



Tropospheric ozone increases over the southern Africa region: bellwether for rapid growth in Southern Hemisphere pollution?

A. M. Thompson^{1,2}, N. V. Balashov², J. C. Witte^{1,3}, J. G. R. Coetzee⁴, V. Thouret⁵, and F. Posny⁶

¹NASA/Goddard Space Flight Center, Code 614, Greenbelt, MD 20771, USA

²Pennsylvania State University Dept. of Meteorology, University Park, PA 16802, USA

³SSAI, Lanham, MD 20706, USA

⁴South African Weather Service, Pretoria, South Africa

⁵Laboratoire D'Aerologie, Obs. Du Midi-Pyrénées, Toulouse, France

⁶Atmosphere and Cyclone Lab, Université de La Réunion, La Réunion, France

Correspondence to: A. M. Thompson (amt16@psu.edu)

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Abstract. Increases in free-tropospheric (FT) ozone based on ozonesonde records from the early 1990s through 2008 over two subtropical stations, Irene (near Pretoria, South Africa) and Réunion (21° S, 55° E; ~2800 km NE of Irene in the Indian Ocean), have been reported. Over Irene a large increase in the urban-influenced boundary layer (BL, 1.5–4 km) was also observed during the 18-year period, equivalent to 30 % decade⁻¹. Here we show that the Irene BL trend is at least partly due to a gradual change in the sonde launch times from early morning to the midday period. The FT ozone profiles over Irene in 1990–2007 are re-examined, filling in a 1995–1999 gap with ozone profiles taken during the Measurements of Ozone by Airbus In-service Aircraft (MOZAIC) project over nearby Johannesburg. A multivariate regression model that accounts for the annual ozone cycle, El Niño–Southern Oscillation (ENSO) and possible tropopause changes was applied to monthly averaged Irene data from 4 to 11 km and to 1992–2011 Réunion sonde data from 4 to 15 km. Statistically significant trends appear predominantly in the middle and upper troposphere (UT; 4–11 km over Irene, 4–15 km over Réunion) in winter (June–August), with increases ~1 ppbv yr⁻¹ over Irene and ~2 ppbv yr⁻¹ over Réunion. These changes are equivalent to ~25 and 35–45 % decade⁻¹, respectively. Both stations also display smaller positive trends in summer, with a 45 % decade⁻¹ ozone increase near the tropopause over Réunion in December. To explain the ozone increases, we investigated a time series of dynamical markers, e.g., poten-

tial vorticity (PV) at 330–350 K. PV affects UT ozone over Irene in November–December but displays little relationship with ozone over Réunion. A more likely reason for wintertime FT ozone increases over Irene and Réunion appears to be long-range transport of growing pollution in the Southern Hemisphere. The ozone increases are consistent with trajectory origins of air parcels sampled by the sondes and with recent NO_x emissions trends estimated for Africa, South America and Madagascar. For Réunion trajectories also point to sources from the eastern Indian Ocean and Asia.

1 Introduction

We are motivated to assess tropospheric ozone trends for two reasons: (1) air quality, where surface data are typically used, and (2) climate perturbations, where free-tropospheric ozone exercises a positive radiative forcing (Shindell et al., 2006). In the troposphere, under the influence of sunlight, ozone is formed by chemical reactions among nitrogen oxides (NO_x = NO + NO₂), carbon monoxide (CO) and volatile organic compounds (VOCs) (Brunekreef and Holgate, 2002). Ozone may also be transported vertically into the free troposphere (FT) from the ozone-rich stratosphere; this mechanism is known as stratosphere–troposphere exchange (STE; Holton et al., 1995). Trend analysis must account for natural variability in tropospheric ozone due to seasonal cycles and climate oscillations that affect both STE and sources of the

ozone precursors, NO_x , CO and VOCs that originate from a range of anthropogenic and natural processes (Oltmans et al., 2013).

Most tropospheric ozone trend studies to date have focused on regional pollution in the Northern Hemisphere, where sources are reasonably well characterized and inter-continental transport links Asia, North America and Europe as a global phenomenon (Cooper et al., 2012; Logan et al., 2012; Parrish et al., 2012, 2013). Ozone measurements from urban and rural background sites are usually used for trend studies (Oltmans et al., 2013), with some mixture of ozone data from ozonesondes and commercial aircraft monitoring (Logan et al., 2012). Trends based on satellite ozone column estimates have been published (Beig and Singh, 2007), but the various data products available are highly uncertain (Doughty et al., 2011; Schoeberl et al., 2007; Stajner et al., 2008; Thompson et al., 2012). Satellite data for the ozone precursors NO_x (van der A et al., 2008; Lourens et al., 2011; Zien et al., 2014) and CO (Worden et al., 2010) are becoming available, but only for the period after 1995. These studies also focus on the Northern Hemisphere. In some cases, satellite trends are based on multiple instruments with differing algorithms and sampling characteristics and thus are highly uncertain.

Data from a handful of South American megacities (Gallardo et al., 2012) and rapidly growing cities in sub-equatorial Africa represent most of our information about the Southern Hemisphere (SH). Trends in South American and African cities are hard to establish because a variety of ozone measurement techniques have been employed, many stations are only a few years old, and calibration checks are sometimes irregular. An exception occurs in South Africa (SA), where the Johannesburg–Pretoria (referred to below as J-P) conurbation (blue star in Fig. 1) may already have attained mega-city status (Lioussé et al., 2012, 2014). Air quality monitoring in some parts of SA began in the 1970s, with adoption of high-quality, regularly calibrated instrumentation in the late 1980s and early 1990s (Rorich and Galpin, 1998). At municipal levels, dozens of stations began operating after 2005 (<http://www.saaqis.org.za>). To the east of J-P, at five monitoring sites over the partly rural, partly industrialized regions of the Gauteng and Mpumalanga Highveld, surface ozone exhibit pronounced sensitivity to the El Niño–Southern Oscillation (ENSO) but little evidence of trends over the period 1990–2007 (Balashov et al., 2014). Oltmans et al. (2013) recently reported that the WMO/GAW (World Meteorological Organization/Global Atmospheric Watch) Cape Point station displayed a 15–20% ozone increase from 1990 to 2000, followed by a period of zero-to-low growth.

In order to examine possible ozone trends in the FT in the J-P region, Clain et al. (2009) used sonde data from the SHADOZ (Southern Hemisphere Additional Ozonesondes; Thompson et al., 2003, 2012) station at Irene (25.9° S, 28.2° E). Clain et al. (2009) also studied FT ozone variability and trends at Réunion (20.8° S, 55.5° E; data from

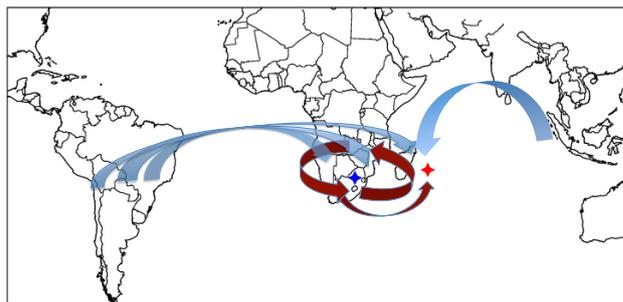


Figure 1. Location of Irene soundings and Johannesburg MOZIC landing/takeoff profiles (blue star) and Réunion soundings (red star). Also illustrated are typical recirculation patterns over southern Africa and an outflow route to the Indian Ocean (maroon arrows). Flows toward the southern African region and eastern Indian Ocean from South America and southern Asia are indicated by blue arrows (see Fig. 12).

1992 to 2008), a SHADOZ station ~ 2800 km northeast of J-P (red star in Fig. 1). A regular linear regression approach was employed to compare the 1990–1993 Irene record with SHADOZ-period (Thompson et al., 2003, 2012; Diab et al., 2004) soundings that spanned 1998–2008. The trends were computed from ~ 1 km above the surface to 16 km for the entire sampling period, with layers 2–6 km thick. On average for Irene, only in the boundary layer (BL, in this case 2–4 km) was there a statistically significant trend, $+14.4 (\pm 4.0) \% \text{ decade}^{-1}$. A similar analysis was performed with the Réunion sonde record, where, conversely, ozone only increased significantly, by $12 (\pm 6) \% \text{ decade}^{-1}$, above 10 km from 1992 to 2008.

Due to a pronounced seasonal cycle of ozone throughout the troposphere, Clain et al. (2009) also computed trends for each season: December–January–February (DJF, summer), March–April–May (MAM, fall), June–July–August (JJA, winter) and September–October–November (SON, spring). There was a barely significant ozone increase in the middle troposphere (MT; 6–10 km, $12.3 (\pm 12.2) \% \text{ decade}^{-1}$) only in JJA. In JJA there was also a significant trend of $18.30 (\pm 9.51) \% \text{ decade}^{-1}$ in the 10–16 km layer. There were no other Réunion trends during individual seasons. In JJA, the Irene increase from 1990 to 2008 at 6–10 km was $11.4 (\pm 5.1) \% \text{ decade}^{-1}$. Taking only the SHADOZ period, 1998–2008, that 6–10 km Irene increase more than doubled in JJA, to $28 (\pm 14) \% \text{ decade}^{-1}$. In the BL (2–4 km, over Irene) there was a statistically significant increase from 1998 to 2008, $+30.5 (\pm 12.5) \% \text{ decade}^{-1}$, also roughly double that over the 1990–2008 period. This $\sim 30 \% \text{ decade}^{-1}$ increase was fairly uniform throughout the year, except for a slightly higher value, $+36 \% \text{ decade}^{-1}$, in MAM. Clain et al. (2009) hypothesized that the Irene and Réunion ozone growth in the lower and middle troposphere could be associated with increases in industrialization and biomass burning.

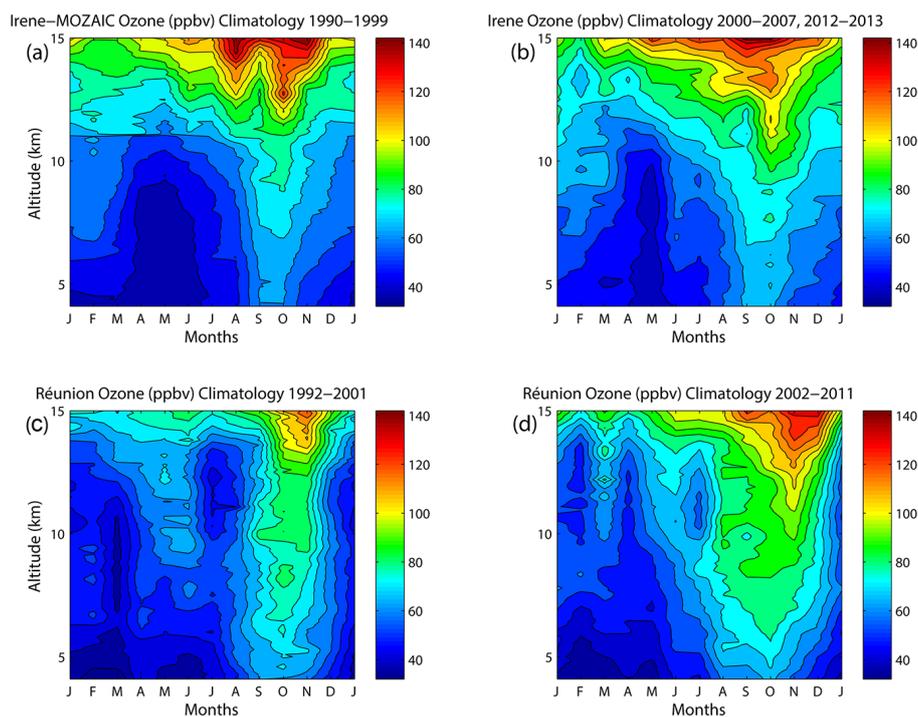


Figure 2. Seasonal cycle of free- and upper-tropospheric ozone over Irene, based on monthly averages for two periods of observations for Irene and Réunion: (a) Irene sondes from 4 to 15 km (1990–1993, 1999) with MOZAIC ozone from 4 to 11 km (1995–1999), (b) Irene (SHADOZ) sondes from 2000 to 2007 and 2012 to 2013, (c) Réunion (pre-SHADOZ and SHADOZ) sondes launched in 1992–2001, and (d) Réunion (SHADOZ) sondes from 2002 to 2011.

However, they pointed out that the Réunion UT ozone increases occur when STE processes are most prevalent.

In this paper, the Irene sondes, with additional J-P ozone profiles (1995–1999) from the Measurements of Ozone by Airbus In-service Aircraft (MOZAIC) project, and extended Réunion ozone profiles (1992–2011) are re-examined and more accurate trends are presented. The BL trends reported by Clain et al. (2009) for Irene are shown to be at least partially an artifact of changing ozonesonde launch times. Second, we merge the Irene and MOZAIC mid-tropospheric (4–11 km) profiles that are unaffected by sampling times. We use a multivariate regression model that accounts for the seasonal cycle, potential vorticity (PV) and ENSO to compute trends based on monthly averaged ozone mixing ratios. A late fall–early winter (May and June) trend in the MT over Irene turns out to be more than twice as large as reported by Clain et al. (2009), with more vertically diffuse regions of increase in summer (November–December). Between 4 and 5 km over Irene, ozone increases suggestive of BL change occur throughout the year, except at the local biomass burning season (SON).

We also calculate ozone trends over Réunion. In that case, we find a winter (July–August) trend from 1992 to 2011 that is larger than over Irene, $+35\text{--}45\text{ decade}^{-1}$, above 8 km. Due to the strength of UT ozone increases over Irene and Réunion, we look for evidence of dynamical changes, using

potential vorticity as a proxy for stratospheric influence. Similarly, assuming that growth in ozone precursors like NO_x and VOCs might account for the distinct ozone increases in May–August, standard emissions databases are consulted. Section 2 describes data sources and analytical methods. Section 3 presents results and discussion. Section 4 provides a summary and conclusions.

2 Data and methods of analysis

2.1 Ozonesonde measurements at Irene and Réunion

The measurements at Irene are made with Vaisala RS-80 radiosondes (prior to 2002) and RS92 radiosondes (from 2002 to 2008) coupled to Science Pump Corporation (SPC) electrochemical concentration cell ozonesondes (Thompson et al., 1996, 2003; Diab et al., 1996). A 1 % buffered KI solution is used; this gives a measurement of tropospheric ozone with 5 % accuracy and precision (Johnson et al., 2002; Smit et al., 2007; Smit and ASOPOS, 2011; Thompson et al., 2007). Comparisons of total column ozone from integration of the Irene sonde data from 1998 to 2008 (minus a gap from 2000 to 2004) with the colocated Dobson no. 89 spectrophotometer, and with Earth Probe TOMS (Total Ozone Mapping Spectrometer, 1999–2004) and OMI (Ozone Monitoring

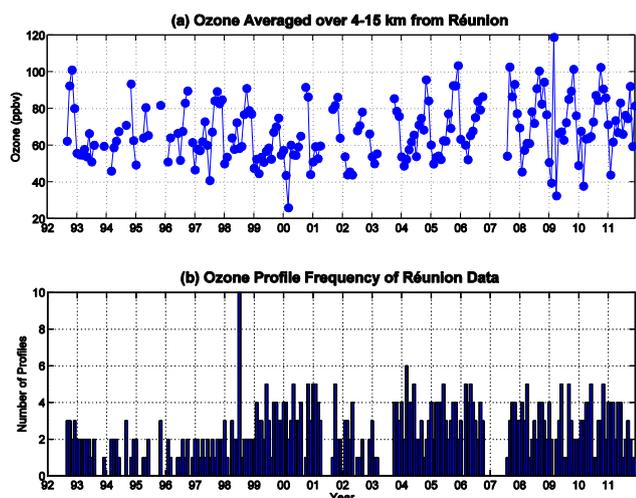


Figure 3. (a) Ozone mixing ratio, averaged over 4–15 km, from the Réunion sonde record that started in 1992. (b) Corresponding data frequency of profiles used in (a) by month.

Instrument, 2005–2008), are within 1 %. This implies that total ozone from the Irene sondes is one of the most accurate records in SHADOZ (see <http://croc.gsfc.nasa.gov/shadoz>; Thompson et al., 2007, 2012).

Figure 2 presents a seasonal climatology of the annual cycle of FT ozone over Irene (Fig. 2a, b) and Réunion (Fig. 2c, d) based on monthly averages for each site. The earlier Irene record, for the years 1990–1999, as in Fig. 2a, is based on the 1990–1993 sondes augmented by the MOZAIC record for 4–11 km for the years 1995–1999; from 1995 until late 1998 there were no sonde launches over Irene. The second Irene climatology (Fig. 2b) is based on SHADOZ soundings for 2000–2007 with about a year of data from September 2012 through October 2013. The most recent sondes followed a hiatus of more than 4 years in Irene launches that started in early 2008. The structure of the two periods depicted in Fig. 2 appears somewhat different in several time and altitude zones. One is within the TTL (tropopause transition layer), which is ~ 13 – 15 km for Irene, during June through December. Second, in the period of active southern African biomass fires (August–November), from ~ 4 to 10 km, ozone appears slightly lower or unchanged in the second period (Fig. 2b) compared with the 1990s (Fig. 2a). Conversely, from April through July or August, ozone below 11 km appears to have increased.

Réunion ozonesondes have been launched since 1992 at St. Denis airport (~ 10 m a.s.l.) (Baldy et al., 1996; Baray et al., 1998, 2006; Randriambelo et al., 1999) using SPC and ENSCI (now Droplet Measurement Technology – DMT) ECC ozonesondes with a 1 % buffered KI solution from 1992 to 1998 and a 0.5 % buffered KI solution after 1998. Several types of radiosondes have been used: Vaisala RS-80 radiosondes (prior to September 2007), Modem M2K2 son-

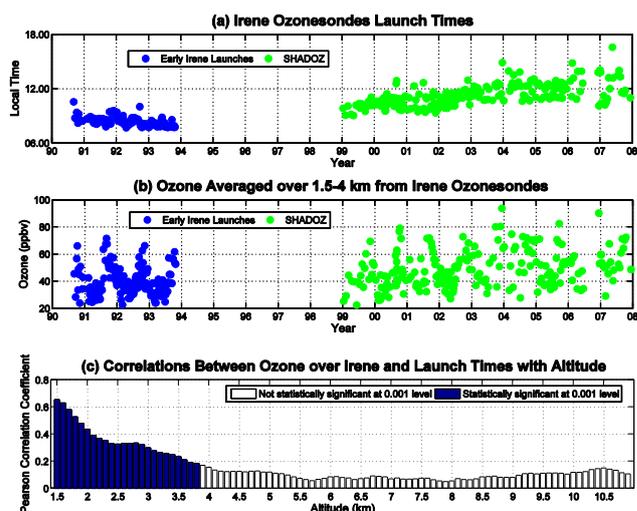


Figure 4. (a) Launch times for Irene, South Africa (25.9° S, 28.2° E), balloon-borne ozonesonde–radiosonde packages during 1990–1993 (blue) and for SHADOZ from 1999 to early 2007 (green). (b) Mean ozone mixing ratio in the 1.5–4 km layer from Irene sondes corresponding to the sampling times in (a), showing the upward trend in ozone mixing ratio as launch times moved later in the day. (c) Correlation between sonde launch times and ozone mixing ratio from the time series in (a) and (b) as a function of altitude in 0.1 km bins from the surface (1.5 km) to 11 km.

des (from September 2007 to March 2013) and Modem M10 (from March 2013 to now). The mean 4–15 km ozone mixing ratio appears in Fig. 3a with the frequency of sonde launches in Fig. 3b. The most recent evaluation of total ozone over Réunion as measured by the sondes averages within 2 % of the satellite reading (Thompson et al., 2012) and the ground-based Système D’Analyse par Observations Zénithales (SAOZ) instrument. Climatologies for 1992–2001 and 2002–2011, based on the soundings depicted in Fig. 3b, are illustrated in Fig. 2c and d. Winter ozone increases above 4 km over Réunion are pronounced in JJA; in the MT there appear to be increases in October and November as well.

The 1990–1993 Irene ozonesondes were launched at 07:30–08:30 local time (LT – UTC +2 h; Fig. 4a). When operations were resumed for SHADOZ in late 1998, launches were conducted $\sim 09:30$ LT. After 2002, launches fluctuated from $\sim 11:30$ to 15:30 LT to accommodate overpasses of ozone instruments on ENVISAT (SCanning Imaging Absorption spectromETER for Atmospheric CHartography – SCIAMACHY) and the Aura satellite (four ozone sensors). The typical mean 1.5–4 km ozone mixing ratio in 1990–1993 (e.g., Fig. 5 in Thompson et al., 1996) was ~ 25 ppbv in summer (DJF), with a spring maximum (SON) at 70 ppbv (Fig. 4b). By 2006 the DJF (low-ozone season) near-surface ozone had drifted upward to 30 ppbv and the mean 1.5–4 km ozone exceeded 80 ppbv, levels not seen in the early 1990s. Thus, the Clain et al. (2009) trend for SON based on comparing the 2–4 km tropospheric ozone

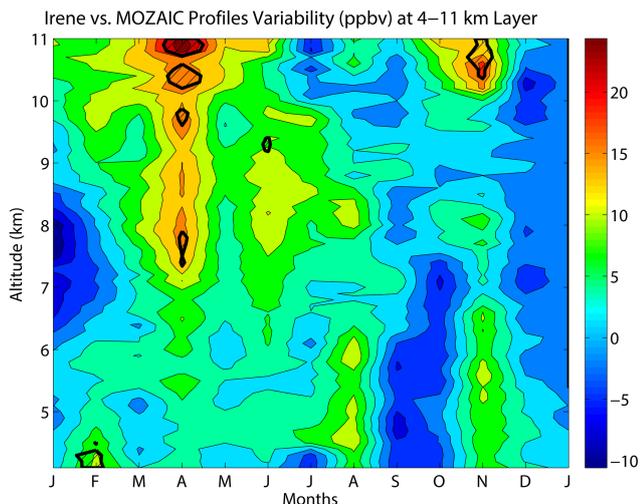


Figure 5. Difference between Irene ozonesonde climatology combined from 1990 to 1993 and 1999 to 2007 and MOZAIC climatology from 1995 to 1999. Hatched areas represent statistically significant deviations of climatologies (places where standard deviation values from two climatologies do not overlap).

column amounts between 1990 and 2008 was a statistically significant increase of $+1.17 (\pm 0.49)$ DU decade⁻¹, equivalent to $15 (\pm 6.2)$ % decade⁻¹. During the SHADOZ period only, 1998–2008, with the sampling times drifting later into the day, the 2–4 km-layer ozone increase for SON calculated by Clain et al. (2009) was $2.4 (\pm 1.5)$ DU decade⁻¹ or $28.9 (\pm 18)$ % decade⁻¹.

Figure 4c shows that, at Irene, ~ 1.5 km above sea level, the correlation between ozone mixing ratio and launch time is 0.6. The correlation drops sharply above 2 km but the correlation coefficient is still > 0.2 at 2 km. Only above 4 km does the ozone–launch-time correlation decrease to < 0.08 . Consequently, trends from sondes based on data below 4 km are assumed to be unreliable. The apparent BL trend noted by Clain et al. (2009) might be observed because midday surface ozone in the Pretoria region (<http://www.saaqis.org.za>) is typically 3–4 times greater than at 07:00 LT due to the daily photochemical ozone cycle.

2.2 MOZAIC data selection

MOZAIC sampling with Johannesburg landing and takeoffs began in 1995 and ended in 2009; coverage after 2001 was less regular than in the 1990s, with some years skipped altogether. The general coherence of the MOZAIC Johannesburg and Irene ozone profiles up to ~ 12 km (200 hPa) has been described by Diab et al. (2003) and Clain et al. (2009). More detailed sonde–MOZAIC comparisons reported by Thouret et al. (1998) found that, above 400 hPa, ozonesondes exhibit higher values than the Airbus instrument. The MT and UT air sampled by the aircraft at beginning of descent and end of ascent is north of Johannesburg, largely over Zambia and

Zimbabwe. Those profile segments correspond to a lower background ozone amount than over Irene, where most sondes travel over the SA Highveld and often encounter higher ozone from mid-latitude air and STE events (see, for example, a comparison of soundings over Lusaka (Zambia) and Irene in September 2000; Thompson et al., 2002). Below 400 hPa, agreement between MOZAIC and Irene profiles is usually within 5 %, the stated uncertainty of the sonde instrument (Thouret et al., 1998). Because ozonesonde data over Irene are missing for most of the 1994–1998 period, we want to fill the gap with 4–11 km measurements from the MOZAIC record. A check for instrument bias between the Irene and MOZAIC ozone profiles appears in Fig. 5, where the difference between the Irene ozonesonde climatology combined from 1990 to 1993 and 1999 to 2007 and mean ozone from MOZAIC in 1995–1999 is presented. Hatched areas represent times and regions where, within the standard deviation for each data set (sonde and MOZAIC), the means of the two climatologies do not overlap. As expected, most of the statistically significant differences are above 9 km. The greatest differences appear in fall (MAM), not in winter, which happens to show the largest ozone trends (Sect. 3). Accordingly, for our analysis, the 1995–1999 MOZAIC and Irene data are merged into a single time series (Fig. 6). Furthermore, because Thouret et al. (1998) found no difference in morning or evening MOZAIC profiles in the FT, all the available data are included in the monthly averages in Fig. 6.

2.3 Dynamical factors and trend analysis

A number of studies point to significant dynamical influences that need to be taken into account in a trend analysis of FT and TTL tropical ozone. For example, examination of tropical tropospheric ozone variability with indicators of ENSO (El Niño–Southern Oscillation) based on satellite and sonde data (Chandra et al., 1998; Thompson and Hudson, 1999; Fujiwara et al., 1999; Thompson et al., 2001; Logan et al., 2008) reveals a positive (increased) ozone response in some regions and negative in others. Time-series analyses of SHADOZ ozone profiles in the troposphere and lower stratosphere (LS) have been carried out by Lee et al. (2010), Randel and Thompson (2011) and Oman et al. (2011). At the sites equatorward of 15° S/N, the ENSO signal exhibits varying characteristics, with stations responding with positive ozone and temperature anomalies (for example, Kuala Lumpur and San Cristóbal), negative at others (Natal and Nairobi in Lee et al., 2010) and with distinct time lags (Randel and Thompson, 2011). Using a different diagnostic, gravity wave frequency (GWF), as inferred from ozone and potential temperature laminae within the ozone and radiosonde profiles, Thompson et al. (2011) found that ENSO signatures during the SHADOZ record were most pronounced in the TTL and less so in the MT. Over subtropical Irene and Réunion, GWF is 2–3 times lower than over Kuala Lumpur, Watukosek and San Cristóbal (Thompson et al., 2011).

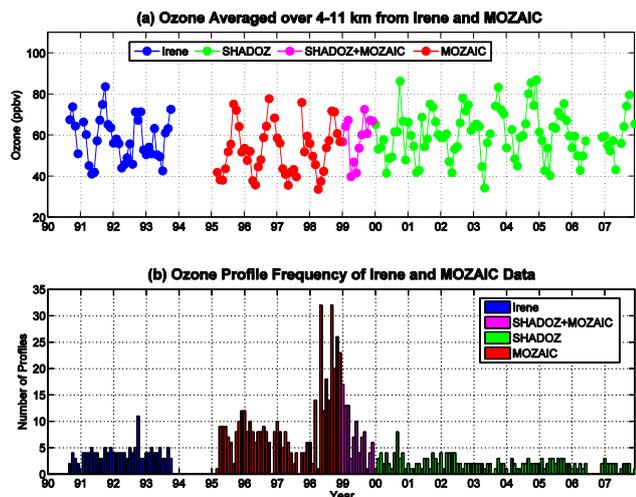


Figure 6. (a) Ozone mixing ratio averaged 4–11 km, from the earlier (1990–1993) Irene record (blue) and the SHADOZ Irene period (1999–2007) (green). The red dots depict averaged ozone mixing ratio, 4–11 km, from MOZAIIC profiles acquired in 1995–1998 from an instrumented commercial jet during landings and takeoffs at Johannesburg (JNB, O. R. Tambo) airport (Thouret et al., 1998; Clain et al., 2009). The magenta dots represent the combined record of MOZAIIC and SHADOZ. (b) Corresponding data frequency of profiles used in (a) by month for Irene and JNB. Equipment changes by the airlines have interrupted the commercial aircraft ozone sampling project in MOZAIIC (now IAGOS). Two field campaigns (SAFARI-92/TRACE-A in September–October 1992; Diab et al., 1996; Thompson et al., 1996) and SAFARI-2000 in September 2000 (Swap et al., 2003; Thompson et al., 2002) gave rise to more frequent Irene launches.

STE is known to affect tropospheric ozone at Irene, especially during the spring. STE processes may occur slowly, as through the Brewer–Dobson circulation (Holton et al., 1995). Alternatively, meteorological phenomena such as intense cumulus convection, tropopause folding associated with upper level troughs, and cutoff lows are the examples of faster STE mechanisms (Rao et al., 2003). It is standard practice to use potential vorticity (PV) as a dynamical tracer of stratospheric air intrusions into FT, as, for example, in tropopause folds, where UT subsidence transports ozone-rich LS air into the mid-troposphere (Keyser and Shapiro, 1986; Beekmann et al., 1994; Rao et al., 2003). Consequently, any diabatic heating processes can alter PV values without affecting ozone.

Accordingly, FT ozone, at both Irene and Réunion is analyzed with a multivariate regression model that includes factors of the semi- and annual cycles, trend, ENSO, and PV variability. Such statistical regression models are common in the atmospheric sciences (Randel and Cobb, 1994; Ziemke et al., 1997). The model can be presented as

$$\hat{T}(t) = \alpha + \beta \cdot t + \gamma \cdot \text{ENSO}(t) + \delta \cdot \text{PV}(t) + \epsilon(t), \quad (1)$$

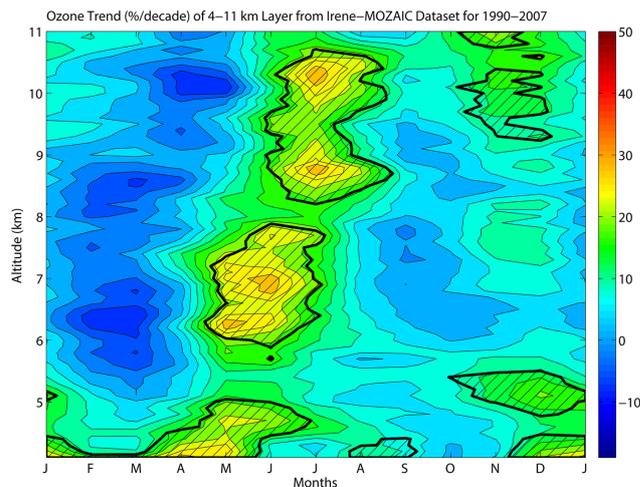


Figure 7. Trend (change in % decade⁻¹) computed from multivariate regression model for combined 4–11 km, Irene–JNB MOZAIIC profile data, 1990–2007. Diagonal shading denotes statistical significance. Increases below 5 km may be related to surface pollution. Note that losses (blue in February–March–April and September–October) are not statistically significant.

where α is the seasonal cycle fit, β is the trend coefficient, t is time in months, γ is the regression coefficient for the time series ENSO(t), δ is the regression coefficient for the PV(t) time series, and finally $\epsilon(t)$ is the residual that is calculated by subtracting the modeled time series $\hat{T}(t)$ from the actual ozone time series $T(t)$. For ENSO, the Southern Oscillation index (SOI, <http://www.esrl.noaa.gov/psd/data/correlation/soi.data>) is used as a proxy. Monthly PV anomalies are calculated from the ECMWF 330 K PV fields over Irene (box bounded by 25.5–32.2° S and 24.8–31.5° E) and from the ECMWF 350 K PV data over Réunion (box within 18–25° S and 49.5–65.25° E) (Dee et al., 2011). Note that including a PV term in Eq. (1) should partially account for any influence of a changing tropopause height (Seidel et al., 2008; Sivakumar et al., 2011). The error for each coefficient is 2 standard deviations (SD) and is estimated using a moving-block bootstrap technique in order to account for auto-correlation in the ozone time series (Wilks, 1997). The model is applied to monthly mean ozone every 100 m from 4–11 km for Irene (Fig. 7) and over 4–15 km for Réunion (Fig. 8). We note that the quasi-biennial oscillation (QBO) also affects tropical ozone (e.g., Witte et al., 2008; Thompson et al., 2011). Adding a term for the QBO in the regression model, Eq. (1), made no difference in the results, presumably because the ozone trends are mostly below 13 km, where QBO impacts are small (Lee et al., 2010).

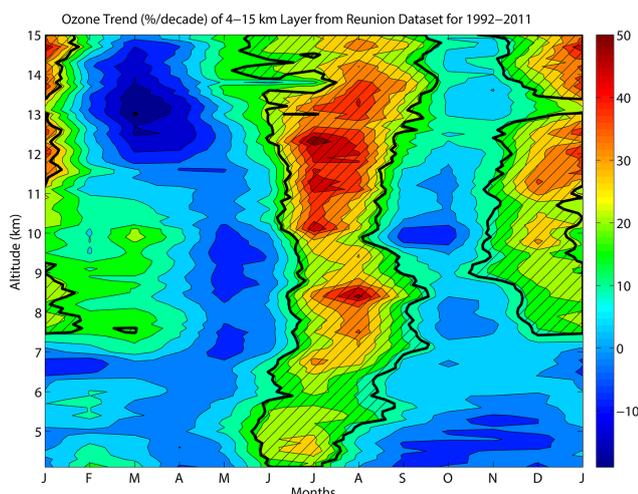


Figure 8. Same as Fig. 7 except trend in Réunion profiles, 4–15 km, from 1992 to 2011.

3 Results and discussion

3.1 Free-tropospheric trends at Irene and Réunion

Figures 7 and 8 display ozone mixing ratio trends (in $\% \text{ decade}^{-1}$) for Irene and Réunion, respectively, based on the 100 m monthly mean ozone averages. Hatched areas, which appear only with positive trends, denote 2-SD statistical significance. At both of these stations, ozone increases are most pronounced in the MT and UT, between 4 and 11 km (Irene, Fig. 7) and between 4 and 15 km (Réunion, Fig. 8) in winter. Ozone increases begin earlier in the year (April, May, June, late fall) between 4 and 6 km over Irene than over Réunion. In addition, in the lower free troposphere (LFT, below 5 km), statistically significant Irene ozone increases occur intermittently after June and into December (Fig. 7). It is possible that surface ozone changes over the urbanizing J-P region play a role in the LFT change. Note that, although Fig. 4 suggests that the Irene data at 5 km are free of sampling artifacts, some contamination in the 4–5 km trends (Fig. 7) might be present.

At Réunion, there is a UT summer increase (Fig. 8; December, January, 8–15 km) that bears some similarity to an Irene increase at 10–11 km in November and December (Fig. 7), but the magnitude of the Réunion ozone change is slightly greater than the Irene signal. In particular, the 13–15 km layer over Réunion shows a significant ozone enhancement during December and January. The PV term described in Sect. 3.2.1 partially accounts for this enhancement. The ozone increase in this layer is likely to be related to STE processes in the UT. A striking result is that there are no significant increases in MT ozone at either site during the southern African biomass burning season, September–October (Fishman et al., 1991, 1996; Thompson et al., 1996; Swap et al., 2002). One reason might be that predominant transport

from the most heavily burning regions south of 20° S at that time of year tends to be southeast toward the Indian Ocean, not along a SA Highveld–Réunion route (Swap et al., 2002; Kanyanga, 2008).

3.2 Possible causes for free-tropospheric ozone increase

We briefly investigate possible reasons for the ozone increases, considering dynamic factors and pollution sources.

3.2.1 Dynamical considerations

The two sources of ozone in the FT are in situ chemical production and transport, where the former cause is generally believed to be at least several times greater than the latter (Stevenson et al., 2006). In this section we consider how meteorological parameters may influence both of these sources. Can the positive trends in TTL and FT ozone be explained by changes in the downward flow that transports ozone into the troposphere from the ozone-rich stratosphere during the wave-breaking process associated with Rossby wave activity (Collins et al., 2003)? Because PV is a convenient dynamical tracer of the stratospheric air parcels, we use it as a proxy for possible changes in STE events. We calculate monthly PV averages at both locations from the daily means of 12Z PV fields (for more details see Sect. 2.3) and use these monthly averaged PV time series to calculate monthly anomalies, which are used as a predictor in our regression model (Eq. 1). A similar approach (but with different goals) is used in Ziemke et al. (1997). Our results are indicated in Fig. 9. Based on evaluating an ozone response to PV changes over Irene, Fig. 9a shows a strong ozone sensitivity to a 330 K PV time series in October and November, when frequent STE episodes associated with wave breaking occur over the SA Highveld (Tyson et al., 1997) and when the ozone tropopause is at its lowest altitude (Sivakumar et al., 2011; Thompson et al., 2012). However, ozone changes at 9–11 km over Irene (corresponding to the 330 K level) are only $\sim 15 \% \text{ decade}^{-1}$ in September and October, less than the winter trends (Fig. 7).

We examined 350 K and 330 K PV May–June–July–August (MJJA) anomalies over Irene (derived from the monthly averaged PV time series described in Sect. 2.3) for the 1990–2007 period to look for potential changes in STE activity during the MJJA period, when the positive ozone trend is most evident (Fig. 10). At the 350 K level (Fig. 10a), there is an indication of slightly decreasing PV; this would be consistent with findings of the well-characterized widening tropical belt (Seidel et al., 2008). However, such a perturbation would tend to favor a higher tropopause, fewer STE events and generally less ozone, the opposite of what is observed (Fig. 7). Figure 10 also presents MJJA anomalies of tropospheric temperature and specific humidity over the 1990–2007 period. These are examined because it is known that up to 300 hPa (Collins et al., 2000) temperature increases may

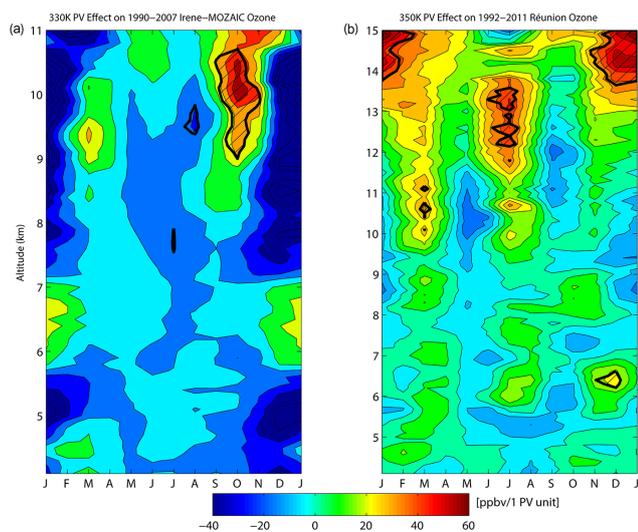


Figure 9. (a) Irene tropospheric ozone (4–11 km layer) sensitivity toward the 330 K potential vorticity time series ($\text{ppbv}/1 \text{ PV unit}^{-1}$) over the box bounded by $25.5\text{--}32.2^\circ \text{ S}$ and $24.8\text{--}31.5^\circ \text{ E}$ for 1990–2007. (b) Réunion tropospheric ozone (4–15 km layer) sensitivity toward the 350 K potential vorticity time series ($\text{ppbv}/1 \text{ PV unit}^{-1}$) over the box bounded by $18\text{--}25^\circ \text{ S}$ and $49.5\text{--}65.25^\circ \text{ E}$ for 1992–2011. Statistically significant response is shaded. Note that the altitude scales are different for the stations.

lead to higher water vapor (H_2O) mixing ratios and enhanced photochemical destruction of ozone through the series of reactions that form OH: $\text{O}_3 + h\nu + \text{H}_2\text{O}$. In Fig. 10, some temperature increases are evident, but there is no consistent, proportional response in specific humidity. Furthermore, if H_2O had increased in the 1990–2007 period, the tendency would be to suppress FT ozone, again the opposite of what is observed (Fig. 7). We conclude that the evidence for dynamical change as the main driver for Irene FT winter ozone trends is not compelling.

At Réunion, a site decidedly more tropical than Irene, the STE effect (Fig. 9b) is statistically significant only during the December–January period in the 13–15 km layer, corresponding to the 350 K PV level (see Fig. 3 in Thompson et al., 2012). Due to this sensitivity we think that the ozone changes in that layer during that time are tied to STE processes. Figure 11 (green curve) suggests that PV influence on MT ozone (5–13 km) over Réunion is smaller than over Irene (Fig. 11, blue curve), but STE events are known to occur at various times throughout the year (Baray et al., 1998; Randriambelo et al., 1999; Clain et al., 2010). In September and October, tropical low-pressure systems and the seasonal lowering of the tropopause are similar to Irene (Sivakumar et al., 2011). Greater PV values at Irene (Fig. 11, blue curve) than at Réunion are not surprising given that Irene is closer to the southern hemispheric subtropical jet. Similar to Irene, we examined tropospheric PV, temperature, and specific hu-

midity anomalies over Réunion for 1992–2011 (not shown) but did not find any noticeable changes.

In summary, there is some evidence for a dynamical role in UT ozone changes over Irene and Réunion, specifically during October–December at Irene and during December–January over Réunion. However, the large winter ozone trends at both locations do not seem to be explained by meteorology.

3.2.2 Photochemistry and pollution

In a number of studies looking at southern African transport in September–October 1992, when intensive radiosonde and ozonesonde launches were made in Namibia and SA as part of Southern African Fire-Atmospheric Research Initiative/Transport and Atmospheric Chemistry near the Equator-Atlantic (SAFARI-92/TRACE-A) experiments (e.g., Diab et al., 1996; Garstang et al., 1996; Thompson et al., 1996; Tyson et al., 1997), the Irene region was found to be in transition. Generally, north of 20° S , easterlies took pollutants toward the Atlantic (Fishman et al., 1990, 1996). On the SA Highveld, where Irene is located, flows in the mid-troposphere were often from the north or northeast, introducing layers of pollution from biomass fires, detected as elevated ozone (Thompson et al., 1996; Tyson et al., 1997). These layers recirculated and often exited Africa southeast toward the Indian Ocean, where pollution was detected in aircraft sampling (Heikes et al., 1996). This transport pattern, designated the “river of smoke” as it appears in MODIS satellite imagery, was confirmed during SAFARI-2000 (Swap et al., 2003). In the mid–upper-tropospheric transition zone, trajectories at 8–12 km showed that many air parcels arriving over Irene during SAFARI-92/TRACE-A (Thompson et al., 1996) originated over South America. Irene soundings displayed ozone layers that resulted from South American biomass fire emissions that traveled toward Africa after they had been lofted to the UT by deep convection (Pickering et al., 1996; Thompson et al., 1997). This mechanism, augmented by NO from lightning (Smyth et al., 1996), was inferred from tracers measured on the DC-8 aircraft. Links between Réunion ozone and biomass fires over Africa and Madagascar are also well established (Baldy et al., 1996; Randriambelo et al., 1999).

Figure 12, which displays air parcel origins for the Irene and Réunion ozone soundings launched in May–August in 1992–2011, suggests that the springtime sources studied in SAFARI-92 and SAFARI-2000 also pertain to winter. Two levels are illustrated. For Irene (Fig. 12a) the 500 hPa level trajectories ($\sim 5.5 \text{ km}$) are in the middle of the 4–8 km zone of $+20\text{--}30\% \text{ decade}^{-1}$ ozone increase in May and June (Fig. 7). The origins of the 500 hPa level air parcels over Irene are mainly located over the South Atlantic and eastern South America. For the 4–8 km ozone increases over Réunion (July and August in Fig. 8), the change is also $\sim 20\% \text{ decade}^{-1}$. The origins of the corresponding air

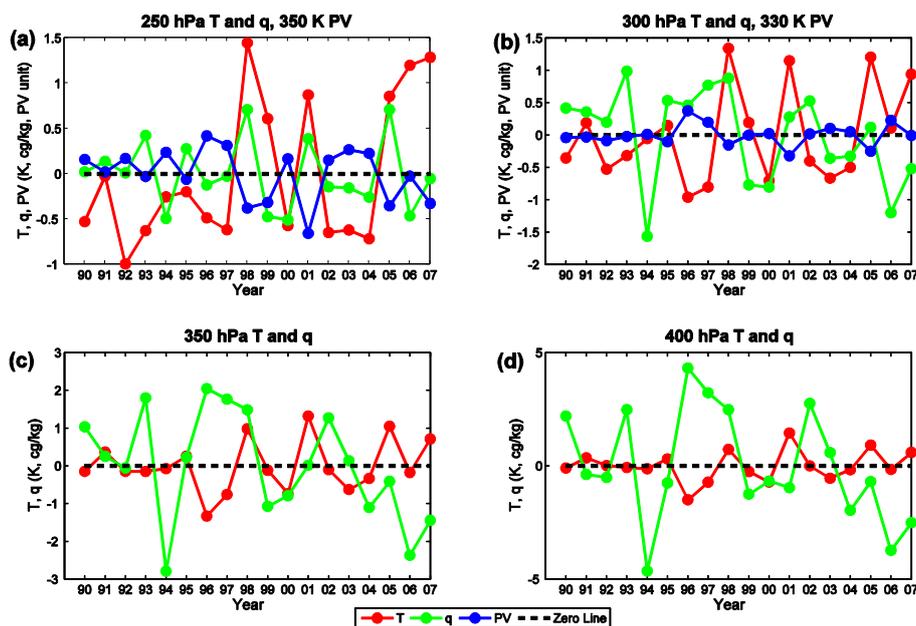


Figure 10. Irene (25.5–32.2° S, 24.8–31.5° E) May–June–July–August (MJJA) temperature (T) and specific humidity (q) anomalies for four pressure levels and potential vorticity (PV) anomalies for two isotropic levels.

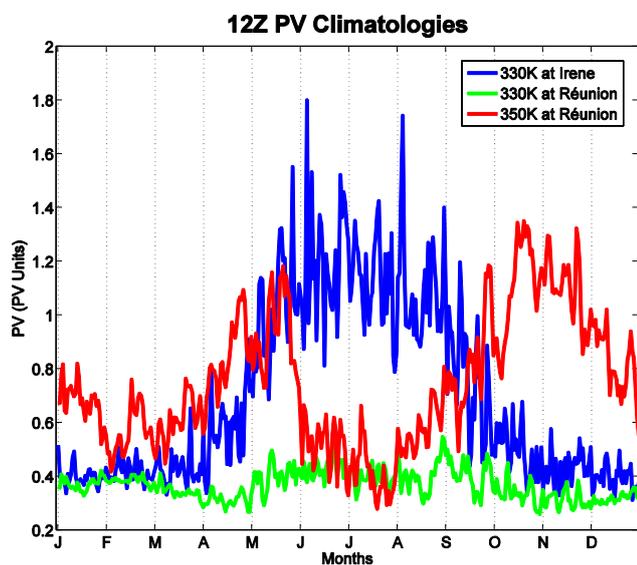


Figure 11. ECMWF potential vorticity (PV) daily climatologies over Irene for 330 K and Réunion for 330 K and 350 K calculated, respectively, over 1990–2007 and 1992–2011, by averaging day-of-year values.

parcels over Réunion (Fig. 12c) are concentrated over Madagascar, southern Africa and the eastern South Atlantic, where tropospheric ozone tends to accumulate year-round due to recirculation within the south Atlantic gyre. Over 5-day transit times from Irene at 300 hPa (Fig. 12b, 150 hPa parcels, not shown), there is a high concentration of origins over South America as well as Africa and the South Atlantic

(Fishman et al., 1990; Thompson et al., 2003; Jensen et al., 2012).

Réunion back trajectories at 300 hPa (Fig. 12d) in addition to South American, Atlantic and African origins include air parcels from the tropical Indian Ocean, which is subject to pollution (Thompson et al., 2001; Chatfield et al., 2004). A study of sources and transport patterns of winter CO over Réunion (Duflot et al., 2010) shows that southern Africa and Madagascar, as well as South America, contribute to CO enhancement in the FT below 11 km. Back-trajectory pathways, determined from FLEXPART, are similar to those illustrated in Fig. 12c and d. Duflot et al. (2011) present MOPITT (Measurement of Pollution in the Troposphere) CO distributions observed over Réunion source regions. During June–August 2007, elevated CO over Réunion is linked to high-CO regions at 250 hPa over South America, the South Atlantic and southern Africa as well as southeast Asia and Indonesia. The CO sources are assumed to be predominantly anthropogenic. Figure 12d also suggests potential Réunion pollution sources from southeast Asia. In September and October there is a shift away from anthropogenic sources to more biomass burning CO, detected by MOPITT near the surface (Duflot et al., 2010), where Irene and Réunion (Figs. 7 and 8) show no trend. The recent study of Zien et al. (2013) on NO₂ transport inferred from GOME-2 (Global Ozone Monitoring Experiment on MetOp-A) in 2007–2011 gives a mostly similar picture to MOPITT. The largest NO₂ plumes in the Southern Hemisphere occur in JJA, with origins densely concentrated over South America, southern Africa and the oceans to the southeast (Figs. 15, 16, 19 in Zien et al., 2013). However,

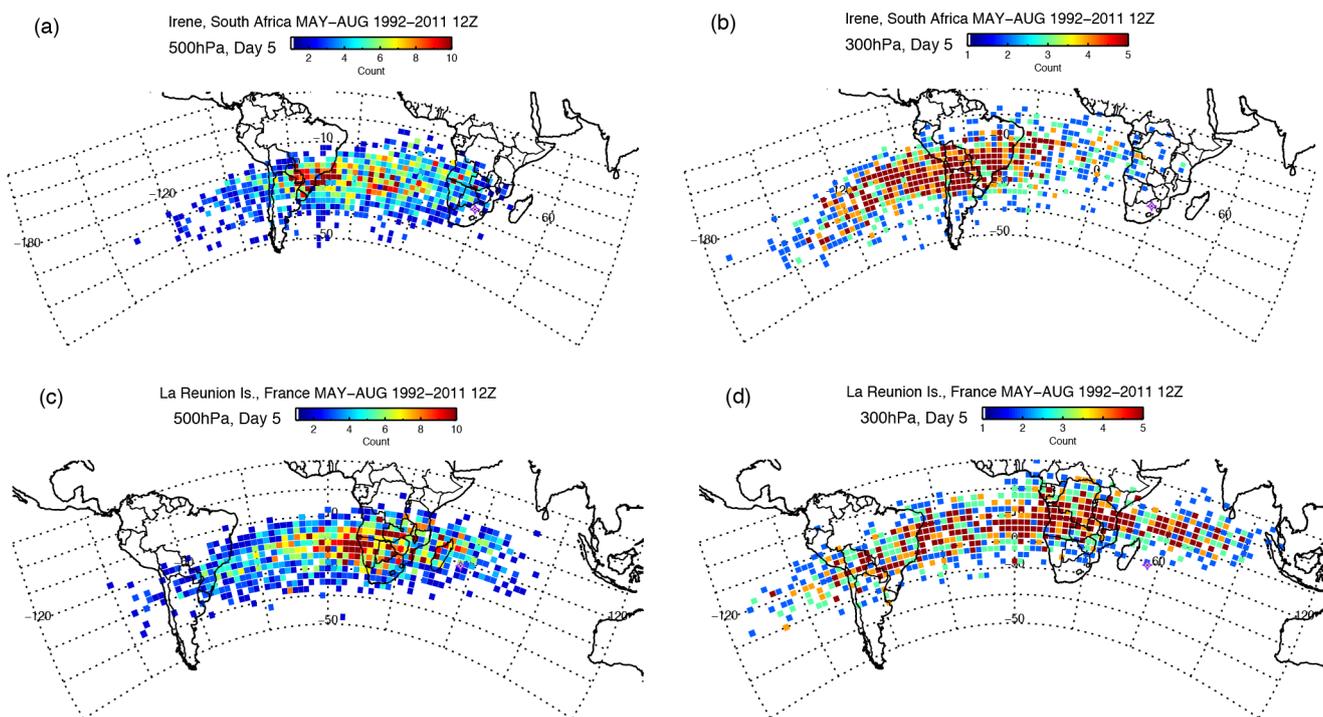


Figure 12. Air mass origins of free-tropospheric ozone over Irene (a) for the sonde launch time at 500 hPa, (b) for 300 hPa and Réunion (c, d). Five-day back trajectories run using NCEP/NCAR re-analysis in the NASA/Goddard kinematic model. The ending points are summed up for a $1^\circ \times 1^\circ$ grid. Note different color bars for the two sites.

due to the shorter NO_2 lifetime, a link to southeast Asia and Indonesia does not appear.

Is there any evidence for increasing pollution over southern Africa and South America in the 1990–2011 period? The evidence is inconclusive. A recent study of global surface and lower tropospheric 20–40-year trends by Oltmans et al. (2013) indicates that ozone at Southern Hemisphere monitoring stations is increasing, apparently due to anthropogenic activity. For Cape Point, SA, which experiences a winter-time brown haze, Oltmans et al. (2013; Fig. 15) showed a $\sim 25\%$ surface ozone increase from 1990 to 2010, most of it in the 1990s. Our recent trend analysis of SA Highveld stations 50–125 km east and southeast of Irene (Balashov et al., 2014) showed little change in surface ozone or NO_x . Is there other evidence that would explain the large FT ozone increases seen in Figs. 7 and 8? Satellite imagery of column NO_2 from SCIAMACHY (2002–2012; A. Richter and J. Burrows, personal communication, 2013) shows no significant change over south-central Africa but a significant increase in a small region over the highveld. Figures 13 and 14 are based on standard emissions data (<http://edgar.jrc.ec.europa.eu/index.php>) that include mobile transport, industrial, domestic and biomass fires. In general, biomass burning over Africa and South America does not appear to be increasing, but industrial emissions are estimated to have increased over these continents 20–30% from 1990 to 2010. Our re-

sults are consistent with these values but suggest that they may be underestimates for winter.

In summary, it is hard to argue that FT ozone increases do not partially result from growing NO_x , but further observations and source-tagged modeling are needed to better establish a link between changing emissions and the strongly seasonal ozone increases observed in the sonde record.

4 Summary and conclusions

The Irene and Réunion free-tropospheric ozonesonde records for 1990–2007 have been analyzed with a multivariate regression model that accounts for the annual cycle, potential vorticity time series and ENSO. In contrast to an earlier study (Clain et al., 2009), by using monthly averaged data, we are able to capture well-defined features throughout the annual cycle. Striking increases throughout the FT, 20–30% decade⁻¹ over Irene and up to 50% decade⁻¹ over Réunion, appear in winter (JJA), with smaller and more vertically diffuse increases in November and December. Below 5 km over Irene, ozone increased 15–25% decade⁻¹ in late fall (April–June) and December. No statistically significant trends appear in September and October, when biomass burning impacts on the SA Highveld are most pronounced. There are subtle differences between the Irene and Réunion ozone changes. The Irene increase starts in April or May and

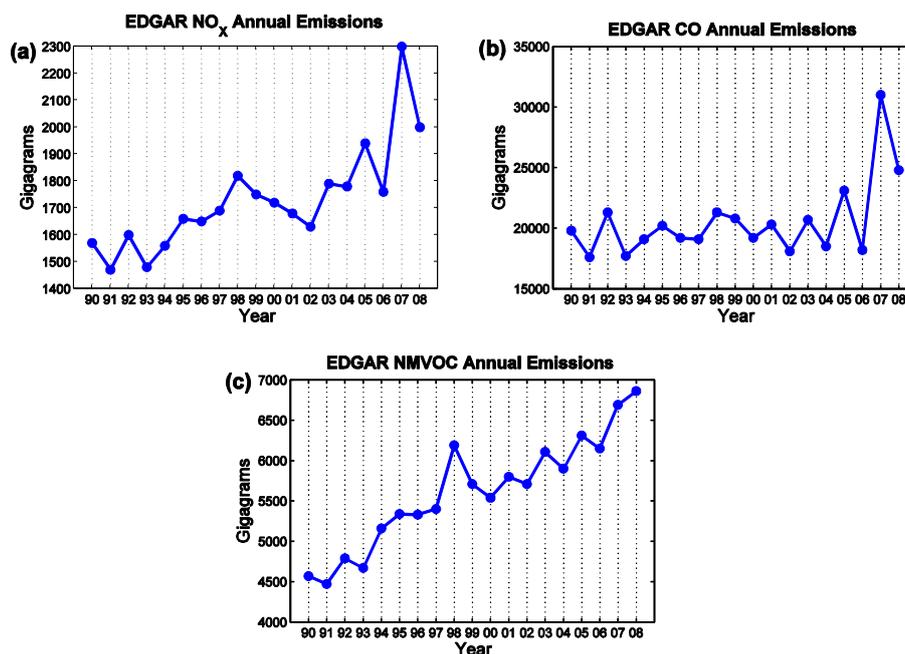


Figure 13. EDGAR annual emissions (total country EDGAR V4.2 emissions from <http://edgar.jrc.ec.europa.eu/index.php>), in Gg (gigagrams) of the principal tropospheric ozone precursors (a) nitrogen oxides (NO_x), (b) carbon monoxide (CO) and (c) non-methane volatile organic compounds (NMVOC) over selected African countries that correspond to trajectory origins in Fig. 12.

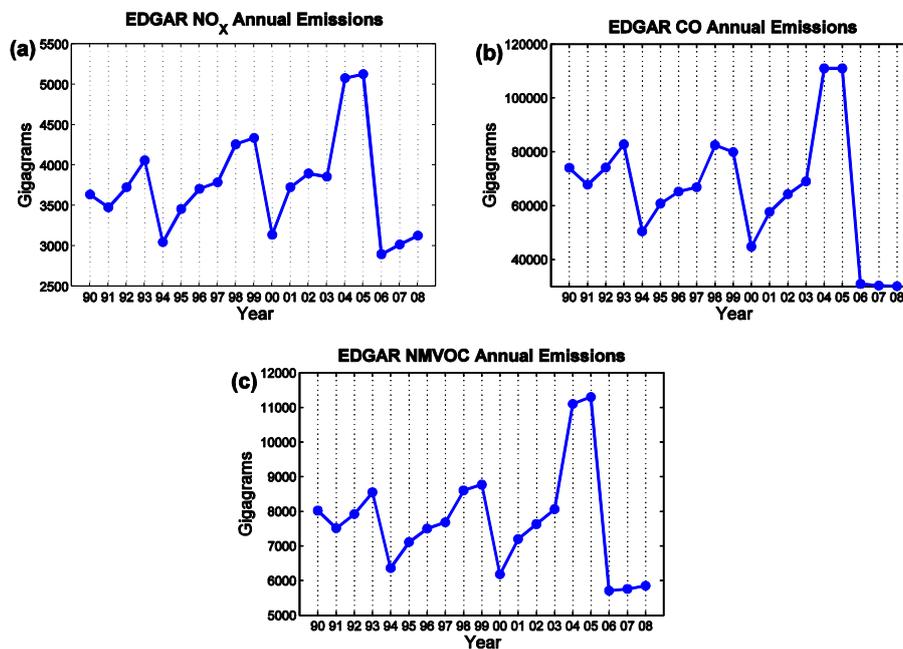


Figure 14. Same as Fig. 13 except for selected South American countries: Bolivia, Brazil, Paraguay and Uruguay. The countries were chosen based on the trajectories in Fig. 12.

is concentrated between 4 and 8 km, almost separate from a June–July zone of ozone growth between 8 and 10.5 km. Over Réunion the ozone increase is largely confined to July and August, with a single feature from 4 to 15 km. The mech-

anism(s) responsible for the ozone growth is not clear. Noting that both sites are in the influence of the subtropical jet, increases above 10 km are suggestive of dynamical changes near the tropopause. However, there is no clear evidence for

the latter; indeed, likely changes in TTL properties would lead to ozone losses, not increases.

Mid-tropospheric ozone increases would be consistent with increases in Southern Hemisphere pollution. Trajectory analysis links Irene and Réunion air parcel origins to regions over Africa and the South Atlantic, where ozone tends to accumulate throughout the year. At the 300 hPa level (9 km), air parcel origins extend over South America and the eastern Pacific. Estimated NO_x emissions increases, 20–30 % from 1990 to 2010, would be consistent with the ozone trends observed over Irene and Réunion. However, surface ozone and NO_x trends over the SA Highveld in 1990 to 2007 do not appear to be consistent with such large growth. More observations are needed, along with a better knowledge of emissions. Model studies are called for as well as further studies of regional dynamics.

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