# Convective and wave signatures in ozone profiles over the equatorial Americas: Views from TC4 (2007) and SHADOZ

Anne M. Thompson<sup>1</sup>, Alaina M. MacFarlane<sup>1,2</sup>, Gary A. Morris<sup>3</sup>, John E. Yorks<sup>1,4</sup>, Sonya K. Miller<sup>1</sup>, Brett F. Taubman<sup>5</sup>, Gé Verver<sup>6</sup>, Holger Vömel<sup>7</sup>, Melody A. Avery<sup>8</sup>, Johnathan W. Hair<sup>8</sup>, Glenn S. Diskin<sup>8</sup>, Edward V. Browell<sup>8</sup>, Jéssica Valverde Canossa<sup>8</sup>, Tom L. Kucsera<sup>10</sup>, Christopher A. Klich<sup>1</sup>, Dennis L. Hlavka<sup>4</sup>

<sup>1</sup> The Pennsylvania State University, Department of Meteorology

- <sup>2</sup> Now at National Weather Service Middle Atlantic River Forecast Center
- <sup>3</sup> Valparaiso University, Dept of Physics and Astronomy
- <sup>4</sup> SSAI; also at NASA/Goddard Space Flight Center
- <sup>5</sup> Appalachian State University, Dept of Chemistry
- <sup>6</sup> KNMI (Royal Dutch Meteorological Institute)
- <sup>7</sup> DWD- Deutscher Wetterdienst, GRUAN Lindenborg
- <sup>8</sup> NASA/Langley Research Center
- <sup>9</sup> Laboratorio de Análisis Ambiental, Escuela de Ciencias Ambientales, Universidad Nacional
- <sup>10</sup> Univ Maryland Baltimore County GEST; also at NASA/Goddard

## **Popular Summary**

During the months of July-August 2007 NASA conducted a research campaign called the Tropical Composition, Clouds and Climate Coupling (TC4) experiment. Vertical profiles of ozone were measured daily using an instrument known as an ozonesonde, which is attached to a weather balloon and launch to altitudes in excess of 30 km. These ozone profiles were measured over coastal Las Tablas, Panamá (7.8N, 80W) and several times per week at Alajuela, Costa Rica (10N, 84W). Meteorological systems in the form of waves, detected most prominently in 100-300 m thick ozone layer in the tropical tropopause layer, occurred in 50% (Las Tablas) and 40% (Alajuela) of the soundings. These layers, associated with vertical displacements and classified as gravity waves ("GW," possibly Kelvin waves), occur with similar structure and frequency over the Paramaribo (5.8N, 55W) and San Cristóbal (0.92S, 90W) sites of the Southern Hemisphere Additional Ozonesondes (SHADOZ) network. The gravity wave labeled layers in individual soundings correspond to cloud outflow as indicated by the tracers measured from the NASA DC-8 and other aircraft data, confirming convective initiation of equatorial waves. Layers representing quasi-horizontal displacements, referred to as Rossby waves, are robust features in soundings from 23 July to 5 August. The features associated with Rossby waves correspond to extra-tropical influence, possibly stratospheric, and sometimes to pollution transport. Comparison of Las Tablas and Alajuela ozone budgets with 1999-2007 Paramaribo and San Cristóbal soundings shows that TC4 is typical of climatology for the equatorial Americas. Overall during TC4, convection and associated meteorological waves appear to dominate ozone transport in the tropical tropopause layer.

Submitted to the TC4 Issue of JGR-Atmospheres (2009JD012909RR)

19 May 2010 2009JD012909RR Submitted to the TC4 Issue of JGR-Atmospheres

#### Convective and wave signatures in ozone profiles over the equatorial 2 Americas: Views from TC4 (2007) and SHADOZ 3

1

4

5

6

7

8 9

10

11 12

13

15 16

17

18

19

20

23

24 25

26

27

- <u>Anne M. Thompson,</u><sup>1</sup> Alaina M. MacFarlane,<sup>1,2</sup> Gary A. Morris,<sup>3</sup> John E. Yorks,<sup>1,4</sup> Sonya K. Miller,<sup>1</sup> Brett F. Taubman,<sup>5</sup> Gé Verver,<sup>6</sup> Holger Vömel,<sup>7</sup> Melody A. Averv,<sup>8</sup> Johnathan W. Hair,<sup>8</sup> Glenn S. Diskin,<sup>8</sup> Edward V. Browell,<sup>8</sup> Jéssica Valverde Canossa,<sup>9</sup> Tom L. Kucsera,<sup>10</sup> Christopher A. Klich,<sup>1</sup> Dennis L. Hlavka<sup>4</sup>
  - <sup>1</sup> The Pennsylvania State University, Department of Meteorology, 503 Walker Building, University Park, PA 16802-5013 USA; anne@met.psu.edu; smiller@psu.edu; cok5018@psu.edu
- <sup>2</sup> Now at National Weather Service Middle Atlantic River Forecast Center, State College, PA 16803; <u>alaina.macfarlane@noaa.gov</u> 14
  - <sup>3</sup> Valparaiso University, Dept of Physics and Astronomy, Valparaiso, IN 46383 USA; gary.morris@valpo.edu
  - <sup>4</sup> SSAI of Lanham, MD 20706 USA; also at NASA/Goddard Space Flight Center, Greenbelt, MD 20771 USA; john.e.vorks@nasa.gov; dennis.l.hlavka@nasa.gov
  - <sup>5</sup> Appalachian State University, Dept of Chemistry, Boone, NC 28608; 828-262-7847; taubmanbf@appstate.edu
- <sup>6</sup> KNMI (Royal Dutch Meteorological Institute), de Bilt, NL; ge.verver@knmi.nl 21
- 22 <sup>7</sup> DWD- Deutscher Wetterdienst, GRUAN - Lindenborg, Germany: Holger.voemel@dwd.de
  - <sup>8</sup> NASA/Langley Research Center, MS 401B, Hampton, VA 23681; melody.a.avery@nasa.gov; glenn.s.diskin@nasa.gov; johnathan.w.hair@nasa.gov; edward.v.browell@nasa.gov
  - <sup>9</sup> Laboratorio de Análisis Ambiental, Escuela de Ciencias Ambientales, Universidad Nacional P.O.Box: 86-3000 Heredia, Costa Rica; 00506-88694960; jvalverde25@gmail.com
- <sup>10</sup> Univ Maryland Baltimore County GEST, Baltimore, MD 21228; also at NASA/Goddard 28 29 Space Flight Center, 301-614-6046; Tom.l.kucsera@nasa.gov 30
- 31 Keywords: Upper Troposphere/Lower Stratosphere; Ozonesondes; Tropical tropopause 32 Layer; Gravity waves; Stratosphere-troposphere exchange

#### Running Head - Thompson et. al.: TC4, SHADOZ O<sub>3</sub> & Waves 33 Thompson et. al.: TC4, SHADOZ O<sup>3</sup> & Waves 34

### 35 36

# Convective and wave signatures in ozone profiles over the equatorial Americas: Views from TC4 (2007) and SHADOZ

37 **Abstract.** During the TC4 (Tropical Composition, Clouds and Climate Coupling) 38 campaign in July-August 2007, daily ozonesondes were launched over coastal Las Tablas, 39 Panamá (7.8N, 80W) and several times per week at Alajuela, Costa Rica (10N, 84W). 40 Wave activity, detected most prominently in 100-300 m thick ozone laminae in the 41 tropical tropopause layer, occurred in 50% (Las Tablas) and 40% (Alajuela) of the 42 soundings. These layers, associated with vertical displacements and classified as gravity waves ("GW," possibly Kelvin waves) by laminar identification, occur with similar 43 44 structure and frequency over the Paramaribo (5.8N, 55W) and San Cristóbal (0.92S, 90W) 45 Southern Hemisphere Additional Ozonesondes (SHADOZ) sites. GW-labeled laminae in 46 individual soundings correspond to cloud outflow as indicated by DC-8 tracers and other 47 aircraft data, confirming convective initiation of equatorial waves. Layers representing 48 quasi-horizontal displacements, referred to as Rossby waves by the laminar technique, are 49 robust features in soundings from 23 July to 5 August. The features associated with 50 Rossby waves correspond to extra-tropical influence, possibly stratospheric, and 51 sometimes to pollution transport. Comparison of Las Tablas and Alajuela ozone budgets 52 with 1999-2007 Paramaribo and San Cristóbal soundings shows that TC4 is typical of 53 climatology for the equatorial Americas. Overall during TC4, convection and associated 54 waves appear to dominate ozone transport in the tropical tropopause layer; intrusions 55 from the extra-tropics occur throughout the free troposphere.

56

### 1. Introduction

57 Ozone in the tropical troposphere reflects an interaction of photochemical and dynamical factors. The marine atmosphere is usually unpolluted, largely because the 58 59 boundary layer (BL; see Appendix for abbreviations) is a region of O<sub>3</sub> photochemical loss [*Piotrowicz et al.*, 1991]. This is a consequence of slow formation (low NO<sub>x</sub> conditions; 60 Zafiriou et al., 1980; Thompson et al., 1993) with loss by HO<sub>x</sub>, or occasionally by rapid O<sub>3</sub> 61 62 destruction by halogens [Read et al., 2008]. In the free troposphere mixed sources 63 converge [*Thompson et al.*, 1996]. Advected pollution, stratospherically influenced air, and lightning add to O<sub>3</sub> formation, the latter at rates according to time since a lightning 64 65 episode (Thompson et al, 1997; see Cooper et al. [2006] and Bertram et al. [2007] for analyses of lightning influence in mid-latitudes). Extra-tropical ozone may also enrich 66 ozone in the tropics [Randel et al., 2007]. 67

68 Examination of ozone profiles from sondes or aircraft over remote tropical sites reveals the free troposphere as a region of low O<sub>3</sub> (< 30 ppbv; *Thompson et al.*, 2003a) 69 70 alternating with layers of elevated O<sub>3</sub> (sometimes > 100 ppbv; *Newell et al.*, 1999). From 71 soundings taken through SHADOZ (Southern Hemisphere Additional Ozonesondes; 72 Thompson et al., 2003a,b; 2010; submitted article available as Supplemental Material), 73 SOWER [Stratospheric Ozone and Water in Equatorial Regions; Hasebe et al., 2007; 74 Takashima and Shiotani, 2007] and related campaigns, much is known about the structure of O<sub>3</sub> in the tropical upper troposphere (UT) and lower stratosphere (LS). Stable 75 76 pollution layers in the free troposphere are frequent over Réunion, Fiji, Samoa, San 77 Cristóbal, and Ascension [Thompson et al., 1996; 2003b; Oltmans et al., 2001; 2004; Randriambelo et al., 2003]. Reduced O<sub>3</sub> layers often characterize the UT and TTL 78 79 (tropical tropopause layer, ~8-14 km; Fueglistaler et al., 2009), where convective outflow of low-O3 BL air occurs. If O3 in the UT or TTL averages to lower concentrations than in 80 the mid-troposphere, an "S-shape" profile results [Folkins et al., 2000]. 81

82The laminar identification (LID) method, based on  $O_3$  and potential temperature83gradients [*Teitelbaum et al.*, 1994, 1996; *Grant et al*, 1998; *Thompson et al.*, 2007a;842008], interprets persistent  $O_3$  layers in terms of two wave-types. In the tropics, Rossby85waves (RW) represent horizontal displacement; these correspond to filaments of extra-86tropical air or pollution from long-range transport. When SHADOZ profiles are analyzed87with the LID technique, RW signatures appear in < 20% of the soundings [*Loucks, 2007; Thompson et al.*, 2010]. Signatures of convectively-generated gravity waves (GW) occur

in 40-90% of SHADOZ soundings, depending on location and season [*Thompson et al.*,
2010a,b]. Near the tropopause, GW are usually identified with Kelvin waves. Transient
Kelvin waves have been observed in O<sub>3</sub> over both eastern and western Pacific [*Fujiwara et al.*, 1998; 2001].

93 Wave activity over the equatorial Americas has received less attention. Robust GW 94 and RW signals were noted during the Milagro/INTEX-B/IONS-06 (Intercontinental 95 Transport Experiment; INTEX Ozonesonde Network Study) campaigns over Mexico City 96 (19N, 99W) and Houston (30N, 95W) in March-May 2006 [Thompson et al., 2008], two 97 locations that are essentially sub-tropical when springtime air parcel flows link them to 98 central America [Fast et al., 2007]. The TC4 (Tropical Composition, Cloud, and Climate Coupling) mission in July-August 2007 offered an opportunity to characterize O3 profiles 99 100 closer to the equator than the IONS-06 soundings. TC4 [Toon et al., 2010] investigated 101 chemical transformation in convective systems and the impacts of deep convection on 102 constituent transport, dehydration and cirrus formation. Sampling from San Jose, Costa 103 Rica, with NASA's DC-8, WB-57 and ER-2 aircraft, was well-suited for comparisons with 104 observations from Las Tablas, Panamá (LTP, 7.8N, 80W), where daily soundings were 105 made from the NATIVE (Nittany Atmospheric Trailer and Integrated Validation 106 Experiment) mobile lab. Most TC4 flights were south of the Intertropical Convergence 107 Zone (ITCZ), which was located at 12-13N during the experiment [*Toon et al.*, 2010]. 108 SHADOZ [Thompson et al., 2003a] soundings from Costa Rica (Alajuela, 10N,84W) were 109 augmented with several launches per week from early July through 9 August 2007.

110 Five TC4 studies are devoted to analysis of ozone transport and wave activity. In 111 Selkirk et al. [2010] temperature anomalies from four-times-daily radiosondes over 112 Alajuela indicate equatorial waves in the TTL. Comparison of TC4 radiosondes and water 113 vapor from cryogenic frost-point hygrometer readings suggests less convection than 114 during the 2005 TCSP (Tropical Convective Systems and Processes) campaign in the same location and time of year. The free troposphere was drier in TC4 than TCSP, and O<sub>3</sub> 115 116 in the mid-upper troposphere was ~35% higher in TC4 (Figures 1, 3 and 4 in Selkirk et 117 al., 2010). Avery et al. [2010] focus on the strong anti-correlation between ozone and 118 condensed cloud water content measured during sampling in active convection, and 119 generalize their findings on convective redistribution of ozone with tracer composites. 120 Convective outflow as indicated by local O<sub>3</sub> minima and elevated lower tropospheric 121 tracers appears to maximize at 10-11 km. Avery et al. [2010] argue that in the DC-8

122	sampling region near the ITCZ, there has been about 50% convective turnover below the
123	TTL, with vertical transport from just above the boundary layer. In <i>Morris et al.</i> [2010]
124	lower-mid tropospheric $\mathrm{O}_3$ within a convectively active region over the Pacific southwest
125	of the Las Tablas (LTP) launch site on 5 August 2007 is investigated in detail. The LTP
126	sounding for that day was caught in a strongly convective cell that bounced the balloon
127	package up and down between 2.5-5 km; the $\rm O_3$ within this layer increased from 30 to 40
128	ppbv before the balloon ascended to the stratosphere. <i>Petropavlovskikh et al.</i> [2010],
129	analyzing the 17 July 2007 DC-8 flight, find that influences on $O_3$ near the TTL are a
130	mixture of convection and advection, the latter including extra-tropical air, some of it
131	possibly of stratospheric origins. The lowest $\rm O_3$ layer occurred at 9-11 km, but low-O_3
132	signatures were also recorded by the UV-DIAL instrument at 2-4 km and 13 km.

133As insightful as the above investigations are, none systematically examines134dynamic influences in ozone structure in the free troposphere and LS day-by-day during135TC4. That is the purpose of the present study. Using the full record of Alajuela (ACR)136and Las Tablas O3 soundings (Section 2), the following analyses are performed:

- Mean O<sub>3</sub> profiles are determined and day-to-day variability is examined in
   curtains of O<sub>3</sub> mixing ratio and in integrated O<sub>3</sub> column amounts.
- 2) Ozone budgets based on LID and expressed as amounts affected by GW and
   RW provide a consistent framework for examining dynamic influences over the course of
   TC4. The climatology of wave signatures at LTP and ACR is compared to those at
   Paramaribo (5.8N,55W) and San Cristóbal (0.92S,90W) sondes, long-term SHADOZ
   stations also in the equatorial Americas (Section 3.1).

144 3) Case studies of soundings and ancillary aircraft measurements are used to
145 corroborate wave designations, with convection for GW and stratospheric influences or
146 pollution for RW (Section 3.2). One episode is among those analyzed by Avery et al.
147 [2010] and Morris et al. [2010]. Others were chosen to illustrate contrasting impacts.

- 4) In Section 4 context for the TC4 observations is given by June-July-August
  (JJA) Costa Rican sondes in 2006, and the 9-year SHADOZ record [*Thompson et al.*,
  2003a,b] at Paramaribo and San Cristóbal. Specifically we ask:
- 151> How does tropospheric  $O_3$  over LTP and ACR in 2007 compare to JJA  $O_3$  over152Costa Rica (Heredia site near Alajuela) in 2006, when an El Niño affected153the eastern Pacific [Arguez, 2007]? How do LTP and ACR  $O_3$  during TC4154compare to  $O_3$  over San Cristóbal in 2007?

- 155
- 156 157

## > How does O<sub>3</sub> over the equatorial Americas in TC4 compare to the 1999-2006 record? Indices based on GW activity are used to quantify interannual variability.

158

## 2. Experimental. Observations and Methods of Analysis.

## 159 2.1 Ground & Aircraft

Continuous surface O3 measurements at Las Tablas (7.8N,80W) were made during 160 161 the period 13 July to 10 August 2007 from the NATIVE mobile lab that also included an ozonesonde ground station. The surface O<sub>3</sub> was measured with a TECO Model 49 C ozone 162 analyzer, along with carbon monoxide (TECO Model 48CTL), NO and NO<sub>v</sub> (TECO Model 163 164 42CY), SO<sub>2</sub> (TECO Model 43C-TLE) and particle size distribution (Scanning Mobility 165 Particle Sizer). All data can be viewed at <<u>http://ozone.met.psu.edu/NATIVE/</u> measurements.html>. Calibrations of O<sub>3</sub>, CO, and SO<sub>2</sub> were made prior to and directly 166 after the campaign with instrument grade gases (Airgas, Inc.). Calibration of NO and NO<sub>v</sub> 167 168 was performed daily with instrument grade NO (Airgas, Inc.). Catalytic conversion 169 efficiency tested before and after TC4 remained close to 100%.

170

2.2

## **Ozone Profiles and P-T-U Profiles**

171 All ozone profile data analyzed here were taken with electrochemical concentration 172 cell (ECC) instruments coupled with standard radiosondes, as described in Thompson et 173 al. [2003; 2007a]. Coordinates of LTP, ACR and the SHADOZ sites referred to here 174 appear in **Table 1**, along with details of the sondes used. At Las Tablas, the 0.5% KI 175 buffered solution with ENSCI ozonesondes is a combination that optimizes tropospheric and stratospheric O3 measurements [Smit et al., 2007; Thompson et al., 2007b; Deshler 176 et al., 2008]. Vaisala radiosondes, Model RS-80, were used to collect P-T-U data. For 177 178 nine of the 25 LTP soundings during TC4 the humidity data are unreliable above ~300-179 500 hPa due to suspected sensor icing. Ozone profiles from LTP are viewable at 180 <http://ozone.met.psu.edu/Panama\_Data/index.html>. Each ozonesonde is calibrated 181 according to standard procedures prior to launch; all LTP sondes were also compared to the TECO O<sub>3</sub> for 5-10 minutes pre-launch; agreement is within the stated precision of 182 183 each technique (5%; Figure 1 in Morris et al., 2010).

184Ozone over Alajuela was measured by ENSCI ECC sondes with 1% KI with reduced185| (0.1%) buffer (Table 1); RS-80 radiosondes with a cryogenic frost-point hygrometer were186used for P-T-U. At both ACR and LTP, most launches took place in early afternoon local187time to capture Aura [Schoeberl et al., 2006], Aqua and CALIPSO satellite overpasses

[*Toon et al.*, 2010]. Images and data for all Costa Rican (late 2005 start), Paramaribo
(1999-present) and San Cristóbal (1999-present) ozonesonde and P-T-U profiles are
available at <<u>http://croc.gsfc.nasa.gov/shadoz></u> and at the World Ozone and Ultraviolet
Data Centre, <<u>http://woudc.org></u>.

192Aircraft data used most often in analysis of the soundings are: O3 from the193FASTOZ in-situ instrument [Avery et al., 2010], uv-DIAL and DACOM CO on the DC-8;194the Cloud Physics Lidar (CPL) and Cloud Radar System (CRS) on the ER-2 [McGill et al.,1952004; Hlavka et al., 2010]. Regional cloud and convective information comes from196meteorological analyses and GOES imagery, as archived by Toon et al. [2010].

197 2.3 Ancillary Data

198 As for IONS-04 [Thompson et al., 2007a] and IONS-06 [Thompson et al., 2008], tracers for O<sub>3</sub> origins include: (1) RH from the radiosonde P-T-U profiles; (2) Ertel's 199 potential vorticity (pv; 1 pvu =  $10^{-6}$  m<sup>2</sup>s-1/K) computed from the Goddard Earth 200 201 Observing System Assimilation Model (GEOS-version 4; Bloom et al., 2005); (3) forward 202 and backward air-parcel trajectories for each launch location and date, calculated with 203 the kinematic version of the GSFC trajectory model [Schoeberl and Sparling, 1995] using 204 GEOS meteorological fields at a 1x1-degree grid. Lightning imagery is also used to 205 describe potential O<sub>3</sub> influences, as are absorbing aerosol data from OMI, trajectoryenhanced aerosol-exposure images and OMI NO2 amounts. All back-trajectories in the 206 207 TC4 region, aerosol and lightning data and trajectory-mapped exposure products are at 208 the GSFC TC4 website: <http://croc.gsfc.nasa.gov/tc4>. In selected cases, additional 209 trajectories were run with the NOAA Hysplit model (Draxler and Rolph, 2003).

210 2.4

Analysis for Wave Influences

In the LID (Laminar Identification; *Thompson et al.*, 2007a; 2008) technique, O<sub>3</sub>
 and potential temperature (θ) laminae, as described in *Teitelbaum et al.* [1994; 1996] and
 *Pierce and Grant* [1998] are used to identify RW and GW signatures as illustrated in
 **Figure 1**. The method is described as follows:

2151) For each sounding, the  $O_3$  and  $\theta$  laminae are isolated through normalization to216running means. A boxcar smoothing over 2.5 km is used to isolate each lamina.217Larger and smaller ranges (from 0.5 to 2.5 km) have been tested with little218difference in laminar statistics. Normalized  $O_3$  is the solid line in Figure 1; the  $\theta$ 219deviations are signified by the dotted line. Because the ozone mixing ratio

7

220 precision is 5% in most of the region of interest, only laminae representing a 221 1 deviation of  $\geq$  10% are included in the analysis (red vertical lines in **Figure 1**). Correlations between  $O_3$  and  $\theta$  gradients are compared to identify GW and RW. 222 2):223 Where the correlations (as in dashed line, Figure 1) exceed 0.7 GW (light green) 224 is defined, based on the reasoning that such correlation between the two quantities 225 signifies a vertical disturbance. Conversely, when horizontal motion affects O<sub>3</sub>, it 226 is poorly correlated with  $\theta$  and RW is specified. We adopt the practice of *Pierce* 227 and Grant [1998] and Teitelbaum et al., 1994], setting the RW limit for anti-228 correlation at +0.3, corresponding to light blue sections in Figure 1. This is a 1 229 fairly conservative criterion; see *Thompson et al.* [2007a] for sensitivity studies.

230 Two analyses are performed with the LID results. First, for an ensemble of soundings, 231 wave frequencies at a given altitude are calculated from the percentage within a sample set 232 that have laminae designated as RW or GW. Second, for each sounding, the contributions 233 of RW and GW above the boundary layer (BL) to the tropopause or to 20 km are 234 computed by integrating the amount of O<sub>3</sub> within a given layer and adding up all the RW 235 and GW segments. Thus, "tropospheric ozone" amounts in this paper are actually free 236 tropospheric column amounts, above a BL top that varies from 1.2 km (San Cristóbal) to 237 1.8 km (Paramaribo). The BL top is determined by taking the most negative second 238 derivative of  $\theta$  with respect to altitude, between 0.4 and 2.5 km [Yorks et al., 2009]. Dobson Units (DU) are used; one DU =  $2.69 \times 10^{16}$  cm<sup>-2</sup>. The amount of O<sub>3</sub> within the 239 240 column not identified with RW or GW is labeled "other" in the budgets.

241 For determination of tropospheric LID O<sub>3</sub> budgets (Section 3), an ozonopause 242 definition of tropopause is employed (white dots, Figure 2; using the method of Browell et al., 1996). This technique, in which O<sub>3</sub> gradients are approached from the stratosphere, 243 244 falls closer to the cold-point tropopause than the ozonopause of Selkirk et al. (2010; their Figure 2, from Alajuela soundings). Thompson et al. [2007a] showed that tropospheric O<sub>3</sub> 245 columns can differ significantly under certain conditions, depending on the use of  $\rm O_{_3}$  or 246 247 thermal tropopause. Such occurrences are infrequent in mid-latitudes (< 10% in IONS-04 248 or IONS-06 soundings) and are negligible in TC4, where Selkirk et al. (2010) showed that 249 the thermal tropopause and chemical tropopause, based on either water vapor from frost-250 point hygrometry or O<sub>3</sub> mixing ratios, was consistently at 350-355 K (147 hPa, 14.2 km);

the cold-point tropopause was always 370-378K (16-17 km). For a 1-2 km difference in
thermal tropopause and the higher ozonopause, the O<sub>3</sub> budget might vary 2-3 DU.

## 253

## 3. Results and Discussion: July-August 2007

254

### 3.1. Overview of Ozone Profiles over LTP and ACR

255 From time-series of O<sub>3</sub> mixing ratio over Las Tablas and Alajuela (Figure 2) the 256 following features emerge: (1) Roughly 10% more  $O_3$  is found in the LTP BL than at ACR 257 due to pollution from Panamá City and occasionally from South American biomass fires. 258 (2) The TTL extends lower over LTP than over ACR. It is customary to assume that when 259 the free tropospheric segment of an ozone profile resembles BL concentrations that 260 convective redistribution has taken place [Kley et al. 1996; Thompson et al., 1997; Newell 261 et al., 1999, Folkins et al., 2006]. Given typical BL concentrations of 20-25 ppbv at the 262 two sites, Figure 2 suggests that there are fewer episodes of high-altitude convection over 263 LTP than ACR (blue shade, 12-14 km), although that inference may be an artifact of LTP having more samples. Consequently, there is less O<sub>3</sub> in the ACR mean O<sub>3</sub> profile between 264 265 11-14 km (Figure 3a) than LTP (Figure 3b; cf Figure 13 in Avery et al., 2010), giving a slight "S" shape in the ACR O<sub>3</sub> profile. The "S" is similar to Pacific SHADOZ profiles 266 267 (*Folkins et al.*, 2000; 2006; cf *Kley et al.*, [1996]) and to IONS-06 soundings (<<u>http://</u> 268 croc.gsfc.nasa. gov/intexb/ionso6.html>) over Mexico City (19N, 99W) that detected the 269 highest O<sub>3</sub> at 8-9 km and minimum O<sub>3</sub> at 12-14 km (*Thompson et al.*, 2008; Fig 5).

270Convective signatures in DC-8 sampling, registered as locally minimum ozone in271profiles from the FASTOZ instrument, were concentrated between 10 and 11 km [Avery et272al., 2010]. Elevated lower tropospheric tracers such as methyl hydrogen peroxide and273organic bromine-containing constituents (Figures 13-15 in Avery et al., 2010) occur274coincidentally with the lower ozone. Mean DC-8  $O_3$  profiles and the soundings (Figure275**3a**) are somewhat divergent. This is not surprising given that the sondes are at fixed276locations whereas the DC-8 deliberately sampled in the vicinity of active convection.

277

### 3.2 Overview of Wave Signatures in the Sondes

Figure 4a shows that the O<sub>3</sub> labeled GW is concentrated throughout the TTL and lower stratosphere over both LTP and ACR, with frequencies similar to those at the Paramaribo and San Cristóbal SHADOZ sites (Figure 4b). The latter depicts wave frequencies averaged for 1999-2007, which are nearly identical to June-July-August statistics. The waves in Figures 4a,b are similar to other SHADOZ tropical [*Thompson et al.*, 2010a,b] and northern hemisphere subtropical locations (Figure 4 in *Thompson et al.*, 2008). As in *Thompson et al.* [2010a,b], the GW signal in the TTL is more frequent at

- 285
  - the station that is closer to the equator (Las Tablas and San Cristóbal, respectively, in 286 Figures 4a and 4b). However, ACR has a higher GW frequency at 3 and 6 km, where 287 convective outflow often occurs (Section 3.3). Ozone associated with GW is 15-20% of 288 the tropospheric column (Table 2). In half the days with TC4 soundings at both LTP and ACR, LTP O $_3$  at 3-6 km is 40-50 ppbv vs ~30 ppbv over ACR (cf Figure 3 mean O $_3$ 289 290 profiles). Thus, column tropospheric  $O_3$  is ~30% higher over LTP than ACR (**Table 2**).
  - 291

#### **Case Studies with Varying Convective and Wave Influence** 3.3

292 Days with coincident launches at LTP and ACR (Figure 5a) offer an opportunity to 293 compare ozone profiles at the two sites and to use TC4 aircraft data, satellite imagery and 294 meteorological products to interpret convective and wave influences. On all dates 295 illustrated in Figure 5a the profiles display convective signatures typically with >10 DU 296 of column O<sub>3</sub> to 20 km designated as GW. The TC4 period started with a phase 297 characterized by active convection over the Costa Rica-Panamá region and the adjacent 298 Pacific (Section 3.3.1); this corresponds to the left-most section relative to the vertical 299 dashed line in **Figures 5b,c**. This is corroborated by satellite and aircraft imagery in 300 flights through 22 July 2007 [Toon et al., 2010]. In a second phase, from 23 July through 301 2 August (Section 3.3.2), between the two dashed lines in Figures 5b,c, TC4 aircraft 302 continued to sample convection but it was less active at ACR and LTP. The fraction of 303 total O<sub>3</sub> designated GW declined in most soundings (Figures 5b,c), as the GW-affected segments in  $\rm O_3$  profiles retreated from the troposphere to above 17 km. The amount of 304 305 column O<sub>3</sub> affected by RW increased compared to the pre-24 July period. More active 306 convection resumed in a third phase (Section 3.3.3) after 2 August, when targeted 307 sampling by the ER-2, DC-8 and WB-57 took place [Toon et al., 2010]. In the following 308 sections episodes illustrative of the three phases are examined to verify the link between 309 the GW designation and convective activity and the relationship of RW to extra-tropical 310 and/or pollution influences.

311

### 3.3.1 13-22 July 2007: Active Convection and Elevated GW

312 13 July. Convective activity at LTP and ACR, as given by GW amount to 20 km, is 313 similar (Figure 5a). The fraction of FT O<sub>3</sub> influenced by GW is similar in both cases 314 (~20%; Figures 5b,c). A typical pair of profiles (Figure 6a) shows that the ACR O<sub>3</sub> concentration averages ~40 ppbv from the surface to the tropopause (14-15 km), whereas 315 O<sub>3</sub> in the upper troposphere over LTP exceeds 50 ppbv. BL O<sub>3</sub> at LTP is less than at ACR. 316 The RH profiles have considerable structure, with moister air over LTP than ACR. 317

- 318 Evidence for convection over ACR comes from the DC-8 flight from California to San Jose, 319 Costa Rica, on 13 July 2007. The last 100-150 km of the flight encompassed a descent 320 near ACR at ~2100 UTC, after the aircraft had crossed the ITCZ. The DC-8 uv-DIAL image of O<sub>3</sub> (Figure 6b) captures the morphology of convective impact throughout the FT 321 322 and TTL. North of the ITCZ (northern edge at 13N), the FT was penetrated by pollution O<sub>3</sub> 323 (>80 ppbv) and aerosols traced to biomass fires interacting with convection. South of the 324 ITCZ, just before descent, FT O<sub>3</sub> dropped to 40-50 ppbv, except for a localized O<sub>3</sub> minimum (< 30 ppbv) around 10 km (Figure 6b), similar to FT O3 structure over ACR 325 326 (Figure 6a), and to the DC-8 FASTOZ O<sub>3</sub> during descent. Note a very thin layer of low 327 ozone at 13 km in the uv-DIAL image, corresponding to an altitude with low O<sub>3</sub> over ACR. 328 A similar low-O3 "bubble" sampled on 17 July 2007 is discussed by Petropavlovskikh et al., 329 2010s. The uv-DIAL aerosols (not shown) corresponding to Figure 6b indicate a "clean" 330 FT south of the ITCZ except for thin cirrus at the tropopause, consistent with the 331 soundings. Convective indicators, elevated CO, methyl-hydrogen peroxide, lightning NO, 332 ultrafine particles (not shown; see flight report at <<u>http://espo. nasa.gov/tc4/docs></u>), 333 penetrated south of the ITCZ. These pollutants came from north of the ITCZ. 334 Interhemispheric transport during convection is well known over the Atlantic [Jonquières 335 et al., 1998; Thompson et al., 2000; Edwards et al., 2003].
- 336 On 13 July (**Figure 5b,c**) about half the tropospheric  $O_3$  over both LTP and ACR 337 corresponds to RW. The corresponding segments in the ACR profile (**Figure 6a**) are 338 locally enhanced in  $O_3$  and reduced in RH, suggesting extra-tropical influence. This is a 339 good example of a sounding that captures both advective and convective signals.
- **<u>22 July.</u>** On this day there is more O<sub>3</sub> in the TTL and LS identified as GW over 340 LTP than ACR (Figures 5a, 7a). There is relatively little tropospheric O<sub>3</sub> associated with 341 342 GW over either one (Figures 5b,c). A convective contrast between LTP and ACR is 343 evident in satellite imagery (see ER-2 flight report for 22 July 07 at <<u>http://espo.</u> 344 nasa.gov/tc4/docs>). When the ER-2 sampled near LTP on 22 July, the cloud and 345 precipitation CPL-CRS imagery (Figure 7b) indicated several levels of convective 346 outflow. For example, there is cirrus with a 13.5-14 km cloud top, coinciding with a GWlabeled segment in the LTP sounding, right above a localized O3 minimum (black profile, 347 348 Figure 7a). The CPL-CRS indicates another cloud outflow layer at 4 km. This region is not designated as GW although there is a local  $\rm O_3$  minimum at 4 km and relatively high 349 350 RH. From 2-5 km the designation is RW; O<sub>3</sub> is 60% greater than at the surface, suggesting 351 possible pollution transport. Surface ozone at LTP, measured in NATIVE on 22 July,

- 352 averaged 15 ppbv (Figure 8a) but the moderately high CO mixing ratio, 135 ppbv,
- 353 supports an interpretation of pollution (Figure 8b).
- 354

3.3.2. 23 July-2 August: Elevated RW

355 During the period 23-28 July most sonde launches were at LTP. At both sites, the soundings from 23 July to 2 August displayed fractionally higher RW O<sub>3</sub> segments in the 356 357 troposphere (Figure 5b,c). An example appears in Figure 9a. The RW signal over LTP 358 extends from 2 to 17 km on 2 August, except for a 2-km region, and there is no GW 359 segment. ACR displays convective influence in terms of GW only from 11-15 km. An RW 360 segment from 5-10 km coincides with a dry layer from 4-9 km; this is suggestive of air 361 from the extra-tropics. Even though convection picks up on 3 August, remnants of the RW 362 feature persist over both sites on that day (Figure 9b).

363During the period of greater RW, there were also changes in surface  $O_3$  and CO at364| Las Tablas (see NATIVE data in Figure 8). On 23 July a normal diurnal  $O_3$  cycle was365observed, with a near-zero nocturnal minimum. LID analysis for the 23 July sounding at366LTP was not valid, indicating active transition and no stable layers. However, on 24 July367the  $O_3$  minimum rises to ~15 ppbv. This causes daily mean  $O_3$  to increase from 17 ppbv on36823 July to 25 ppbv on 24 July. At this time, CO dropped below 90 ppbv (Figure 8b), one369of the lowest values at NATIVE during TC4.

370

## 3.3.3 3-10 August: Return of Active Convection. Elevated GW

371 **3 August.** The fractions of GW and RW tropospheric segments over Las Tablas 372 and Alajuela are nearly the same (Figures 5b,c) and the wave structures are similar 373 (Figure 9b). Over LTP the GW signal that was absent on 2 August returns at 13-20 km 374 (Figure 9b). The DC-8 and ER-2 sampled not far from LTP near active convection (refer 375 to GOES image with flight tracks for all three aircraft on 3 August; Figure 16 in Toon et al. 376 [2010]). The DC-8 profiles in **Figure 10a** were taken over NATIVE from 1705-1735 UTC 377 during the convective period that was sampled less than 50 km away by the ER-2; the LTP launch took place at 1741 UTC. The upper of two O3 minima over LTP (10-15 km, Figure 378 379 **9b**), corresponds to cloud outflow recorded by satellite imagery (not shown) and to cirrus 380 in the ER-2 CPL-CRS product (Figure 10b) at 13-15 km. A second O<sub>3</sub> minimum with 381 elevated CO at 5-6 km (Figure 10a) is also located at a cloud outflow layer (lower bar 382 arrow in **Figure 10b**). Over ACR, O<sub>2</sub> mixing ratios averaged > 80 ppbv in the 6-13 km 383 1 segment (Figure 9b). Above 8 km, the RH drops off sharply, suggesting extra-tropical 384 air. The elevated O<sub>3</sub> coincides with a mostly RW segment that brackets the tropopause, which is 1.5 km higher over LTP than ACR (Figure 2). 385

- 386 **5** August. During the period 3-5 August there was a sharp transition in the LTP 387 and ACR profiles that is reflected in the O<sub>3</sub> budgets (Figures 5a-c); the GW O<sub>3</sub> budgets to 388 20 km are nearly identical over the two stations on 4 August (Figure 5a). The upper tropospheric O3 mixing ratios decline over both sites, from a mean of ~75 ppbv on 3 389 390 August to 45 ppbv on 5 August (Figures 9b,c); during the transition, LTP free 391 tropospheric O3 declines to 22 DU on 4 August, the lowest O3 column in the TC4 period (Figure 5b). From 4 to 5 August there are further transitions in vertical O<sub>3</sub> structures 392 393 over ACR and LTP (Figure 9c). The GW signal that starts over LTP (ACR) at 12 km (11 394 km) on 4 August (not shown) retreats to 15 km on 5 August. Over Las Tablas a several-km 395 thick layer that is 20 ppbv above background coincides with RW (Figure 9c; also Figure 396 1). DC-8 aircraft sampling near LTP on 5 August confirmed the possibility of extra-397 tropical origins at 8-10 km, where O<sub>3</sub> mixing ratios were 50-70 ppbv in a relatively dry 398 layer [Avery et al., 2010]. However, just above this layer, at 11 km, the DC-8 noted cleaner 399 than usual conditions, signifying convective outflow of marine boundary layer air (upper 400 outflow on Figure 10c). Near the surface, the DC-8 detected pollution due to biomass 401 fires (Flight notes at <http://www.espo.nasa.gov/tc4/flightDocs.php>).
- 402 The 5 August ozonesonde launch at LTP (1505 UTC) was timed for nearby DC-8 403 spiral (~1540 UTC) and ER-2 sampling of convective cells to the southwest (Figure 10c; 404 cf Figure 19 in Toon et al., 2010). Between 2.5 km and 5.1 km, the sonde bounced up and 405 down five times within a convective cell while  $O_3$  concentrations increased by ~10 ppbv. 406 Morris et al. [2010] use satellite imagery, lightning data, radar and OMI NO2 maps, along 407 with DC-8 measurements to demonstrate that lightning NO production is responsible for 408 much of the increase. The lower outflows in Figure 10c correspond to the region of the 409 bouncing sonde. The profile in Figure 9c is based on the final sonde ascent from 2.5 to 410 5.1 km; the GW signal is not detected.
- 411

## 4. Waves in the Equatorial Americas: 1999-2007. TC4 in Context.

412 A perspective for interpreting convective influence over LTP and ACR is provided 413 by wave frequencies over Paramaribo and San Cristóbal (Figure 4b), SHADOZ sites 414 operating since 1999 [Thompson et al., 2003a,b]. The amplitudes of individual layers and 415 wave structure at Paramaribo and San Cristóbal resemble those for LTP and ACR (Figure 416 1) as do the structure of the GW frequencies at LTP and ACR (Figures 4a,b). Similar GW 417 structure appears over equatorial Indian Ocean sites, eg Watukosek, Kuala Lumpur, that 418 display the highest annually averaged GW frequency, ~60% [Thompson et al., 2010a]. The higher GW frequency at San Cristóbal leads to a larger GW fraction of tropospheric O<sub>3</sub> 419

- 420(Figure 11). Although the tropospheric  $O_3$  column averaged 25 DU in 2007, compared to42128 DU for LTP, 25% of  $O_3$  is GW-affected at San Cristóbal compared to 15% at LTP (Table4222). TC4 was timed for the onset of the sub-tropical convective season and the North423American monsoon. Figure 4c, a summary of monthly averaged GW over Paramaribo,424shows that JJA has about half the maximum GW frequency, typically a December425occurrence.
- 426 An interannual view of ozone budgets and convective influence appears in **Figure** 427 11, where the mean JJA tropospheric  $O_3$  column (with segments for RW and GW) is 1 428 displayed for Costa Rica (2006 only), Paramaribo and San Cristóbal from 1999-2007. At 429 San Cristóbal, 2006 is a low-O, year compared to the six others, possibly due to a 430 moderate El Niño [Arguez, 2007]. In the eastern Pacific, El Niño tends to enhance 431 convective activity, mixing lower O<sub>3</sub> air from the BL throughout the troposphere. [Logan 432 et al., 2008]. The GW-affected tropospheric ozone amount in 2006 is only slightly lower 433 than normal over San Cristóbal but the total tropospheric column dropped from a mean 434 22-23 DU (1999-2005; Figure 11) to 18 DU so the GW fraction is magnified. At Heredia (20 km away) 2006 tropospheric  $O_3$  is lower than over ACR in 2007 (Figure 11). 435
- 436 General meteorological conditions at Paramaribo (6N), Panamá (8N), and Alajuela 437 (10N) are similar, with the ITCZ migrating over each. The SHADOZ wave climatology 438 [Loucks, 2007; Thompson et al., 2010] shows GW frequency diminishing with increasing 439 latitude. A GWI (Gravity Wave Index; Figure 12), based on the fraction of the O<sub>3</sub> column 440 to 20 km denoted as GW, provides a quantitative comparison of site-to-site and 441 interannual variability. GWI is larger at San Cristóbal than Paramaribo until 2004 when 442 data gaps at San Cristóbal compromise the record. The gaps also preclude conclusive 443 linkage of GWI to signals associated with an El Niño.

444 <u>5. Summary</u>

445 During TC4, in July and early August 2007, ozonesondes and radiosondes were 446 launched several times/week at Alajuela, Costa Rica (10N,84W) to characterize convective 447 influences in the tropical tropopause layer (TTL). At Las Tablas, Panamá (7.8N, 8oW), a coastal site 300 km southwest of Panamá City, O<sub>3</sub> profiles from daily sondes, surface O<sub>3</sub>, 448 449 CO and other tracers are analyzed. Laminar identification provides a systematic approach 450 to classifying wave signatures in sounding data, giving a statistical perspective on the TC4 451 period and the longer-term SHADOZ sounding record at Paramaribo and San Cristóbal. 452 The findings are summarized:

- GW influences, possibly due to semi-permanent Kelvin waves in the TTL and lower
   stratosphere (cf *Grant et al.*, 1998; *Thompson et al.*, 2010a) appeared in 50%
   (40%) of Las Tablas (Alajuela) sondes. The GW structure and frequency are similar
   to those over SHADOZ stations at San Cristóbal and Paramaribo.
- On average there is 35-40% more tropospheric column O<sub>3</sub> at LTP than ACR during
   TC4 and 20% more at LTP than at San Cristóbal, a remote marine station, 1400 km
   southwest of LTP.
- June-July-August O<sub>3</sub> budgets at Paramaribo and San Cristóbal suggest that 2007
   was a "typical" year in terms of tropical equatorial O<sub>3</sub> amount and convective
   activity expressed in GW frequency. During 1999-2006, Paramaribo and San
   Cristóbal display O<sub>3</sub> column amounts and convective influence that bracket the TC4
   ACR and LTP values.

465 Classification of wave types through LID is validated through case studies in which 466 aircraft observations support interpretation of convective influences (with the GW designation) and extra-tropical impact, corresponding to RW. Laminae of low-O3 surface 467 468 air convectively injected into the free troposphere are detected by LID, frequently 469 interleaved with the richer-O<sub>3</sub> layers; subtle day-to-day variations are captured. The 470 pattern of convection inferred from LID is consistent with the meteorological evolution of 471 the campaign [Toon et al., 2010]. The early part of TC4, to 22 July 2007, was 472 characterized by persistent GW throughout the free troposphere and TTL. After a less active period, from 23 July until approximately 2 August, with lower GW signals and 473 474 greater RW, GW increased in frequency along with convection.

475 Sonde and aircraft data established further the convection-GW linkage and demonstrated the prevalence of extra-tropical laminae interleaved with layers from 476 477 convective outflow throughout the equatorial Americas. In terms of TC4 objectives, our 478 analysis of ozone structure strengthens the case for convection as a dominant mechanism 479 for water vapor transport and cirrus formation in the TTL. The persistence of higher-O<sub>2</sub> 480 laminae in the troposphere requires further investigation to determine the extent to which 481 these layers are remnants of extra-tropical filaments or associated with localized 482 equatorial waves.

<sup>483</sup>Acknowledgments.We are grateful to NASA's Upper Air Research Program and Aura Validation (M. J.484Kurylo; K. W. Jucks) that sponsored the Las Tablas and Alajuela TC4 soundings and ground-based485measurements at Las Tablas. These programs, with NOAA support, also sponsor SHADOZ at Costa Rica486and San Cristóbal. The Paramaribo station is sponsored by KNMI and the Suriname Meteorological487Department. Additional analysis support came from NASA's Tropospheric Chemistry Program (J. H.

- 488 Crawford, J. A Al-Saadi). Las Tablas measurements with the NATIVE trailer were assisted by A. Pino and
- 489 L. Jordan (University of Panamá); A. M. Bryan and D. Lutz (Valparaiso Univ); Z. Chen and J. L. Tharp
- 490 (PSU). Costa Rican launches were made by UNA students K. Cerna, V. H. Beita, D. Gonzalez. Thanks to
- 491 Mission Scientists M. R. Schoeberl and P. A. Newman for flight notes and to K. E. Pickering for
- 492 discussing lightning data. Thanks to EAB, BvdW, AOG (PSU) for analysis.

#### 493 APPENDIX. ABBREVATIONS AND ACRONYMS

- 494 ACP= Alajuela, Costa Rica (10N, 84W)
- 495 BL = Boundary Layer, here determined from radiosondes (*Yorks et al.* 2009)
- 496 CALIPSO = Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation
- 497 CPL = Cloud Physics Lidar (ER-2 instrument)
- CRS = Cloud Radar System (ER-2 instrument) 498
- $DU = Dobson Unit (1 DU = 2.69 \times 10^{16} cm^{-2})$ 499
- ECC = Electrochemical Concentration Cell (ozonesonde type) 500
- 501 FT = Free Troposphere
- 502 **GOES** = Geostationary Operational Environmental Satellites
- GSFC = Goddard Space Flight Center 503
- 504 GWI = Gravity Wave Index
- 505 INTEX = Intercontinental Transport Experiment (-A, 2004; B, 2006)
- 506 IONS = INTEX Ozonesonde Network Study < http://croc.gsfc.nasa.gov/intex/ions.html; ... 507 intexb/ionso6>
- 508 ITCZ = Intertropical Convergence Zone
- JJA = June-July-August 509
- 510 LTP = Las Tablas, Panamá (7.8N, 80W)
- 511 NASA = National Aeronautics and Space Administration
- 512 **OMI** = Ozone Monitoring Instrument
- 513 P-T-U = Pressure-Temperature-Humidity
- 514 RH = Relative Humidity
- 515 RWI = Rossby Wave Index
- 516 SHADOZ = Southern Hemisphere Additional Ozonesondes 517
  - <http://croc.gsfc.nasa.gov/shadoz>
- 518 SOWER = Stratospheric Ozone and Water Vapor in Equatorial Regions
- TC4 = Tropical Composition, Clouds and Climate Coupling (2007) 519
- 520 <http://espo.nasa.gov/tc4>
- 521 TCSP = Tropical Convective Systems and Processes (Costa Rica, 2005) 522
  - TTL = Tropical Tropopause Layer (sometimes tropopause transition layer)
- 523 UV-DIAL = Ultraviolet Differential Airborne Lidar [Laser Detection and Ranging]

524 Table 1. Stations for which data are used. Further technical details given in Table A-1 in 525 Thompson et al. (2003a) and in Thompson et al. (2007b).

526	Station I	atitude,	Instrument 7	Type,	Radiosond	le Co-Investigator/
527	L	ongitude S	Sensing Solut	tion		Sponsor
528	Las Tablas	7.8N, 80W	ENSCI, 0.5%	KI, buffered	RS-80-15N	G. A. Morris, A. M. Thompson
529	Heredia/Alaj	uela, 10.0N,	84 W ENSCI, 1	% KI,	RS-80&	H. Vömel; J. Valverde Canossa
530			buffere	d Cry	ogenic Frost	-point hygrometer
531	San Cristóba	l 0.92S, 89	.6W ENSCI	2% unbuffe	red RS-80	H. Vömel. INAMHI (National
532			to 2000	5; 1%, reduce	ed	Inst. of Hydrology and
533			buffer,	2006-		Meteorology of Ecuador), M. V. A.
534						Reyes [Johnson et al., 2002; Thompson
535						<i>et al.</i> , 2007b]
536	Paramaribo	5.8N,55V	V SPC, 1	% KI buffere	d RS-80 to 2	2005 G. Verver & Met. Service
537					RS-92, 200	5- Suriname [Peters et al.,
538						2003; Fortuin et al., 2006]

540		<b>Table 2.</b> Free tropospheric ozone columns during June-July-August						
541	2007. ACR mean omits 28 July sounding where data ended below the tropopause.							
542	Station	GW O <sub>3</sub>	RW O <sub>3</sub>	Other O <sub>3</sub>	Total			
543	ACR - DU	2.9	8.2	9.3	20.4			
544	ACR - %	14	40	46	100			
545	LTP - DU	3.94	13.2	10.8	28			
546	LTP - %	15	47	38	100			
547	San Cris DU	5.5	7.5	12	25			
548	San Cris %	24	28	48	100			

#### 549 References

539

558

559

560

561

562

563

564

565

566

567

568

569

570

571 572

573

574

575

576

577

578

579

580

581

582

583

550 Arguez, A., ed. (2007): State of the climate in 2006. Bull. Am. Meteor. Soc, 88, S1-S135.

551 Avery, M. A., J. Joiner, C. Twohy, D. McCabe, E. Atlas, D. Blake, P. Bui, J. Counse, J. Dibb, G. 552 Diskin, R. Gao, P. Lawson, M. McGill, D. Rogers, G. Sachse, R. Salawitch, E. Scheuer, 553 K. Severance, A. M. Thompson, C. Trepte, P. Wennberg, J. Ziemke, (2010) Convective 554 distribution of tropospheric ozone and tracers in the central American ITCZ Region: 555 Evidence from observations during TC4, J. Geophys. Res., doi: 10.1029/2009 556 JD013450, in press. Manuscript available at TC4 website. Contact 557

btoon@lasp.colorado.edu for password.

- Bertram, T., et al. (2007), Direct measurements of the convective recycling of the upper troposphere, Science, 315, 816-820, doi:10.1126/science.1134548.
- Bloom, S., et al. (2005), Documentation and validation of the Goddard Earth Observing System (GEOS) data assimilation system - Version 4. Technical Report Series on Global Modeling and Data Assimilation 104606.
- Browell, E. V., et al. (1996), Ozone and aerosol distributions and air mass characteristics over the South Atlantic Basin during the burning season, J. Geophys. Res., 101, 24,043-24,068.
- Cooper, O. R., et al. (2006), Large upper tropospheric ozone enhancements above mid-latitude North America during summer: In situ evidence from the IONS and MOZAIC ozone networks, J. Geophys. Res., 111, D24S05, doi: 10.1029/2006JD007306.
  - Deshler, T., et al. (2008), Balloon experiment to test ECC-ozonesondes from different manufacturers, and with different cathode solution strengths: Results of the BESOS flight, J. Geophys. Res., 113, D04307, doi:10.1029/2007JD008975.
  - Dougherty, K. M. (2008), The effect of ozonopause placement on tropospheric ozone budgets: An analysis of ozonesonde profiles from selected IONS-06 sites, MS Thesis, The Pennsylvania State University.
- Draxler, R. R., and G. D. Rolph (2003), HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model, http://www.arl.noaa.gov/ready/hysplit4.html, NOAA Air Resour. Lab., Silver Spring, MD.
- Edwards, D. P., et al. (2003), Tropospheric ozone over the tropical Atlantic: A satellite perspective, J. Geophys. Res., 108, 4237, doi: 10.1029/2002JD002927.
- Fast, J. D., et al. (2007), A meteorological overview of the MILAGRO field campaign, Atmos. Chem. Phys. 7, 2233-2257.
- Folkins, I., S. J. Oltmans, and A. M. Thompson (2000), Tropical convective outflow and nearsurface equivalent potential temperatures, Geophys. Res. Lett., 27, 2549-2552.

- 584Folkins, I., P. Bernath, C. Boone, K. Walker, A. M. Thompson, and J. C. Witte (2006), The585seasonal cycles of O3, CO and convective outflow at the tropical tropopause, Geophys.586Res. Lett., 33, L16802, doi:10.1029/2006GL026602.
  - Fortuin, P., et al. (2007), Origin and transport of tropical cirrus clouds observed over Paramaribo, Suriname (5.8°N, 55.2°W), *J. Geophys. Res.*, **112,** D09107, doi:10.1029/2005JD006420.

587

588

589

593

594

595

596

597

598 599

600

601

602

603

604

605

606

607

608

609

610

611

612

613

614 615

616

617

618

619

620

621

622

623

624

625

626

627

628

629

630

631

632

- Fueglistaler, S., A. E. Dessler, T. J. Dunkerton, I. Folkins, Q. Fu, and P. W. Mote (2009),
   Tropical tropopause layer, *Rev. Geophys.*, 47, RG1004, doi:10.1029/2008RG000267.
   Fuijwara, M., K. Kita, and T. Ogawa (1998). Stratosphere-troposphere exchange of ozone
  - Fujiwara, M., K. Kita, and T. Ogawa (1998), Stratosphere-troposphere exchange of ozone associated with the equatorial Kelvin wave as observed with ozonesondes and rawinsondes, *J. Geophys. Res.*, **103**, No. D15, 19,173-19,182.
    - Fujiwara, M., F. Hasebe, M. Shiotani, N. Nishi, H. Vömel, and S. J. Oltmans (2001), Water vapor control at the tropopause by equatorial Kelvin waves observed over the Galápagos, J. Geophys. Res., 28, 3143-3146.
    - Grant, W. B., R. B. Pierce, S. J. Oltmans, and E. V. Browell (1998), Seasonal evolution of total and gravity wave induced laminae in ozonesonde data in the tropics and subtropics, *Geophys. Res. Lett.* **25**, 1863-1866.
    - Hasebe, F., M. Fujiwara, N. Nishi, M. Shiotani, H. Vömel, S. Oltmans, H. Takashima, S. Saraspriya, N. Komala, and Y. Inai (2007), In situ observations of dehydrated air parcels advected horizontally in the Tropical Tropopause Layer of the western Pacific, *Atmos. Chem. Phys.*, 7, 803-813.
      - Hlavka, D., L. Tian, W. Hart, L. Li, M. McGill, and G. Heymsfield (2010), Vertical cloud climatology during TC4 derived from high-altitude aircraft merged lidar and radar, J. *Geophys. Res.*, this issue.
    - Johnson, B. J., S. J. Oltmans, H. Vömel, T. Deshler, C. Kroger, and H. G. J. Smit (2002), ECC ozonesondes pump efficiency measurements and sensitivity tests of buffered and unbuffered sensor solutions, *J. Geophys. Res.*, *107*(D19), 4393, doi: 10.1029/2001JD000557.
    - Jonquières, I., A. Marenco, A. Maalej, and F. Rohrer (1998), Study of ozone formation and transatlantic transport from biomass burning emissions over West Africa during the airborne Tropospheric Ozone Campaigns TROPOZ I and TROPOZ II, *J. Geophys. Res.*, **103**, 19,059–19,073.
      - Kley, D., P. J. Crutzen, H. G. J. Smit, H. Vömel, S. J. Oltmans, H. Grassl and V. Ramanathan (1996) Observations of near-zero ozone over the convective Pacific: Effects on air chemistry, *Science*, 274, 230-233.
      - Logan, J. A., I. Megretskaia, R. Nassar, L.T. Murray, L. Zhang, K.W. Bowman, H.M. Worden, and M. Luo (2008), Effects of the 2006 El Nino on tropospheric composition as revealed by data from the TES, *Geophys. Res. Lett.*, **35**, L03816, doi:10.1029/2007GL031698.
    - Loucks, A. L. (2007), Evaluation of dynamical sources of ozone laminae in the tropical troposphere and tropical tropopause layer, M.S. Thesis, Penn State University.
  - McGill, M. J., L. Li, W. D. Hart, G. M. Heymsfield, D. L. Hlavka, P. E. Racette, L. Tian, M. A. Vaughan, and D. M. Winker (2004), Combined lidar-radar remote sensing: Initial results from CRYSTAL-FACE, *J. Geophys. Res.*, **109**, D07203, doi:10.1029/2003JD004030.
    - Morris, G. A., et al. (2010), Observations of ozone production in a dissipating convective cell during TC4, *J. Geophys. Res.*, doi: 10.1029/2009JD 014098, submitted. Manuscript available at TC4 website. Contact <u>btoon@lasp.colorado.edu</u> for password.
    - Newell, R. N., V. Thouret, J. Y. N. Cho, P. Stoller, A. Marenco, and H. G. Smit (1999), Ubiquity of quasi-horizontal layers in the troposphere, *Nature*, **398**, 316-319.
- 634 Oltmans, S.J., et al. (2001), Ozone in the Pacific tropical troposphere from ozonesonde
   635 observations, J. Geophys. Res., 106, 32503-32526.

636 Oltmans, S. J., et al. (2004), Tropospheric ozone over the North Pacific from ozonesonde 637 observations, J. Geophys. Res., 109, D15S01, doi: 10.1029/2003JD003466. 638 Peters, W., P. Fortuin, H. Kelder, C.R. Becker, J. Lelieveld, P.J. Crutzen, and A.M. Thompson 639 (2004), Tropospheric ozone over a tropical Atlantic station in the Northern 640 Hemisphere: Paramaribo, Surinam (6°N, 55°W), Tellus, 56, 21-34. 641 Petropavloskikh, I., E. Ray, S. M. Davis, K. Rosenlof, G. Mannev, R. Shetter, S. Hall, K. 642 Ullmann, L. Pfister, J. Hair, M. Fenn, M. Avery, and A. M. Thompson, (2010) Low ozone 643 bubbles observed in the tropical tropopause layer during the TC4 campaign in 2007, J. 644 Geophys. Res., doi: 10.1029/2009JD012804, in press. Manuscript available at TC4 645 website. Contact btoon@lasp.colorado.edu for password. 646 Pierce, R. B., and W.B. Grant (1998), Seasonal evolution of Rossby and gravity wave induced 647 laminae in ozonesonde data obtained from Wallops Island, Virginia, Geophys. Res. 648 Lett., 25, 1859-1862. 649 Piotrowicz, S. R., H. Bezdek, G. Harvey, and M. Springer-Young (1991), On the ozone minimum 650 over the equatorial Pacific Ocean. J. Geophys. Res. 96, 18679-18687. 651 Randel, W. J., D. J. Seidel, and L. L. Pan (2007), Observational characteristics of double 652 tropopauses, J. Geophys. Res., 112, D07309, doi:10.1029/2006JD007904. 653 Randriambelo, T., J-L. Baray, S. Baldy, A. M. Thompson, S. J. Oltmans, and P. Keckhut (2003), 654 Investigation of the short-term variability of tropical tropospheric ozone, Annales 655 Geophysiques, 21, 2095-2106. 656 Read, K. A. et al. (2008), Extensive halogen-mediated ozone destruction over the tropical 657 Atlantic Ocean, Nature, 453, 1232-1235, doi: 10.1038/nature07035. 658 Schoeberl, M. R., and L.C. Sparling (1995), Trajectory modeling: Diagnostic tools in 659 atmospheric physics, S. I. F. Course CXVI, edited by G. Fiocco and C. Visconti, North-660 Holland, Amsterdam. 661 Schoeberl, M. R., et al. (2006), Overview of the EOS aura mission, IEEE Trans., 44 (5), 1066-662 1074, doi:10.1109/TGRS.2005.861950. 663 Selkirk, H. B., H. Vömel, J. M. Valverde Canossa, L. Pfister, J. A. Diaz, W. Fernández, J. 664 Amador, W. Stolz, and G. Peng, The detailed structure of the tropical upper troposphere 665 and lower stratosphere as revealed by balloonsonde observations of water vapor, ozone, 666 temperature and winds during the NASA TCSP and TC4 Campaigns, J. Geophys. Res., 667 in press. \*\* Manuscript available at TC4 website. Contact btoon@lasp.colorado.edu for 668 password. 669 Smit, H. G. J., et al. (2007), Assessment of the performance of ECC-ozonesondes under quasi-670 flight conditions in the environmental simulation chamber: Insights from the Jülich 671 Ozone Sonde Intercomparison Experiment (JOSIE), J. Geophys. Res., 112, D19306, doi: 672 10.1029/2006JD007308. 673 Takashima, H., and M. Shiotani (2007), Ozone variation in the tropical tropopause layer as 674 seen from ozonesonde data, J. Geophys. Res., 112, D11123, 675 doi:10.1029/2006JD008322. 676 Teitelbaum, H., J. Ovarlez, H. Kelder, and F. Lott (1994), Some observations of gravity-wave-677 induced structure in ozone and water vapour during EASOE, Geophys. Res. Lett., 21, 678 1483-1486. 679 Teitelbaum, H., et al. (1996), The role of atmospheric waves in the laminated structure of ozone 680 profiles at high latitude. Tellus, 48A, 442-455. 681 Thompson, A. M., et al. (1993), SAGA-3 ozone observations and a photochemical model 682 analysis of the marine boundary layer during SAGA-3, J. Geophys. Res., 98, 16955-683 16968. 684 Thompson, A. M., et al. (1996), Where did tropospheric ozone over southern Africa and the 685 tropical Atlantic come from in October 1992? Insights from TOMS, GTE/TRACE-A and 686 SAFARI-92, J. Geophys. Res., 101, 24,251-24,278. 687 Thompson, A. M., W.-K. Tao, K. E. Pickering, J. R. Scala, and J. Simpson (1997), Tropical deep 688 convection and ozone formation, Bull. Amer. Met. Soc., 78, 1,043-1,054.

- Thompson, A. M., B. G. Doddridge, J. C. Witte, R. D. Hudson, W. T. Luke, J. E. Johnson, B. J.
  Johnson, S. J. Oltmans, and R. Weller (2000), A tropical Atlantic paradox: Shipboard
  and satellite views of a tropospheric ozone maximum and wave-one in JanuaryFebruary 1999, Geophys. Res. Lett., 27,3317-3320.
- 693Thompson, A. M., et al. (2003a), Southern Hemisphere Additional Ozonesondes (SHADOZ)6941998-2000 tropical ozone climatology. 1. Comparison with TOMS and ground-based695measurements, J. Geophys. Res., 108, 8238, doi: 10.1029/2001JD000967.
- 696Thompson, A. M., et al. (2003b), Southern Hemisphere Additional Ozonesondes (SHADOZ)6971998-2000 tropical ozone climatology. 2. Tropospheric variability and the zonal wave-698one, J. Geophys. Res., 108, 8241, doi: 10.1029/2002JD002241.
- Thompson, A. M., et al. (2007a), IONS (INTEX Ozonesonde Network Study, 2004). 1.
  Summertime UT/LS (Upper Troposphere/Lower Stratosphere) ozone over northeastern
  North America, J. Geophys. Res., 112, D12S12, doi: 10.1029/2006JD007441.
  Thompson, A. M., J. C. Witte, H. G. J. Smit, S. J. Oltmans, B. J. Johnson, V. W. J. H. Kirchhoff,
  - Thompson, A. M., J. C. Witte, H. G. J. Smit, S. J. Oltmans, B. J. Johnson, V. W. J. H. Kirchhoff, and F. J. Schmidlin (2007b), Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2004 tropical ozone climatology. 3. Instrumentation, station variability, evaluation with simulated flight profiles, J. Geophys. Res., 112, D03304, doi: 10.1029/2005JD007042.
  - Thompson, A. M., J. E. Yorks, S. K. Miller, J. C. Witte, K. M. Dougherty, G. A. Morris, D. Baumgardner, L. Ladino, and B. Rappenglueck (2008), Tropospheric ozone sources and wave activity over Mexico City and Houston during Milagro/Intercontinental Transport Experiment (INTEX-B) Ozonesonde Network Study, 2006 (IONS-06), Atmos. Chem. Phys., 8, 5113-5125.
    - Thompson, A. M., A. L. Loucks, S. Lee, S. K. Miller (2010a), Gravity and Rossby wave influences in the tropical troposphere and lower stratosphere based on SHADOZ (Southern Hemisphere Additional Ozonesondes) soundings, 1998-2007, J. Geophys. Res., doi: 10.1029/2009JD013429, submitted.
      - Thompson, A. M., S. J. Oltmans, D. W. Tarasick, P. Von der Gathen, H. G. J. Smit, J. C. Witte (2010b), Strategic ozone sounding networks: Review of design and accomplishments, *Atmos. Environ.*, in press.
      - Toon, O. B., et al. (2010), Planning and implementation of the Tropical Composition, Cloud and Climate Coupling Experiment (TC4), *J. Geophys. Res.*, this issue. Manuscript available at TC4 website. Contact <u>btoon@lasp.colorado.edu</u> for password.
    - Torres, A. L., and A. M. Thompson (1993), Nitric oxide in the equatorial Pacific boundary layer: SAGA-3 measurements, *J. Geophys. Res.*, **98**, 16949-16954.
    - Yorks, J. E., A. M. Thompson, E. Joseph, and S. K. Miller (2009), The variability of free tropospheric ozone over Beltsville, Maryland (39N, 77W) in the summers 2004-2007, *Atmos. Environ.*, **43**, 1827-1838.
    - Zafiriou, O. C., M. McFarland, and R. H. Bromund (1980) Nitric oxide in seawater, Science, **207**, 637-639, 1980.

### FIGURE CAPTIONS -

703

704

705

706

707

708

709

710

711

712

713

714

715

716

717

718

719

720

721

722

723

724

725

726

727

728

Fig 1 Application of laminar identification (LID) method to typical sounding from Panamá. Illustrated are normalized  $O_3$  (solid line), potential temperature (dotted line) and correlation between the two quantities (dashed). Correlation criteria for Rossby waves (RW) are within vertical lines between -0.3 and +0.3 (light blue). The latter designation is used in discussion of profiles and budgets. Gravity wave (GW) criterion of *Pierce and Grant* (1998; see their Figure 1) and *Thompson et al.* (2007a; Figure 3) calls for normalized  $O_3$  and  $\theta$  correlation to reach 0.7 (vertical line; light green for budgets). For

computation of the GW Index, a more restrictive criterion is used, namely, the corresponding O<sub>3</sub> layer amplitude must exceed 0.1 (10%), as in the darker green. An RW Index, not used here, is based on counting only ozone within dark blue. Fig 2 Curtain plots of O<sub>3</sub> mixing ratio to 18 km during TC4 over (a) Alajuela, Costa Rica (ACR); (b) Las Tablas, Panamá (LTP). White dots refer to the ozonopause as described in the text. Fig 3 Mean profiles of ozone, temperature, relative humidity (RH) from surface to 20 km for: (a) Alajuela, Costa Rica (ACR); eight O<sub>3</sub> profiles with slight interference from volcanic SO<sub>2</sub> have been smoothed at 3 km. For comparison, mean DC-8 profiles from the FASTOZ ozone instrument (green dots) are displayed. The profiles include landing and takeoffs from San Jose airport near Alajuela. (b) Las Tablas, Panamá. In the latter case, seven questionable RH profile segments are omitted from mean. Fig 4 (a) Frequency of GW occurrence over LTP, ACR during July-August 2007 TC4 sampling; (b) mean GW frequency over Paramaribo and San Cristóbal, based on all 1999-2007 profiles. For (b) J-J-A and full year means are virtually the same because J-J-A frequencies fall about halfway between the annual maximum and minimum frequencies. Paramaribo did not launch during TC4; (c) annual GW frequency at Paramaribo. The latter is typical of near-equatorial SHADOZ sites [Thompson et al., 2010a]. Fig 5 (a) Amounts of O<sub>3</sub> (in DU) from top of the BL to 20 km, affected by GW, RW determined by LID [Thompson et al., 2007a] based on O3 and P-T-U soundings from days with both Las Tablas (LTP) and Alajuela (ACR) launches during TC4. (b) Same as (a) except for free tropospheric O<sub>3</sub> segment of all LTP soundings during TC4. The free troposphere is defined from the top of the BL to the ozonopause, as illustrated in Figure 2; (c) same as (b) for O<sub>3</sub> over ACR. The vertical dashed line distinguishes phases of convective activity (greater before 23 July 2007 and after 2 August, diminished in between), as detected in the sondes. (a) Ozone, RH, temperature profiles at ACR and LTP for 13 July 2007. Vertical bars refer to RW Fig 6 (blue) and GW (green) as described in Figure 1. (b) Uv-DIAL image of ozone from DC-8 flight from California to Costa Rica. Ozone < 40 ppbv, purple, is near surface and also at cloud outflow level, ~ 10 km, south of the ITCZ; the latter is the cloudy region at 1945 UTC.

Note a thin cloud-outflow ozone lamina at 13 km.

- Fig 7 (a) Ozone, RH, temperature profiles at ACR and LTP for 22 July 2007. (b) convective cells with outflow layers denoted by arrows on 22 July 2007 near LTP from ER-2 Cloud Physics Lidar and Cloud Radar System composite image [*Hlavka et al.*, 2010].
- Fig 8 Daily mean mixing ratios of (a)  $O_3$ ; (b) CO, from NATIVE in Las Tablas, Panamá (7.8N,80.0N). NATIVE CO readings are higher than the median DC-8 profile data (Figure 2 in *Avery et*

	al., 2010), although NATIVE NO/NO $_{\rm y}$ and SO $_{\rm 2}$ suggest that pollution is infrequent,
Fig 9	Profiles from August 2007 TC4 sampling (a) 2 August 2007; (b) 3 August; (c) 5 August.
	Labels as in Figure 6a. For 5 August, the DC-8 $\mathrm{O_3}$ measurement from profiling near LTP
	displayed a high-O3, low-CO layer [ <i>Avery et al.,</i> 2010] at 8-10 km. Also on 5 August, the
	ozonesonde package, caught in dissipating convection, was buffeted in updrafts and
	downdrafts between 2 and 5 km, presumably due to balloon icing [Morris et al., 2010].
	Only the final ascent profile appears in (c), so a GW signal indicating convection does not
	appear below 7 km. However, the RW segment may denote ozone from pollution.
Fig 10	(a) Ozone, CO from DC-8 spiral on 3 August 2007 at 1505-1535 UTC, suggests extra-
	tropical influence at 6-8 km, with convection at 5 km and above 8 km. (b) 3 Aug 2007 ER-
	2 sampling produced composite CPL-CRS image with convective cells (outflow at
	horizontal arrows) at 7.5N, 80.5W. Vertical arrows mark LTP sonde launch. (c) Same as
	(b) except for 5 August.
Fig 11	Averaged ozone amounts (in DU) in the free troposphere affected by GW, RW determined
	by the laminar method using all $\mathrm{O_3}$ and P-T-U sounding from J-J-A 1999-2007 for San
	Cristóbal, Galapagos (0.89S,90W) and Paramaribo, Suriname (5.8N,55E) and, since 2005,
	for two Costa Rican launch sites near San Jose (Heredia in 2005-2006; Alajuela, ~20 km
	distant, in 2007). The 2007 data at Las Tablas, Panamá, are from TC4. BL $O_3$ amounts
	(not shown) are 2 DU at San Cristóbal, 3.5 DU at Paramaribo and the Costa Rican sites.
Fig 12	Gravity wave Indices (GWI) based on $O_{_3}$ and P-T-U soundings from the Paramaribo and San

Cristóbal SHADOZ sites.































FIGURE 9 (continued)







# Mean J-J-A Free Tropospheric Ozone



Location and Year

