RESEARCH ARTICLE

Characterizing ozone throughout the atmospheric column over the tropical Andes from in situ and remote sensing observations

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In this study, we characterize atmospheric ozone over the tropical Andes in the boundary layer, the free troposphere, and the stratosphere; we quantify each contribution to total column ozone, and we evaluate the performance of the multi-sensor reanalysis (MSR2) in the region. Thus, we present data taken in Ecuador and Peru (2014–2019). The contribution from the surface was determined by integrating ozone concentrations measured in Quito and Cuenca (Ecuador) up to boundary layer height. In addition, tropospheric and stratospheric column ozone were quantified from ozone soundings (38) launched from Quito during the study time period. Profiles were compared against soundings at Natal (SHADOZ network) for being the closest observational reference with sufficient data in 2014–2019. Data were also compared against stratospheric mixing ratios from the Aura Microwave Limb Sounder (Aura MLS). Findings demonstrate that the stratospheric component of total column ozone over the Andes (225.2 ± 8.9 Dobson Units [DU]) is at similar levels as those observed at Natal (223.3 ± 8.6 DU), and observations are comparable to Aura MLS data. In contrast, the tropospheric contribution is lower over the Andes (20.2 ± 4.3 DU) when compared to Natal (35.4 ± 6.4 DU) due to a less deep and cleaner troposphere. From sounding extrapolation of Quito profiles down to sea level, we determined that altitude deducts about 5–7 DU from the total column, which coincides with a 3%–4% overestimation of the MSR2 over Quito and Marcapomacocha (Peru). In addition, when MSR2 data are compared along a transect that crosses from the Amazon over Quito, the Ecuadorian coast side, and into the Pacific, observations are not significantly different among the three first locations. Results point to coarse reanalysis resolution not being suitable to resolve the formidable altitude transition imposed by the Andes mountain chain. This work advances our knowledge of atmospheric ozone over the study region and provides a robust time series of upper air measurements for future evaluations of satellite and reanalysis products.

Keywords: Ozone layer, Stratospheric ozone, Ozonesondes, Andes, Ecuador, Peru

1. Introduction

From the boundary layer through the free troposphere and into the stratosphere, ozone is relevant to the global environment and the climate system. In the ambient air, ozone is an air pollutant whose concentration is regulated in most countries. In the stratosphere, ozone effectively shields harmful ultraviolet (UV) radiation that otherwise would place life on Earth in peril. Furthermore, due to its radiative properties, ozone (in the troposphere and stratosphere) plays a major role in the global energy budget of the Earth-atmosphere system (Forster et al., 2007). Thus, ozone monitoring throughout the atmospheric column is a major endeavor that calls for scientific efforts worldwide. However, looking into data sources and relevant literature that deal with ozone distribution and abundance, most studies are concentrated in the Northern Hemisphere (NH). For example, recent global assessments of tropospheric ozone mostly focus on observations in the United States, Europe, and East Asia (e.g., Fleming et al., 2018; Young et al., 2018). Similarly, observations of total column ozone (TCO) dominate in the NH as is evident from global data archives (e.g., World Ozone and Ultraviolet Data Center [WOUDC], 2020). Meanwhile, there are vast regions in the world, home to millions of people, such as the tropical Andes in South America, where reliable ozone measurements (discussed in this article) are yet to be incorporated in global and regional studies that expand analyses to a more extensive reality. Hence, this work is committed to studying ozone...
in the atmospheric column over the tropical Andes using data from different sources.

Tropospheric ozone is important in the study area from the perspective of air quality as well as from the standpoint of its contribution to TCO. The Andes mountain chain is a remarkable topographic feature that presents an abrupt transition from the Amazon into the Pacific, which has an impact on the interpretation of TCO as opposed to regions located at sea level. Thus, there is less tropospheric column over the Andes due to high altitude for which the tropospheric component of TCO is lower than at sea level. However, little has been studied in this regard (Kirchhoff, 1998; Cazorla, 2017), which is partially explained due to a lack of in situ measurements. In addition, tropical Andean cities, in spite of their equatorial latitude, have low surface ozone when compared with urban areas in the NH. This reality, not as broadly known as the one in the NH, also influences the abundance of ozone in the atmospheric column at this tropical region, which we explore in this article along with the altitude factor.

TCO observations and studies over the Andes are also important from a public health perspective, as due to latitude and altitude this region is exposed to some of the highest UV indexes recorded in the globe (Zaratti et al., 2014). In humans, overexposure to UV is hazardous for risks ranging from tanning and skin burn to premature aging, skin cancer, and cataracts (International Agency for Research on Cancer, 2012). A recent study demonstrates that in Quito (Ecuador), the UV index can be greater than 16 during up to 10 days per month, while 40 years’ worth of satellite data (1979–2018) indicates that TCO over Quito varies between 251.3 \( \pm \) 21.6 Dobson Units (DU; Parra et al., 2019). Hence, continuous TCO monitoring is critical to better understand the UV index temporal variability at Andean sites and to provide environmental authorities with a proper scientific basis that underlies advisories and public health campaigns.

An additional angle that makes this study relevant is the need for validation of satellite products in the region. Over the tropical Andes, satellite data is a critical source of information to monitor ozone precisely because the density of measurements is lacking. In this study, we present a reliable and continuous source of ozone soundings that can be used for satellite comparisons.

With the above motivations, we present an analysis that includes surface ozone measurements, ozonesonde data, remote sensing observations, and reanalysis products that particularly focus on Ecuador and Peru for the 2014–2019 period. Surface ozone includes data taken at Universidad San Francisco de Quito (USFQ) as well as in the city of Cuenca (located in Southern Ecuador) by the local government. Ozonesonde data, taken at USFQ, augment regional observations as they can be compared with TCO measurements in Marcapomachocha, Peru. We also compare the Quito soundings with Microwave Limb Sounder (MLS) stratospheric mixing ratios and against profiles taken at Natal (Brazil) from the SHADOZ (Southern Hemisphere Additional Ozonesondes) network (Thompson et al., 2004). Finally, we complement our investigation using data from the multi-sensor reanalysis (MSR2) by the Tropospheric Emission Monitoring Internet Service (TEMIS, 2020; Royal Netherlands Meteorological Institute). This product is of interest to our region as TCO was evaluated using Peruvian observations (Van der A et al., 2015a, 2015b) and the historical UV index was recently assessed against measurements of UV index in Quito (Parra et al., 2019). The scientific questions we pursue in this work are the following:

1. What is the contribution of boundary layer ozone to tropospheric column ozone (TrCO) over the equatorial Andes from measurements taken in Quito and Cuenca, Ecuador?
2. From comparisons of Quito soundings against SHADOZ Natal as well as MLS stratospheric mixing ratios, what can be said in regard to the contribution of tropospheric and stratospheric ozone to TCO over the study region?
3. How well does the MSR2 compare to measurements in the study region?

This work is organized as follows: The Methods section contains details of measuring sites, data sources, and processing techniques. The Results section contains the main findings along with a discussion that places data within a regional context. In the Conclusions section, we incorporate the main lessons learned from this consolidated analysis.

2. Methods

2.1. Data sets

2.1.1. Surface ozone

Quito, Ecuador

Ground-level ozone has been monitored continuously at USFQ’s Atmospheric Measurement Station (EMA, Spanish acronym) since 2014 (Cazorla, 2016). EMA is a rooftop facility located within USFQ’s main campus at coordinates 0.19°S, 78.4°W, and 2,414 masl. Figure 1 indicates EMA’s location in Ecuador. Ozone data are continuously measured with a 49i Thermo Scientific ozone sensor. Data quality control is performed continuously through intercomparisons against observations taken at a neighboring station run by the Quito’s Air Quality Network (details in Supplemental Information). In addition, intercomparisons against conditioned ozonesonde measurements at the surface are done periodically to further ensure data quality (for details on instrumentation, refer to Cazorla, 2016, 2017). In this work, raw data (1-s) were reduced to 10-min resolution, and the latter were used to produce 1-h averages. We present data from June 2014 to December 2019 (available at https://observaciones-iaa.usfq.edu.ec). Additional details on measurements and instrumentation at EMA can be found elsewhere (Cazorla and Tamayo, 2014; Cazorla and Juncosa, 2018).

Cuenca, Ecuador

Cuenca’s air quality network has an automatic station at its historical center, at coordinates 2.89°S, 79.00°W, and
2,500 masl, (location in Figure 1). This station belongs to the Municipality of Cuenca and measures, among other pollutants, ambient O₃ as well as meteorological variables. According to technical documentation, monitoring is based on methods established in the Ecuadorian air quality regulation, under the responsibility of the local government, which is the official entity accredited by the National Environmental Authority for monitoring air quality. As part of its operation, quality assurance and control activities are routinely performed. The instrument used is a Teledyne model 400e analyzer, and data are acquired every minute (Empresa Pública Municipal de Movilidad, Tránsito y Transporte de Cuenca, 2020). For this study, hourly O₃ concentrations were provided to us by the Cuenca’s Air Quality Network (data available at https://observaciones-iia.usfq.edu.ec).

2.1.2. Ozonesonde data

Quito, Ecuador
We present 38 ozonesoundings launched between June 2014 and November 2019 from EMA USFQ (https://observaciones-iia.usfq.edu.ec). Specific details pertaining instrumentation, ozonesonde conditioning, and launching protocols as well as geographical features of the launching site can be found elsewhere (Cazorla, 2016; Cazorla and Juncosa, 2018). Briefly, at EMA we use iMet radiosondes coupled with EN-SCI ozonesondes conditioned following NOAA’s methodology (Johnson and Davies, 2013). Figure 2 depicts the time line of EMA launches. Flight details are specified in the Supplemental Information, Table S1.

Natal, Brazil
Ozonesonde data from the SHADOZ Natal (Brazil) station (5.40°S, 35.20°W, 42 masl) were obtained from the public archive (https://tropo.gsfc.nasa.gov/shadoz). These data were compared directly against Quito soundings. Thus, selected profiles correspond to ozonesondes launched on the same day or closest in date to EMA’s launches for the period June 2014–2019. Figure 2 shows the selected Natal soundings with respect to EMA’s launching time line (exact dates in the Supplemental Information, Table S2).

2.1.3. Ground-based remote sensing data

Marpomacocha, Perú, and Natal, Brazil
Daily TCO measurements in the Peruvian Andes were downloaded from the WOUDC website (https://woudc.org/data/explore.php). According to the data source, observations were taken with a Dobson Beck instrument (#87) in Marcapomacocha (Mar) at coordinates 11.40°S, 76.32°W, and 4,500 masl. Data were available from February 10, 2015, to July 1, 2018.

Similarly, daily TCO data for the Natal station at coordinates 5.83°S, 35.20°W, and 42 masl were obtained from the same website. Observations were also taken with a Dobson Beck instrument (#93), and the available dates were from January 2, 2014, to December 30, 2019.

2.1.4. Satellite data

MLS mixing ratios
Stratospheric ozone mixing ratios measured by the MLS instrument on board of the Aura satellite were compared against ozone sounding data taken in Quito for the study time period. Data were obtained from the Goddard Earth Sciences Data and Information Services Center (2020) website (https://disc.gsfc.nasa.gov/). The data set used was “MLS/Aura Level 2 Ozone (O3) Mixing Ratio V004 (ML2O3 004).” Data were averaged over a domain that surrounds EMA station and is bounded by meridians...
79.3°W and 78.0°W and parallels 1.5°S and 1.1°N (if no data were found, the domain was extended to meridians 81.3°W–76.5°W). Quality flags were applied following community recommendations (Livesey et al., 2020), and invalid data points were discarded accordingly.

Ozone Monitoring Instrument (OMI) TCO
OMI TCO data were downloaded from the GES DISC website (https://disc.gsfc.nasa.gov/). Thus, daily files (Hierarchical Data Format—Earth Observing System [HDF-EOS5]) were obtained for the product "OMI/Aura Ozone (O3) DOAS Total Column L3 1 day 0.25°×0.25° V3 (OM-DOAO3e 003)" for the 2014–2019 period (Goddard Earth Sciences Data and Information Services Center, 2021).

Data were extracted for the EMA coordinates and compared with TCO from ozonesondes and MSR2 data. This comparison was done to contrast the MSR2 spatial resolution against finer resolution data.

2.1.5. Reanalysis data

MSR2 TCO
TCO from the MSR2 data set (TEMIS, 2020) was obtained from the public archive (http://www.temis.nl/protocols/o3field/o3field_msr2.php). Data (1°×1°) were downloaded for each day of the period 2014–2019 for coordinates that coincide with EMA USFQ, Marcapomacocha, and Natal (Figure 1). In addition, TCO MSR2 data were downloaded for cells at the same latitude of EMA station but located at points along a transect from the Pacific Ocean (P1, 0.125°S, 82.125°W), the Ecuadorian coast side (P2, 0.125°S, 79.675°W, 200 masl), and the Amazon (P4, 0.125°S, 76.875°W, 300 masl) as marked in Figure 1 (P3 corresponds to EMA coordinates). These data were used to compare the reanalysis product along this transect with respect to data over Quito.

2.2. Data processing and analysis

2.2.1. Surface ozone

Ground-level ozone in Quito and Cuenca (1-h data) were overlapped in 24-h plots for every month. Statistics were applied to both data sets in order to obtain the ozone diurnal variation in the 5th, 50th, and 95th percentiles. In order to determine the contribution of boundary layer ozone to TCO, the following procedure was applied:

1. The average depth of the planetary boundary layer (PBL) in Quito and Cuenca at midday was calculated for every month of the year. For Quito, the monthly mean PBL depth was obtained using surface observations (2014–2019) following the empirical model proposed by Cazorla and Juncosa (2018; details in the Supplemental Information, Figure S1). For Cuenca, we used previous research that focused on finding the most suitable physical schematic for the PBL in the WRF-Chem model (Weather Research and Forecasting with the Chemistry module) for simulating air quality in September 2014 (Parra, 2018). Thus, an average midday PBL depth from the simulation with the best schematic was chosen (Supplemental Information, Figure S2), and this value was used for all months.
2. The PBL depth at each location was divided in 50-m layers. Density at the center of every layer was calculated using temperature and pressure vertical profiles for each month from soundings taken at EMA. The same vertical profiles were used for both sites in the Ecuadorian highlands.

3. We used a well-mixed volume approach to determine the ozone column in the boundary layer. Thus, ozone number density (molecules cm$^{-3}$) in every layer was calculated using ozone ground station observations (ppbv), air density in every layer, and Avogadro’s number. We used the monthly ozone maxima measured at the surface in order to estimate the greatest observed contribution to TrCO (we also included all data with indication of the 5th and 95th percentiles). Hence, ozone column (molecules cm$^{-3}$) was obtained by integrating ozone number density from the surface to the top of the boundary layer, and values were transformed to DU. Data are presented and discussed as yearly patterns.

2.2.2. Ozonesonde data

Ozone profiles at EMA were reduced from their original resolution (5-m) to 50-m averages. Time series were statistically processed to obtain profiles in the 5th, 50th, and 95th percentiles. TrCO was obtained from each sounding by integrating ozone abundance from the surface up to tropopause level. The chemical definition of tropopause was applied as in Thompson et al. (2003b) and Cazorla (2017). Thus, tropopause height was marked at the level at which ozone mixing ratio reaches 100 ppbv when searched from below. TCO for each sounding was found which ozone mixing ratio reaches 100 ppbv when searched from below. TCO for each sounding was found by integrating ozone up to balloon burst altitude and adding the corresponding climatology following McPeters et al. (2012). Stratospheric column ozone (SCO) was found from the difference between TCO and TrCO.

Similarly, Natal soundings were processed in order to obtain TrCO, SCO, and TCO, although tropopause levels with the chemical definition were searched from above as pollution layers in the mid-troposphere are common at this site as reported previously (Thompson et al., 2003b; Cazorla, 2017). Comparisons against Quito soundings were done for dates in which data at Natal were available, as indicated in Section 2.1.2. Thus, TrCO, SCO, and TCO at both stations were overlapped as time series and in 1-year plots in order to find the seasonal variability. Finally, data were averaged by trimesters starting in February (FMA, MJJ, ASO, NDJ), and direct comparisons of these averages were performed. We present a discussion in terms of tropospheric and stratospheric contributions to TCO at both locations.

2.2.3. MLS comparisons

Quito soundings were compared against stratospheric mixing ratios for MLS pressure levels from 70 to 10 hPa. For comparisons, both data series were overlapped. In addition, direct comparisons were performed for specific flight dates. The time line of date comparisons is presented in Figure 2 with dates of available MLS data at or close to dates for Quito soundings. When there were missing MLS data points on the day of an EMA flight, the average of the closest MLS measurements before and after the sounding was used (refer to Table S2). From this comparison, a profile of the percentage difference (EMA-MLS)/EMA × 100 is presented.

2.2.4. MSR2 and OMI comparisons

TCO from the MSR2 reanalysis was evaluated by comparing against data taken at each location (Quito soundings as well as ground-based remote sensing TCO at Macaophoca and Natal). Comparisons were done by looking at overlapped time series, finding linear correlations between data sets, and finding the distribution of percentage differences between measurements and reanalysis data. In addition, comparisons among data taken in Quito and MSR2 along a transect that crosses from the Pacific, over the Andes (at EMA’s coordinates), and into the Ecuadorian Amazon were performed in order to explore whether satellite reanalysis identifies differences in measurements over the high and narrow Andes chain.

Finally, a comparison of TCO was done using OMI observations, ozonesonde measurements, and MSR2 TCO at EMA. This comparison was performed to contrast results obtained with MSR2, whose spatial resolution is coarse, with satellite data with finer resolution such as OMI. As before, a linear correlation and percentage differences were found between OMI and ozonesonde data. Also, overlapped data for the three time series is presented in a 1-year plot.

3. Results and discussion

3.1. Surface ozone and its contribution to TrCO

Ground-level ozone measured in Quito and Cuenca (2014–2019) is depicted in Figure 3. Data are overlapped in 24-h plots. The average ozone diurnal variation (50th percentile) is depicted by solid curves for both sites (blue and red, respectively), while the colored shading indicates the 5th and 95th percentile boundaries. From diurnal variations, average levels of ambient ozone in Quito usually remain at or below 40 ppbv (1-h data), as indicated by the 50th percentile profile in every month. When looking at the 95th percentile, ozone generally remains below 50 ppbv except in September, when the curve reaches a maximum just under 60 ppbv. Likewise in Cuenca, seasonal variability is similar to Quito with the highest levels taking place in September, although concentrations are generally lower. Thus, overlapped data in Cuenca show that ozone maxima (1-h) usually remain below 30 ppbv during the first semester, while in the second semester, concentrations are just under 40 ppbv. Correlating surface ozone at both locations by trimesters (Supplemental Information, Figure S3) indicates that ozone in Cuenca is generally...
The greatest correlation takes place in September, during the month of the equinox, when insolation at the surface peaks, leading to more active photochemistry (Parra et al., 2019). In contrast, during the March equinox, ozone events decrease due to the presence of persistent clouds associated with the rainfall season (Tobar and Wyseure, 2017; Cazorla and Juncosa, 2018). As presented, most of the time ozone concentrations at these Andean urban areas meet the national air quality standard of 50.9 ppbv (100 m$gm^{-3}$ in standard conditions as an 8-h mean), which coincides with the World Health Organization guideline for ozone. Looking at individual days in recent years, there were few episodes in Quito when ozone was higher than usual. For example, there were 3 days in 2015 when 1-h data at midday was above 65 ppbv, reaching a maximum of 82 ppbv on September 14. In addition, November 2, 2016, September 19–20, 2017, and October 1, 2018, had 1-h maxima at about 65 ppbv, although 10-min spikes neared 80 ppbv (Supplemental Information, Figure S4). These cases have been associated to transport of air masses from wildfires in the surrounding woods (Daza et al., 2019), although more research needs to be conducted in this regard. One of the objectives of this work is to characterize concentrations of ozone at the surface in order to estimate the boundary layer contribution to TrCO, while the chemical nature of ambient ozone in Quito and Cuenca has been explored in previous research. Below, we briefly summarize previous findings in regard to boundary layer evolution and the chemistry of ozone production at the study site.

The diurnal evolution of the PBL in Quito as well as its seasonal variability was studied in depth in a previous study (Cazorla and Juncosa, 2018). Briefly, surface conditions directly influence the growth and mixing of atmospheric species in the boundary layer. In regard to typical weather patterns, there are two cloudy and rainy seasons in March–April and October–November, while the warm season runs from late June to mid-September. As presented in previous work (Cazorla, 2016; Parra, 2017; Cazorla et al., 2020; Parra and Espinoza, 2020) under regular traffic conditions, the regime of ozone production is NO$_x$-saturated. Ambient NO in the rush hour can be 50 ppbv or higher (10-min data), which contributes not only to titrating ozone but to favoring termination reactions between radicals and NO$_x$ species. A comparison of ozone levels in Quito against other cities can be found elsewhere (Cazorla, 2016). A complete discussion of the chemistry of ozone formation in Quito, that uses a 0-dimension photochemical box model, can be found in Cazorla et al. (2020).

From observations of 1-h surface ozone and boundary layer depths in 2014–2019, the contribution of ozone in the PBL to TrCO and its seasonal variability is presented in Figure 4. These estimations comprise the entire range of pollution and mixing conditions in the boundary layer derived from the multyear data set. Hence, curves for maxima and minima are depicted with dashed lines (blue for Quito and red for Cuenca), while the shaded areas indicate data within the 5th and 95th percentiles at each location. Thus, in Quito, the maximum contribution to TrCO varies between 5 and 9 DU with the highest values
happening in September (upper dashed blue line in Figure 4). However, most of the time, the ozone column in the PBL is lower, as indicated by the blue shading, whose range is 1–7.3 DU. This variability is due to ozone levels being lower in March to May and the midday PBL shallower, while in the summer ozone levels are higher and the PBL is deeper. For example, the maximum value of 9.2 DU in the PBL in Quito happened on September 14, 2015. As described earlier, during this pollution episode, surface ozone was 80.2 ppbv and the depth of the mixing layer was 1,821 m. On the other hand, low surface ozone (below 25 ppbv) combined with shallow boundary layers (less than 1,000 m) yield ozone columns of 1 DU or even less. To further illustrate these results, we included in Figure 4 all the midday ozonesonde measurements (11) of the ozone column in the PBL at EMA (black stars in Figure 4). Ozonesonde observations are snapshots of the atmosphere at a given time. From this set of observations, which only collects a subset of mixing and pollution conditions, the PBL ozone column ranges between 1.2 and 5.8 DU. Therefore, looking into the entire set of estimations performed with 2014–2019 data, sounding observations fall within the entire range of estimations. Similar to what was observed in Quito, the maximum contribution of boundary layer ozone to TrCO in Cuenca ranges from 4.5 to less than 8 DU, with a peak also in September and minima from May to July. Figure 4 also shows the entire range of ozone column calculations in the PBL in Cuenca, given by different mixing and pollution conditions from data between 2014 and 2019.

From the above analysis, we report that the maximum contribution of ozone in the PBL to TrCO in Andean cities in Ecuador is less than 7 DU on average, while the full range varies from less than 1 to up to 9 DU. This range depends on pollution and weather conditions that vary seasonally and influence the evolution and abundance of ozone in the PBL.

The results presented above are important over the tropical Andes as they have an impact on the interpretation of TrCO and TCO over this high-altitude region. Hence, the TrCO contribution to TCO is low not only due to a less deep troposphere but also because boundary layer ozone is generally low. Furthermore, this contribution varies seasonally with values in September doubling those of May to July. More discussion and comparisons on this particular topic are elaborated further below, when Quito soundings are compared to those in Natal.

3.2. Quito ozone soundings: Features and comparisons

3.2.1. Ozone profile structure

High resolution data for the 38 profiles collected at EMA are depicted in Figure 5 along with profiles in the 5th, 50th, and 95th percentiles. These data show that ozone levels in the free troposphere over the tropical Andes are generally well-mixed up to tropopause height and average tropospheric levels are at 50 ppbv or lower, as given by the 50th percentile. There is a general absence of pollution layers in the mid-troposphere, which results in a structure different from the “S” shape established in previous work as a characteristic of ozone profiles in the tropics (Folkins et al., 2002). These results are consistent with previous work that compiled the first year of data (Cazorla, 2017). In addition, events of near-zero ozone in the upper troposphere have not yet been observed to the present, which also differs from observations at other sites, in particular in the Tropical West Pacific (Solomon et al., 2005). However, Newton et al. (2016) reported concentrations not lower that 12–13 ppbv in that region and indicated that
ozonesonde conditioning and data processing could influence measurements of low ozone in the UT/LS.

From profile statistics (Figure 6), the tropopause height from the thermal definition is generally found at 17.02 ± 0.53 km, while from the chemical definition it is located at 16.97 ± 0.63 km. Thus, tropopause levels determined with both definitions are well-mixed up to the cold point tropopause (CPT). Finally, the mean CPT found at EMA (~82.2 ± 2.5°C) is consistent with the annual mean encountered by Kim and Son (2012), and the seasonal variability (CPT is less cold from July to September) is also consistent with data in previous work (Sivakumar et al., 2011).

3.2.2. Comparisons with SHADOZ Natal

At the moment, EMA in Quito is the only ozone sounding station in the tropical Andes. At a close latitude, the SHADOZ Natal station collects data regularly (although at sea level in the Atlantic) for which it is the nearest observational reference to compare ozone profiles in the troposphere and stratosphere during the proposed time period (the SHADOZ station in Galapagos [Ecuador] has not been collecting data since early 2016). Thus, measurements of TrCO, SCO, and TCO taken in Quito and Natal are presented in Figure 7a-f overlapped in 1-year plots and averaged by trimesters.

As presented, TrCO is greater over Natal than over Quito throughout the times series. A wider ridge from September to December is noticeable in the Natal data set. Averaging measurements by trimesters shows that TrCO in ASO and NDJ is 16–18 DU higher in Natal than in Quito, while in FMA and MJJ, the difference is of about 12 DU. Previous work demonstrates that over this region, transport from biomass burning regions, as well as urban and biogenic emissions, are important sources of O3 precursors and can lead to local and regional pollution (Pacifico et al., 2015). Precisely, the biomass burning season in the Amazon runs from July to November with September being the peak month for fires (Jensen et al., 2012; Gonzalez-Alonso et al., 2019; Butt et al., 2020). In
addition, long range transport from biomass burning in southern and Sub-Saharan Africa can lead to elevated ozone in the Brazilian northeast during the last trimester (Bela et al., 2015). In contrast, profiles over Quito do not show, until the moment, long-range pollution features. Earlier work (Cazorla, 2017) included an analysis of ozonesondes in Natal and a robust ozonesonde time series taken in San Cristobal, where clear differences in ozone profile structure shows pollution layers at both sites, but an absence of such features in the Quito profiles. Thus, it was proposed that the Andes form a natural barrier that prevents polluted mid-tropospheric air masses from the east to mix with air over the Andes (Cazorla, 2017). Moreover, low surface ozone presented in this work, combined with vertical mixing, are apparent reasons for lower TrCO over the Andes, although further investigation needs to be performed to better quantify convective and dynamic conditions over this area.

Opposite to differences in TrCO, SCO data over Quito and Natal generally overlap (Figure 7b). Averaging measurements by trimesters shows that there are no significant differences in measurements at both sites as indicated by 1-s absolute uncertainty error bars in Figure 7e (5% error bars for ozonesonde measurements in the stratosphere and 8% in the troposphere; SPARC 1998; Johnson et al., 2002; Thompson et al., 2003a; Fioletov et al., 2006; Hassler et al., 2014; Cazorla, 2017). However, higher TrCO over Natal leads to apparent higher TCO in the time series. Nevertheless, when data are averaged, the difference is marginal mainly in the fourth trimester due to greater TrCO over Natal. As a result, over the Andes, the percentage contribution of SCO to TCO is greater as TrCO is significantly lower and SCO is the same as Natal.

In 2002, Kirchhoff and Guarnieri determined that the difference due to altitude in TrCO over La Paz, located at 3,420 masl, was of about 8.9 DU when compared to a sea level profile. From simple proportionality, this finding implies that over EMA station and Quito (2,400–2,800 masl), a less deep troposphere subtracts some 6–7 DU from the TrCO. Extrapolating EMA profiles down to sea level (Supplemental Material Figure S5) yields a difference of 5–7 DU, which is consistent to the work by Kirchhoff and Guarnieri. Hence, the high-altitude factor combined with the low surface ozone from the boundary layer need to be carefully taken into account when interpreting TCO observations over this unique region. Therefore, we propose that using solely an absolute value of TCO to discuss ozone in the atmospheric column over the Andes without clarification that SCO is within normal levels could be misleading as TCO absolutes overlook clear differences due to a less deep and cleaner troposphere.

Finally, it is important to mention that ENSO (El Niño Southern Oscillation) has an influence on atmospheric ozone in the study region. Previous research explored this topic at sites close in latitude and longitude to the study region. Work conducted by Ziemke et al. (2015) shows that in the tropics (20°N–20°S) the variability of the tropospheric ozone column in longitudes 70–80°W due to ENSO is about 1 DU and does not exceed 2 DU even in extreme ENSO events. Additionally, Lee et al. (2010) analyzed the ENSO-related variability in ozone in the troposphere and the tropical UT/LS. They found that at San Cristobal (Galapagos), which is practically at the same latitude as EMA, ozone anomalies are negative (down to −10 ppbv in the UT and −200 ppbv in the LS), while Natal exhibits positive ozone anomalies (up to 6 ppbv in the

Figure 7. Measurements (2014–2019) of total (TCO), stratospheric (SCO), and tropospheric (TrCO) column ozone taken at EMA (blue squares) and SHADOZ Natal (red stars) overlapped in one year plots (left panels) and averaged by trimesters (right panels). DOI: https://doi.org/10.1525/elementa.2021.00019.f7
UT and 140 ppbv in the LS). In regard, to the ENSO influence in surface ozone, Cazorla and Herrera (2020) found indication that episodes of transport-associated high ozone in the San Cristobal ambient air occur under conditions unrelated to ENSO because transport of air masses rich in precursors requires easterly air flow from biomass burning regions. Being at high altitude in continental South America, between two sites where ENSO studies have been conducted (San Cristobal and Natal), future studies need to address the specific question of the ENSO influence in the atmospheric ozone column over the Andes.

3.2.3. MLS comparisons

Time series of EMA observations and MLS measurements in the stratosphere are presented in Figure 8. The EMA time series generally overlap with MLS mixing ratios at all pressure levels. The average of EMA profiles between 70 and 10 hPa is presented in Figure 9a along with average MLS profiles for all data and for dates that coincide with EMA launches (Figure 2). The percentage difference (EMA – MLS)/EMA × 100 is presented in Figure 9b. For matching dates, between 30–10 hPa and at 46 hPa, the difference is 0.2 to –4%. At 38 hPa, the percentage difference is –8.5%; at 56 hPa, –15%; and at 68 hPa, 5.2%. Differences using the average profile obtained with all MLS data are lower. The magnitude of these differences is consistent with previous work that validates MLS measurements using ozonesonde data (Jiang et al., 2007). The latter article uses soundings at Paramaribo, Natal, and San Cristobal, all at sea level. Given the particular conditions of the Andes mountain chain that we have documented in this investigation, the data from the EMA station can provide a valuable source of information for future satellite validations. Finally, it is important to comment about recent work that identified a drop-off in stratospheric ozone measurements taken by electrochemical concentration cells, which was observed at several ozone sounding stations around the globe between 2014 and 2016 (Stauffer et al., 2020). In this regard, we document that we have not observed this artifact in measurements at EMA station.

3.2.4. Comparisons against Marcapomacocha

Quito in Ecuador and Marcapomacocha in Peru share the high-altitude conditions of the Andes although Marcapomacocha is 1,500 m higher than Quito. Also, Marcapomacocha is a rural environment, whereas Quito is a busy urban center. Marcapomacocha is the only other site in the tropical Andes where TCO measurements are available although only until July 2018 taken with a ground-based spectrometer. A comparison of TCO from sounding data in Quito against Marcapomacocha measurements is presented as overlapped data in a 1-year plot (Figure 10a). In the time series, TCO over Quito on August 27, 2015, was 39 DU higher than in Marcapomacocha. On September 11 and 30, 2015, TCO was 20 DU higher and on September 6, 2016, this difference was 15 DU higher. It is possible that increased TrCO over Quito’s urban environment around August and September in years that were dry and polluted is partially the reason for larger TCO when compared to more pristine regions such as Marcapomacocha. For example, on the referred dates, TrCO over Quito was 27.4, 26, 23.47, and 22.3 DU, respectively. However, more research and a longer time series is needed to explain individual differences. As per the rest of the data, for matching dates, difference is within a 5% (Figure 10b) between both data sets. Likewise, when sounding data are averaged by trimesters (as in Figure 7d) and compared against all Marcapomacocha observations also averaged by trimesters, differences are not significant within a 5% level of uncertainty (1–σ; graph not shown). Hence, we conclude that TCO measurements at both sites are within similar levels.

3.3. MSR2 TCO evaluation

The MSR2 incorporates a wealth of satellite observations particularly useful in regions such as the tropical Andes, where in situ measurements are scarce. Comparing MSR2
TCO and Quito data (38 ozone soundings) yields a linear regression with a slope of 0.871 and an $R^2$ coefficient of 0.56 (Figure 11a). Thus, the MSR2 data set overestimates TCO by 3.1% (252.9 DU vs. 245.4 DU, $\pm 7.5$ DU) on average with respect to measurements in Quito, as indicated by the distribution of percent age differences presented in Figure 11b. These results are consistent with a previous study by Parra et al. (2019), which reported that MSR2 UV index over Quito is underestimated in 3.4% with respect to ground-based measurements taken independently by a multichannel radiometer (Biospherical Instruments Inc., located at coordinates 0.16°S, 78.48°W) that belongs to the Quito’s Air Quality Monitoring Network (Secretaría de Ambiente, 2010).

Earlier, we discussed that due to high altitude, TCO over the Quito region is 5–7 DU lower than at sea level. Thus, we propose that the difference with MSR2 is partially related to the coarse reanalysis resolution ($1^\circ \times 1^\circ$), which cannot capture the abrupt transition from the Amazon into the steep and narrow Andean terrain. To further explore these differences, we looked into reanalysis data across a transect from the Pacific, the Ecuadorian coast side, EMA station, and the Ecuadorian Amazon (Figure 1, points P1, P2, P3, and P4, respectively). A profile for each location, obtained overlapping daily MSR2 data (2014–2019) in a one year plot, is presented in Figure 12. As depicted, yearly profiles over EMA and the Amazon do not show major differences even though there is an altitude gap of 2,200 m. From data statistics (Table S3), the mean difference in MSR2 data between Quito and the Amazon by trimesters in DU is 2.6, 1.9, 2.9, and 3.1 for FMA, MJJ, ASO, and NDJ, respectively. Given uncertainty in reanalysis products (2% RMS error, reported by Van der A et al. (2010), but likely larger over the Andes), there is no real difference between satellite observations in the Amazon and over our urban area in the Andes. A similar situation can be observed when comparing data between EMA and an area at low altitude in the Ecuadorian coast side. In this case, differences are slightly larger, which probably has to do with gridded data coming from interpolation with measurements over the Pacific. For example, the mean difference in MSR2 data between P1 and P3 is 6 DU. This finding is useful for practical purposes because the MSR2 product is important to our region due to the

Figure 9. (a) Mean stratospheric ozone profiles from ozone soundings at EMA USFQ (red line) and MLS all data (blue) and using only dates that coincide or are close to EMA soundings (green). (b) Percentage differences (EMA – MLS)/EMA $\times 100$ with all data (blue stars) and matching dates (green circles). DOI: https://doi.org/10.1525/elementa.2021.00019.f9

Figure 10. (a) Total column ozone from EMA soundings (blue squares) overlapped with Marcapomacocha (Mar) spectrometer measurements. All Mar data are depicted with green circles, and dates that coincide with EMA soundings are circled with a black line. (b) Percentage difference (EMA – Mar)/EMA $\times 100$ for matching dates. DOI: https://doi.org/10.1525/elementa.2021.00019.f10
reasons explained earlier. Hence, we report that the MSR2 product overestimates TCO above the Ecuadorian Andes with 6–7 DU. Taking into account this overestimation, we propose that applying a simple correction of –7 DU to the MSR2 improves the percentage difference (EMA – MSR2)/EMA to the following by trimesters: 0.08, –1.22, 2.74, and 0.46 for FMA, MJJ, ASO, and NDJ, respectively.

From an observational perspective, the results discussed above report for the first time an overestimation encountered in MSR2 TCO when compared to data over the Ecuadorian Andes. However, reanalysis products come from models that assimilate data from a number of individual satellite sensors. Hence, finding the underlying factors responsible for the observed differences implies a more intensive scrutiny than a simple macroscopic characterization. Although a dedicated comparison against every individual satellite product that is assimilated in the reanalysis is beyond the scope of this article, we included a comparison of ozone sounding data against OMI measurements with the purpose of finding potential differences due to spatial resolution. Figure 13a shows the linear correlation between TCO from OMI and 29 balloon-borne measurements at EMA (there were sounding dates when OMI did not have data). Although data dispersion is greater than with MSR2 (correlation against OMI has a lower $R^2$ coefficient), scattering happens more uniformly over and under the 1:1 line. As a result, the percentage difference (OMI – EMA)/EMA × 100 is about

Figure 11. (a) Linear correlation between MSR2 and EMA soundings and (b) Distribution of percentage differences between both data sets. (b) and (c) The same, but between MSR2 and Marcapomacocha (spectrometer data). (d) and (e) Similar, but between MSR2 and Natal (spectrometer data). DOI: https://doi.org/10.1525/elementa.2021.00019.f11
1\% as indicated in Figure 13b (Figure S6 shows overlapping data for the three data sets in a 1-year plot). Considering solely the spatial resolution factor, the OMI data set, whose resolution is finer (0.25° × 0.25°), yields a better comparison against the analyzed set of ozonesondes. However, these findings raise new questions in regard to the performance of other satellite and reanalysis products in this region of the world. Future research needs to tackle such questions in particular with longer ozonesonde time series at EMA.

As opposed to what happens in the Andes, in continental South America, closest to the equator, ozone satellite observations and reanalysis products have been historically validated against spectrometer and ozone sounding measurements at Natal. It is not surprising, therefore, that comparisons of MSR2 against ground-based measurements of TCO yield high correlation and linearity as indicated by the regression and the distribution of percentage differences in Figure 11e and f.

Finally, the comparison of MSR2 data against TCO measurements in Marcapomacocha yields a low correlation ($R^2$ coefficient of 0.42), as presented in Figure 11c and d. In this case, the MSR2 product overestimates measurements by 3.6\% (248.3 DU vs. 239.6, +8.7 DU). This difference is consistent with MSR2 performance over Quito. Since the comparison of sounding and spectrometer data between Quito and Peru showed that mean differences are generally not significant, we partially attribute this offset to coarse resolution and altitude. However, additional research and comparisons are needed to identify specific causes for differences with reanalysis and satellite products and also to further explore TCO differences between Quito and Marcapomacocha due to latitude.

4. Conclusions

In this work, we present a characterization of ozone throughout the atmospheric column, and we quantify the contributions of the boundary layer, the troposphere, and the stratosphere to TCO using measurements taken at Andean sites in Ecuador and Peru. We propose that the interpretation of TCO over the study region needs to emphasize on the fact that apparent low values (when compared with TCO at tropical sea-level sites) are unrelated to differences in stratospheric ozone but are due to a less deep troposphere and also due to low surface ozone. For example, over Quito, the difference due to altitude is of about 5–7 DU. In addition, the maximum contribution of boundary layer ozone to TCO, on average, is less than 7 DU even over urban areas. From sounding data taken in Quito, the mean $TrCO$, by trimesters, ranges between 17 and 24 DU with the greater column in the months of ASO,
which is significantly lower than, for example, at Natal, where values range between 30 and 40 DU. In contrast, the contribution of stratospheric ozone over the Andes (225.2 ± 8.9 DU) is similar to the one over Natal (223.3 ± 8.6 DU) from sounding data at both sites. Likewise, comparisons of stratospheric ozone sampled from Quito against MLS mixing ratios demonstrate matching levels of stratospheric ozone as well as the consistency and quality of EMA soundings over time. In regard to evaluating MSR2 TCO, we conclude that the 3%–4% higher values in the reanalysis, when compared to measurements in Ecuador and Peru, partially arrive from coarse spatial resolution. The latter observation is evident when looking at average differences among points in a transect from the Amazon, over Quito, Ecuador’s coast side, and into the Pacific. Thus, similar values between the Amazon, Quito, and the coast side indicate that the MSR2 product overestimates TCO above the Ecuadorian Andes with 7 DU. For practical purposes, this difference can be applied to the MSR2 data as an altitude correction exclusively for the Ecuadorian Andes. However, further research that compares individual satellite products against measurements is needed to investigate in more depth underlying reasons for the observed differences. Finally, we would like to remark on the importance of continuing efforts to maintain and expand observations over the tropical Andes as well as incorporating this information into evaluations of satellite and reanalysis products.

Data accessibility statement

Surface and sounding data from Ecuador can be accessed at https://observaciones-iaa.usfq.edu.ec. SHADOZ data can be accessed at https://tropo.gsfc.nasa.gov/shadoz. Spectrometer data at Natal and Marcapomacocha can be accessed at https://woudc.org/data/explore.php.

Supplemental files

The supplemental files for this article can be found as follows:

- Data quality control for EMA station. Figure S1–S6. Table S1–S3. Docx

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Author contributions

Contributed to conception and design: MC, RP.
Contributed to acquisition of data: MC, RP, EH, FRDs.
Contributed to analysis and interpretation of data: MC, RP, EH.
Drafted and/or revised the article: MC, RP.
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