Low ozone bubbles observed in the tropical tropopause layer during the TC4 campaign in 2007.

Petropavlovskikh I.[1,2], E. Ray[1,2], S. M. Davis[1,2], K. Rosenlof[2], G. Manney[3], R. Shetter[4], S. Hall[4], K. Ullmann[4], L. Pfister[5], J. Hair[6], M. Fenn[7], M. Avery[6]

[1] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80305, USA

[2] Earth Systems Research Laboratory, NOAA, Boulder, Colorado, USA

[3] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA,

also at New Mexico Institute of Mining and Technology, Socorro, NM, USA

[4] National Center for Atmospheric Research, ESSL, Atmospheric Chemistry Division, Boulder, Colorado, USA

[5] NASA Ames Research Center, Moffett Field, California, USA

[6] NASA Langley Research Center, Hampton, Virginia, USA

[7] Science Systems and Applications, Inc., Hampton, VA, 23666, USA

I. Petropavlovskikh, NOAA/ESRL/GMD

325 Broadway, Boulder, CO, USA, irina.petro@noaa.gov

Abstract:

In the summer of 2007 the NASA DC8 aircraft took part in the Tropical Composition, Cloud and Climate Coupling (TC4) campaign based in San Jose, Costa Rica. During this campaign, multiple in-situ and remote-sensing instruments aboard the aircraft measured the atmospheric composition of the Tropical Tropopause Layer (TTL) in the equatorial region around Central and South America. Partial ozone column measurements above the aircraft were derived from the CCD Actinic Flux Spectrometer (CAFS) instrument and column ozone profiles were derived from the Differential Absorption Lidar (DIAL) instrument. During the July 17 flight off the Ecuadorian coast, these instruments detected well-defined "bubbles" of anomalously low ozone concentration (~ < 75 ppbv) above the aircraft in the TTL. Backward trajectories from meteorological analyses and the aircraft in situ measurements suggest that the ozone-depleted airmass came from deep convection in the Equatorial Eastern Pacific and/or Panama Bight regions at least 5 days before observation by the DC-8. Although the precise origin of the airmass can not be identified with any degree of confidence, the coherence of this low-ozone airmass after such a long period of time has implications for the chemical composition and mixing in the TTL.

Introduction.

One of the NASA science objectives is to continuously monitor natural and anthropogenic variability of atmospheric composition in response to climate change. Various satellite programs, including the A-train satellites, provide atmospheric data necessary to meet this objective. While satellite data help with the global view of the changing atmosphere, the quality of these measurements is assured by comparisons with suborbital and ground-based measurements. Strong vertical gradients exist in the ozone distribution near the tropical tropopause that are not well resolved by most satellite measurements due to the coarse vertical resolution. Studies have shown that ozone changes in the tropical lower stratosphere are important for determining the magnitude and sign of the ozone radiative forcing [*IPCC*, 2001; *Ramaswamy et al.*, 2001]. Additionally, as noted in Gettelman et al. [2009], modeled tropopause height levels and cold point temperatures are sensitive to the amount of ozone near the tropopause. The photochemical lifetime of ozone in the tropical tropopause layer (TTL) is several months, so transport is the primary cause of changes in ozone mixing ratios. Because the TTL serves as the gateway for air entering the stratosphere, it is of interest to study processes that impact the distribution of radiatively active gases in that region.

The Aura satellite has multiple instruments providing global column or profile ozone information [*Schoeberl et al.*, 2006; *Schoeberl et al.*, 2008]. The Aura Validation experiment (AVE) project mission was designed to provide correlative measurements from NASA aircraft at a variety of locations covering the satellite's spatial and altitude coverage [*Froidevaux*, 2001; *Newman*, 2001]. During the past Aura ozone validation activities, including AVE, P-AVE, CR-AVE, TC-4, and ARCTAS, the UV actinic flux was measured by the CAFS (CCD based Actinic Flux Spectroradiometer) instrument (R. Shetter and S. Hall, NCAR) aboard the NASA WB-57 and DC-8 aircraft platforms. The Absorption Lidar (DIAL) system (J. Hair, NASA/Langley) has been flown on the NASA DC-8 in P-AVE and TC4 missions.

In the summer of 2007 the NASA DC8 aircraft took part in the Tropical Composition, Clouds and Climate Coupling (TC4) campaign based in Costa Rica. Multiple in-situ and remote-sensing instruments aboard the aircraft were flown to measure atmospheric composition of the TTL. The layer was first defined by Highwood and Hoskins [1998] and Folkins et al. [1999], and the definition was refined by Fueglistaler et al. [2009]. It is a region in the tropics (~12-18 km) which is significantly impacted by deep convection, and whose properties are transitional between the troposphere and stratosphere. Questions still remain regarding the exact impact of convection as well as the time scales for chemistry and transport that affect the composition of the TTL.

Measurements and data.

The TC4 campaign was based out of San Jose, Costa Rica during July and August 2007. Measurements were coordinated between three aircraft, providing coverage of the stratosphere (ER-2), upper troposphere (WB-57), and low to middle troposphere (DC-8). In this study, we exclusively use measurements from the DC-8, as the flight of interest did not have simultaneous measurements from the other two aircraft. The DC-8 aircraft was equipped with both in-situ and remote-sensing instruments. Measurements of ozone, aerosol, cloud, water vapor, and other trace gasses were taken from aboard the aircraft.

Figure 1 shows the combined picture of all flight tracks accomplished by the NASA DC-8. The DC-8 sampled the atmosphere over a very large region near equatorial Central and South America. However, the phenomena we discuss in this paper, a low-ozone bubble near the coast of Ecuador, was the only one observed during the TC4 mission.

The integrated ozone column (DU) above the DC-8 aircraft is derived from the CCD Actinic Flux Spectroradiometer CAFS measurements during each flight [*Petropavlovskikh et al.*, 2007]. Also, a Differential Absorption Lidar (DIAL) system provides continuous measurements of ozone number density, aerosol scattering and depolarization distribution above and below the aircraft level [*Browell et al.*, 1998]. The DIAL measured number concentration is converted to mixing ratio by using modeled molecular density for the latitude and month. In situ ozone (FastOz, NASA Langley Research Center [*Avery*, this issue]), CO (DACOM, NASA Langley Research Center [*Sachse et al.*, 1987]), MHP (CIMS, Caltech [*Eisele and Tanner*, 1991; *Mauldin et al.*, 1998; *Mount et al.*, 1997]) measurements were made from aboard the NASA DC8.

Launches of ozone and water vapor sondes were coincident with most of the TC4 flights. The launches were done from Juan Santa Maria airport, Costa Rica, San Cristobal of Galapagos Islands, Ecuador and from Las Tables, Panama (the last location is part of the NATIVE campaign, P.I. A. Thompson). Ozone profiles are available from all three sites as well as relative humidity from a standard operational radiosonde. Research quality water vapor measurements from a frost point balloon were only taken at the Costa Rica and Galapagos sites.

Below, we use GOES-12 satellite (located over the equator at 75º W) images from the TC4 region for identification of deep convection, and for moisture and temperature analysis. Both visible (Channel 1) and IR (channel 4 at 10.5 microns) images are used in this study. Brightness temperatures (from Channel 4) below -35 C) are designated by colors – 10 C for each color change (green is between -65 and -75 C). All images shown here have been degraded to a 6 km resolution from the original 1 km visible and 4 km IR data.

This study focuses on analysis of measurements taken during one DC-8 flight. The flight was on July 17, 2007, and the track is shown in dark lavender on Figure 1 and also overlaid on a visible satellite image in Figure 5 (a). In particular, we examine one unusual ozone feature and hypothesize on its origins.

NASA DC8 Observations

A depleted ozone column above the DC-8 aircraft was detected by both DIAL and CAFS near the Ecuador coast on July 17, 2007. The total ozone column was also measured by the OMI instrument aboard the Aura satellite. The OMI surface tracks on July 17 2009 (similar to location of MLS tracks in Figure 5) were located in close proximity to the depleted ozone episode location. The OMI data were then interpolated to the latitude of the DC-8 flight tracks. Figure 2 shows time series of CAFS ozone columns (green) derived above the altitude of the DC-8 for July 17 2007 flight. In addition, the co-located OMI-TOMS v2.2 data are shown as total ozone column above the clouds (magenta) and ozone columns above the surface (blue). The depleted ozone column above the DC8 aircraft is found at about 17 UT (vertical red line in Figure 2). The extension of the CAFS-derived partial ozone column data (green) with ozone climatology [*Bhartia*, 2002] estimated below the DC-8 altitude (orange) creates a total ozone column dataset (black symbols) that matches a similar reduction in the OMI-TOMS total ozone column time series (seen in both blue and magenta symbols). It suggests that the reduction in OMI-TOMS total ozone column is entirely confined to the altitudes above the aircraft.

This anomaly in the CAFS and OMI ozone column observations occurs at the same time that the DIAL vertical profile data shows a bubble of depleted ozone between 14 and 16 km. Figure 3 shows the time altitude contour plot of the DIAL ozone mixing ratio for the part of the flight between 16:00 and 17:20 UT. This portion of the flight was flown at an altitude of 11.3 km (until about 17:00 UT when the aircraft turned and descended to 10.3 km altitude). Note that FASTOZ data are shown as thin line at altitude of the NASA DC-8 aircraft (it is also shown in Figure 4). The ozone anomaly between 14 and 16 km altitude is measured twice in this time series (centered around 16:53 UT on the south bound leg, and again around 17:05 on a parallel track heading north 0.4 degrees longitude farther to the west). The variation in ozone noted here is approximately a factor of 2, from a high value in the 15 km region of ~0.125 ppmv (or 125 ppb) to a low value of ~0.06 ppmv (60 ppb).

In-situ ozone measurements were collected by the FastOz instrument [*Avery*, this issue] aboard the DC-8. During most of this flight an average 40 ppb of ozone mixing ratio was measured while sampling inside the cloud and 63 ppb when out of cloud (as determined by ozone correlations with the Counterflow Virtual Impactor data aboard DC-8, [*Noone et al.*, 1988; *Twohy et al.*, 1997]). Figure 4 shows FastOz data during the portion of the flight when the DIAL observed the low ozone events at 15 km altitude. Note, the FASTOZ data are plotted at various aircraft altitudes: at 11.3 km from 16:00 to

17:02 UT, and at 10.3 km from 17:05 to 17:15 UT (the period of the DC-8 descent is indicated by two solid vertical lines). An intermediate ozone concentration during the flight near the Ecuador coast (marked by two vertical dashed lines between 16:42 and 16:55 UT) at 11.3 km altitude is in the range of 50 ppbv. The absence of large gradients in the ozone mixing ratio suggests mixed air and not fresh convection. Therefore, it implies that the depleted ozone at 15 km altitude is not related to the local convection that would have altered the ozone mixing ratios at the 11.3 km flight level.

Two of the other chemicals measured aboard the NASA DC-8 are CO (Carbon Monoxide) and MHP (Gas Phase Methyl Hydrogen Peroxide or CH_3OOH), which can be used as indicators of vertical transport. Both CO and MHP have significant effects on hydroxyl (OH) radicals in the atmosphere by reducing their abundance and increasing tropospheric ozone concentration [*Andreae et al.*, 1988; *Crutzen and Andreae*, 1990]. Elevated CO and MHP concentrations in troposphere in the tropics can be a consequence of biomass burning [*Lee et al.*, 1997; *Wennberg et al.*, 1998]. At the same time, tropospheric ozone distribution in tropics is also altered through interactions of pollution with large-scale circulation and deep convection [*Newell et al.*, 1997; *Thompson et al.*, 2003]. Therefore, these chemicals can be used as tracers for vertical transport.

Figure 4 shows CO mixing ratios remaining unchanged when sampled directly below the depleted ozone features (low-ozone time period is indicated by the first two vertical dashed lines). CO and ozone data were anti-correlated during most of the flight. The lack of the elevated MHP concentrations in the upper troposphere prior to 17:05 UT, while high concentration (~500 pptv) levels were measured near the surface (spiral portion of the DC-8 flight between ~17:20 and 18:40 UT, not shown), suggests that DC-8 sampled airmass at 11.3 km was different from the polluted marine boundary layer. The period of the DC-8 flight between 17:05 and 17:10 is co-incident in time with the second DIAL sampling of the low ozone feature (between the second solid vertical line and the right edge of the plot). The period of decreased in-situ ozone with increased CO and MHP occurs right after a short descent from 11.3 to 10.3 km (indicated by two solid lines), which suggests possible convective influence at the DC-8 aircraft level. Since the DC8 was at a lower altitude and different longitude for the second pass it likely encountered different dynamical conditions. Although high clouds were seen in the nadir looking DIAL aerosol channel (with cloud top heights just below 10 km) up to 16:42 UT and after 17:05 UT, the satellite images near the time of the aircraft flight do not indicate any deep convection reaching up to the 14-16 km levels (see the following section for more discussion). The depleted ozone at the NASA DC-8 level appears to be a narrow layer located above the cloud tops and just above a slight enhancement in the DIAL nadir aerosol image (not shown). There seemed to be an intercept of the upper outer fringe of this layer at 16:57 UT, whereas the aircraft was on the lower outer fringe when it leveled out at 10.3 km at 17:05 UT. There could very likely be the influence of shallower convection at the DC-8 levels, with the possibility of transport from the East (see the later section on back trajectories), but that convection isn't getting up to the levels where the depleted ozone is detected. Moreover, the DIAL data show a disconnect in vertical distribution with increased ozone mixing ratios at 13 km (Figure 2). Therefore, the MHP and CO observations at the NASA DC-8 aircraft flight level provide supporting evidence that the depleted ozone is not related to local vertical transport.

GOES data and NCEP analysis.

The Aura satellite surface tracks are shown in Figure 5, where the HIRDLS (H), TES (+), and MLS/OMI (M) instrument sampling tracks are plotted over the GOES-12 satellite IR image at 17:45 UT. Channel 4 is the traditional IR window channel that "sees" to the ground except where there are clouds; it is centered at 10.5 microns wavelength band. The colors on the plot are used to indicate the cloud system, where the colder the cloud - the brighter the white color on the plot. Brightness temperatures below -35C are designated by colors with -10C for each color change, such that the green is between -65 and -75 C. Thus, areas of bright colors represent deep convection. The three most prominent areas of deep convection are located over the Pacific coast of Mexico, Panama and northern South America.

A combination of NCEP analysis and GOES images were used to create convective influence plots for the area under question [*Pfister et al.*, 2001]. The back trajectories were run for 8 days prior to the event on July 17, 2007, and were stopped when found to be convectively influenced. The geo-location of the air parcels was checked against the GOES images for bright clouds that are indicative of deep convection events. Based on the DIAL ozone curtain plots, it appears that the depleted ozone area ranges from about 14.9 (or ~49 kft) to 15.7 km (or ~52 kft) geometric altitude. Therefore, the lower limit for trajectories was placed at a pressure of 134 mb, while the upper limit was extended to 117 mb.

Back Trajectory Analysis of the low-ozone air mass

In this section, backwards trajectory calculations and satellite data are analyzed to examine the evolution and identify the likely source region of the low-ozone airmass observed from the DC-8 on the July 17 flight.

For the analysis presented here, 10-day back trajectory calculations were performed using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [*Darxler*, 1998; *Draxler et al.*, 1997; *Draxler*, 2003]. The input meteorological data for HYSPLIT are from the NCEP Global Data Assimilation System (GDAS, 1° x 1° resolution, http://www.emc.ncep.noaa.gov/modelinfo/index.html). Isentropic back trajectories were initialized at 17 UT on 17 July 2007 over a matrix of 9 latitudes and 8 longitudes spanning the bounding latitude/longitude box of the region over which the DC-8 observed the low-ozone bubble (near Ecuador coast, 3 degrees S and 82 degrees W, between 16:30 UT and 17:00 UT). Additional model runs (not shown) were performed using combinations of the GDAS omega vertical velocity as well as different initialization times (16 Z and 18Z) to investigate the sensitivity of the results. Although the endpoints of these runs differ slightly from the nominal run, the results below are not sensitive to these small perturbations in initialization time or vertical velocity assumptions. The trajectories were stopped whenever the convective influence analyses (described in the previous section) suggested the intercept with the deep convective system.

Figure 5 shows the nominal back trajectory runs initialized at the altitude of the low-ozone bubble (15.4 km, top panel) and at the mean altitude of the DC-8 during the low-ozone bubble measurement (10.4 km bottom panel).. The backward trajectory analysis plots illustrate that the air-masses at the DC-8 altitude and 15 km are of significantly different origin, with the flight-level air-mass originating from the East over

South America, and the 15 km air-mass originating from the West and ultimately North/Northeast over the Panama Bight region.

The 15-km back trajectories were tracked backwards in time to the point at which they intercepted convection, as defined by low brightness temperatures (< 238 K, or blue colors in the figures shown here) in GOES Channel-4 imagery. As the trajectories make their turn and head north, we find convective influence in the time range > 5 days old. All trajectories intercepted convection between the 10 and 12 July, between 5 and 7 days before being measured by the DC-8. The southernmost trajectories (black through light blue colors) encountered convection in the Panama Bight and E. Pacific region, whereas the northernmost trajectories encountered convection off of the East coast of Columbia, over Columbia, and over Venezuela (green through red colors). Although the convective source of the trajectories at a given initialization latitude is somewhat sensitive to the start time and vertical velocity used (i.e., isentropic vs. omega), all of the combinations of backward trajectories yield convective sources in the vicinity of Panama and Columbia. Because the GOES brightness temperatures are consistently lower over Panama for the trajectories considered here, we hypothesize that the low-ozone bubble airmass originated over this region. Overall, these back trajectories support the idea that low-ozone air detrained from deep convection over the South and Central America regions can be transported through the TTL over long times (~7 days) and distances (~1000 km) in a coherent manner (i.e., without significant mixing).

Satellite observations.

In support of our hypothesis of long-range transport from the Panama region, we present data from the two coincident times over the course of the 10-day trajectories in which the air parcels were located in the proximity of Aura/HIRDLS measurements [*Gille et al.*, 2008]. The trajectory locations over GOES IR imagery are shown in (a) panels of Figures 6 and 7, while the HIRDLS ozone data for these times are shown in (b) panels of Figures 6 and 7.

The HIRDLS V4 ozone profile data covers a wider range of latitudes, while profiles are about 100 km apart, so its resolution does not contain the fine horizontal details observed by DIAL. However, the vertical resolution of HIRDLS is about 1 km, which should be sufficient for identifying the vertical ozone gradient. The sequence of two HIRDLS ozone pressure-latitude cross sections accompanied by the GOES IR images and trajectories is shown in Figures 6 and 7. Figure 6 (a) shows the trajectory locations on 16 July over the Eastern Pacific ocean, far from the regions of persistent convection off the coasts of Central America. Also, a region of low-ozone air close in space and time to the altitude of the back trajectories (~15.25 km) is present in the HIRDLS data taken at ~21:20 UT (see panel (b) in Figure 6). Because of the lack of convective clouds in this region of low ozone, as evidenced by the high brightness temperatures in the GOES imagery, we hypothesize that this low-ozone region in the HIRDLS data is the same airmass measured on 17 July by the DC-8. The region below 15 km where no data exist (white) may be due to the presence of clouds or where ozone concentrations are below the HIRDLS detection limit [*Nardi et al.*, 2008].

Figure 7 (a) shows the trajectory locations at 21 UT on 10 July plotted over GOES-12 IR image (upper panel), as well as data from the HIRDLS overpass at ~20:25 UT (lower panel). This time is within one day after the trajectories (purple and blue in the figures) intercepted convection in the region. The HIRDLS data indicate a widespread region of low-ozone air over Central America. Part of this data is associated with convective clouds north of 10° along the HIRDLS track (i.e., the yellow dashed line in Figure 7 (b)), whereas some of the data comes from regions free of convection at the time of measurement. It is likely that this large region of low-ozone air seen from 5 – 15°N on 10 July contributed to the low-ozone air-mass observed on 17 July by the DC-8, although a definitive attribution is not possible.

The above results support our hypothesis that the episodes of low ozone found in the DC-8 measurements in the non convective region originate from long-range transport of convectively-influenced, low-ozone air that has maintained some integrity for several days. These results suggest that quasi-horizontal mixing processes in the Upper Tropical Troposphere (UTT) are relatively slow. Deep convection over Panama is likely the source of the observed low ozone "bubble".

RDF (reverse domain filling) analysis

The BT analysis discussed above suggested the possibility of the long-range adiabatic transport of the low concentration ozone "bubble" to the Ecuador coast from the Panama region where it was generated by the deep-convection mechanism. The DIAL and CAFS instruments detected a low ozone bubble between 14 and 16 km altitude around 17 UT during the NASA DC-8 aircraft flight on June 17 2007. In this section we attempt to validate our long-range transport hypothesis by using reverse domain filling (RDF) calculations [*Sutton et al.*, 1994] [*Manney et al.*, 1998] driven by GEOS-5 data assimilation system meteorological analyses [*Reinecker*, 2007].

The RDF analysis was used to infer the transport of ozone features noted here. In the calculations, trajectory calculations using the GEOS-5 winds are started on a dense grid (0.25 degrees latitude by 0.40 degrees longitude) and run back 8 days; at that time, gridded MLS or HIRDLS data are interpolated to the parcel locations to provide an estimate of the ozone that was transported to the starting locations of the trajectories. Thus, the RDF maps/profiles from MLS/HIRDLS are based on transport by GEOS-5 winds and initialization with a single day of MLS or HIRDLS gridded data. Figure 8 (a) shows the MLS initialized run, which looks consistent with the location of the DC-8 found low ozone bubbles near Ecuador on July 17 2007. Gradients comparable to those observed from the DC-8 are seen in the RDF generated ozone field, indicating that transport over 8 days can indeed generate features like those observed. The RDF procedure was also applied to several other chemical species measured by MLS (H_2O, CO and HNO_3, results are not shown), which show strong consistency in the morphology of the RDF fields with those for ozone; this is evidence that the RDF calculations are largely showing transport of real atmospheric features, since the "noise" (i.e., spurious values) would not in general be expected to be correlated in all the species.

Results in Figure 8 (a) suggest that the low ozone feature in the RDF analysis near the coast of Ecuador at the 360 K potential temperature level (near 15 km altitude, see Figure 3) are similar to the DIAL-observed low ozone mixing ratios between 14 and 16 km altitude. The light blue colored filament of ozone that represents low ozone mixing ratio of 50 ppbv extends to the west from the Ecuador coast (DC-8 tracks are marked by white line) and then loops under the red-colored (higher mixing ratio) ozone feature in the middle of the plot, and then extends to the north up to the Coast of Mexico. The ozone feature may be smoothed out because of the initialization with MLS low resolution ozone, but it is still indicative of the transport-related ozone residuals between 14 and 16 km altitude.

Results of an RDF analysis "transporting" equivalent latitude [*Butchart and Remsberg*, 1986] are shown in Figure 8 (b). The equivalent latitudes are the latitudes that would enclose the same area as the PV contours, thus showing at what equivalent latitude the air at each point in the plot originated 8 days previously. The light sand colored filaments seen near the south end of the DC-8 flight track (shown as white line) suggest that the low ozone "bubble" most likely originated at about 10 degrees N. The RDF analyses support our hypothesis of the origination of the low ozone "bubble" in the InterTropical Convergence Zone (ITCZ) zone as the region of the deep convective processes at low northern latitudes.

Discussion and Conclusions

The TTL is a region that is infrequently perturbed by convection [*Gettelman et al.*, 2002]. This allows ozone mixing ratios in the TTL to be significantly greater (red color in DIAL data in Figure 3) than in the free tropical troposphere below 14 km, a region heavily influenced by convective mixing as noted by the ozone gradients in the DAIL data shown in Figure 3. A typical tropical ozone profile during the TC4 campaign showed low ozone through the bulk of the troposphere (up to ~16 km, or the approximate height of the tropopause), with a sharp gradient increasing to maximum values near 30 km. All the ozone measurements from the Panama site taken during TC4 are shown in the Figure 9. There is significant variability near 15 km, not unlike the range noted in the single DC-8 flight with the DIAL measurements. The temporal variation at Panama is comparable to the spatial variation seen in the DIAL measurements, with minimums on the order of 0.05 ppmv and maximums as high at 0.15 ppmv. Five of the Panama sondes launched during TC4 show low values (below 0.07 ppmv) in the 14-16 km level, which is

~20% of the time. This indicates that such phenomena are not an uncommon occurrence, and hence likely contribute to the overall ozone budget in the UTT. Because of this, it is of interest to study this particular case observed by the DC-8 in further detail.

One goal of the TC4 mission was to characterize the chemical boundary conditions below the TTL, particularly for ozone. In the UTT the chemical lifetime of ozone is about 50 days, and is much longer than the mixing time due to frequent strenuous ITCZ related convection. In situ measurements from aircraft were analyzed to characterize the statistical vertical distribution of ozone created by the convective redistribution of ozone [*Avery*, this issue]. The statistics of ozone measured during the mission between 7º S and 17º N and between 270º and 290º W shows that very fresh convective outflow chemically more closely resembles in situ ozone sampled at about 3 km than it does at the surface, suggesting that vertical transport in the middle troposphere is predominantly 3-10 km, and that entrainment/detrainment is more complicated than just moving boundary layer air up to the tropopause.

The back trajectory analyses indicate that the low ozone features observed by DIAL were the result of deep convective upwelling in the ITCZ, followed by roughly isentropic transport to south of the equator. It is somewhat surprising that the low ozone features were so pronounced after moving around the UT for a week or more, which may reveal information on mixing time scales in the TTL. This is not inconsistent with results recently published in James and Legras [2009], which show mixing times on the order of a month in the subtropics above 350K.

One may question why this type of feature (unmixed low ozone) did not appear in other DC-8 observations. As noted in Figure 1, very few flights ventured outside of the convectively influenced region near the Panama bight. Hence, no distinct regions that were convectively influenced would show up in the DIAL data (everything looks the same). Such low ozone values in the TTL between 14 and 16 km are not completely rare; low ozone values in the TTL were seen in DIAL data during the PEM-A and PEM-B campaigns [*Browell et al.*, 2001; *Browell et al.*, 2003]. However, it should be noted that the previous observations did not observe a similar spatially coherent low ozone "blobs" seen during TC4. Because of the winds in this case, there is a contribution from convection that is north of the equator and likely from the Panama region.

Some other points may be useful for further discussion. For example, the DIAL ozone data on July 17 show large ozone values just below the ozone bubble, larger than at similar altitudes on either side of the low-ozone area. It suggests the possibility of some sort of exchange between the troposphere and stratosphere. However, on the other hand the vertical and horizontal winds at the TTL levels were very slow, indicating that this is also likely a horizontally transported feature.

There are other possibilities we have considered that could have caused the low ozone features noted above 14 km on July 17th in the DIAL measurements. The DC-8 was flying in close proximity to the volcanic outflow from Ecuador. The chemical reaction involving volcanic SO2 -> H2SO4 particles could be the reason for the ozone destruction through the activation of chlorine. However, if that was the case, we would expect to see aerosols present in the low ozone air mass. The contours in Figure 3 show aerosols in the regions of elevated ozone in the 14-16 km levels, indicative of an aged air mass, but there are no aerosols detected by DIAL in the low ozone bubble, hence supporting the idea that it is a relatively "freshly" pumped up air mass.

Yet another mechanism of ozone destruction could be related to the combination of high H_2O mixing ratios and occurrence of clouds below (apparent from backscatter in

DIAL aerosol backscatter data). It could lead to high photochemical destruction of ozone through photochemical loss $J(O_3) \rightarrow O(^1D) + H_2O \rightarrow OH$, followed by additional ozone loss through the HO_2/OH catalytic cycle. However, the DIAL/LASE system did not detect high mixing water vapor above the DC-8 level, negating this as possible for this case.

To summarize, based on the back trajectories (Figure 5 (a) coherent low ozone bubble observed in the south part of the DC-8 flight of July 17, 2009 by the DIAL instrument at ~17 UT between 14 and 16 km (green color in Figure 3) most likely resulted from non local convection occurring in the Caribbean Sea, with possibly some contribution from the Panama Gulf. Supporting evidence for the non locality and subsequent transport comes from the fact that a low ozone region crossing the back trajectories is seen in satellite observations in the absence of convection several days after the convective event (Figure 6). There is also distinct difference in direction of trajectories derived above aircraft level (Figure 5 (a)) and at aircraft level (Figure 5 (b), South America), also supporting the non locality of the source. Therefore, ozone depletion above the aircraft and elevated/reduced ozone mixing ratios at the aircraft level, and increased ozone below the aircraft are governed by different processes. Further work is needed to assess the magnitude of the contribution of convection to the ozone budget of the tropospheric portion of the TTL.

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Figures

Figure 1. Composite of DC-8 tracks during the TC4 campaign in July-August of 2007 (courtesy of the NASA Langley DIAL team).

Figure 2. Ozone column data time series are shown for NASA DC-8 flight on July 17 2007. The co-incident OMI-TOMS v2.2 total ozone column data above the clouds (magenta) and above the surface (blue) are plotted for comparisons with the combined CAFS total ozone column (black): a combination of the CAFS-derived ozone column above (green) and climatological ozone column below the NASA DC-8 aircraft level (orange, offset by 150 DU). The approximate time of the low ozone value encounter (at 17 UT) is marked by red vertical line. The dashed vertical line marks the Aura satellite overpass time at 19:30 UT.

Figure 3. Ozone mixing ratio profiles (ppbv) as derived by the DIAL instrument on board the NASA DC-8 flight on July 17, 2007 are plotted as function of altitude and time. The colors indicate different levels of ozone. The depleted ozone layer between ~14 and 16 km is marked with black oval. The corresponding latitude and longitude coordinates of the DC-8 platform are also provided at the bottom of the plot. The aerosol contours are potted (white lines) over the ozone field to show the co-incident aerosol scattering measurements.

Figure 4. In situ ozone (FastOz), carbon dioxide (CO, DACOM) and MHP (Gas Phase Methyl Hydrogen Peroxide, CIMS) mixing ratios are shown at the aircraft level for portion of the NASA DC-8 flight on July 17 2009. The time period between 16:45 and 16:55 UT (marked by two dashed vertical black lines) is co-incident with the DIAL low ozone measurements at 14-16 km altitude range. The descent of the DC-8 from 11.3 to 10.3 km is pointed out by the two vertical solid black lines. The period of the DC-8 flight between 17:05 and 17:10 is co-incident with the second DIAL sampling of the low ozone feature. The decreased ozone, elevated CO and MHP levels suggest possible deep convection influence.

Figure 5. (a) Backward trajectories initialized at the altitude and latitude/longitude of the low-ozone air-mass (~15 km) are plotted over the GOES Channel 4 brightness temperature imagery taken at 17:45 UT (colors from black to red indicate the starting latitude of the trajectory, and diamonds are plotted at 00:00 UT on each day of the trajectories). The DC-8 flight track is shown in white. **(b)** Same as **(a)**, but for trajectories initialized at the DC-8 altitude (~ 10 km).

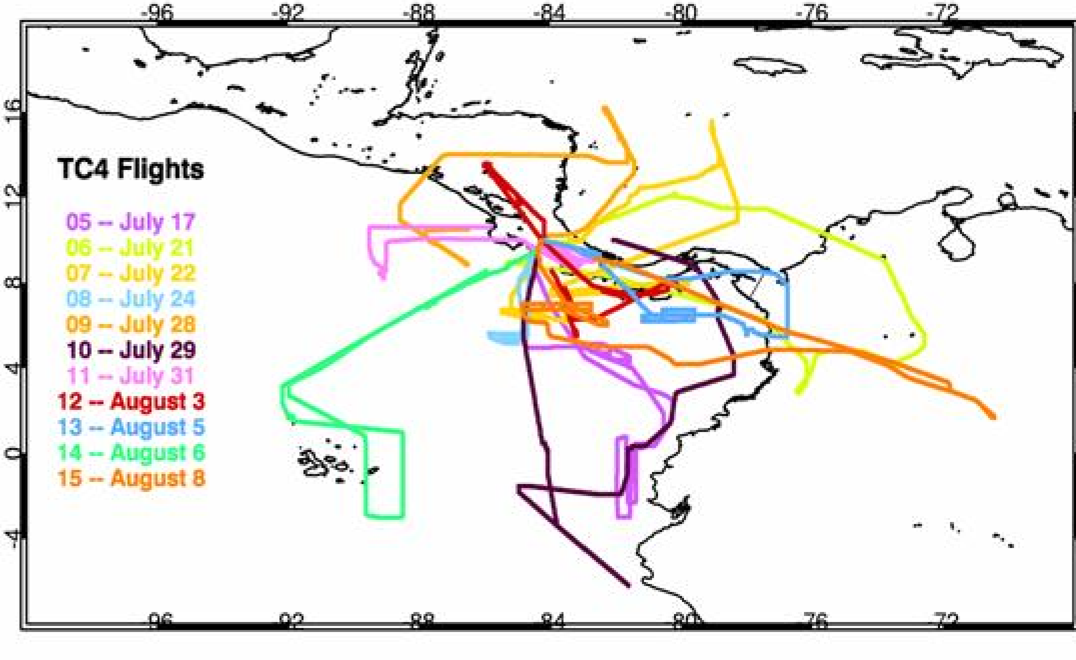
Figure 6. (a) GOES channel 4 imagery with back trajectory locations ending at 22 Z (+ signs) on 16 July, with HIRDLS measurement track plotted (H's and dashed yellow line). **(b)** HIRDLS data, with yellow dashed line corresponding to location in top figure, and plotted at the mean altitude of the back trajectories at the time of HIRDLS overpass (21:20 UT). Black dashed line is the HIRDLS cloud-top altitude.

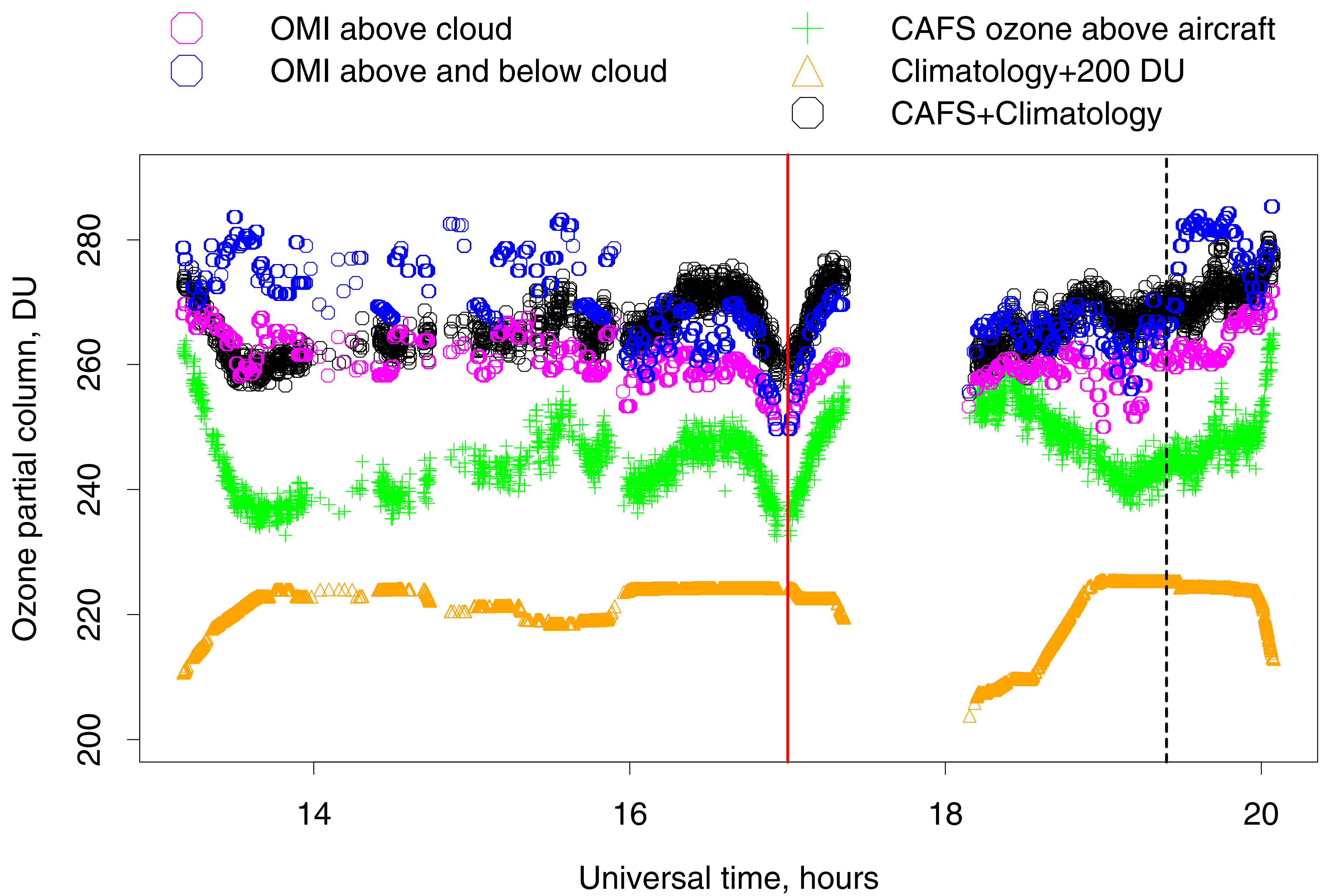
Figure 7. **(a)** GOES channel 4 imagery with back trajectory locations ending at 21 Z (+ signs) on 10 July, with HIRDLS measurement track plotted (H's and dashed yellow line). **(b)** HIRDLS data, with yellow dashed line corresponding to location in top figure, and plotted at the mean altitude of the back trajectories at the time of HIRDLS overpass (20:25). Black dashed line is the HIRDLS cloud-top altitude.

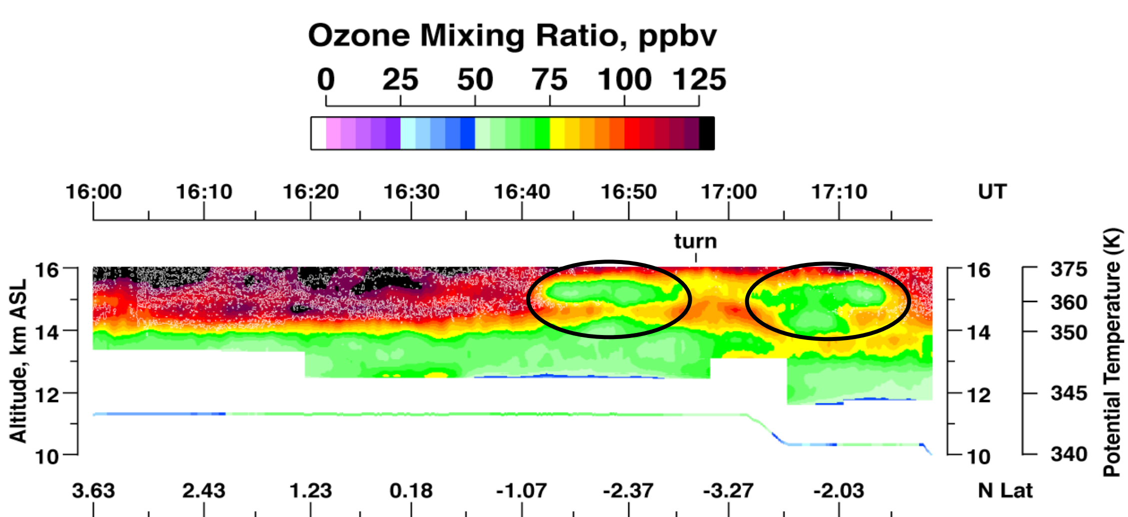
Figure 8. **(a)** The latitude/longitude cross-section of the 8-day RDF analysis of the GEOS-5 isentropically advected ozone mixing ratios at 360 K level. The MLS ozone field was used to initiate RDF analysis. The DC-8 flight tracks are shown as white lines in the middle of the plot. **(b)** The same as **(a),** but for equivalent latitude data.

Figure 9. Ozone sounding mixing ratio measurements are plotted as function of time and altitude. Las Tablas, Panama, NATIVE campaign (7.75 N, 80.25 W).

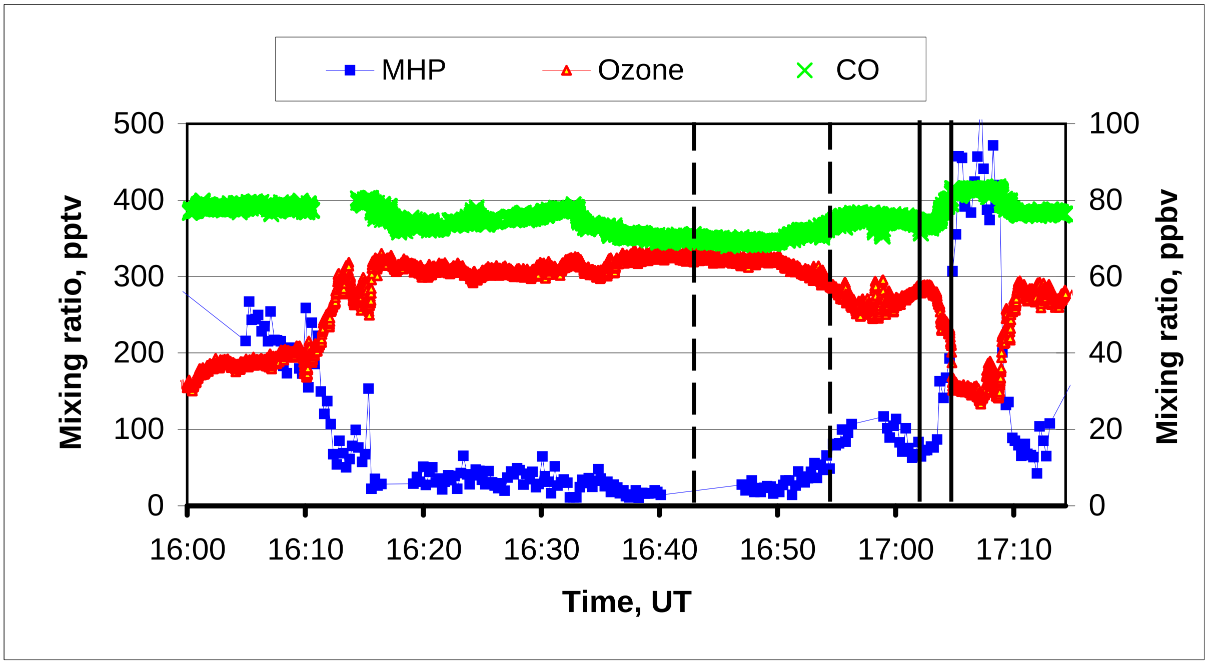
DC-8 Composite Flight Tracks
TC4: July 17 - August 8, 2007




OMI above cloud
OMI above and below cloud
CAFS ozone above aircraft
Climatology+200 DU
CAFS+Climatology
Ozone partial column, DU
200
220
240
260
280
14
16
18
20
Universal time, hours

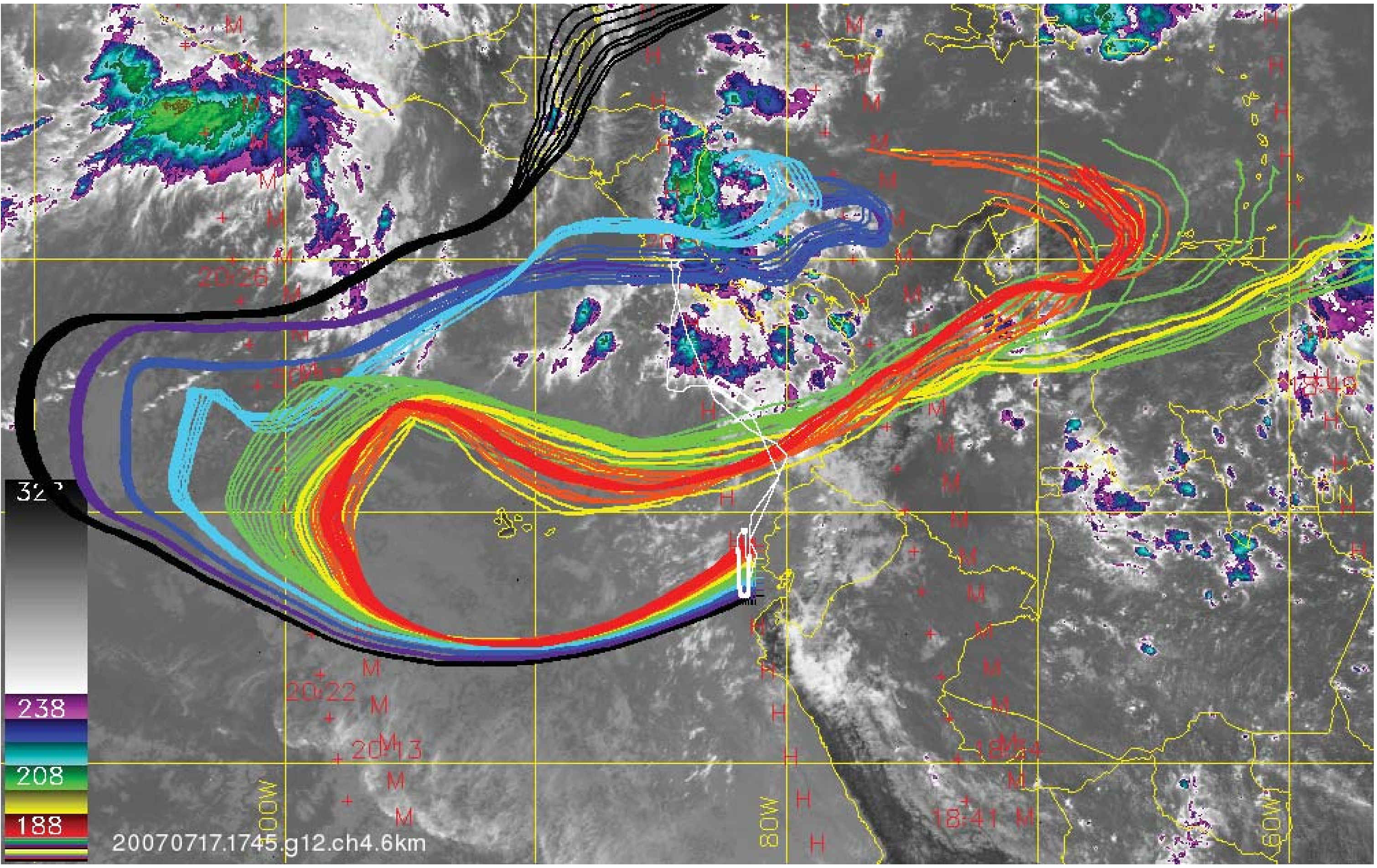


Ozone Mixing Ratio, ppbv
0
25
50
75
100
125
16:00
16:10
16:20
16:30
16:40
16:50
17:00
17:10
UT
turn
Altitude, km ASL
16
14
12
10
Potential Temperature (K)
375
360
350
345
340
3.63
2.43
1.23
0.18
-1.07
-2.37
-3.27
-2.03
N Lat
-81.31
-80.78
-80.42
-81.22
-81.52
-81.56
-81.90
-81.96
E Lon

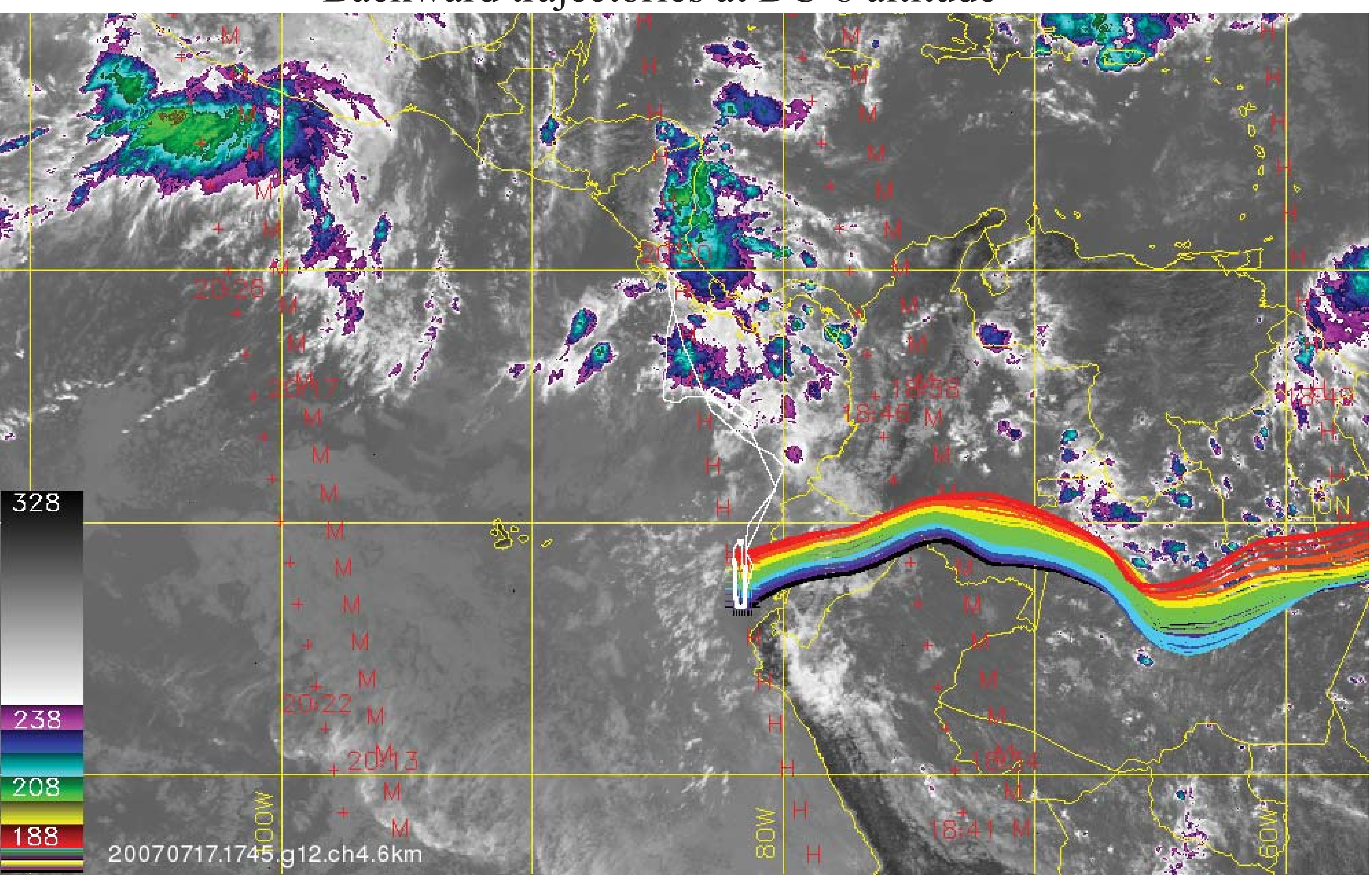


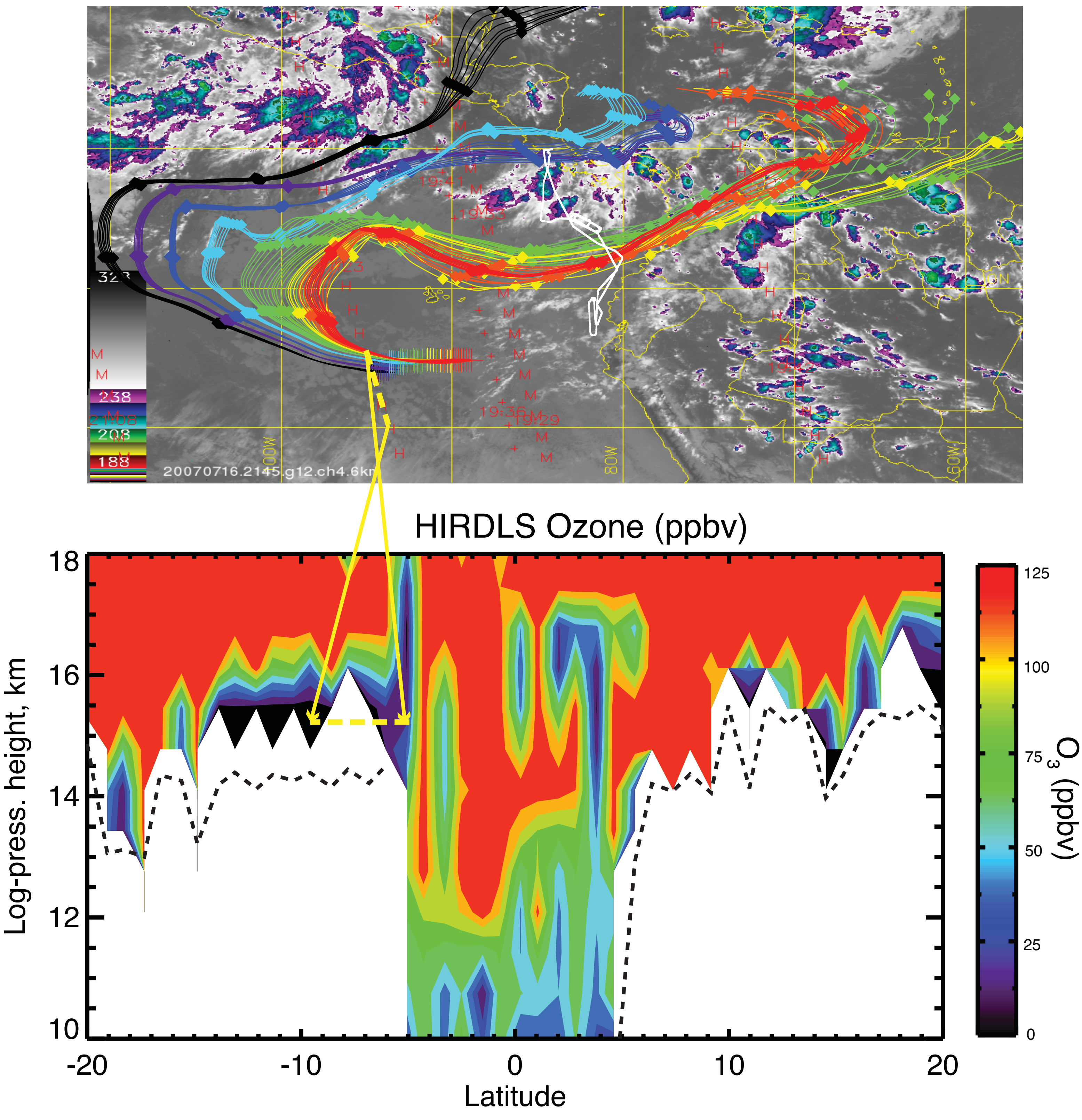
MHP
Ozone
CO
Mixing ratio, pptv
Mixing ratio, ppbv
Time, UT
0
100
200
300
400
500
0
20
40
60
80
100
16:00
16:10
16:20
16:30
16:40
16:50
17:00
17:10

Backward trajectories at low-ozone bubble altitude

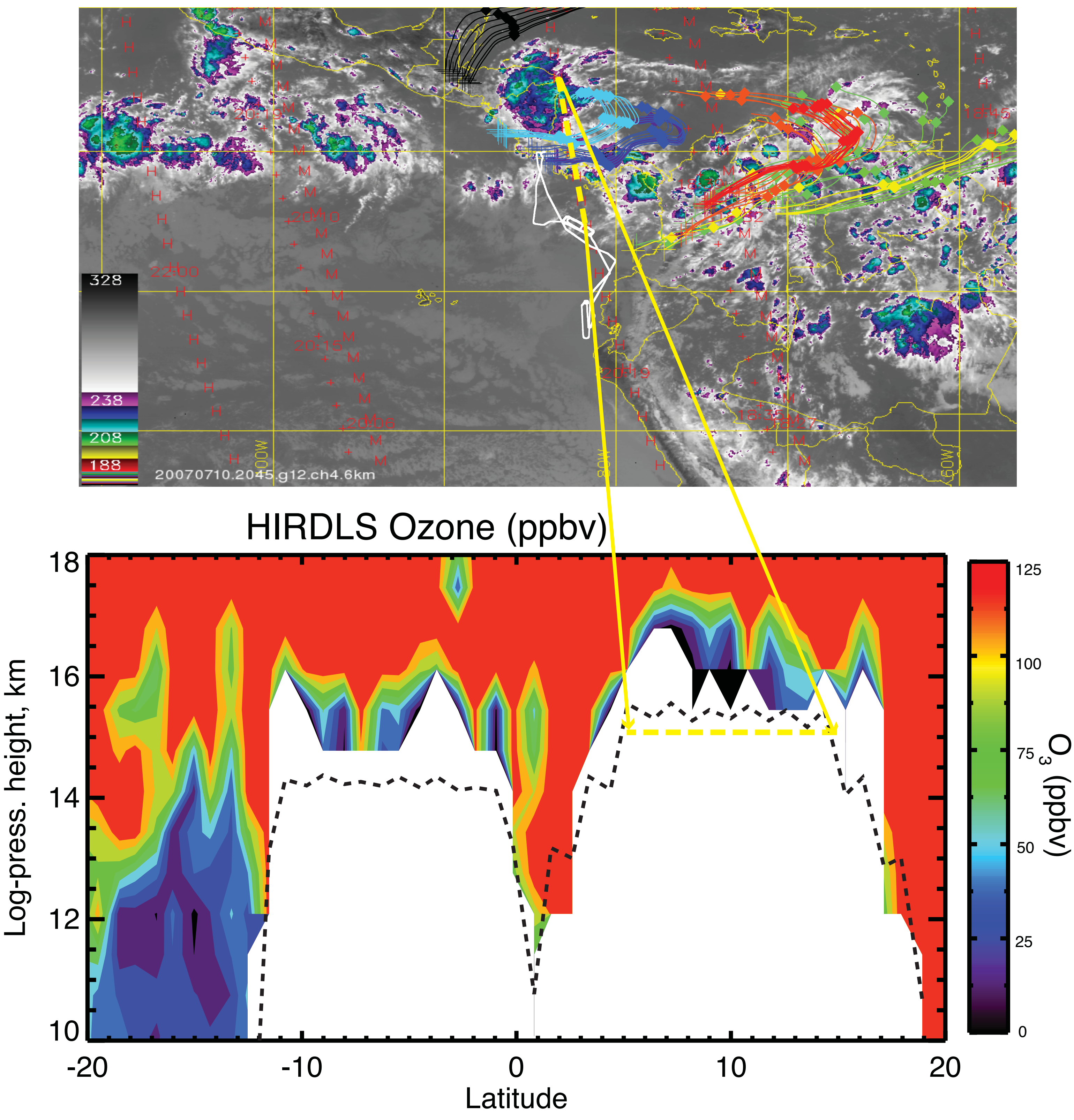


Backward trajectories at DC-8 altitude

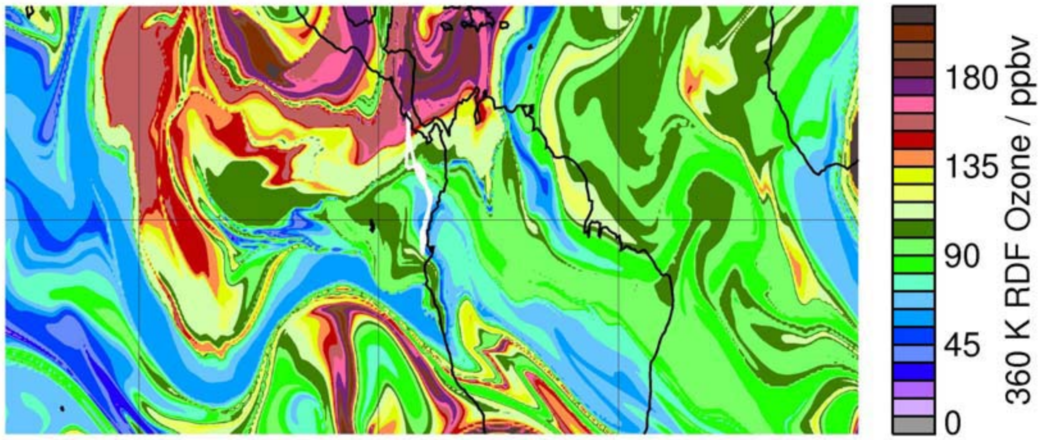




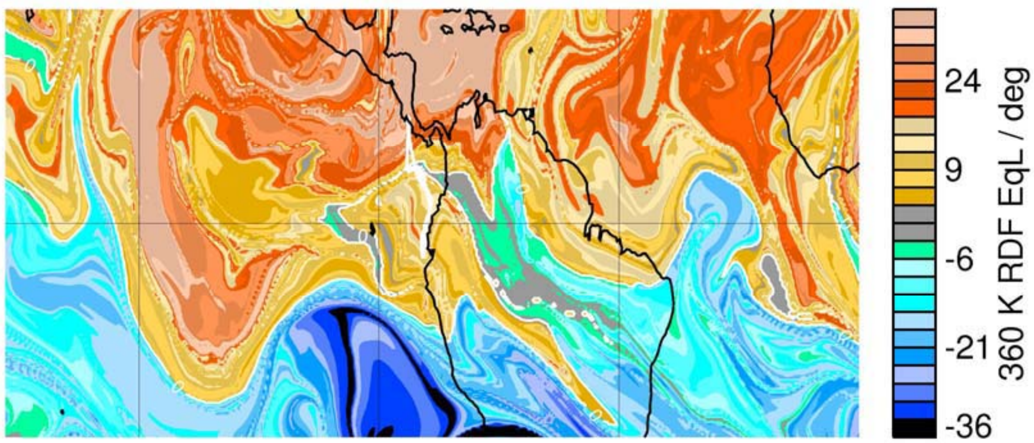
20070716.2145.g12.ch4.6km
100W
80W
60W
238
208
188
HIRDLS Ozone (ppbv)
Log-press. height, km
Latitude
O3 (ppbv)



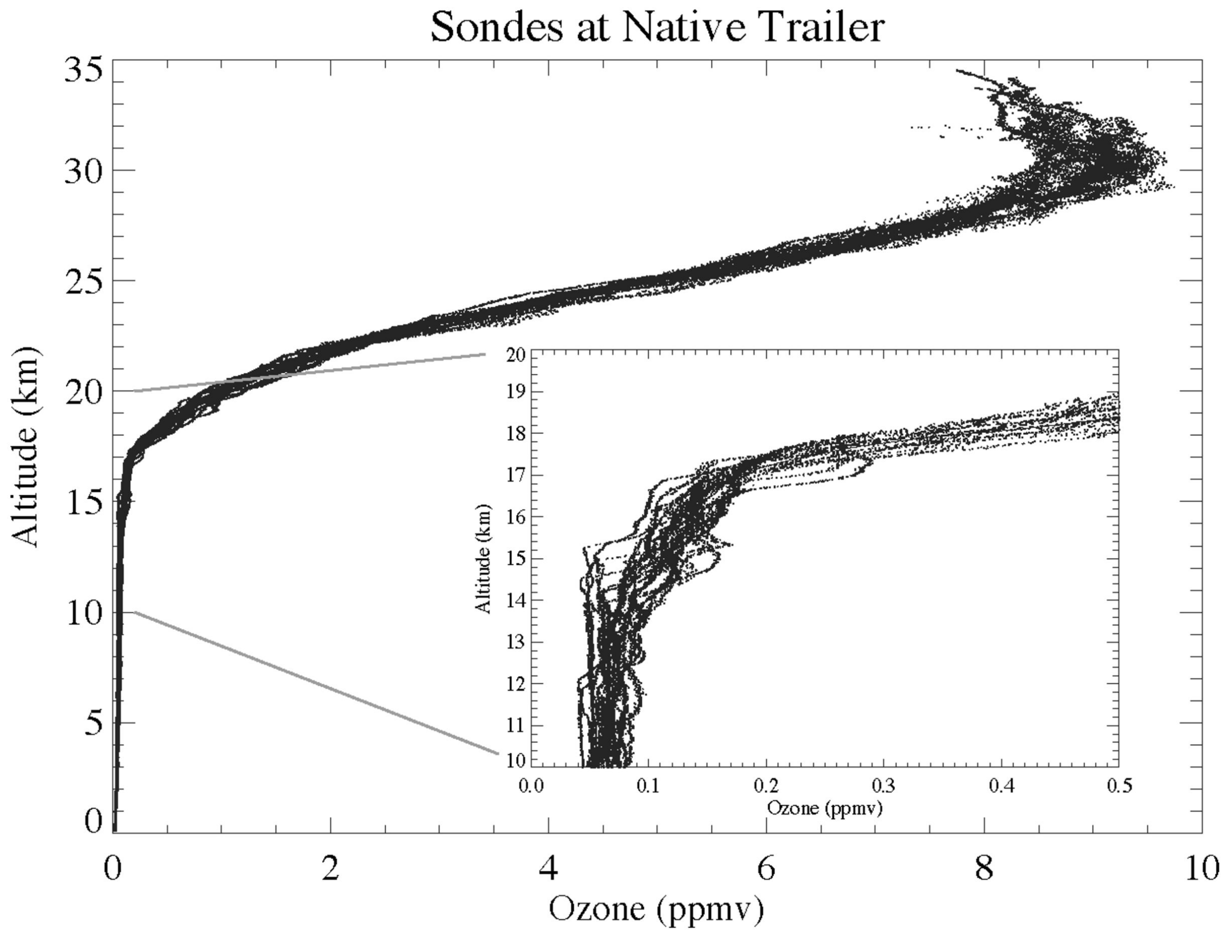
328
238
208
188
20070710.2045.g12.ch4.6km
HIRDLS Ozone (ppbv)
Log-press. height, km
Latitude
O3 (ppbv)



(a)



(b)



Sondes at Native Trailer
Altitude (km)
Ozone (ppmv)
0 2 4 6 8 10
0 5 10 15 20 25 30 35
Altitude (km)
Ozone (ppmv)
0.0 0.1 0.2 0.3 0.4 0.5
10 11 12 13 14 15 16 17 18 19 20