a lifetime between 11 minutes and 46 hours [Marandino et al., 2013]; CH$_3$I a lifetime of ~4 days and CHBr$_3$ a lifetime of ~15 days [Carpenter et al., 2014]; that of CHBr$_2$Cl is about three months, and CH$_2$BrCl, CH$_2$Br$_2$ and CH$_2$Cl$_2$ have lifetimes of the order of six months [Montzka et al., 2010; Mellouki et al., 1992;
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 and 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 sample data from the entire CAST, CONTRAST and ATTREX campaigns yield the plots in figure 3.17. Necessarily the vast majority of these points are from the Northern Hemisphere, away from the very low ozone concentrations described in section 3.1.5.2. 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.

\((\text{CH}_3)_2\text{S}, \text{CH}_3\text{I}, \text{CHBr}_3\) and \(\text{CHBr}_2\text{Cl}\) all show enhancements when ozone concentrations were less than 20 ppbv compared to when ozone concentrations were greater than 20 ppbv, suggesting that the more ozone-deficient air has encountered the marine boundary layer, where these molecules are produced, more recently than the more ozone-rich air. Meanwhile, \(\text{CH}_2\text{BrCl}\) and \(\text{CH}_2\text{Cl}_2\) show no difference when ozone is low and when ozone is high because they have a much longer lifetime than the other VSLSs measured, and \(\text{CH}_2\text{Cl}_2\) also has large industrial emissions.

The remaining species that were measured with the whole air samplers from CONTRAST and ATTREX are plotted in the supplementary material. These thirty-three molecules show expected enhancements in the typically polluted high-ozone régime for those of industrial origin, and enhancements in the typically cleaner low-ozone régime for those of marine origin.

Very few WAS samples were taken in the Southern Hemisphere—only two were taken by the FAAM BAe 146, 60 by the Global Hawk, and 134 by the Gulfstream V, compared to the Northern Hemisphere where 302 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.
3.1.8 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.

3.1.9 Acknowledgements

We thank the NERC Facility for Airborne Atmospheric Measurements (FAAM) for the CAST aircraft data, and the Centre for Data Archival (CEDA) for supporting meteorological data. The project was supported by Natural Environment Research Council (NERC) grant NE/J006173/1. Richard Newton is a NERC-supported research student.

END

3.2 Closing remarks

A supplementary materials section was produced in association with this journal article, containing plots of the whole air sample (WAS) data that was not plotted in
the article. This can be found in the supplementary materials chapter of this thesis in section 6.2.
Chapter 4

The distribution of low ozone events in WRF-Chem

4.1 Introduction

The WRF (Weather Research and Forecasting) model was used to simulate the conditions that caused the low-ozone event that was observed by the ozonesondes that was described in detail in chapter 2. The WRF-ARW (Advanced Research WRF) core was used, with passive tracers from the WRF-Chem system.

4.1.1 Preliminary work

Before WRF could be used to simulate the low-ozone event, the setup of the WRF model had to be modified to best represent the observed conditions. WRF has a number of physics and dynamics options, which can have a large effect on the solutions of the model simulation, therefore a considered approach to choosing the most effective physics options based upon measurements made within the model domain is required.

To investigate the differences in model solutions when changes in physics schemes are made, a control run that was known to be stable was used as a first attempt. Then the physics schemes could be changed one by one and the differences of each individual physics scheme could be evaluated. The physics options that were investigated were the microphysics scheme, and the planetary boundary layer (PBL) and surface layer schemes. In addition, the number of vertical levels in the simulations was investigated.

The control run used the Morrison 2-moment microphysics scheme, the Yonsei University (YSU) PBL scheme and Revised MM5 surface layer scheme, the Grell 3-d cumulus scheme, and the RRTMG longwave and shortwave radiation schemes. The control run had issues with underestimating the amount of outgoing longwave
radiation (OLR), thus overestimating the amount of cloud cover, and a steady reduction in sea-level pressure over time.

The microphysics scheme tested were the WRF single-moment 6-class scheme, the WRF double-moment 6-class scheme and the Eta-Ferrier scheme, and were compared to the Morrison 2-moment scheme in the control run. The WRF single-moment and double-moment schemes produced almost identical results, and both of them increased the outgoing longwave radiation (OLR) to a more representative level (figure 4.1). The WRF double-moment scheme was used in the final runs.

The planetary boundary layer and surface layer schemes are interdependent, and have to be changed together. The Miller-Yamada-Janjić (MYJ) PBL scheme

![Outgoing longwave radiation](image1)

![Outgoing longwave radiation difference](image2)

![Outgoing longwave radiation](image3)

**Figure 4.1:** Outgoing longwave radiation from the control run (top), the run with the WRF double-moment 6-class microphysics scheme (bottom), and the difference between the two (middle).
with the Monin-Obukhov Eta Similarity surface layer scheme, the Mellor-Yamada-Nakanishi-Niino (MYNN) PBL and surface layer schemes, and the Quasinormal Scale Eliminatot (QNSE) PBL and surface layer schemes, were tested and compared to the Yonsei University (YSU) PBL scheme and Revised MM5 surface layer scheme. The QNSE/QNSE was unstable with this setup, even with timesteps less than one second. The surface pressure improved when the MYJ/Monin-Obukhov combination was used, and improved further when the MYNN/MYNN combination was used (figure 4.2). Therefore the MYNN/MYNN combination was used in the final runs.

The Grell 3-d cumulus scheme was the only cumulus scheme compatible with the WRF-Chem tracers that were used. In the control run, the Grell 3-d cumulus scheme

![Image of sea level pressure maps](image)

**Figure 4.2:** Sea level pressure from the control run (top), which is an underestimation of the actual sea level pressure, with the difference between the control run and the MYJ/Monin-Obukhov combination (middle) and the MYNN/MYNN combination (bottom).
Figure 4.3: Comparison between tracer #1 concentrations in the inner domain, when the region of interest was placed in the outer domain only (left plot) and in the inner domain only (right plot). The tracer-free air in the left plot have diffused into the inner domain through the lateral boundaries, suggesting the convection parameterization scheme is overestimating the amount of surface air uplifted.

was activated in both domain 1 and domain 2. It was found that at a resolution of 4·447 km that domain 2 did not require the cumulus scheme—the mesoscale convective system (MCS) that was being modelled was much larger, so sub-grid scale convection (<4 km) was insignificant compared to the MCS, which was over 100 km in diameter. Therefore in the final run, the Grell 3-d cumulus scheme was active in domain 1, but turned off in domain 2—domain 2 was considered to be convection resolving. Although the outer domain would have been capable of resolving an MCS over 100 km in diameter, but studies have shown convection is underestimated at lower resolutions [Chemel et al., 2009; Arteta et al., 2009b] and as high resolution as practicable was used in the model simulation of this study.

In the control run, the regions of interest of tracers #1 and #2 were placed at the surface and the boundary layer respectively (see section 4.2.3.2) in both domain 1 and domain 2. However, it was found that the convective parameterization scheme was uplifting much more tracer-free air into the TTL than the amount uplifted in domain 2. This excess of tracer-free air was diffusing through the lateral boundaries into domain 2. Figure 4.3 illustrates this, which compares one run with the region of interest in domain 1 only (where the only tracer-free air has diffused through the lateral boundaries) and another run with the region of interest in domain 2 only. It was therefore concluded that regions of interest should not be placed in the outer domain with convective parameterization, and in the experiment simulations the regions of interest were in the inner domain only.

The Goddard longwave and shortwave radiation schemes was compared with the RRTMG longwave and shortwave radiation schemes. The temperature profile in
Figure 4.4: An example temperature profile comparing the RRTMG (blue) and Goddard (red) radiation schemes. Little difference is found below the mid-stratosphere.

Figure 4.4 shows the tropopause location and temperature is almost identical, and there is little difference between the two schemes below the mid-stratosphere. As a result, the RRTMG was used for the radiation schemes.

Finally, the control run had 49 vertical levels with a model top of 7.5 hPa. A preliminary simulation was made with 98 vertical levels—double the number of levels as the control run. Little difference was found between the control run and the run with 98 vertical levels, apart from the simulation with 98 vertical levels ran approximately half as quickly. Therefore, the final run used 49 vertical levels.

The WRF system was then setup to produce the runs in which the experiments were done, which were used to simulate the low-ozone event observed by the ozonesondes. Table 4.1 summarizes the physics options that were tested, and the reasoning behind choosing the physics options that were used in the experiments.

It should be noted that not every physics option was tested, and other combinations may provide equally valid, but different solutions. The aim was to produce a stable run, which produced representative results, which was successfully attained. A future study on the sensitivity of this type of tracer analysis should be considered with not only the sensitivity to model physics options (similar to the investigation by Arteta et al. [2009a]), but to variables such as model start time (similar to the investigation by Frey et al. [2015]), and vertical and horizontal resolutions (similar to the investigation by Arteta et al. [2009b] and Chemel et al. [2009]). This would be a separate study due to the large scope of this possible investigation.
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<td></td>
<td>Eta-Ferrier</td>
<td>Also underestimates OLR</td>
</tr>
<tr>
<td></td>
<td>WRF single-moment</td>
<td>Better OLR representation</td>
</tr>
<tr>
<td></td>
<td>6-class</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>WRF double-moment 6-class</strong></td>
<td>Little difference from WRF single-moment in performance and computing time</td>
</tr>
<tr>
<td>PBL/surface layer</td>
<td>YSU/Revised MM5</td>
<td>Sea level pressure too low</td>
</tr>
<tr>
<td></td>
<td>MYJ/Monin-Obukhov</td>
<td>Sea level pressure improved slightly compared to YSU/Revised MM5</td>
</tr>
<tr>
<td></td>
<td><strong>MYNN/MYNN</strong></td>
<td>Best sea level pressure improvement compared to YSU/Revised MM5</td>
</tr>
<tr>
<td></td>
<td>QNSE/QNSE</td>
<td>QNSE was unstable, and simulation crashed</td>
</tr>
<tr>
<td>Cumulus convection</td>
<td><strong>Grell 3-d</strong></td>
<td>Only scheme compatible with tracers</td>
</tr>
<tr>
<td>Radiation schemes</td>
<td>RRTMG</td>
<td>Most differences are in mid-to-upper stratosphere. Choice of radiation scheme not important</td>
</tr>
<tr>
<td></td>
<td>Goddard scheme</td>
<td></td>
</tr>
<tr>
<td>Vertical levels</td>
<td>49 vertical levels</td>
<td>Little difference, but half the computing time to run</td>
</tr>
<tr>
<td></td>
<td>98 vertical levels</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Table of physics options that were tested in the test runs. The options in bold were selected for the experiment runs.

4.1.2 Journal article

The following manuscript is a journal article currently, at the time of writing, in preparation for publication, anticipated to be acceptable for the Atmospheric Chemistry and Physics journal. The article investigates the low-ozone event of 17–23 February that was found in the ozonesonde data (chapter 3), using the aforementioned WRF setup. The co-authors on this article were Geraint Vaughan and Charles Chemel. I was responsible for preparing and running the WRF model, with assistance on running WRF from Charles Chemel. Geraint Vaughan and I were responsible for analyzing the data.
4.2 Journal Article: Modelling transport from the boundary layer to the tropopause region in the Tropical Warm Pool

4.2.1 Abstract

A modelling study of a low-ozone event that was measured by ozonesondes on Manus Island between 17 February and 23 February 2014 was performed using the Weather Research and Forecasting (WRF) model. The simulation of the region from 17–22 February showed that the low-ozone event originated from a mesoscale convective system (MCS) to the east of Manus Island that uplifted ozone-deficient air into the tropical tropopause layer (TTL), where an easterly jet advected it westward.

A comparison was made between the 17–22 February simulation and a simulation of 3–7 February when conditions were less convective, and the difference between the two contrasting meteorological situations was able to be quantified. A mass flux calculation determined that $4.7 \times 10^4$ kg of surface air was uplifted into the TTL in the 17 February run after 88 hours, whereas only $1.03 \times 10^4$ kg was uplifted in the 3 February run in the same amount of time. The simulated ozone concentrations derived from passive tracers for the 7 February run showed 18.6% of the TTL in the domain was less than 20 ppbv, with 1.87% less than 10 ppbv, whereas for the 3 February run, only 0.36% of the TTL in the domain was below 20 ppbv.

The inflow and outflow of the MCS was investigated for unmixed uplift of surface air and direct injection into the stratosphere through overshooting convection, though no evidence of either were found in the model simulation. Instead, the inflow came from a well-mixed boundary layer, whilst the outflow is capped by the cold-point tropopause (CPT). Air is injected, however, above the level of zero net radiative heating, which will enter the stratosphere on a much longer timescale.

The results confirm that the MCS was responsible for the low-ozone concentrations measured by the ozonesondes from Manus, and that the MCS considerably changed the composition of the tropical tropopause layer over a large area of the West Pacific around Papua New Guinea.

4.2.2 Introduction

Convection in the tropics has a profound influence on the atmospheric circulation, through the transport of latent and sensible heat from the Earth’s surface, the redistribution of water vapour, and its effect on the radiation budget. It is also of central importance in determining the composition of the stratosphere, providing a mechanism for chemical species from the lower troposphere to enter the stratosphere.
and be distributed globally by the Brewer-Dobson circulation [e.g Arteta et al., 2009a].

Troposphere-to-stratosphere transport in the tropics falls into two categories. The first is through convective uplift of air into the tropical tropopause layer (TTL) above the level of zero net radiative heating [Brewer, 1949] but below the cold-point tropopause (CPT); air uplifted above the level of zero net radiative heating will eventually reach the stratosphere [Gettelman et al., 2004] through the large-scale ascent driven by extratropical wave pumping [Holton et al., 1995]. This process is slow—the timescale at which air can be lifted from 150 hPa to 100 hPa is of the order of 1–2 months [Sherwood and Dessler, 2001]. The second category is direct injection into the stratosphere by overshooting cloud tops [Hosking et al., 2010], which is a much quicker process: air can be transported into the lower stratosphere from the boundary layer in 30 minutes or less [Thompson et al., 1997]. Overshooting convection has been observed primarily in the West Pacific and Maritime Continent, Western Africa, Brazil, and the Indian Monsoon [Liu and Zipser, 2005; Pan and Munchak, 2011].

The Brewer-Dobson circulation lifts tropospheric source gases for ozone-destroying radicals such as NO\(_x\), ClO\(_x\) and BrO\(_x\) into the stratosphere. Many of these gases, such as N\(_2\)O and CFCs, are very long lived and well-mixed in the troposphere; the flux reaching the stratosphere is largely independent of the details of tropospheric transport. On the other hand, very short-lived substances (VSLSs), which normally break down in the troposphere through reaction with the hydroxyl radical (OH), can only contribute to the stratospheric halogen budget if lifted by deep convection above the level of zero net radiative heating. There is considerable uncertainty about the flux of VSLSs into the tropopause region, which motivated the field campaign described below that forms the basis for this paper.

Measurements of ozone in the tropics have found very low ozone concentrations in the TTL over tropical oceans, consistent with uplift of boundary-layer air and therefore of VSLSs from near the surface directly into the tropopause region. For example, ozonesondes launched during the 1993 CEPEX (Central Pacific Experiment) campaign observed minimum ozone concentrations of ~10 ppbv at around 15 km, attributed to vertical mixing of lower-tropospheric air through deep convection [Kley et al., 1996; Vömel and Diaz, 2010]. Similarly, ozonesondes launched during the ACTIVE (Aerosol and Chemistry Transport in Tropical Convection) campaign from Darwin in 2005-6 observed ozone concentrations of less than 10 ppbv above 15 km [Vaughan et al., 2008; Heyes et al., 2009]. Subsequent back-trajectory investigation led Heyes et al. [2009] to conclude that the TTL composition is determined by ‘hot-spots’ of convection, which uplift air from the lower troposphere followed by advection in the TTL over considerable distances, so that the composition of the troposphere in these ‘hot-spot’ regions can determine the TTL composition over
a wide area. Lastly, ozonesondes from the TransBrom campaign in October 2009 also observed ozone minima in the TTL below 15 ppbv, coincident with minima of OH, concluding that low concentrations of OH increases the lifetime of VSLSs and promotes their transport into the stratosphere [Rex et al., 2014].

These ozonesonde observations of low ozone concentrations in the TTL in the West Pacific give no indication of the spatial extent of a particular event. Modelling studies have been used to further investigate the effects of deep convection on the distribution of trace species, and provide more spatial information than the ozonesondes. Lawrence et al. [1999] attempted to reproduce the CEPEX ozonesonde observations to the MATCH-MPIC (Model of Atmospheric Transport and Chemistry—Max Planck-Institute for Chemistry Version) model, concluding that the simulation was able to reproduce some of the observed features, but was unable to quantitatively reproduce the ozone concentrations as described by Kley et al. [1996]. However, Vömel and Diaz [2010] reprocessed the CEPEX ozonesonde data to remove a low bias, meaning that the model may have had better skill at reproducing the ozone concentrations than first expected.

The Hector thunderstorm in the Tiwi Islands, off the coast of Darwin, Australia, has been extensively modelled [e.g Connolly et al., 2006; Chemel et al., 2009; Cummings et al., 2013; Frey et al., 2015], due to its predictability in time and location [Allen et al., 2008]. Chemel et al. [2009] considered the effect of overshooting convection in the Hector thunderstorm on the moisture content of the stratosphere, concluding that Hector has a moistening effect on the lower stratosphere above the storm. However, the authors note that the relative importance of gradual radiative uplift versus episodic, overshooting convection on troposphere-to-stratosphere transport is still unknown. Meanwhile Frey et al. [2015] observed both hydration and dehydration in different parts of Hector. They also found that in the WRF model, passive tracers released in the boundary layer layer were uplifted with greater efficiency than passive tracers released in the free troposphere. A passive ozone tracer showed a reduction up to $\theta = 360$ K (up to $\sim 15$ km) due to uplift of ozone-deficient air from the boundary layer up to TTL level, and an enhancement above that, due to subsidence from the stratosphere. Marécal et al. [2006] and Rivière et al. [2006] investigated a severe convective storm over Bauru, Brazil, concluding that the RAMS (Regional Atmospheric Modeling System) model produced no overshooting into the stratosphere, but model output of ozone precursors including VSLSs [Marécal et al., 2006] and ozone [Rivière et al., 2006] are consistent with boundary layer-to-TTL transport up to $\sim 15$–17 km.

Therefore, there is further evidence in modelling studies for direct injection of boundary layer air into the TTL. However, such a study has not, to our knowledge, been conducted in the West Pacific Warm Pool region. Furthermore, there is a need
to complement ozonesonde measurements, which produce a one-dimensional profile of the ozone concentrations in the atmosphere, with other studies of the wider area.

The motivation for this paper arises from ozone measurements conducted by the CAST (Coordinated Airborne Studies in the Tropics) campaign [Harris et al., 2017], an intensive measurement campaign that took place around the West Pacific Warm Pool in January–March 2014. The main component of CAST, an aircraft campaign involving the FAAM (Facility for Airborne Atmospheric Measurements) BAe 146-301 ARA (Advanced Research Aircraft), was based out of Guam alongside its sister campaigns, CONTRAST (Convective Transport of Active Species in the Tropics) and ATTREX (Airborne Tropical Tropopause Experiment) [Pan et al., 2017; Jensen et al., 2017]. The second component of CAST involved ozonesonde flights from Manus Island, Papua New Guinea (2°07'S, 147°4'E). These are described in detail in Newton et al. [2016], but the findings are summarized here. Thirty-nine ozonesondes were launched between 2 February and 25 February 2014, of which 34 gave good ozone profiles. A region of anomalously low ozone concentrations were found in the TTL in the latter part of the campaign, with ozone minima around 12 ppbv at 15–16 km altitude over five days between 18 and 22 February, and in one instance on 21 February, the ozone minimum was 8.3 ppbv.

Figure 4.5 shows a time series of ozone measured by the CAST ozonesondes, with the low-ozone event visible at ~15 km between 18 and 22 February. The salient features of the lower tropospheric ozone distribution are the general increase with height and the increase in time from ~10 ppbv to ~20 ppbv from 10 February to 20 February. This means that during the low-ozone event in the TTL, the concentrations are lower than those found in the boundary layer over Manus: ~13–20 ppbv. In figure 4.5 the contouring obscures the fact that in the lowest 200 hPa of the profile the ozone fell below 15 ppbv; see Newton et al. [2016] for the surface ozone time series on Manus during the CAST campaign. Together with the strong easterly jet in the TTL between 17 and 24 February [Newton et al., 2016], this points to advection of a layer of low ozone concentrations over Manus. In this paper we examine how a mesoscale convective complex to the east of Manus could have generated this layer.

To this end, we use the WRF model to reproduce the conditions that produced the low-ozone event in the TTL over Manus on 18–22 February 2014, and answer the following questions:

- can WRF differentiate between a convective situation where low ozone concentrations can be observed, and a non-convective situation where more typical, background ozone concentrations can be observed in the TTL?
- how large was the extent of the low-ozone event: was it locally constrained to a small area around Manus Island, or did it extend throughout large swathes of the West Pacific?
Figure 4.5: 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 2014. Green bars along the top denote launch times of ozonesondes. For further details see Newton et al. [2016].

• was the ozone uplifted unmixed from the surface to the TTL, and was there significant injection into the stratosphere from overshooting convection?

The paper is organized as follows: the design of the simulations is described in section 4.2.3, with a description of the model setup in section 4.2.3.1 and a description of the passive tracers in section 4.2.3.2. The results are in section 4.2.4, with results from the 3 February run in section 4.2.4.1 and results from the 17 February run in section 4.2.4.2, and finally a summary of the findings are in section 4.2.5.

4.2.3 Design of the numerical experiments

4.2.3.1 Model setup

Simulations were made using the WRF model, version 3.5.1 [Skamarock et al., 2008]. Two one-way nested domains were used: the outer domain (d01) contained 750×200 grid points at 22.235 km resolution with a timestep of 15 seconds, while the second domain (d02) contained 1000×800 grid points at 4.447 km resolution with a timestep of 3 seconds. Both model domains had 49 vertical levels with a model top of 7.5 hPa. The locations of the model domains, and the WRF landmask are shown in figure 4.6.

Initial and lateral boundary conditions for the outer domain were derived from the European Centre for Medium Range Weather Forecasts (ECMWF) gridded analyses available every 6 h with a horizontal resolution of $\frac{1}{4}^\circ$. The sea-surface
temperature was updated every 6 h using the Real Time Global, SST High-Resolution (RTG_SST_HR) analyses available daily at a resolution of $\frac{1}{12}^\circ$ [Gemmill et al., 2007].

The physics options used in the model simulation were chosen after testing several settings for each. The Grell 3-d cumulus parameterization [Grell, 1993; Grell and Dezső, 2002] was used in the outer domain only; at a resolution of $4.47 \text{ km}$ domain 2 resolves the mesoscale convective system (MCS), which is the focus of this study. The Grell 3-d ensemble scheme was used because it is compatible with the implementation of the tracers described in section 4.2.3.2. Other physics options settings were tested, such as the microphysics scheme, in which the WRF double-moment 6-class scheme [Lim and Hong, 2010] was chosen ahead of the WRF single-moment 6-class scheme, the Morrison 2-moment scheme and the Goddard scheme. The WRF double-moment 6-class scheme produced a more realistic outgoing longwave radiation (OLR) field: the Morrison 2-moment scheme especially overestimated the amount of cirrus cloud in the domain. The MYNN (Mellor-Yamada-Nakanishi-Niino) Level 3 planetary boundary layer (PBL) physics scheme and the MYNN surface layer physics scheme combination [Nakanishi and Niino, 2006, 2009] was used ahead of the MYJ (Mellor-Yamada-Janjić)/Eta Similarity scheme and the YSU (Yonsei State University scheme)/Revised MM5 combinations. It was found that while the MYNN/MYNN combination was computationally expensive compared to the other schemes, it provided a better representation of the surface pressure field with respect to the the synoptic charts of this region, and remained stable for longer.

Finally, the RRTMG (Rapid Radiative Transport Model—Global) longwave and shortwave radiation schemes [Iacono et al., 2008] were used, and the Unified Land Surface Model (LSM) [Tewari et al., 2004] and the Urban Canopy Model [Chen et al., 2011] were used as the land surface option and the urban surface option respectively.

The model setup and the physics options chosen produce a simulation that adequately represents the synoptic conditions in the area and remains stable over five days, which was the time period over which the model was run, whilst remaining within the computational limits of the resources available.

Table 4.2 summarizes the settings used.
Physics option & d01 & d02 \\
\hline
\text{timestep} & 15 \text{s} & 3 \text{s} \\
\text{horizontal resolution} & 22.235 \text{km} & 44.47 \text{km} \\
\text{microphysics} & \text{WRF double-moment 6-class} & \text{ditto} \\
\text{longwave radiation} & \text{RRTMG} & \text{ditto} \\
\text{shortwave radiation} & \text{RRTMG} & \text{ditto} \\
\text{surface layer physics} & \text{MYNN} & \text{ditto} \\
\text{land surface physics} & \text{Unified Noah LSM} & \text{ditto} \\
\text{urban physics} & \text{Urban Canopy Model} & \text{ditto} \\
\text{PBL physics} & \text{MYNN Level 3} & \text{ditto} \\
\text{cumulus physics} & \text{Grell 3-d} & \text{None} \\
\text{model top height} & 7.5 \text{hPa} & 7.5 \text{hPa} \\
\hline

\textbf{Table 4.2: Table of physics options and settings used in the model simulation}

\subsection*{4.2.3.2 Tracers}

Passive tracers were used to simulate the transport of ozone around the model domain. The tracers were implemented with an arbitrary background value of 1 ppb placed everywhere in the domain, and regions of interest prescribed with a value of 0 ppb, which become the ‘emission points’. The regions of interest can be at any location and altitude within the domain. The domain is therefore filled with tracer, and a small region of interest emits clean, tracer-free air around the domain, analogous to the region being filled with ozone, and areas of clean, ozone-free air being emitted from certain regions of interest, typically in contact with the surface.

The model updates the tracer distribution in three phases:

\begin{itemize}
  \item[i.] update of the meteorology,
  \item[ii.] advection of the tracer by the updated winds,
\end{itemize}

\textbf{Figure 4.7: A schematic of the tracer implementation. Tracers are initialized to zero in an area of interest (in white—left image) in the initialization phase, the tracers are then advected around the domain in the advection phase (middle image), and the grid-points that were initially set to zero are reset back to zero again during the reset phase—the other grid-points retain their new value (right image).}
iii. reset of the tracer to 0 in the designated regions of interest only.

Thus the tracer concentrations in the region of interest remained at 0 throughout, while they evolved in the rest of the domain according to the meteorology. The schematic in figure 4.7 shows a simplified pictorial depiction of the three phases.

The tracers were initialized only in the inner domain, as the regions of interest were in the inner domain only, and the inner domain was convective permitting whereas the outer domain had parameterized convection, which would have unwanted consequences on tracer transport.

The tracers were placed as follows:

- tracer #1: at the surface (vertical level 0) throughout the whole of domain 2,
- tracer #2: at the top of the boundary layer (vertical level 11) throughout the whole of domain 2,
- tracer #3: at the surface (vertical level 0) in a limited area bounded by longitudes 151°10'E (x=528) and 167°10'E (x=928) and latitudes 8°46'S (y=164) and 11°54'N (y=664),
- tracer #4: at the top of the boundary layer (vertical level 11) in the same limited area as tracer #3,
• tracer #5: in the whole of the boundary layer (vertical levels 1 to 11) in the same limited area as tracer #3 and #4.

The limited area for tracers #3, #4 and #5 was designed to capture the MCS responsible for producing the low-ozone event over Manus on 18–22 February. The top of the boundary layer for tracers #2, #4 and #5 was determined by locating the temperature inversion im the vertical profiles obtained from the WRF output (see figure 4.8). An inversion occurs at ~700 hPa, which corresponds to model level II.

Moreover, the tracers were designed such that a comparison could be made between the uplift from the boundary layer and lower troposphere, and uplift from the surface (i.e. tracer #1 vs. tracer #2; and tracer #3 vs. tracer #4), so conclusions can be drawn on whether air is being uplifted unmixed from the surface or otherwise mixing within the boundary layer. In addition, tracers #1 and #2 allow the uplift in the whole region to be studied and compared to the uplift in just the MCS (tracers #3 and #4), in order to evaluate the relative contribution of the MCS to that of the entire region. Finally, tracer #5 was designed to allow comparison of the WRF tracers with the ozone measurements from the CAST ozonesondes from Manus Island.

4.2.4 Results

4.2.4.1 3 February run

The first simulation was initialized on 3 February 2014 at 00:00 UTC and run for five days until 8 February at 00:00 UTC. The meteorology at this time showed very little indication of convection around Manus Island, and the only precipitation during this period was a short shower on 4 February at around 00:00 UTC (10:00 PGT) (see figure 4.9). Most of the convection during the period was south of Manus Island close to Australia and over the Coral Sea (see satellite image in figure 4.10).
The simulation captures convection in a similar place to that found in the satellite image in figure 4.10: of the little amount of convection found in the inner domain, most of it was found in the Arafura Sea and the Coral Sea. The outgoing longwave radiation image derived from the WRF output (see figure 4.11) shows large concentrations of cloud in the same areas as the satellite image.

Throughout the whole run, very little of the tracer-free air from the surface was transported into the TTL. Brief episodes of tracer-free air do appear in the TTL on
Figure 4.12: Tracer #1 at tropopause level (∼112 hPa) on 4 February at 08:00 UTC, at the greatest extent of tracer uplift during the run.

A few occasions, but it was always constrained to within the Arafura and Coral Seas in the area of convective activity. Such episodes were short-lived, with the air either dissipating or sinking back into the mid-troposphere after a short time.

Figure 4.12 shows an example, using tracer #1, of one of these episodes at its

Figure 4.13: Map showing extent of tracer #1 (surface tracer—in red) compared to tracer #2 (boundary layer tracer—in green) on 7 February 2014 at 12:00 at 112 hPa altitude, showing that the boundary layer tracer is uplifted much more vigorously than the surface tracer.
greatest extent at 08:00 UTC on 4 February. The episode began at \( \sim 06:00 \) UTC, before dissipating at \( \sim 10:00 \) UTC, so there is a reduction in tracer concentration in the tropopause for around 4 h before background concentrations of tracer return to the area again.

However, the reduction in tracer #2 concentration in the TTL was more pronounced, suggesting for that period convection was lifting air from the boundary layer rather than from the surface. Figure 4.13 illustrates one of these periods at 12:00 UTC on 7 February showing the difference in extent between tracers #1 and #2. The mass of air from the tracer-free region of interest that was transported to the TTL was calculated using the density of air derived from the WRF temperature and pressure fields (equation 4.1), multiplied by the reduction in tracer concentration (equation 4.2), and summed throughout the whole domain (equation 4.3).

\[
\rho_{i,j,k} = \frac{p_{i,j,k}}{R_{\text{specific}} T_{i,j,k}} \tag{4.1}
\]

\[
m_{i,j,k} = (1 - C_{t,j,k}^{\text{tracer}}) \rho_{i,j,k} \cdot \delta x_{i,j,k} \cdot \delta y_{i,j,k} \cdot \delta z_{i,j,k} \tag{4.2}
\]

\[
m_k = \sum_{i,j} m_{i,j,k} \tag{4.3}
\]

where \( R_{\text{specific}} = 287 \cdot 058 \text{ J kg}^{-1} \text{ K}^{-1} \) is the specific gas constant for dry air, \( p_{i,j,k} \) and \( T_{i,j,k} \) are atmospheric pressure and temperature, respectively at grid point \( i, j, k \), \( C_{t,j,k}^{\text{tracer}} \) is the tracer concentration, and \( \delta x_{i,j,k} \), \( \delta y_{i,j,k} \) and \( \delta z_{i,j,k} \) are the grid spacings (i.e. cell dimensions) in the \( x \), \( y \) and \( z \) directions, respectively. Finally, \( m_{i,j,k} \) is the mass of tracer in each grid cell, and \( m_k \) is the total mass in each vertical layer. The total mass for the TTL, defined as the total mass between layer 24 (166·2 hPa) and layer 28 (98·3 hPa) (i.e. \( \sum_{k=24}^{28} m_k \)), of tracer #1 after 88 hours of model time, at 16:00 UTC on 7 February, was calculated to be \( 1.03 \times 10^4 \text{ kg} \). A similar calculation for tracer #2 yielded a value of \( 1.55 \times 10^4 \text{ kg} \).

Cross-sections were plotted along the largest area of deep convection, which for this period was along 12\(^\circ\)S. Figure 4.14 shows the cross-section of tracer #2 at 08:00 UTC on 4 February 2014; the black line in the figure shows the simulated height of the cold-point tropopause. It was found that neither the surface tracer (tracer #1) nor the boundary layer tracer (tracer #2) cross the tropopause, so there is no troposphere-to-stratosphere transport taking place.

### 4.2.4.2 17 February run

The second run was initialized on 17 February 2014 at 00:00 UTC and run for four days until 21 February at 00:00 UTC. During this period, the Southern Pacific Convergence Zone (SPCZ) was active around the latitude of Manus Island (2\(^\circ\)),...
forming an MCS to the northeast of Papua New Guinea and the Solomon Islands. This system was found, by Newton et al. [2016], to be the origin of the low-ozone event described in section 4.2.2, according to the back-trajectories using the HYSPLIT model [Stein et al., 2015]. Figure 4.15 shows the MTSAT satellite image for 20 February at 12:00 UTC, with the MCS visible in the image.

On 17 February, the model showed little convective activity throughout the day, although some of this was as a result of the spin-up required for the model simulation to begin to form organized convection. However, the convection built up throughout the day on 18 February in the area where the MCS was observed. By 20 February, the MCS was fully mature, and covered much of the domain west of New Guinea. Figure 4.16 shows the OLR image derived from the WRF output from 20 February at

![Figure 4.14](image)

**Figure 4.14**: Cross-section of the concentrations of tracer #2 at 12:00 UTC on 4 February 2014. These tracers, and also the surface tracers, do not penetrate into the stratosphere.

![Figure 4.15](image)

**Figure 4.15**: MTSAT infra-red satellite image for 20 February 2014 at 12:00 UTC. Convection is found mostly to the east of Manus, which resulted in the low-ozone event observed above Manus over the following few days. The magenta asterisk marks the location of Manus.
12:00 UTC, showing comparable features to the satellite image in figure 4.15.

The CAST ozonesondes observed an easterly jet with winds of up to 40 m·s$^{-1}$ in the tropopause layer above Manus. Back-trajectories from the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) model suggest the jet passed through the MCS and so transported ozone-deficient air from the MCS towards Manus. The WRF model simulation resolved this easterly jet, with winds originating from a convergence zone at around 155°E, 0°N and flowing across the model domain into

![Figure 4.16: Outgoing longwave radiation (OLR) on 20 February 2014 at 12:00 UTC derived from the WRF output.](image)

![Figure 4.17: Wind simulated by WRF at TTL level (~112 hPa) on 19 February 2014 at 12:00 UTC, showing the easterly jet along 2°S.](image)
Figure 4.18: Two-hourly WRF model output of tracer #1 concentrations from 12:00 to 22:00 UTC on 18 February 2014 at 112 hPa, when the surface tracer was abundant in the TTL.

The convection that built up throughout 18 February onwards prompted the appearance of tracer-free surface air from the region of interest of tracer #1 in the tropopause layer. The first indication of the tracer-free air reaching the tropopause layer was at 12:00 UTC on 18 February; figure 4.18 shows the situation at 2-hourly intervals from 12:00 UTC to 22:00 UTC, showing the evolution of the convective event as it progressed. By 12:00 UTC on 19 February, the tracer-free surface air had advected from the convective system via the easterly jet over to Manus (see figure 4.19).

The surface ozone on Manus Island at this time ranged from $\sim8$–13 ppbv, and marine surface ozone concentrations were likely to have been even lower (see Newton et al. [2016] for details). By the end of the simulation at 00:00 UTC on 21 February, 0.53 ppb of tracer #1 (noting that 1 ppb is the background value and 0 ppb is the value at the surface) was measured in the TTL over Manus, with most of the domain to the west of the convection affected by this event. If the tracer were rescaled to representative values, setting the tropospheric background to 30 ppbv, and the surface to 5 ppbv of ozone, then 0.53 ppb of tracer would correspond to a value of 18 ppbv. The minimum tracer #1 value in the domain was $\sim0.4$ ppb (discounting three grid-points in the convective core of 0.1 ppb), corresponding to an ozone concentration of 15 ppbv—in comparison the lowest concentrations that the CAST
Figure 4.19: Concentrations of tracer #1 simulated by WRF at TTL level (∼112 hPa) from 19 February at 12:00 UTC.

Figure 4.20: Concentrations of tracer #1 simulated by WRF at TTL level (∼112 hPa) from 20 February 2014 at 12:00 UTC, rescaled to simulate estimated ozone concentrations throughout the domain.

Ozonesondes measured over Manus were 12 ppbv, and one ozonesonde measured a minimum of 8⋅3 ppbv on 21 February. Figure 4.20 shows the approximate TTL ozone concentrations for 12:00 UTC on 20 February when tracer #1 is rescaled in the same way as described earlier; the low-ozone event can be seen to extend throughout large swathes of the West Pacific and Maritime Continent, suggesting uplift of ozone-deficient surface air alone can produce the observed low ozone concentrations in the
TTL. 18.6% of this layer at this time was less than 20 ppbv, and 1.87% was less than 10 ppbv; the respective values for the 3 February run using the data for figure 4.12 was 0.36% was less than 20 ppbv, and no gridpoints had a value less than 10 ppbv.

A calculation of the mass of tracer-free air in the TTL using equations (4.1)–(4.3) was done for 20 February 2014 at 16:00 UTC, 88 hours after the start of the run such that it is directly comparable to the calculation for 6 February 2014 at 16:00 UTC, which was also 88 hours after the start of the 3 February run. The calculation yielded a value for tracer #1 of $4.70 \times 10^4$ kg, compared to $1.03 \times 10^4$ kg for the 3 February run, and the value for tracer #2 was $5.84 \times 10^4$ kg, compared to $1.55 \times 10^4$ kg for 3 February run. Therefore it can be concluded that the model is capable of differentiating a convective period where uplift of boundary layer, and surface, air to the TTL occurred in large quantities and a less convective period with little surface-to-TTL uplift.

Figure 4.21 shows a comparison of a profile of the concentrations of WRF tracer #5 with CAST ozonesonde 31 launched at 17:43 UTC on 20 February 2014 from Manus Island. The WRF profile was derived from the average of the 41×41 gridpoint square centred upon Manus Island bound by the coordinates 2.74°S, 1.14°S; 146.42°E, 148.02°E, at 18:00 UTC. The WRF profile shows good agreement with that from the ozonesonde, and ozone concentrations are diminished most between 200 hPa and 100 hPa in both cases. Due to the way the tracers were implemented, they do not have a stratospheric component, so ozone concentrations in figure 4.21 are

![Figure 4.21](image)

**Figure 4.21:** Comparison of the concentrations of ozone from CAST ozonesonde 31 launched on 20 February 2014 at 17:43 UTC from Manus Island and tracer #5 averaged over a 41×41 gridpoint square centred on Manus Island from 18:00 UTC on 20 February. The height of the CPT is also indicated.
Figure 4.22: Concentrations of tracer #5 simulated by WRF at TTL level (~112 hPa) from 20 February 2014 at 18:00 UTC—at the time of the ozonesonde launch—rescaled to ozone concentrations. The black rectangle shows the tracer release area for tracers #3, #4 and #5, and the smaller magenta rectangle shows the area used to produce the average profile in figure 4.21.

assumed to reach stratospheric levels above the CPT at level 30 (85 hPa), and set to the same value as the ozonesonde. At 85 hPa, the ozone concentration measured by ozonesonde 31 was 300 ppbv. The extent of tracer #5 at 18:00 UTC on 20 February, and the location of the square used to produce the WRF tracer profile and the rectangle showing the region of interest for tracer release, are shown in figure 4.22.

Figures 4.23 and 4.24 show cross-sections of the domain along 2°N, such that the cross-section passes through the largest area of uplift of boundary layer air around (2°N, 152°E), at 18:00 UTC on 20 February (the same time as figures 4.21 and 4.22). The tracer-deficient region of interest for tracer #3 was placed at the surface where the MCS was located, and the region of interest for tracer #4 was placed in the same region but at the top of the boundary layer. The cross-sections of tracers #3 and #4 support the hypothesis from the use of the HYSPLIT back-trajectory model that ozone-deficient air was uplifted from near the surface into the TTL, and once in the TTL the air was then advected along the easterly jet in the TTL along 2°N. The cross-sections also show that the tracers do not cross the tropopause in the region of the MCS, so no direct stratospheric injection of tropospheric air was found in the model. Both the surface tracer and the boundary layer tracer produce similarly shaped cross-sections with differences only in their relative abundances in the upper troposphere, which suggests air is drawn from a well-mixed boundary layer rather than directly from the surface.
4.2.5 Conclusions

The overall aims of this modelling study were to investigate whether the low-ozone event of 21–23 February could be reproduced using the Weather Research and Forecasting (WRF) model, and investigate the properties of the low-ozone event including its spatial extent and the nature of the uplift into the stratosphere.
It was shown that WRF reproduced the low-ozone event by comparing the 17–21 February to 3–7 February when convective activity was inhibited. Firstly, the mass of tracer-free air from the surface in tracer #1, and the boundary-layer in tracer #2, was much larger for the 17–21 February run compared to 3–7 February (see table 4.3 for values), confirming more uplift took place in the period of 17–21 February. Despite there being convection in the seas between Australia and Papua New Guinea in the 3 February run associated with the Southern Pacific Convergence Zone (SPCZ), the mesoscale convective system (MCS) found in the 17 February run caused much more boundary layer-to-tropopause transport.

<table>
<thead>
<tr>
<th></th>
<th>3 Feb</th>
<th>17 Feb</th>
</tr>
</thead>
<tbody>
<tr>
<td>tracer #1</td>
<td>1.03×10^4 kg</td>
<td>4.70×10^4 kg</td>
</tr>
<tr>
<td>tracer #2</td>
<td>1.55×10^4 kg</td>
<td>5.84×10^4 kg</td>
</tr>
</tbody>
</table>

**Table 4.3:** Mass of tracer-free air from the respective regions of interest of tracers #1 and #2 in the TTL after 88 hours in 3 February run and 17 February run.

As the WRF model was able to reproduce the low-ozone event, its properties could be investigated. The WRF model confirms the hypothesis that the low-ozone event originated in the mesoscale convective system (MCS) to the east of Manus Island, which uplifted ozone-deficient air into the TTL before advecting within an easterly jet. WRF suggests the easterly jet spread the ozone-deficient air to Manus, where it was measured by the ozonesondes, and also throughout large swathes of the tropical West Pacific to the west of the MCS. A large area had ozone concentrations below 20 ppbv in the TTL, and in the core of the MCS ozone concentrations were less than 10 ppbv.

The final question concerned whether surface air was being uplifted unmixed through the convective system, and whether direct injection into the stratosphere was observed. No evidence for either was found; firstly the simulation suggests air was mixed in the boundary layer and lifted from there instead of directly from the surface. Finally, no boundary layer air was found above the cold-point tropopause (CPT) either in the core of the MCS in the 17 February run or in the Southern Pacific Convergence Zone (SCPZ) in the 3 February run, so it is expected the wave-driven large-scale ascent is the only mechanism for troposphere-to-stratosphere transport in this region at this time.
4.3 Closing remarks

4.3.1 Discussion of uncertainties

The set-up of the WRF model is subject to several variables that contribute to the uncertainty of the simulation. These include, but are not limited to the following, listed from least to most significant causes of model uncertainty:

- **Physics options**—as shown in section 4.1.1, the choices of physics options have a large effect on the model simulation. The effect of the convection parameterization scheme was not tested due to only the Grell 3-d scheme being compatible with the tracers, and Arteta et al. [2009a] suggests that the Grell 3-d scheme strongly underestimates the amount of surface rainfall due to convection compared to the Arakawa-Schubert and Kain-Fritsch schemes. This is therefore a significant, yet unavoidable source of uncertainty.

- **Horizontal and vertical resolution**—horizontal resolutions of ∼1km are able to resolve convection well, and grid-spacings less than 1km are useful for providing more detail, such as horizontal convective rolls [Chemel et al., 2009]. However, coarser resolutions than 1km are known to underestimate the amount of convection within a storm, and coarser vertical resolutions have a similar effect [Arteta et al., 2009b]. Sun et al. [2013] found that for a particular tropical cyclone in 2006, the maximum intensity of the cyclone increased, with maximum wind speeds increasing by ∼18% from 55 m·s\(^{-1}\) at 5 km resolution to 65 m·s\(^{-1}\) at 1 km resolution, but the area of maximum intensity decreased, with the radius of maximum wind reducing by ∼22% from 45 km at 5 km resolution to 55 km at 1 km resolution. Therefore the uncertainty in convective uplift is likely to be significant, but much less than 18% in all of the WRF output variables.

- **Start time**—the model start time has an effect on the input boundary conditions used to initialize the WRF model, and the evolution of the modelled convection. This was studied by [Frey et al., 2015], who observed that the Hector thunderstorm was weaker or even non-existent when an earlier start time was used and thus the time between the start of the model run and the development of Hector was lengthened. In addition, due to the lack of sinks for the passive tracers to be removed in the model, different start times will result in different amounts of passive tracer being present at following times during the simulation.

- **Positioning of domains**—the placing and size of domains have an effect on where the lateral boundaries are, and the boundary conditions upon them. The
error due to the differences in boundary conditions will be small, except in circumstances where a convective storm is found on, or near, the boundary itself.

4.3.2 Suggested expansion to the study

The tracer implementation leaves scope for stratospheric tracers, such that the surface/boundary layer region of interest is set to 0 ppb, the background is set to 1 ppb, and the stratosphere is set to ∼10 ppb, but a complicated modification to the WRF code would have to be made. As it was expected that negligible downwelling of high-ozone concentrations from the stratosphere would occur, the implementation in the journal article where it was added in artificially at the post-processing stage should not contribute much to the errors of the WRF model.

This study could be expanded in the future, given increased computing power: as mentioned in the conclusions in section 4.2.5 the Brewer-Dobson circulation, which is important to troposphere-to-stratosphere transport, requires a global model to resolve. Therefore to study the regional large-scale ascent in the West Pacific Warm Pool, a simulation of the whole globe is needed.

Moreover, the limited computing power enabled the inner domain of the model to be run at a relatively coarse resolution for modelling convection of 4.447 km, which is only able to resolve some of the larger convective systems. With extended computing power, it would have been advantageous to run the model at ≲1 km, such that all of the convection could be resolved more precisely. This would, however, require either a higher resolution outer domain, or numerous nested domains, which would increase the computational expense of the simulation markedly.

Further suggestions for future research motivated by this study, and the other studies in chapters 2 and 3 can be found in chapter 5.
Chapter 5

Conclusions

5.1 Summary of salient results

The overarching objectives of the studies described was to investigate the mechanisms of transport of ozone deficient air into the tropical tropopause layer from below, including how and from where the air is uplifted. This was investigated using ozonesonde measurements from Manus Island, Papua New Guinea as part of the CAST campaign and complementary measurements from the CAST, CONTRAST and ATTREX flight campaigns using the FAAM BAe 146, the NCAR Gulfstream V and the NASA Global Hawk based out of Guam, in addition to simulations of the West Pacific Warm Pool region using the WRF (Weather Research and Forecasting) model.

From the ozonesonde campaign, numerous insights into the procedures and post-processing of the data were found, and the following recommendations for ozonesonde standard operating procedures (SOP) were made:

- the ozonesonde SOPs should be amended to avoid exposure to ozone during preparation, especially after adding the anode and the cathode solutions. This will help reduce background currents.

- if an ozonesonde background current of \(\leq 50\) nA is not achieved during the day-of-flight preparation, the anode and the cathode solutions should be replaced, and the preparation to be performed again.

- if a background current of \(>50\) nA is used, then the hybrid background current correction should be used in post-processing the data (equation 5.1). Moreover, ozonesondes launched historically that have background currents in excess of 50 nA should be reprocessed with the hybrid background current correction.

- the limit-of-detection for ozonesondes should be revised down to 5 ppbv, consistent with the uncertainty on the ozonesonde measurements.
\[ I_{bg} = 50 \text{ nA} + \left( I_{meas}^{bg} - 50 \text{ nA} \right) \frac{p}{p_0} \] (5.1)

The observations that were made by the ozonesondes on Manus Island produced the following conclusions:

- no extremely low ozone concentrations of \( \lesssim 5 \text{ ppbv} \) that have been measured in the TTL in previous campaigns were found, and it is expected that these low-ozone measurements were artefacts of an inappropriate background current correction.

- an ozone minimum of \( \sim 12\text{–}13 \text{ ppbv} \) was found in the TTL on 18–22 February, which was shown to have originated from the outflow of a mesoscale convective system (MCS) to the east of Manus and advected over to Manus in an easterly jet in the TTL. Ozone concentrations of \( \lesssim 12\text{–}13 \text{ ppbv} \) were seen only at the surface on Manus, suggesting uplift of unmixed surface air occurred within the MCS.

- the choice of background current correction, with a constant correction for ozonesonde background currents \( \lesssim 50 \text{ nA} \) and the new hybrid correction for background currents \( \gtrsim 50 \text{ nA} \) was verified using collocated measurements with the Gulfstream V, which agreed within 5 ppbv of the ozonesonde measurements.

The subsequent studies investigated the low-ozone phenomenon in other measurements, firstly the CAST/CONTRAST/ATTREX aircraft data, which surveyed the West Pacific at the same time as the ozonesonde campaign. The conclusions from the investigation of the aircraft data were as follows:

- the Global Hawk measured similar values of minimum ozone concentration in the Southern Hemisphere, of between 10·5 ppbv and 14·2 ppbv.

- in the Northern Hemisphere, no low ozone concentrations below 15 ppbv were found. This was hypothesized to be as a result of more convective activity in the Southern Hemisphere than the Northern Hemisphere. In addition, previous measurement campaigns have observed a difference in boundary layer ozone concentrations between the two hemispheres, so in the Southern Hemisphere convection uplifts lower ozone concentrations than in the north.

- data on very short-lived substances (VSLSs) measured by the whole air samplers (WAS) show that VSLSs of marine origin were enhanced when ozone concentrations were low, consistent with convective uplift from the surface.

The third and final study involved investigating the low-ozone event of 18–22 February that was observed by the ozonesondes using the WRF model. The conclusions from this modelling study were as follows:
• WRF was able to differentiate between the 18–22 February conditions and the 3–7 February conditions when convective activity was inhibited. The mass of surface air that was transported to the TTL was $1.03 \times 10^4$ kg for 3–7 February and 4.70 kg for 17-22 February, and similar differences in the values were obtained for boundary layer air.

• the low ozone event of 18–22 February was observed in the WRF model simulation to extend throughout most of the West Pacific; 18.6% of the modelled area had simulated ozone concentrations less than 20 ppbv and 1.8% less than 10 ppbv, and so the MCS had a considerable effect on the composition of the TTL in the region during its lifetime.

• no evidence for air from the boundary layer penetrating into the stratosphere was found, meaning the only mechanism for troposphere-to-stratosphere transport is via the Brewer-Dobson circulation, which occurs on a timescale longer than the lifetimes of VSLSs.

• no evidence was found for uplift of unmixed surface air entering the TTL, and the most likely mechanism for surface-to-TTL transport is uplift of air from a well-mixed boundary layer during this time instead.

5.2 Suggestions for further study

Chapter 2 introduced new insights into the ozonesonde measurement technique, and measurements from the West Pacific where few measurements have been made. Further research related to this study should be made, including:

• reprocessing the historical ozonesonde data with the hybrid background current, which would provide information on whether the low-ozone concentrations are plausible, or likely to be an artefact of the background current correction used. An estimate of the ozone budget in the TTL with the new hybrid correction should be made to see how much difference this makes to the established values.

• as the hybrid background current has only been used for the CAST campaign, further research is required to ensure it is robust and valid for other ozonesondes, including using multiple independent collocated measurements to compare and validate the ozonesonde measurements. The values in the TTL are especially important, so focusing on collocating measurements with high-altitude aircraft such as the Global Hawk in the TTL is essential.
• as the CAST ozonesondes showed, the low-ozone events are short-lived—the one in the TTL above Manus lasted approximately 5 days. Therefore the long-term monthly ozonesonde launches, such as those from the SHADOZ dataset, are too infrequent to capture the variability of ozone, and the frequency of launches should be increased. If a climatology of ozone in the TTL could be made, the frequency of ozonesonde launches could be increased during periods of favourable conditions.

Chapter 3 regard low ozone concentrations that were measured in the TTL in the Southern Hemisphere in the ATTREX flight that crossed the equator. If the experiment were to be repeated, the following should be taken into consideration if the low-ozone phenomenon is to be central to the campaign:

• the aircraft should take measurements in both hemispheres equally, which would require a base close to, or on the equator. Flights should be performed that survey both sides of the equator in a short amount of time, so that a comparison of near-simultaneous measurements in both hemispheres can be made.

• more collocation of aircraft, such that measurements are made in the same geographic area in both the boundary layer and the tropopause layer simultaneously. This would allow information on whether the reported contrast between the Northern and Southern Hemispheres is as a result of differences in boundary layer ozone concentrations, or more convective activity was observed in the Southern Hemisphere when the measurements were made.

• whole air samplers (WAS) should be focused towards sampling air with low ozone concentrations to determine the composition of ozone-deficient air and if it is consistent with rapid uplift of surface air. Very few WAS samples were taken in the Southern Hemisphere where the lowest ozone concentrations were found, so the composition of this very low-ozone is still not known fully.

• in the long term, continuous measurements over a long period of time are required to investigate the effects of periodic oscillations, such as the El Niño–Southern Oscillation (ENSO) and the Quasi-Biennial Oscillation (QBO), on convective transport of low-ozone air. Future campaigns should consider re-locating multiple aircraft in the West Pacific area so that repeated measurements can be made over the long-term in multiple seasons (such as biomass burning season, monsoon season etc.), meteorological conditions and ENSO/QBO régimes.

• making long-term high resolution observations of chemical species important to the ozone formation and destruction in the troposphere would be beneficial
for full chemical analysis of ozone in the West Pacific. The study in chapter 4, and those described in Arteta et al. [2009a], Arteta et al. [2009b] and Frey et al. [2015] used passive tracers for this reason.

In chapter 4, it was demonstrated that WRF was able to reproduce the MCS that produced the low-ozone event measured by the CAST ozonesondes between 18–22 February as a case study. This study can be expanded by:

- applying the same modelling technique to other instances of convective activity to reproduce other low-ozone events. It remains unknown how frequently these low-ozone events occur, how large they are on average and their size distribution, and whether they contribute significantly to the redistribution of ozone on both a local and a global scale.

- building up a model climatology of low-ozone events, including the effects of ENSO and the QBO. This would determine when the periods of favourable conditions are for these low-ozone events, which would allow measurement campaigns to focus on intensively surveying during these periods.

- expanding the modelling study to other parts of the world. As ozone is higher in most other parts of the tropics, the same boundary layer-to-TTL transport would have different effects on TTL composition.

- utilizing an ensemble of WRF model runs with different sets of physics options, which would provide a better understanding of the possible scenarios that could have produced the low-ozone event, and the uncertainties on the WRF output.
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Chapter 6

Supplementary information

6.1 Supplementary material to chapter 2

6.1.1 Manus ozonesonde profiles

Figures 6.1 to 6.6 show the profiles of all the ozonesondes that were obtained from the CAST campaign on Manus Island. In the first fourteen ozonesondes, which were contaminated, the hybrid background current correction was used, and the resulting profile is shown as a black solid line. The other corrections are also shown for comparison, namely the constant (black dashed line), pressure-dependent (blue dashed line) and the Vömel and Diaz [2010] correction (green dashed line). From ozonesonde 15 onwards, the ozonesondes were prepared clean, and the constant background correction was used, though for clean ozonesondes with low background currents the constant and hybrid corrections are identical. In these ozonesondes, the profile resulting from a constant correction is shown as a black solid line, and the hybrid correction is not shown. In all of the ozonesonde profiles, the ground level ozone is shown as a black asterisk, measured by the TECO-49 ozone monitor on the ground on Manus Island.

Tables 6.1 and 6.2 list the ozonesonde launches and their launch times.

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<thead>
<tr>
<th>#</th>
<th>Launch time (UTC)</th>
<th>Notes</th>
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<tbody>
<tr>
<td>1</td>
<td>2 February 04:23</td>
<td>Background current too high</td>
</tr>
<tr>
<td>2</td>
<td>3 February 00:43</td>
<td>Background current too high</td>
</tr>
<tr>
<td>3</td>
<td>3 February 06:41</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4 February 05:09</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5 February 00:24</td>
<td></td>
</tr>
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Table 6.1: Table of the CAST ozonesonde launches and launch times.
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<thead>
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<th>Notes</th>
</tr>
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<tbody>
<tr>
<td>6</td>
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<td>Coincided with CONTRAST flight RF09</td>
</tr>
<tr>
<td>7</td>
<td>6 February 00:23</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6 February 06:54</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>6 February 23:55</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7 February 07:08</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>8 February 05:44</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>8 February 23:57</td>
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<td>13</td>
<td>9 February 07:11</td>
<td></td>
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<td>14</td>
<td>10 February 00:11</td>
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<td>15</td>
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<td>16</td>
<td>11 February 00:59</td>
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<td>17</td>
<td>12 February 01:06</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>12 February 07:00</td>
<td>Unusually low stratospheric ozone—presumed to be a leak in the ozonesonde</td>
</tr>
<tr>
<td>19</td>
<td>13 February 00:16</td>
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</tr>
<tr>
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<td>25</td>
<td>17 February 01:54</td>
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<td>26</td>
<td>18 February 00:01</td>
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<td>27</td>
<td>18 February 07:24</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>19 February 02:34</td>
<td>Ozonesonde blew over in heavy wind and solution emptied from sonde</td>
</tr>
<tr>
<td>29</td>
<td>19 February 05:55</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>20 February 01:58</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>20 February 07:43</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>21 February 01:01</td>
<td>Ozonesonde leaked</td>
</tr>
<tr>
<td>33</td>
<td>21 February 05:20</td>
<td></td>
</tr>
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<td>22 February 01:31</td>
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</tr>
<tr>
<td>35</td>
<td>22 February 04:49</td>
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<td>36</td>
<td>23 February 01:51</td>
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</tr>
<tr>
<td>37</td>
<td>24 February 00:39</td>
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</tr>
<tr>
<td>38</td>
<td>24 February 06:57</td>
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</tr>
<tr>
<td>39</td>
<td>25 February 00:32</td>
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</tr>
</tbody>
</table>

*Table 6.2: Table of the CAST ozonesonde launches and launch times continued.*
Figure 6.1: Ozonesondes 4 to 9. Ozonesondes 1 to 3 were too heavily contaminated, and are not shown; ozonesonde 6 was coincident with Gulfstream V flight RF09.
Figure 6.2: Ozonesondes 10 to 15. Ozonesonde 15 was the first ozonesonde that was entirely unaffected by contamination.
Figure 6.3: Ozonesondes 16 to 22. Ozonesonde 18 leaked and is not shown.
Figure 6.4: Ozonesondes 23 to 29. Ozonesonde 28 was launched after falling over and emptying its solution canisters and is not shown.
Figure 6.5: Ozonesondes 30 to 36. Ozonesonde 32 leaked and is not shown; ozonesondes 34 and 35 were coincident with Gulfstream V flight RF14.
Figure 6.6: Ozonesondes 37 to 39.
6.2 Supplementary material to chapter 3

6.2.1 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 ($\text{CHCl}_3$) was 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 6.7a 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 15 of the accompanying article. Likewise the profile for trichloromethane is found in figure 6.7b.

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].

6.2.1.1 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 6.7c),

- ethyne ($\text{CH}≡\text{CH}$):
  lifetime = $\sim$2–4 weeks (figure 6.7d),

- propane ($\text{CH}_3\text{CH}_2\text{CH}_3$):
  lifetime = $\sim$2 weeks (figure 6.7e),

- methylpropane ($\text{CH}_3\text{CH}($CH$_3$)$_2$):
  lifetime = $\sim$1 week (figure 6.7f),

- butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$):
  lifetime = $\sim$5 days (figure 6.8a),
• 2-methylbutane \((CH_3CH_2CH(CH_3)_2)\):  
  lifetime = 4 days (figure 6.8b),

• pentane \((CH_3CH_2CH_2CH_2CH_3)\):  
  lifetime = \(\sim\)3 days (figure 6.8c)

• isoprene \((CH_2\xrightarrow{\beta} C(CH_3)CH\xrightarrow{\alpha} CH_2)\):  
  lifetime = \(\sim\)minutes–hours (figure 6.8d)

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.

### 6.2.1.2 Haloaliphatic compounds

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

#### CFCs

• CFC-12 \((CCl_2F_2)\):  
  [dichlorodifluoromethane]  
  lifetime = \(\sim\)100 years (figure 6.8e)

• CFC-11 \((CCl_3F)\):  
  [trichlorofluoromethane]  
  lifetime = \(\sim\)50 years (figure 6.8f)

• CFC-112 \((CCl_2FCCl_2F)\):  
  [tetrachloro-1,2-difluoroethane]  
  lifetime = \(\sim\)60 years (figure 6.9a)

• CFC-112a \((CCl_3CClF_2)\):  
  [tetrachloro-1,1-difluoroethane]  
  lifetime = \(\sim\)50 years (figure 6.9b)

• CFC-113 \((CCl_2FCClF_2)\)  
  [1,1,2-trichloro-1,2,2-trifluoroethane]  
  lifetime = \(\sim\)90 years (figure 6.9c)
• CFC-114 (CClF₂CClF₂)
  [1,2-dichlorotetrafluoroethane]
  lifetime = ~190 years (figure 6.9d)

**HCFCs**

• HCFC-22 (CHClF₂)
  [chlorodifluoromethane]
  lifetime = ~12 years (figure 6.9e)

• HCFC-141b (CH₃CCl₂F)
  [1,1-dichloro-1-fluoroethane]
  lifetime = ~10 years (figure 6.9f)

• HCFC-142b (CH₃CClF₂)
  [1-chloro-1,1-difluoroethane]
  lifetime = ~18 years (figure 6.10a)

**HFCs**

• HFC-134a (CH₂FCF₃)
  [1,1,1,2-tetrafluoroethane]
  lifetime = ~14 years (figure 6.10b)

• HFC-365mfc (CH₃CF₂CH₂CF₃)
  [1,1,1,3,3-pentafluorobutane]
  lifetime = ~9 years (figure 6.10c)

**Halons**

• Halon-1211 (CBrClF₂)
  [bromochlorodifluoromethane]
  lifetime = ~16 years (figure 6.10d),

• Halon-2402 (CBrF₂CBrF₂)
  [1,2-dibromotetrafluoroethane]
  lifetime = ~30 years (figure 6.10e)

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.

**Others**

- chloromethane \((\text{CH}_3\text{Cl})\)
  lifetime = \(\sim 12\) months (figure 6.10f),

- bromomethane \((\text{CH}_3\text{Br})\)
  lifetime = \(\sim 9\) months (figure 6.11a),

- 1,1,1-trichloroethane \((\text{CH}_3\text{CCl}_3)\)
  lifetime = \(\sim 6\) years (figure 6.11b),

- tetrachloromethane \((\text{CCl}_4)\)
  lifetime = \(\sim 26\) years (figure 6.11c),

- 1,2-dichloroethane \((\text{CH}_2\text{ClCH}_2\text{Cl})\)
  lifetime = \(\sim 3\) months (figure 6.11d),

- trichloroethene \((\text{CHCl}=\text{CCl}_2)\)
  lifetime = \(\sim 5\) days (figure 6.11e),

- tetrachloroethene \((\text{CCl}_2=\text{CCl}_2)\)
  lifetime = \(\sim 5\) months (figure 6.11f)

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.

### 6.2.1.3 Aromatic compounds

- benzene \((\text{C}_6\text{H}_6)\)
  lifetime = \(\sim \)months (figure 6.12a)

- chlorobenzene \((\text{C}_6\text{H}_5\text{Cl})\)
  lifetime = \(\sim 2\) weeks (figure 6.12b)
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.

6.2.1.4 Sulfides

- carbonyl sulfide (OCS)
  
  lifetime $= \sim 35$ years (figure 6.12c)

Like dimethyl sulfide, shown in figure 15 of the accompanying article, carbonyl sulfide, shows a slight enhancement in the low-ozone, clean régime.
Figure 6.7: WAS plots page 1
Figure 6.8: WAS plots page 2
Figure 6.9: WAS plots page 3
Figure 6.10: WAS plots page 4
Figure 6.11: WAS plots page 5
Figure 6.12: WAS plots page 6
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