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- First continuous, long-term measurements of O_3 in the Equatorial Eastern Pacific Boundary Layer
- Analysis and interpretation of the diurnal and seasonal cycles
- Description of ozone intraseasonal variability and possible link to tropical instability waves

Supporting Information:

- Supporting Information S1

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On the variability of ozone in the equatorial eastern Pacific boundary layer

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Abstract Observations of surface ozone (O_3) mixing ratios carried out during two ground-based field campaigns in the Galápagos Islands are reported. The first campaign, Primera Investigación sobre la Química, Evolución y Reparto de Ozono, was carried out from September 2000 to July 2002. The second study, Climate and HALogen Reactivity tropical EXperiment, was conducted from September 2010 to March 2012. These measurements complement the Southern Hemisphere ADDitional OZonesonde observations made with weekly to monthly frequency at Galápagos. In this work, the daily, intraseasonal, seasonal and interannual variability of O_3 in the marine boundary layer are described and compared to those observed in other tropical locations. The O_3 diurnal cycle shows two regimes: (i) photochemical destruction followed by nighttime recovery in the cold season (July to November) and (ii) daytime advection and photochemical loss followed by nighttime depositional loss associated to windless conditions in the warm season (February to April). Wavelet spectral analysis of the intraseasonal variability of O_3 reveals components with periods characteristic of tropical instability waves. The O_3 seasonal variation in Galápagos is typical of the Southern Hemisphere, with a maximum in August and a minimum in February–March. Comparison with other measurements in remote tropical ocean locations shows that the change of the surface O_3 seasonal cycle across the equator is explained by the position of the Intertropical Convergence Zone and the O_3 levels upwind.

1. Introduction

In the last 40 years a wealth of data has been accumulated from measurements of surface ozone (O_3) and vertical profiles at multiple observatories in remote locations around the globe. For instance, surface measurements at stations of the U.S. Geophysical Monitoring for Climate Change network started 40 years back [Oltmans and Levy, 1994], and the Southern Hemisphere ADDitional OZonesondes (SHADOZ) program [Thompson et al., 2011] has collected and made public ozonesonde data acquired at tropical locations since 1998. Also, numerous ship- and aircraft-based atmospheric observations of trace gases relevant for the tropospheric O_3 budget have been carried out since the seventies [e.g., Fabian and Pruchniewicz, 1977; Piotrowicz et al., 1986; Winkler, 1988; Johnson et al., 1990; Paluch et al., 1995; Gregory et al., 1996; Schultz et al., 1999; Browell et al., 2001; Wang et al., 2001; Shiotani et al., 2002; Conley et al., 2011]. These measurements have enabled comprehensive studies of the background atmosphere, which have elucidated the main mechanisms controlling the natural O_3 budget and its variability across different time scales. Despite of the fact that O_3 and trace gas observations are still limited and sparse over the open ocean, a better picture of global O_3 distribution is now available, which permits assessing more confidently changes that may be attributed to human activity.

Globally, the remote marine boundary layer (MBL) and in particular the tropical Pacific MBL is an atmospheric O_3 sink. The existence of an equatorial surface O_3 minimum has been demonstrated by several research cruises [Piotrowicz et al., 1986; Winkler, 1988; Johnson et al., 1990]. In this low NO_x regime, the O_3 budget is determined by transport and its main photochemical losses. The daily variability of the O_3 profile shows a characteristic pattern encompassing photochemical daytime depletion and nighttime replenishment [Johnson et al., 1990; Oltmans and Levy, 1994; Ayers et al., 1997; Dickerson et al., 1999; Nagao et al., 1999;

Figure 1. Daily averages of surface O_3 mixing ratios recorded during the PIQUERO and CHARLEX campaigns (black line), concurrent ozonesonde surface measurements (empty circles), and daily averaged sea surface temperature from MODIS Aqua and Terra observations (blue) and from in situ measurements at Santa Cruz (red) and San Cristóbal (green).

emitted from the ocean surface to O_3 depletion in the MBL, and the free troposphere (FT) has also been quantified [Dickerson *et al.*, 1999; Read *et al.*, 2008; Saiz-Lopez *et al.*, 2012]. The photochemical lifetime of O_3 in the equatorial Pacific MBL has been estimated to be of the order of 6.5 days [Conley *et al.*, 2011]. Surface O_3 sources are horizontal transport [de Laat and Lelieveld, 2000], entrainment from the FT [Ayers *et al.*, 1997; Hu *et al.*, 2010; Conley *et al.*, 2011], and some limited NO_x chemistry.

The impact of convection on free-tropospheric O_3 is apparent in the structures of moist, low O_3 layers sandwiched between dry, high O_3 layers frequently found in ozonesonde profiles and aircraft surveys, resulting from convection followed by horizontal advection in the middle troposphere [Shiotani *et al.*, 2002]. Due to the link between water vapor and O_3 , and to enhanced convection, the seasonal cycle of MBL and tropospheric O_3 in the tropical Pacific [Thompson *et al.*, 2003] is related to the sea surface temperature (SST) seasonal variation. On interannual time scales, El Niño–Southern Oscillation (ENSO) is the dominant mode of tropical tropospheric O_3 variability [Ziemke *et al.*, 2010; Randel and Thompson, 2011]. Chemical transport models (CTM) driven by meteorological reanalysis fields reproduce the main features of locally observed seasonal variations in O_3 [Wei *et al.*, 2002] as well as the ENSO-related interannual variability and the intraseasonal variability of the tropospheric column O_3 (TCO) above the Pacific [Ziemke *et al.*, 2015]. By contrast, chemistry climate models (CCM), usually constrained by SST observations, reproduce ENSO interannual variability but struggle to reproduce shorter time scale changes [Oman *et al.*, 2011; Ziemke *et al.*, 2015].

The intraseasonal variability of tropospheric O_3 in the Pacific has been studied using satellite data, and it has been found to contain the signature of the Madden-Julian Oscillation (MJO) [Ziemke *et al.*, 2015]. MBL O_3 variability on this time scale is perhaps not as well studied, mainly due to the sparse spatial coverage of observatories and sparse time coverage inherent in ship and aircraft campaigns. Continuous measurements at specific locations are required to observe changes related to oscillation patterns such as the MJO. For example, continuous surface measurements at Samoa display a ~ 15 day period pattern throughout the year [Oltmans and Levy, 1994], which remains to be studied in detail. A previous study of selected sections of this data set did not reach firm conclusions about the cause of such variability [Piotrowicz *et al.*, 1991] but suggested that large-scale circulation patterns could determine the characteristics of the equatorial western Pacific O_3 minimum.

In this paper, the first ground-based continuous observations of surface O_3 in the eastern tropical Pacific are reported. The first part of these observations was carried out in the period 2000–2002, and a second set of measurements was acquired 10 years later in the period 2010–2012. The variability of O_3 on the daily, intraseasonal, and seasonal time scales is investigated and discussed in the context of background O_3 in the tropical MBL across the globe.

de Laat and Lelieveld, 2000; Hu *et al.*, 2010]. Photochemical losses are dominated by O_3 photolysis followed by the $H_2O + O^1D$ reaction and HO_x reactions [Liu *et al.*, 1983; Thompson *et al.*, 1993]. This loss mechanism is favored by high insolation over warm sea water and is subjected to seasonal changes. In remote locations the maximum amplitude of the daily cycle is associated to the insolation maximum, although this may be obscured by seasonal continental outflows [Oltmans and Levy, 1994]. Higher O_3 mixing ratios also tend to favor larger amplitudes of the daily cycle, since O_3 depletion depends on odd oxygen radicals generated by O_3 photolysis [de Laat and Lelieveld, 2000]. The contribution of halogens

Figure 2. Correlation plots between UV and ECC surface measurements for (top) PIQUERO and (bottom) CHARLEX. Black lines are linear fits and dashed lines the corresponding 95% prediction limits.

April 2001 to 24 May 2001 and 29 March 2002 to 25 April 2002 has been removed due to values exceeding systematically the contemporary ECC measurements by more than a factor of 2, which is possibly due to a local pollution source. Meteorological measurements carried out at the observatory from 2000 to 2002 include air temperature, wind speed (WS), and relative humidity (RH). Only monthly averages of SST are available for the 2000–2010 period.

CHARLEX (Climate and HALogen Reactivity tropical Experiment) was a ground-based study of the composition and chemistry of the MBL carried out at Puerto Villamil, Isabela Island (0.96°S, 90.97°W) from September 2010 to June 2011 and at the meteorological observatory in San Cristóbal from July 2011 to February 2012 [Gómez Martín *et al.*, 2013] (see Figure 1). Its main goal was to study the temporal evolution of reactive halogens in the eastern Pacific MBL. Combined with spatially resolved data from the same region [Mahajan *et al.*, 2012] and other locations around the world [Prados-Roman *et al.*, 2015], the results of CHARLEX have provided new field insights into the emission of reactive iodine precursors from the ocean [Carpenter *et al.*, 2013; MacDonald *et al.*, 2014] and the contribution of iodine and bromine to surface O₃

2. Instrumentation

A summary plot of the two campaigns is presented in Figure 1, showing surface O₃ daily averages and surface ozonesonde measurements plotted alongside concurrent satellite and in situ SST observations for seasonal contextualization. The SHADOZ program started regular ozonesoundings at San Cristóbal, Galápagos (Ecuador) in March 1998 and is ongoing up to the present, albeit with some interruptions. This program was augmented by the PIQUERO (Primera Investigación sobre la Química, Evolución y Reparto de Ozono) project, which measured surface O₃ at San Cristóbal from September 2000 to July 2002. Vertical profiles were measured using standard Electrochemical Concentration Cell (ECC) ozonesondes [Thompson *et al.*, 2007]. Surface O₃ was measured using an ultraviolet absorption (UV) detector (2B Technologies, serial number 16), which was colocated with the ozonesonde launch program at the meteorological observatory at San Cristóbal (0.90°S, 89.61°W). The inlet of the surface O₃ monitor at the meteorological observatory was placed 1 m above the roof of the two story observing building and approximately 14 m above mean sea level using Teflon tubing to the instrument. The SHADOZ ECC measurements at the surface were employed to validate the UV measurements (Figure 2, top). Based on this comparison, UV data from 15

depletion [Saiz-Lopez *et al.*, 2014]. A detailed description of the measurement sites can be found in Gómez Martín *et al.* [2013]. Surface O₃ measurements were performed with two UV absorption detectors (2B Technologies, models 202 and 205, accuracy 1.5 and 1.0 ppbv, respectively), one of which was sent for refurbishing and recalibration to the manufacturer during the campaign and then sent back for replacing the other a month later. At Isabela, the Teflon tubing inlet was guided using a pole pointing southward, sampling air 2 m away from the laboratory walls and about 5 m directly above sea level. In San Cristóbal the inlet was set up in a similar manner on the top of a two storey building (5 m above ground level) within the meteorological station compound. Data were acquired every 2 s and continuously logged into a computer. The data were subsequently averaged in 10 min bins for preliminary analysis and quality control, and finally, 1 h averages and the 1 day averages, shown in Figure 1, were calculated for the analysis presented in this paper. A wealth of ancillary data were acquired in situ during the campaign (meteorological variables, NO_x, and global irradiance) [Gómez Martín *et al.*, 2013]. A set of ozonesondes (Science Pump Corp, Model 6A) was launched mainly during the warm season in 2011 (see Figure 1), which was necessary because the SHADOZ program at San Cristóbal had been interrupted in 2008. The ozonesondes were attached to meteorological radiosondes (Vaisala), which provided pressure, temperature, and humidity data. The entire system was flown on a TOTEX balloon (TX-1200) filled with helium. Chemical sensing solutions were prepared following the manufacturer's recommendations. The standard cathode solution used was 1% potassium iodide buffered [Komhyr *et al.*, 1995]. An O₃ generator (Science Pump Corporation, TSC-1) was used for calibration and preparation of the sondes [Komhyr, 1986]. Laboratory studies indicate that ECC ozonesondes operated according to standard procedures yield 3–5% precision and 5–10% accuracy up to 30 km altitude [Smit *et al.*, 2007]. Simultaneous ozonesondes launched from Isabela and San Cristóbal at 12:00 local time (LT) during April and May 2011 were essentially in agreement and showed that the vertical structure of the MBL and the lower free troposphere (LFT) above the two locations is similar. A collection of colocated ECCs was used as surface instruments to validate the UV absorption measurements in the period when the surface monitors were replaced, with both techniques being in good agreement (Figure 2, bottom).

The SHADOZ O₃ profiles obtained at San Cristóbal between 1998 and 2012 [Thompson *et al.*, 2003] have been employed to contextualize the O₃ measurements at Galápagos. Contemporary remote sensing observations from Moderate Resolution Imaging Spectroradiometer (MODIS) Terra (2000–2002) and MODIS Aqua (2002–2012), as well as the NOAA OI SST V2 High Resolution Dataset (1981–present) [Reynolds *et al.*, 2007], have been used for investigating connections between surface O₃ and SST. The averaging regions or “boxes” of MODIS SST satellite data around Galápagos are shown in Gómez Martín *et al.* [2013, Figure 2a] and also defined in the supporting information of the present work (Table S1). To compensate for the lack of daily meteorological and SST data at San Cristóbal during PIQUERO, records belonging to other locations such as the Charles Darwin Station at Santa Cruz Island (0.75°S, 90.32°W) and the two easternmost equatorial TAO buoys (0°S and 2°S, 95°W) [McPhaden *et al.*, 2009] have been compiled.

3. Observations

The regional climate around the Galápagos Archipelago is determined by the interaction of ocean currents and winds, governed by the seasonal shift of the ITCZ, and strongly influenced by ENSO. The year is divided climatologically into two seasons: the rainy and warm season lasting from January–February to April and the dry colder season lasting the remainder of the year [Alpert, 1963]. This division does not only determine the O₃ seasonal cycle but also modulates the intraseasonal and the daily variability.

3.1. Daily Variability

The O₃ daily cycle in the Galápagos has two distinct regimes. From July to November, i.e., during the cold season and when O₃ seasonal maximum occurs, a photolytic destruction regime is observed, with O₃ peaking early in the morning (7:00–8:00 LT), decaying during the day, and recovering during the night (the average daily profile of the two campaigns for September–November is shown in Figure 3a as a solid black line with black circles). A permanent strong inversion exist during the cold season (see section 3.3), which suggest that advection is the main mechanism for nighttime O₃ replenishment [de Laat and Lelieveld, 2000]. Trajectory analysis shows that air masses spend several days over the Pacific cold tongue before being advected into the Galápagos area [Sorribas *et al.*, 2015]. Note in Figure 3a that a small increase of O₃ is observed between 6:00 and 7:00 LT, which corresponds to peak NO₂ levels of ~100 pptv early in the morning. Some rush hour

Figure 3. Monthly averaged hourly values of surface O_3 (black), NO_2 (green squares), global irradiance (red), and wind speed (blue) (the axes titles are color coded). The large squares represent NO_2 mixing ratios above the detection limit of the instrument. (a) Monthly averaged daily profiles for October 2010. The average daily profile of O_3 of the two campaigns for September–November is represented by the dotted black line. (b) Monthly averaged daily profiles for February 2011. The dotted black line represents here the average daily profile of O_3 for February–April.

anthropogenic emissions close to the site caused by ship traffic were observed on the spot, but the NO_2 cycle is driven mainly by radiation. The evening peak gives an idea of the total NO_x levels, which are at the limit of what normally is considered a low NO_x environment [de Laat and Lelieveld, 2000]. The average O_3 daytime decrease for the two campaigns in the cold season is ~ 1 ppbv d^{-1} . The monthly average daytime decrease for October 2010 is 2.3 ppbv d^{-1} (solid black line in Figure 3a). This daily cycle may also appear during the transition months between the warm and the cold seasons (May–July and November–January), although generally a flat profile is observed. The estimated contribution of HO_x photochemistry to O_3 photochemical loss is $\sim 70\%$ [Gómez Martín et al., 2013], with the rest corresponding to halogens (IO_x and BrO_x).

Figure 4. Monthly averages of O_3 changes. Black squares: O_3 at 17:00 LT minus O_3 at 7:00 LT. Negative values indicate O_3 (photochemical) loss and tend to appear in the cold periods. Red squares: O_3 at 10:00 LT minus O_3 at 5:00 LT. Positive values indicate O_3 increase (advection) and tend to be larger in the warm periods.

The amplitude of the daily cycle at Galápagos also has some interannual variability. Figure 4 shows the time series of monthly averaged daily O_3 loss from 7:00 LT to 17:00 LT. Net photolytic O_3 destruction (black squares, negative values) was observed through the cold seasons of 2000, 2001, and 2010. In 2011 photolytic O_3 loss was only seen in July and not in the following months, when a large cold season negative anomaly occurred (see interannual variability, section 3.4).

In the warm months (February through April, Figure 3b), and sometimes in the preceding transition period (end of December and January), a completely different O_3 daily cycle emerges, which appears to be mainly

driven by the wind daily cycle. Figure 3b (blue line) shows that during night time the wind is very low. Surface dry deposition to the land surface surrounding the measurement site during the windless periods is therefore a primary cause of the observed nighttime O_3 reduction. At dawn, wind starts blowing again from the south and flushes the stagnant air mass bringing O_3 -richer open ocean air, causing a 5–6 ppb increase between 6:00 LT and 10:00 LT. The replenishment of O_3 is followed by daytime photochemical destruction. The relative changes between 10:00 and 17:00 LT are similar between Figures 3a and 3b, suggesting similar photochemical destruction in the warm and cold period.

The higher levels of NO_x in the warm period (the green squares in Figure 3b correspond to NO_2) are possibly due to the increase in ship traffic during the peak tourist season, while the higher NO_2 nighttime levels (0.4 ppb) may result from a combination of increased fuel consumption and the low winds. NO_2 and NO spikes of the order of 1 ppb are observed in the early morning and the evening. The reaction of O_3 with NO is probably responsible for the absence of nighttime NO . This may also contribute to the removal of O_3 , although the NO_2 levels observed are lower than the O_3 nighttime depletion (~4 ppb), which shows that this cannot be the main O_3 sink. The Pearson correlation coefficients between nighttime (18:00–5:00 LT) O_3 , NO_2 , and wind speed in the January–April 2011 period are $R(O_3 - NO_2) = -0.434$, $R(O_3 - WS) = 0.425$, and $R(NO_2 - WS) = -0.571$ ($p < 0.01$). Visual inspection of the hourly averaged data confirms that some very low O_3 (even complete destruction) events coincide with high NO_x episodes (up to 3 ppbv) but also that high NO_x episodes with nonzero wind do not lead to large nighttime O_3 depletion. Thus, it can be concluded that low wind favors accumulation of NO_x and depletion of O_3 , but ultimately, it is another process (most likely dry deposition to the land surface) that leads to the O_3 loss. Figure 3 also shows some evidence of transient O_3 production related to the high NO_x early morning and evening events. Figure 3a shows a sharper increase of O_3 between 6:00 LT and 7:00 LT in October. The onset of O_3 increase in the February average in Figure 3b matches very well the onset of wind, but the February–April average (black dots) shows that some O_3 production (~1 ppb) occurs at dawn between 5:00 LT and 7:00 LT during the NO_x spike before the wind starts blowing at 7:00 LT. There is also some indication in Figure 3b that the NO_x spike in the evening forms some extra O_3 just before dusk. In any case, it seems clear from the data in Figure 3 that advection is the major source of O_3 during the warm season. It is worth noting that despite the large O_3 increase between 6:00 and 8:00 LT, the total mixing ratios are still very low, at levels similar to those at Samoa [Oltmans and Levy, 1994]. Figure 4 shows the time series of monthly averages of daily advection of O_3 between 5:00 LT and 10:00 LT. It can be seen that the deposition-advection process occurs systematically from February to April (red squares, positive values).

Figure 5 shows average vertical profiles for some of the most frequent launching times at Galapagos from the SHADOZ database, with August–October averages plotted in Figure 5a and February–April averages in Figure 5b. In the warm season the profile at 6:00 LT reaches the highest MBL O_3 at 1 km and the lowest at the surface. The departure of the 6:00 LT profile from the dependence on altitude of the daytime profiles below 0.6 km reinforces the conclusion that O_3 is depleted near the land surface around the measurement site during nighttime due to the low surface wind regime. By contrast, the cold season profiles are roughly in the same order though the MBL and the inversion layer (IL). Figure 5d shows daily profiles from the ozonesondes at selected heights for February–April, emphasizing the distinct behavior at the surface in the warm season, which contrasts with photochemical depletion between 0.6 and 2 km. The daily variation in the cold season is fairly homogeneous through the MBL, with photochemical production between 6:00 and 8:00 LT, followed by photochemical destruction through the day and recovery in the evening.

3.2. Intraseasonal Variability

3.2.1. Surface Data Correlations in the Frequency and Time Domains

The daily averages of SST and O_3 in Figure 1 contain oscillations with amplitude of up to 4°C and 10 ppbv respectively within periods of 2–4 weeks. The intraseasonal variability can be better visualized by applying a 5 day running average to the daily average time series in order to remove noise and then subtracting the monthly average from the daily average time series. The resulting data sets for surface O_3 and H_2O vapor mixing ratios, wind meridional component (v), and SST during CHARLEX are shown in Figure 6. O_3 peaks separated by 15–30 days are concurrent with SST and water vapor minima.

Due to the nonstationary nature of time series of atmospheric and oceanic variables (amplitude and phase varying with time), wavelet analysis is a suitable technique for spotting their underlying oscillation patterns

Figure 5. (a) August–October average vertical profiles for some of the most frequent launching times of the SHADOZ database. Thick lines: O_3 , thin lines: temperature (for simplicity only two temperature profiles out of four are shown). (b) The same for February–April. (c) Daily profiles at selected altitudes for August–October, plotted alongside the surface UV average profile for September–October (no August data are available for PIQUERO and CHARLEX). (d) The same for February–April.

Figure 6. Deseasonalized, five day moving-averaged time series of (a) O_3 mixing ratio, (b) water vapor mixing ratio in parts per cent by volume (ppcv), (c) meridional wind component, and (d) in situ SST for the CHARLEX campaign.

Figure 7. Wavelet power spectrum (using the Morlet wavelet) of (a) surface O_3 mixing ratio anomalies and (b) in situ SST for the period 17 September 2010 to 31 January 2012 (CHARLEX campaign). (c) The wavelet power cross spectrum and (d) the wavelet squared coherence of these two variables. The black contours denote the 95% a priori confidence limit with respect to red noise. The shaded areas indicate the cone of influence, where edge effects might distort the picture. Arrows indicate the phase lag between the two variables.

and resolve their amplitude variations with time. Figure 7 shows the power wavelet spectrum [Torrence and Compo, 1998] of O_3 (Figure 7a) and in situ SST (Figure 7b) during CHARLEX, and the O_3 -SST cross power wavelet spectrum (Figure 7c) and wavelet coherence (Figure 7d) [Grinsted et al., 2004] for the CHARLEX campaign. Relative phase is shown as arrows (in-phase pointing right, antiphase pointing left, and 90° pointing down). During CHARLEX, O_3 and SST have oscillations with periods between 15 and 33 days (Figure 7a and 7b). Global wavelet spectra and time series of variance in selected frequency ranges are useful to visualize this variability. The global wavelet spectra for O_3 (Figure S1) and satellite and in situ SST (Figures S2 and S3, respectively) have peaks 95% significant against red noise for periods of 17 and 33 days, and 17, 33, and 56 days, respectively.

Figure 8. Wavelet power spectrum (using the Morlet wavelet) of (a) surface O₃ mixing ratio anomalies and (b) in situ SST for the period September 2000 to April 2001 (PIQUERO campaign). (c) The wavelet power cross spectrum and (d) the wavelet squared coherence of these two variables. The black contours denote the 95% a priori confidence limit with respect to red noise. The shaded areas indicate the cone of influence, where edge effects might distort the picture. Arrows indicate the phase lag between the two variables. (e–h) The same for the period September 2001 to March 2002.

Besides the observation of significant frequency components in different variables, it is important to establish if these are simultaneous and coherent. There is significant O₃-SST common power in the ~15 and ~30 day bands, mainly during the two cold seasons (Figure 7c). Significant coherence also exists for these bands (Figure 7d), from the beginning of the measurements to the end of November 2010 and between mid-July and early November 2011. There is significant cross power around the 16 day period in January–February 2011 but no coherence. Significant coherence seems then to be restricted to the cold season, even though significant cross power also exist in the early warm season. Within the intervals of significant cross power and coherence, the phase lag is 180–225° in the 15 and 30 day bands in the cold season of 2010, while in the cold season of 2011 is ~90° and ~225° in the 17 and 30 day bands, respectively. The wavelet spectra and cross-spectral relationships of O₃ and H₂O mixing ratios for the CHARLEX period are shown in Figure S4. The picture is very similar to that in Figure 7, and in fact SST and H₂O have significant cross power and squared coherence and are in phase in both cold seasons of the CHARLEX campaign. The generally anti-phase behavior of O₃ and SST (H₂O) in the frequency domain has its time domain counterpart in negative correlation between this variables (see below), as suggested by Figure 6, and it fits with the fact if that water vapor increases, this may enhance O₃ photolytic depletion.

Figure 8 shows the corresponding wavelet spectra for PIQUERO in the period September 2000 to March 2002 (with an interruption in between). Unfortunately, discontinuities in the data preclude an analysis of the whole campaign, and a good part of both cold seasons is impacted by the data edges. The results for the PIQUERO period do not show the same features than in the CHARLEX period or at least not as clearly. Significant oscillations in O₃ and SST are missing in the cold season of 2000. But, on the other hand, O₃ oscillations have significant power in the 17 and 33 day bands in the cold season of 2001. SST significant power in these bands falls in the cone of influence region. Significant cross power exists from October to December. In the warm

Figure 9. Vertical distribution of O_3 in the MBL and LFT during the cold season. Figures 9a–9c (1999) show O_3 mixing ratio contour plot and inversion altitude (black points) from the (a) SHADOZ record, (b) surface O_3 anomalies from SHADOZ, and (c) satellite SST. Figures 9d–9f show the same for 2000; Figure 9b also shows surface O_3 anomalies from and PIQUERO in red. The satellite SST series have been obtained from the NOAA OI SST V2 High Resolution Dataset by averaging $1/4^\circ$ pixels around San Cristóbal Island. The SST concurrent with the ozonesonde measurements is highlighted by blue dots connected with thick lines. The triangles indicate which vertical profiles corresponding to high SST (triangle) and low SST (inverted triangle) anomalies are used to calculate the average vertical profiles shown in Figure 10 (2000) and Figure S10 (1999).

season of 2001, significant power between 8 and 20 day periods is observed in O_3 . This high variability precedes the period from 15 April 2001 to 24 May 2001 screened due to factor of 2 deviations with respect with the collocated ECCs at San Cristóbal (see section 2). This high-frequency variability was not observed at Isabela Island.

In order to show how these frequency relationships translate into the time domain, Pearson correlation coefficients between the anomalies of surface O_3 and other variables have been computed (Table S1). Correlation coefficients have been determined for the entire period of measurements, for all the cold (warm) season periods together and for each individual season. When the complete time series or the warm season subsets are considered, the correlations between O_3 and other variables are poorer or less significant than for the cold (warm) seasons subsets considered together or individually. Enhanced correlations for separated seasons and the anticorrelation of SST and O_3 in the cold periods reflect the time-dependent frequency and phase relationships described above. However, these correlation coefficients are generally smaller than 0.5, so these variables explain individually only a small fraction of the O_3 variability. Results of multivariate linear regression of O_3 anomalies versus the available environmental and meteorological variables are listed in Table S2. This analysis yields more than one significant regression coefficient for cold season data segments. The most significant increase in the explained variance of O_3 anomalies with respect to the simple correlations in Table S1 occurs for the first CHARLEX cold season, where the explained variance rises from 32% with only water vapor to 59% by adding linear terms to the regression (v , SST, Rad, and NO_2). Note that this is the only period of the campaign during which all in situ variables were measured.

3.2.2. Intraseasonal Variability in the Vertical Distribution of Ozone

The low sampling rate of the SHADOZ ozonesondes (average of three sondes per month between 1998 and 2008) precludes a study of the weekly to monthly variability of the O_3 profile using spectral analysis

Figure 10. Average vertical profiles of (a) temperature, (b) O_3 mixing ratio, (c) relative humidity (bottom axis) and H_2O mixing ratio in parts percent by volume (top axis, thin lines) for positive (red) and negative (blue) SST anomalies in the cold season of year 2000 (indicated by triangle and inverted triangle symbols in Figure 9f). The blue (red) dashed lines indicate the range of the inversion layer during negative (positive) SST anomalies.

techniques. However, during the PIQUERO period and the year before, the number of ozonesondes launched was higher (weekly). Figure 9 (and Figure S5) show contour plots of O_3 vertical distribution versus time (a and d), surface O_3 (b and e), and SST (c and f). The figures include examples for two cold periods (warm periods in Figure S5). The altitude of the main inversion (altitude of maximum absolute lapse rate) is overlaid on the O_3 contour plot. Inspection of Figure 9 reveals ~20–30 day period oscillations on the structure of the MBL and FT at different altitudes. In 2000, the inversion height (black circles) changes roughly following the oscillations of SST. The O_3 mixing ratios within the MBL and the IL experience oscillations as well. Using the data in Figures 9d–9f in the period where oscillations are observed (J153–J337, i.e., from 1 June to 2 December 2000), the Pearson correlation coefficient between the O_3 anomalies (0–300 m average) and MBL height is $R = -0.432$ ($p = 0.022$). This increases to $R = -0.610$ ($p = 0.006$) for the J153–J265 period (1 June–21 September). Correlation of MBL height with SST is also significant: $R = -0.568$ ($p = 0.014$) for J153–J265. The anticorrelation between O_3 and SST anomalies (i.e., the blue dots in Figures 9e and 9f) is weak and not significant at 95% level, except if the data point at J272 is screened. The data in Figure 9a–9c (1999) show significant correlation between O_3 and SST anomalies in the J189–J301 period ($R = -0.497$, $p = 0.016$) but no significant correlation between SST and MBL height. The ozonesonde data for the cold period of 2001 does not show significant correlations. In Figure 10, the averaged air temperature, O_3 mixing ratio and RH vertical profiles corresponding to negative and positive anomalies of SST during the cold season of 2000 (Marked with triangles in Figures 9e and 9f) are compared. It can be seen that low surface O_3 coincides with a higher inversion (by up to ~500 m, Figure 10a) and higher water content of the MBL (Figure 10c).

Figure S5 shows how in the eastern Pacific warm season (March–May) the height of the inversion and the O_3 mixing ratios are not correlated to variations of SST. An alternation of periods of capped/uncapped MBL occurs separated by ~20 days, and the absence of inversion is generally associated with a decrease of O_3 through the MBL–IL–LFT column due to convection.

3.3. Seasonal Variability

Figure 11 shows average vertical profiles of T (a), O_3 (b), and RH (c) for March, June, September, and December. The annual cycles of O_3 and H_2O mixing ratios in the MBL, the IL, and the LFT using the full

Figure 11. Average vertical profiles for the 1998–2014 period of (a) temperature, (b) O_3 , and (c) relative humidity for the months of March, June, September, and December during the 1998–2014 period, using SHADOZ and CHARLEX ozone sondes. The vertical thick lines indicate the average thickness of the IL for the respective months (see text for definition of the IL). (d and e) The seasonal cycle of O_3 and water vapor averaged over different layers (surface, average MBL, IL, and LFT) are shown, respectively. Fourier series expansion with terms fitted to the O_3 seasonal variation at the surface and the FT is shown in red in Figure 11d. (f) The seasonal variation of the inversion altitude and maximum lapse rate at the inversion are plotted (the size of the symbols indicates the fraction of capped MBL profiles relative to the total number of sondes launched, with the largest size indicating 100%).

SHADOZ data set (1998–2014) plus the CHARLEX ozonesondes (2011) are shown in Figures 11d and 11e, respectively. The annual cycles of inversion height and lapse rate calculated from ozonesonde data are plotted in Figure 11f. The cycles of surface wind and SST are plotted in Figures 12g and 12h, respectively. The IL is defined here by the interval of positive lapse rates ($-dT/dz$) around the altitude of the maximum lapse rates, while the MBL and the LFT are defined as the layers between the surface and the IL and between the IL and 4 km, respectively.

Seasonal anticorrelation between surface O_3 and SST ($R = -0.848$) and H_2O ($R = -0.882$) and positive correlation with wind ($R = 0.719$, mostly with v) can be seen in Figures 11d and 11e and Figures 12 (12e–12h). Surface O_3 is also anticorrelated with the inversion layer height and positively correlated with the lapse rate (Figure 11f). The seasonal variation of O_3 in the MBL, IL, and FT shows a secondary maximum in the warm season that is not observed at the surface. The water vapor mixing ratio only shows a strong seasonal dependence in the MBL.

For the purpose of comparison with seasonal cycles in other locations [Parrish *et al.*, 2016], a sine function of the form $y = y_0 + A_1 \sin(\chi + \phi_1) + A_2 \sin(\chi + \phi_2)$ has been fitted to the seasonal cycles of O_3 in Figure 11d. This is equivalent to derive a Fourier series expansion with a fundamental and a second harmonic term. The resulting parameters for surface O_3 are $y_0 = 12.8 \pm 0.5$ ppbv, $A_1 = 5.3 \pm 0.8$ ppbv, $\phi_1 = -2.74 \pm 0.13$ rad, $A_2 = 0.8 \pm 0.7$ ppbv, and $\phi_2 = -0.7 \pm 1.0$ rad (95% confidence limits). The increase in the quality of the fit by including a second harmonic is marginal ($R = 0.986$ versus $R = 0.972$). The seasonal cycle above the surface presents a significant second harmonic component. The fitted parameters for the LFT O_3 cycle are: $y_0 = 24.2 \pm 0.3$ ppbv, $A_1 = 4.4 \pm 0.4$ ppbv, $\phi_1 = 2.69 \pm 0.09$ rad, $A_2 = 3.0 \pm 0.4$ ppbv, and $\phi_2 = -1.21 \pm 0.14$.

3.4. Interannual Variability

Figure 12 shows composites or continuous series of deseasonalized monthly averages of O_3 , water vapor, WS, and SST. The O_3 series has been constructed by concatenating the SHADOZ monthly averages with the

Figure 12. Monthly mean values of deseasonalized observations of (a) O_3 , (b) water vapor, (c) wind speed, and (d) SST (in situ in black and satellite in red). The small panels on the right column show the seasonal cycle of each variable. A Fourier series expansion with 5 terms fitted to the O_3 seasonal variation is shown in red in Figure 12e. For the O_3 record (black dots in Figure 12a), the size of the symbol is scaled to the number of observations. During PIQUERO and CHARLEX the UV and ECC data are averaged, and therefore, the number of observations is much larger.

monthly averages of the data acquired during the CHARLEX campaign. The surface data acquired during the PIQUERO campaign (filtered as explained in section 2) is averaged with the SHADOZ data obtained during the same period to obtain the corresponding monthly averages. The water vapor, wind speed, and SST monthly averages are calculated from the measurements at San Cristobal. The correlation between O_3 and the other series in Figure 12 is not larger than 0.5 but statistically significant at the 99% confidence level. The sign of correlation with SST (Figure 12d) and water vapor (Figure 12b) is negative. Regression of O_3 against several variables does not enhance the amount of explained variance beyond 25%.

4. Discussion

4.1. Daily Variability

Of all tropical and subtropical stations where data are available, Samoa is the one resembling more closely the behavior of surface O_3 at Galápagos, except for the February–April warm period. In Samoa there is a small seasonal dependence of the amplitude of the daily cycle, which is larger in June–November (~ 2 ppbv), coincident with the insolation and the O_3 maxima. Higher O_3 mixing ratios tend to favor larger amplitudes of the daily cycle because the primary removal mechanism (photolysis and reaction of O^1D with water) is first order in O_3 . In Galápagos, net photolytic destruction peaked in the cold season of 2000, 2001, and 2011 (Figure 4, black squares negative values). The small amplitude of the daily cycle in August–November 2011 is possibly related to the generally low O_3 mixing ratios during the 2011 cold season.

The O_3 daily cycle in Galápagos during the warm season resembles the daily cycle and absolute levels observed at Paramaribo (Suriname, 6°N , 55°W) through the year [Maas, 2004]. The actual background surface O_3 levels in the warm season are obscured by the losses caused by nighttime stagnation of the sampled air masses. The amplitude of the seasonal cycle at a similar location such as Samoa is 10 ppbv (Figure 13), which suggests that the average O_3 in the warm season at Galápagos could be around 8–9 ppbv using the seasonal O_3 maximum as a reference. Extrapolation of the average vertical profiles at 8:00 and 12:00 LT (Figure 5a) from 0.6 km downwards also suggests average surface values around 7–10 ppbv, i.e., between the night time minimum and the daytime maximum. Thus, daily averages of the surface UV measurements, and also

Figure 13. Seasonal cycle (January to December) of surface O_3 , outgoing longwave radiation (OLR) (NOAA), meridional (v) and zonal (u) wind (SCOW) and SST (NOAA) for several remote ocean locations in the tropical Pacific, Atlantic and Indian Oceans. Panels grouped in sets of four, one panel for each variable and one set for each station. Multiyear O_3 data from SHADOZ (Galápagos, Ascension, Reunion) and NOAA/Earth System Research Laboratory (ESRL) (Hawaii, Samoa, and Barbados). O_3 data at Kiritimati (Christmas Island) from Clarke *et al.* [1996], Takashima *et al.* [2008], and Conley *et al.* [2011] (different months from 1994 to 2007). O_3 data at Cape Verde (2007) from Lee *et al.* [2009]. O_3 data at Paramaribo (2003) from Maas [2004] and the STAR project (<http://projects.knmi.nl/star/intern/researchschool.htm>).

monthly averages of ECC measurements combining launch times before and after 6:00 LT, may not be far from the background O_3 mixing ratios.

Of those ozonesondes launched at San Cristóbal from January to April, 28 were launched between 5:00 and 7:00 LT and 45 were launched between 8:00 and 18:00 LT. Measurements taken during the low wind periods at night during warm months show systematically lower O_3 mixing ratios (Figure S6) and cannot be considered as representative of the oceanic background conditions

4.2. Intraseasonal Variability

The oscillation periods observed in the O_3 daily anomalies in the cold season are close to the periods of tropical instability waves (TIWs) [Legeckis, 1977; Chelton *et al.*, 2000]. TIWs are westward propagating nonstationary waves with 17 day period and 1 m s^{-1} phase speed near the Equator, and 33 day period and 0.5 m s^{-1} phase speed north of the equator [Lyman *et al.*, 2007]. They are caused by meridional and vertical shear of the equatorial oceanic current system and are observed in oceanic variables such as SST [Chelton *et al.*, 2000]. TIWs modify the stability of the MBL, influencing meridional and zonal wind [Hayes *et al.*, 1989; Chelton *et al.*, 2001; Hashizume *et al.*, 2002], as well as water vapor and boundary layer height [Hashizume

et al., 2002]. Pacific TIWs show significant amplitudes during the equatorial eastern Pacific cold season and disappear in the warm season, when the cold tongue vanishes [Hayes *et al.*, 1989]. TIWs within the Galápagos archipelago have been previously reported [Sweet *et al.*, 2009]. Wavelet spectral analysis of archive SST and wind data known to display TIWs [e.g. Halpern *et al.*, 1988], as well as of data contemporary to the PIQUERO and CHARLEX campaigns (supporting information, p.8), confirms that significant TIWs passed through Galápagos during the CHARLEX campaign. The identification of the 17 and 33 day SST components with TIWs and the significant cross power and coherence between SST and O_3 in these bands (Figure 7) in the equatorial eastern Pacific cold season suggest that the coupling of TIWs into the MBL may also result in O_3 oscillations.

Figure 10 shows that high SST coincides with a higher inversion and higher water content of the MBL in 2000. These are effects of the coupling of SST TIWs to the MBL structure previously found during the Shoyo-maru 1999 cruise [Hashizume *et al.*, 2002], although an impact on O_3 was not reported [Shiotani *et al.*, 2002]. The cruise track at 2°N intercepted several crests and troughs of the SST waves. The impact of TIWs on the MBL was characterized by launching four radiosondes per day, but only one in four was coupled to an ozone-sonde. Note that increases in MBL height and decreases in O_3 mixing ratio occur consistently in both datasets (see Figure S10).

The generally antiphase relationship for the significant cross power and coherence intervals (Figure 7) and the anticorrelation in the time domain of O_3 with SST and H_2O mixing ratio suggest that the mechanism behind the impact of TIWs on O_3 may be photochemical. However, understanding the intraseasonal variability of O_3 in relation to meteorology is a complex topic requiring a detailed analysis of spatiotemporal meteorological variability combined with CTM or CCM simulations. Such detailed analysis is beyond the scope of this paper and will be subject of a follow-up study.

4.3. Seasonal Variability

The seasonal pattern of surface O_3 at Galápagos is characteristic of the Southern Hemisphere (SH), with a minimum in February and a maximum in August (see annual cycles for Samoa, Ascension, and Reunion in Figure 13). Comparison of the parameters of the Fourier series fit to the seasonal cycle to those of other locations [Parrish *et al.*, 2016] highlights the similarity between Galapagos and Samoa, including the annual average (y_0), the amplitude and phase of the first harmonic, and the low significance of the second harmonic. Barbados shows an analogous tropical Northern Hemisphere (NH) behavior, with a factor or ~ 2 higher annual average, same amplitude and 6 months phase shift of the first harmonic, and low significance of the second harmonic. The second harmonic in the MBL has been attributed by [Parrish *et al.*, 2016] to photolytic loss of O_3 , driven by the annual cycle of actinic flux. The range of insolation experienced within the course of a year at low latitudes is narrower than at higher latitudes, which explains why the second harmonic is less significant in Galápagos.

However, the ozonesonde data shows the presence of a strong second harmonic aloft. Fourier expansion fits of the seasonal cycles in Figure 11d show that the first harmonic has similar phase angle from the surface through the IL, albeit with decreasing amplitude, becoming nonsignificant in the IL. The first harmonic is again significant in the FT, but the phase and amplitude are completely different from those at the surface. Both the amplitude and phase parameters of the second harmonic are similar from the higher layers of the MBL through the FT. The inversion altitude annual cycle (Figure 11f) is correlated to SST, with the strongest (and lowest) inversions occurring during the cold months (the maximum lapse rate at the inversion is also plotted in Figure 11f). All the radiosonde profiles indicate a capped MBL during the August–November period (see T and RH climatological profile for September in Figures 11a and 11c). By contrast, in the warm season conditions compatible with vertical exchange. Thus, it can be concluded that in the warm period, the MBL receives influence of the FT, which causes a secondary maximum, whereas in winter the MBL remains isolated from the FT. The double sinusoid in the FT cycle is an interesting feature which should be addressed in future work. Analysis of FT O_3 in the eastern Pacific [Kim and Newchurch, 1996; Oltmans *et al.*, 2001] suggests that the maximum in August–September results from transport of O_3 -rich continental air masses during the South American biomass burning season, but the secondary maximum in January–March has not been discussed yet.

The comparison between Galápagos and other tropical locations in Figure 13 sheds light into how the seasonal cycle of surface and MBL O_3 varies across the equator. Open ocean NH locations like Cape Verde

[Lee *et al.*, 2012], Barbados, or Hawaii also have a single sinusoidal annual cycle which describes the majority of the seasonal variation [Parrish *et al.*, 2016] but with a maximum in January–April, i.e., ~6 months shifted with respect to the SH cycle. The equatorial location of the Galápagos Islands does not lead to the surface O_3 seasonal cycle being an average between, e.g., the cycles at Samoa (Pacific Ocean, 14°S) and Barbados (Atlantic Ocean, 13°N). The relative position of the ITCZ, which influences SST and wind (note that OLR, SST, and wind components are plotted in Figure 13 for each station), determines the surface O_3 seasonal cycle. Barbados is always north of the ITCZ, while the two Pacific locations are generally always at the southern side of it. Barbados is always under North Easterlies and Galápagos and Samoa generally always under South Easterlies. In July, the ITCZ is well north of the equator and Barbados is at its northern edge. Under these circumstances the NE trade winds weaken and SST and water vapor concentration in the MBL are high, thus causing O_3 to decrease. At the same time the other two locations are far south of the ITCZ and fully under SE trade winds, and therefore, O_3 is high. The situation inverts in January, when the ITCZ migrates south and both Galápagos and Samoa are at its southern edge. Samoa and Galápagos surface O_3 annual cycles are almost identical due to the ITCZ being curved toward the south in the Pacific Ocean and the situation of Galápagos at the north of the Pacific cold tongue, which implies higher levels of ozone upwind.

Figure 13 shows measurements at two equatorial locations other than Galápagos. Paramaribo is half of the year at each side of the ITCZ and consequently displays a double O_3 maximum, with two minima occurring when the ITCZ passes above [Maas, 2004]. Kiritimati (Christmas Island, 2°N, 157°W), which is similarly situated than Galápagos with respect to the latitudinal shift of the ITCZ (see OLR cycle, Figure 13), shows a hint of a surface O_3 seasonal cycle, at least according to the rather sparse data available [Clarke *et al.*, 1996; Takashima *et al.*, 2008; Conley *et al.*, 2011]. The likely explanation for a weaker seasonal cycle in Kiritimati than in Galápagos is that the former is located at the tip of the Pacific cold tongue, with a dominating zonal wind component and warm waters to the south, which essentially precludes the replenishment of ozone-rich air from higher latitudes during austral winter-spring. In October, O_3 is 10–15 ppbv at 10°S, 150°W [Piotrowicz *et al.*, 1986] and 20–30 ppbv at 10°S, 85°W [Helmig *et al.*, 2012]. Thus, the seasonal variation of the Pacific cold tongue probably explains why the low O_3 region that extends across the equatorial Pacific in January–April becomes restricted to west of 150°W in July–December [Piotrowicz *et al.*, 1986].

4.4. Interannual Variability

Concurrent low SST and water vapor and enhanced O_3 occurred during the 2007 and 2010 La Niña events (Figure 12). Before 2015 no major El Niño was registered in the available O_3 record. The 2015–2016 El Niño has not caused extraordinary O_3 anomalies according to the few SHADOZ ozonesondes launched from San Cristóbal in June–October 2015, with surface values of 13–20 ppbv during the seasonal maximum. These are slightly low but still larger than the values observed during the cold season of 2011 (ENSO-neutral year). Thus, there seems to be a stronger response of O_3 to low than to large SST anomalies in the longer time scales, although a clear relationship is not apparent in the sparse data available.

5. Summary and Conclusions

Continuous surface O_3 mixing ratios measurements at the Galápagos Islands in 2000–2002 (PIQUERO campaign) and 201–2012 (CHARLEX campaign) have been used to identify modes of O_3 variability in different time scales ranging from a few days to seasonal variations. The daily variability of surface O_3 at Galápagos has two distinct regimes: (i) a cycle of average photochemical destruction followed by nighttime recovery in the cold season and (ii) a pronounced cycle in the warm season encompassing daytime advection and photochemical loss followed by nighttime loss associated with deposition and local NO_x emissions under windless conditions. On the intraseasonal time scale, evidence of a possible impact of the 17 and 33 day period TIWs on surface O_3 mixing ratios is reported for the first time. The impact of TIWs throughout the MBL makes this environment particularly suitable for carrying out quantitative studies on the O_3 budget and provides modelers with a challenging test bed.

On the seasonal scale, it has been shown that Galápagos is situated in the chemical SH and that the change in the seasonal cycle in surface O_3 across the equator depends on the location with respect to the ITCZ and also

on the O₃ levels in the subtropics. Galápagos is situated at the north of the Pacific cold tongue and as a consequence does not display during austral winter and spring the low O₃ levels observed in the Pacific warm pool at similar latitudes around the year [Piotrowicz *et al.*, 1991].

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