March 22, 2004

Popular Summary -

"TROPOSPHERIC OZONE CLIMATOLOGY OVER IRENE, SOUTH AFRICA, FROM 1990-1994 AND 1998-2002"

Paper for *JGR-Atmospheres*

R.D. Diab[1], A.M. Thompson[2], K. Mari[1], L. Ramsay[1] and G.J.R. Coetzee[3]

[1]School of Environmental Sciences, University of KwaZulu-Natal, Durban 4041, So. Africa
[2]NASA/GSFC, Laboratory for Atmospheres, Greenbelt, Maryland, USA
[3]South African Weather Service, Pretoria, South Africa

This paper describes ozone profiles from sonde data during the period of NASA's TRACE-A (Transport and Atmospheric Chemistry near the Equator - Atlantic) campaign (1990-1993) and the more recent SHADOZ (Southern Hemisphere Additional Ozonesondes) period. The data were taken by the South African Weather Service at the Irene (25°54'S; 28°13'E) station near Pretoria, South Africa, an area that is a unique mixture of local industry, heavy biofuels use and importation of biomass burning ozone from neighboring countries to the north. The main findings are:
(1) With its geographical position at the edge of the subtropical transition zone, mid-latitude dynamical influences are evident at Irene, predominantly in winter when upper tropospheric ozone is enhanced as a result of stratospheric-tropospheric exchange.
(2) There has been an increase in the near-surface ozone amount between the early 1990's and a decade later, presumably due to an influx of rural population toward the Johannesburg-Pretoria area, as well as with industrial growth and development.
(3) Most significant for developing approaches for satellite ozone profile climatologies, cluster analysis has enabled the delineation of a background and 'most polluted' profile. Enhancements of at least 30% occur throughout the troposphere in spring and in certain layers increases of 100 % are observed.

Support: ACMAP, TOMS Project

TROPOSPHERIC OZONE CLIMATOLOGY OVER IRENE, SOUTH AFRICA FROM 1990-1994 AND 1998-2002

R.D. Diab[1], A.M. Thompson[2], K. Mari[1], L. Ramsay[1] and G.J.R. Coetzee[3]
[1]School of Environmental Sciences, University of KwaZulu-Natal, Durban 4041, South Africa
[2]NASA/GSFC, Greenbelt, Maryland, USA
[3]South African Weather Service, Pretoria, South Africa

Submitted to JGR, March 04

Abstract

Ozonesonde measurements over Irene in South Africa are reported for the period 1990 to 1994 and a more recent period, 1998 to 2002, when the station became part of the SHADOZ network. Irene displays the characteristic Southern Hemisphere springtime tropospheric ozone maximum but its seasonal features are modulated by both tropical and mid-latitude influences due to its subtropical location (25°54'S; 28°13'E). The tropical savanna biomass burning signature, *viz.* the spring maximum, is less developed than at stations further north in Africa, although long-range transport and re-circulation in the subtropical anticyclonic gyre over southern Africa permit the build-up of relatively high springtime tropospheric ozone. Mid-latitude dynamical influences are evident, predominantly in winter when upper tropospheric ozone is enhanced as a result of stratospheric-tropospheric injection of ozone. Urban-industrial sources are also significant and most likely account for the observed increase in surface and lower tropospheric ozone between the two time periods. A classification of ozone profiles using a cluster analysis has enabled the delineation of a background and 'most polluted' profile. Enhancements of at least 30% occur throughout the troposphere in spring and in certain layers increases of 100 % are observed. The classification results substantiate the findings for Johannesburg located close to Irene, based on MOZAIC data.

Introduction

Ground based measurements, such as ozonesondes, provide detailed information on the vertical distribution of ozone in the troposphere and lower stratosphere. They have been used to provide insights into ozone trends and dynamical and photochemical processes. However, the paucity of stations in some regions, particularly in the Southern Hemisphere and the tropical and subtropical latitudes, has hampered investigations. Against this background, the Southern Hemisphere Additional Ozonesondes (SHADOZ) project was initiated in 1998 to augment the frequency of ozonesonde launches at existing stations. Irene (25°54'S; 28°13'E) in South Africa became part of the SHADOZ network in October 1998 and ozonesonde launches have continued on a bi-monthly basis till the present. Tropospheric ozone variations at SHADOZ stations, including Irene, have been reported by *Thompson et al.* [2003a,b].

Prior to becoming part of the SHADOZ programme, regular weekly ozonesonde launches were made at Irene from June 1990 to August 1993, but were curtailed at the end of the SAFARI-92 (Southern African Fire-Atmosphere Research Initiative)/TRACE-A (Transport and Atmospheric Chemistry near the Equator-Atlantic) campaigns. General characteristics of tropospheric ozone from this earlier period have been described by *Zunckel et al.* [1992] and within the context of the SAFARI-92 by *Diab et al.* [1996a,b] and *Thompson et al.* [1996]. A few launches were undertaken in May 1994 as part of SA'ARI-94 (Southern African Atmospheric Research Initiative), to characterize the vertical distribution of trace gases and aerosols during the non-fire season and have been reported by *Helas et al.* [1995]. These

soundings also formed the basis of an analysis of stratospheric-tropospheric exchange (STE) by *Combrink et al.* [1998].

Irene is located in the Southern Hemisphere subtropics and whilst it displays Southern Hemisphere tropospheric ozone seasonality (austral spring maximum), it differs from other ozonesonde stations in the African tropics (for example Brazzaville and Ascension) [*Cros et al.*, 1992; *Fishman et al.*, 1991] in that its biomass burning signature is less well developed. Situated in the subtropical regime, the tropospheric ozone record displays an interesting combination of tropical and mid-latitude influences, which are reported here.

In terms of both its subtropical and African location, the Irene ozonesonde record is most valuable. This paper reports the factors governing the climatology of tropospheric ozone, including seasonality and vertical distribution. Comparisons between the two time periods, 1990-1994 and 1998-2001 are made and an increase of ~10 ppbv in surface ozone between the two time periods highlighted. The influence of synoptic weather systems on ozone concentrations is reported, emphasizing the dominance of the subtropical anticyclonic re-circulation on the enhancement and vertical stratification of ozone, and the role of mid-latitude cyclones on STE and the invasion of relatively clean, ozone-poor air from the Atlantic Ocean. Finally, results of a classification of ozone profiles similar to the study undertaken by *Diab et al.* [2003] are presented in order to highlight contrasts between background and 'most polluted' profiles.

Data and Methodology

Irene is situated ~ 20 km south of the urban-industrial centre of Pretoria at an altitude of 1523 m. Between July 1990 and October 1993 ozonesondes were launched on a weekly basis, with 4 launches being undertaken in May 1994 as part of SA'ARI-94. Since 1998, launches have been made twice a month. A total of 172 profiles were available from the earlier period and 122 profiles from the recent period, covering 1998 to 2002. Release times of the sondes were 06:00 UTC (08:00 local time) for the earlier period and 08:00 UTC (10:00 local time) for the recent period.

The station uses Science Pump Type 6A (5A for the period 1990-1994) electrochemical cell (ECC) sondes, which are interfaced with Vaisala RS 80-15NE radiosondes to provide pressure (hPa), temperature (°C), humidity (%), and ozone partial pressure (mPa) measurements. Data were recorded at 2-second intervals and were subsequently averaged over 100 m height intervals.

A measure of total tropospheric ozone (TTO) was obtained by integrating the ozone concentration from the surface to 16 km. A threshold of 16 km, although not necessarily corresponding exactly with the height of the meteorological or chemical tropopause has been found to be appropriate for estimating TTO and has been used before [*Diab et al.*, 1996a]. The troposphere was also apportioned into 2 km layers and ozone within each layer estimated.

A classification of SHADOZ ozone profiles from the late 1998 through 2002 period using a cluster analysis was undertaken in the manner described by *Diab et al.* [2003]. The intention was to seek pattern and order in the ozone profiles and to determine mean profiles representative of background and highly polluted conditions. A generic cluster analysis technique available as part of the SPSS package (Statistical Package for the Social Sciences, Version 11, 2001) was utilized. It represents an agglomerative technique rather than the

divisive classification of TWINSPAN (Two Way Indicator Species Analysis) utilized in the first study by *Diab et al.* [2003] for Johannesburg. A comparison of the results using these different techniques concluded that the agreement was significant at the 95% level [*Ramsay*, 2003; *Ramsay et al.*, 2004]. As an agglomerative technique, SPSS is based on the fusion of a set of n entities into groups according to the difference between the units being clustered. A Euclidian distance measure is considered the most appropriate measure when all the variables are quantitative [*Abeyasekera*, 2002]. The method of clustering that was used in this study was the within-group linkage, which involves the addition of an element to the group that will result in the smallest increase in the total within-group distance. In the classification, only data between the surface and 12 km were utilized in order to retain compatibility with the study of *Diab et al.* [2003] based on MOZAIC (Measurement of Ozone and Water Vapor aboard In-service Aircraft) data.

Context: Climate and Regional Sources of Ozone Precursors

Irene's subtropical location ("I" in Figure 1) means that the atmospheric circulation is dominated by the subtropical anticyclone, which at the surface is centered at ~32°S in summer and about 6° further north in winter [*Taljaard*, 1953]. Large scale subsidence and re-circulation within the sub-continental scale anticyclonic gyre are responsible for the build-up of pollutants over long periods of time and large spatial scales [*Garstang et al.*, 1996; *Tyson et al.*, 1996; *Piketh et al.*, 2002]. The result is the formation of a widespread haze layer over the African subcontinent that extends to a depth of ~5 km and is capped by a persistent absolutely stable layer produced by subsidence within the subtropical anticyclonic circulation [*Cosijn and Tyson*, 1996]. During SAFARI-92, conditions suited to the collection of ozone as a result of the persistent stable layers lasted for 40 days (*Garstang et al.*, 1996]. The anticylonic pattern is particularly dominant during autumn and winter and has a 79% frequency in June and July and an 11% frequency in December [*Tyson and Preston-Whyte*, 2000]. Disruption of the anticylonic gyre occurs as a result of the passage of mid-latitude westerly waves that traverse the southern section of the subcontinent causing the 5 km absolutely stable layer to dissipate.

Within the haze layer, trace gases and aerosols are re-circulated until ultimately they exit the subcontinent towards the east as a giant plume (Figure 1), approximately 1000 km wide, and centred at 31°S along the east coast [*Garstang et al.*, 1996; *Tyson et al.*, 1996]. Irene is situated to the north of this plume. More than 75% of the transport off the subcontinent between the surface and 500 hPa is directed towards the east [*Tyson et al.*, 1996].

During summer, Irene comes under the influence of the tropical easterlies, which penetrate southwards as the Intertropical Convergence Zone (ITCZ) shifts meridionally. Easterly winds from the Indian Ocean cause moist air to be advected across the station. In summer, intense convective activity is a common mid-afternoon phenomenon that could give rise to the rapid vertical redistribution of surface-generated pollutants and possible enhancement of ozone production in the mid- to upper troposphere as noted by *Pickering et al.* [1990; 1993; 1996]. Lightning activity, which frequently accompanies these convective storms, could also lead to upper tropospheric ozone enhancement as noted by *De Caria et al.* [2000].

In terms of regional sources of tropospheric ozone precursors, it is noted that Irene is located on the eastern side of the African subcontinent to the south of the main biomass burning region over Africa. The burning pattern spreads from west to east across the continent (Figure

1) as the dry season progresses from June to October [*Cahoon et al.*, 1992]. Isolated fires extend fairly far south (~20°S), however, greater ozone enhancement is expected further north. This has been confirmed by *Kirkman et al.* [2000], who on the basis of aircraft sampling south of latitude 15°S during SAFARI-92, noted highest ozone values over a grid square in north-east Zimbabwe (between 15-20°S and 30-35°E). Recently, based on ozonesonde launches at Lusaka (15°30'S; 28°E) as part of SAFARI-2000, *Thompson et al.* [2002] reported very high surface ozone values and total tropospheric ozone (TTO) greater than 50 Dobson Units (DU; 1 DU = 2.69 x 10^{16} mol/cm^2). They suggested that Zambia is a collector area for regional pollution. Indeed, one of the most polluted Irene profiles is compared with a typical springtime Lusaka profile [Fig. 2 in *Thompson et al.*, 2002] and shows Irene to be much cleaner. Notwithstanding these observations, Irene is still likely to experience the impact of biomass burning through long-range transport in the anticyclonic gyre. The results of SAFARI-2000, conducted after an anomalously wet period, served to underscore the importance of biomass burning on the southern African subcontinent [*Swap et al.*, 2003a].

Urban-industrial sources in the region are also significant. Irene is situated between the large urban-industrial complexes of Pretoria and Johannesburg ("J" in Figure 1), and is also ~100 km downwind of the major power generating region of South Africa where 11 large coal generating power plants (~30 GW total generating capacity) are situated. Domestic usage of biofuels also contributes to emissions of ozone precursors in the region. Both industrial and domestic emissions peak in winter.

The importance of biogenic (vegetative and microbial) emissions has recently been emphasized by *Swap et al.* (2003b). It was suggested that the rapid release of NO_x and hydrocarbons following the onset of the first spring rains, referred to as 'pulsing', was more important in the tropospheric ozone budget than previously thought.

Seasonality in Total Tropospheric Ozone

Monthly variations in TTO (surface to 16 km) and integrated ozone within 2 km layers are depicted in Figures 2 and 3 respectively. A spring maximum in TTO is evident and confirms the well established Southern Hemisphere seasonal trend observed at many stations, for example Natal in Brazil (5.9°S; 35.2°W) [*Kirchhoff et al.*, 1991], Brazzaville in the Congo (4°S; 15°E) [*Cros et al.*, 1992; *Nganga et al.*, 1996; *Diab et al.*, 1996a; *Thompson et al.*, 1996], Ascension Island (8°S; 14°W) [*Cros et al.*, 1992; *Diab et al.*, 1996a], Reunion Island (21°S, 55°E) [*Baldy et al.*, 1996; *Taupin et al.*, 1999] and Watukosek in Indonesia (7.5°S;112.6°E) [Komala *et al.*, 1996; *Fujiwara et al.*, 1998, 1999, 2000]. The spring maximum has been variously attributed to photochemical sources such as biomass burning, biogenic emissions and lightning production, as well as to stratospheric injection of ozone-rich air, or some combination of the above. The relative importance of these sources has not been specifically addressed in these papers. However, a recent modelling study by *Marufu et al.* [2000], suggested that over Africa, pyrogenic sources, including biomass burning, accounted for 16% of tropospheric ozone abundance on an annual basis compared with 26% by stratospheric input. Urban-industrial sources were estimated to contribute 19%, biogenic sources 12% and lightning 27%.

The same spring maximum is evident in each 2 km-layer below 10 km (Figure 3a-e). In the lower troposphere (< 4 km) (Figure 3a-b), ozone values are fairly steady in the first half of the

year and start to rise in mid-winter (July), peak in spring and then level off again. The 4-6 km and 6-8 km layers display particularly well developed seasonal cycles with amplitudes of ~3.5 DU (Figure 3c-d). A secondary maximum is observed in late summer (February/March) for each of these mid-tropospheric layers (4-6 km and 6-8 km). This finding supports the results of *Diab et al.* [2003] who found a summertime mid-tropospheric ozone maximum between 6 and 8 km at Johannesburg, which is located close (< 50 km) to Irene. Above 10 km, the seasonal cycle is not well defined and there is no clear ozone maximum (Figure 3f-h).

The secondary maximum present in the 4-6 km and 6-8 km layers is not reflected in the TTO record of Irene, in contrast to the pattern at Brazzaville and Ascension where secondary TTO maxima were observed in March/April and were attributed to Northern Hemisphere biomass burning [*Diab et al.*, 1996a]. The southwards movement of the ITCZ, particularly the Zaire Air Boundary (ZAB), during summer to almost 20°S [*Taljaard*, 1972] means that Southern Hemisphere stations close to the equator can easily come under the influence of Northern Hemisphere biomass burning at this time of the year.

Comparing results between the earlier period (1990-1994) and the more recent period (1998-2002) for TTO and 2-km layers (Figure 2), it is noted that the maximum has shifted from September to October and has increased by up to 2 DU. It has also changed from a broadly based maximum extending from September to November in the early period to a distinct October maximum in the recent period. Below 8 km, values differ little between the two periods with the exception of the October increase. Indeed, the October increase is best developed between the surface and 2 km and 2-4 km, suggesting that surface-based photochemical sources are largely responsible for the increase. In the 8-10 km and 10-12 km layers, values have increased little (generally ~1 DU) over the greater part of the year (between May and December). A slightly greater difference is observed in the upper troposphere, between 12 and 16 km, particularly between June and October.

Figure 4 summarizes the seasonality of ozone profiles over Irene during the SHADOZ period. Five years of monthly averaged ozone mixing ratios based on 0.25 km means are illustrated. The variable tropopause is most apparent. Referring to the 100-130 ppbv contours as the 'tropical tropopause layer' (or TTL), it is noted that the January-February TTL is above 15 km. The altitude of the TTL, on average, declines through the year, reaching a minimum around 12 km in October. The latter marks the end of the winter and spring transition season when breaks or folds in the tropopause in association with the subtropical jet permit ozone-rich stratospheric air to penetrate into the troposphere [*Baray et al.*, 1998].

Most of the free troposphere over Irene is typified by 55-65 ppbv. This is modified by the injection of lower values (45-55 ppbv contours up to 8 km) in May, which marks the season when relatively low ozone maritime air masses are advected across the subcontinent in association with mid-latitude westerly waves. Pollution from biomass fires, both regional and imported from countries to the north [*Thomspon et al.*, 2002], as well as lightning from the nascent wet season and biogenic emissions, contribute to the higher ozone throughout the lower troposphere during the August through November period.

In comparison with other Southern Hemisphere stations, for example Reunion [*Baldy et al.*, 1996; *Diab et al.*, 1998], Okaukuejo and Brazzaville [*Diab et al.*, 1996a], where seasonal ranges in TTO were estimated from satellite data, the seasonal range in TTO at Irene is relatively small (13.1 DU in the earlier period and 19.7 DU between 1998 and 2002 (Figure 2). The largest annual range (34 DU) is observed at Reunion. Irene appears to be less

influenced by a seasonally varying tropospheric source of ozone such as biomass burning than stations that are further to the north and closer to the major regions of biomass burning on the African subcontinent [*Diab et al.*, 1996a] or stations that are situated downwind of major source regions, such as Reunion. It is also possible that a non-seasonally fluctuating source such as urban-industrial emissions is dominant at Irene due to its location close to two major metropolitan areas.

Vertical Distribution of Tropospheric Ozone

Mean annual and mean seasonal tropospheric ozone profiles from the two time periods (1990-1994 and 1998-2002) are displayed in Figure 5. Surface ozone values are consistently greater in the more recent period by about 10 ppbv (except in summer) and most likely reflect the increased contribution from anthropogenic sources. It is assumed that urban-industrial emissions of ozone precursor gases would have increased over this period as a result of an increase in population in the greater metropolitan Pretoria area (within which Irene is located) from ~0.5 million in 1991 [*National State of the Environment Report*, 1998] to a population of ~ 2 million according to the latest census statistics [*Statistics South Africa*, 2001] and a consequent increase in industrial and vehicular activity. A similar trend was noted by *Zunckel et al.* [1992] in a comparison of ozone profiles between the 1960s and the early 1990s and was attributed to an increase in urban-industrial emissions. The absence of a surface trend in summer suggests that a non-summer source, for example emissions from domestic cooking and heating, is responsible for the increase. Indeed, the use of biofuels, particularly the burning of coal for domestic cooking and wintertime heating, is recognised as a significant contributor to air pollution in the greater Pretoria area [*http://www.iclei.org/cities21/pretoria.pdf*]. However, it is well known that more favourable near-surface dispersion conditions in summer [*Tyson et al.*, 1976] would lessen the impact of increased emissions from whatever source and this could account for the absence of a summer trend.

It is also noted from Figure 5 that there has been an increase in ozone in the upper troposphere (> 10 km) in the winter months. The most likely source of a winter upper tropospheric enhancement is STE. With the limited data to hand, however, it is not possible to state whether the frequency of such events has increased over time.

Composite plots of seasonal profiles (Figure 6) show that throughout the troposphere, mean spring values are enhanced by about 20 ppbv compared with the average during the remainder of the year. There is a remarkable consistency in the vertical profiles up to 10 km outside of the spring season. Mean ozone values range between 40 and 60 ppbv, suggesting that this is the average background tropospheric loading, which increases during spring when a temporally varying source such as biomass burning accounts for the seasonal enhancement. Above 10 km, there is less seasonal consistency. However, the higher ozone values in winter and spring (Figure 5) are possible evidence of greater STE activity, which is known to maximise in these seasons [*Poulida et al.*, 1996; *Baray et al.*, 1998; *Gouget*, 1999].

Influence of Synoptic Weather

There is considerable variability in the vertical distribution of ozone (Figure 7). Maxima approaching 150 ppbv and occasionally 200 ppbv are common (except in summer), mainly in

the mid- to upper-troposphere. These appear as yellow and orange features above 8 km in Figure 7. In summer, there is a relatively tight envelope of profiles surrounding the mean, indicative of a consistency in the origin of tropospheric ozone. It is well known that tropospheric ozone amounts fluctuate in response to weather changes [*Diab et al.*, 1992; *Barsby and Diab*, 1995; *Diab et al.*, 1996b; *Tyson et al.*, 1997]. Strongly stratified ozone profiles occur in association with anticyclonic circulations, with peaks in ozone coinciding with absolutely stable layers. In cases where these layers are at least 0.25 km thick, they appear in Figure 7, sometimes as isolated blue or green features. Uniformly low ozone profiles occur in association with the passage of a mid-latitude westerly wave in which 'ozone-poor' air from the South Atlantic Ocean is advected across the country. In the lower troposphere, the mixing ratios are well under 50 ppbv, appearing as blue or purple in Figure 7.

During the SAFARI-2000 campaign (September 2000), there was opportunity to examine day-to-day variability inherent in ozone profiles over Irene (Figure 8). Given the magnitude of changes at various altitides within the sequence illustrated, the difficulty of summarizing the vertical distribution in terms of a mean profile are obvious. For example, in the lower troposphere (< 5 km), ozone increased from ~50 ppbv to ~90 ppbv in 3 days (1-4 September i.e. a rate of increase of ~17 ppbv/day). This is the scale of photochemical ozone formation in the 0-4 km altitude range over southern Africa observed during SAFARI-92/TRACE-A [*Jacob et al.*, 1996; *Thompson et al.*, 1996]. On 8 September, upper tropospheric ozone increased by almost 100 ppbv compared with the previous day, whilst values below 10 km remained almost unaffected. Similar changes were observed over Lusaka in a series of daily launches between 6 and 11 September 2000 [*Thompson et al.*, 2002].

The variability poses a challenge in the estimation of a mean profile and a concern as to what it represents. The next section presents results of a cluster analysis, in which profiles were grouped according to the magnitude and altitude of ozone maxima and minima in order to discern meaningful patterns inherent in the data.

Results of the Classification of Ozone Profiles

Results of the application of a cluster analysis to Irene ozone profiles are displayed in Figure 9. A full discussion of the results and a comparison with classification results obtained at Johannesburg using MOZAIC data and a different cluster analysis technique [*Diab et al.* 2003] are given by *Ramsay* [2003] and *Ramsay et al.* [2004]. For the purposes of this paper, it is pertinent to highlight 4 relevant patterns, although 6 distinct groups of Irene ozone profiles were identified.

The first and dominant pattern is that represented in Figure 9a. This group comprises 48% of all profiles and is arguably the 'typical' or most representative Irene ozone profile (compare with mean profile in Figure 5). Interestingly, this pattern of vertical ozone distribution occurs throughout the year and is characterized by a steady rise in ozone concentration from a mean surface value less than 30 ppbv to a mean of 70 ppbv at 12 km, although individual values at this level tend to approach 90 ppbv. This pattern is most similar to the profile named 'steady tropospheric increase' by *Diab et al.* [2003] at Johannesburg. Identification of a 'typical' pattern is useful in that it represents the norm and may be more valuable than the mean because it is not obscured by extreme values.

A second group, distinguished from the former by the marked increase in ozone that occurs in the upper troposphere (> 9 km), is presented in Figure 9b. Mean ozone values above 100 ppbv and individual values that approach 120 ppbv characterize the upper troposphere. The dominance of winter profiles (> 50%) in this group suggests a relationship with a lowered tropopause and/or an increased occurrence of STE. This is most likely an expression of Irene's subtropical location where mid-latitude influences are experienced to a greater extent in winter as the mid-latitude westerlies and associated frontal patterns shift northwards. However, it is important to note that whatever the process that is giving rise to enhanced upper tropospheric ozone, it is not confined to the winter season. Indeed, 21% of the profiles occur in spring and 14% each from summer and autumn. A comparison between this profile and the mean winter profile for the recent SHADOZ (1998-2002) period presented earlier (Figure 5) highlights this distinction. The latter is a profile dominated by a temporal period (winter in this case), whereas the former profile is most likely the product of a particular process that occurs predominantly in winter but can occur at other times throughout the year as well.

The next group of interest is that denoted by Figure 9c as it represents background tropospheric ozone conditions at Irene and therefore provides a useful baseline against which to evaluate seasonal or episodic enhancements. Mean ozone values are less than 50 ppbv throughout most of the troposphere (< 10 km) and display relatively little variability about the mean. Profiles occur preferentially in autumn (60%), which is not unexpected as this is the season of lowest TTO values (Fig. 2). Comparison with the mean autumn profile (Figure 4), however, shows this group to be cleaner (less polluted) as individual polluted profiles have been removed from the group.

A fourth category is that which represents the most polluted conditions in the troposphere (Figure 9d). Characteristic features are the elevated surface ozone values (> 45 ppbv) and consistently high mean ozone values (70-80 ppbv) above 2 km. As expected, this category is dominated by spring profiles but not exclusively. A comparison between the mean of Group 4 with the spring mean from the recent period (Figure 5) reveals differences, which again highlights the benefits of delineating the most polluted profiles as a separate grouping by means of a classification procedure.

Differences between average background (least polluted) and 'most polluted' profiles are highlighted in Figure 10. Lower-tropospheric and mid-tropospheric background ozone values approximate 25 ppbv and 50 ppbv respectively. The enhanced profile displays values between 70-80 ppbv for most of the troposphere. Percentage enhancements at 500 m intervals are also displayed in Figure 10. Throughout the troposphere, enhancements of at least 30% occur and are above 70% most of the time. Maximum enhancements close to 100% are experienced in some layers.

Discussion and Conclusion

Since Irene is on the boundary of zonally defined meteorological regimes, *viz.* tropical and mid-latitude zones, atmospheric conditions are influenced by a range of dynamic processes during different periods of the year. This is expressed in tropospheric ozone characteristics. Similar conclusions regarding dynamical influences on satellite-derived tropospheric ozone data were drawn by *Hudson et al.* [2003].

TTO seasonality is characterized by a spring maximum, typical of all Southern Hemisphere tropical stations where biomass burning is a dominant feature, but is modulated by Irene's more subtropical location. Specifically, the seasonal range in TTO (< 20 DU) is less than tropical stations further to the north and less than Reunion, which is downwind of southern Africa, indicating that Irene is less affected by a seasonally varying source of tropospheric ozone such as biomass burning. It is suggested in this paper that TTO seasonality at Irene is strongly influenced by a non-seasonally fluctuating source such as urban-industrial emissions due to its proximity to major metropolitan and industrial areas. Furthermore, the summertime secondary TTO maximum, characteristic of African stations in the tropics (e.g. Brazzaville), is evident only as an enhancement in mid-tropospheric layers, 4 to 8 km, again indicating the absence or modulation of tropical influences in the lower and upper troposphere.

Comparison between the two time periods, *viz.* 1990-94 and 1998-2002 showed an increase of ~10 ppbv in surface ozone in all seasons except in summer. The most likely contributing factor is an increase in urban-industrial emissions over this period. An increase in the domestic use of biofuels for heating in poor urban settlements is expected to account for the contrasts between summer and other seasons.

Considerable day-to-day variability in the vertical distribution of tropospheric ozone was evident. Enhancements approaching 150-200 ppbv in the mid- and upper troposphere were attributed to the complexity of photochemical and dynamical contributions from both the tropics and the mid-latitudes. The dominance of the subtropical anticyclone facilitates the build-up of photochemically generated ozone and the superimposition of dynamical mid-latitude influences causes *inter alia,* the invasion of ozone-poor maritime air from the west in association with westerly waves, increased vertical mixing resulting in less vertical stratification and the possibility of STE into the upper troposphere.

The inherent variability in tropospheric ozone vertical distribution is the rationale for a classification of ozone profiles by means of a cluster analysis, which permits the identification of archetypal ozone profiles. A background profile, in which ozone values lay below 50 ppbv throughout the troposphere, provided a baseline against which the magnitude of seasonal or episodic enhancements could be evaluated. A 'most polluted' profile on the other hand, occurred mainly in spring and displayed relatively high surface ozone (> 40 ppbv), and a sharp near-surface increase to values between 70-80 ppbv above 2 km. Enhancements of at least 50% can be expected during spring, and in certain layers (~2.5 - 4 km), enhancements of 200% occur.

Acknowledgements

RDD acknowledges the National Research Foundation, Pretoria for funding this research. F. Sokolic and J.C. Witte are thanked for their assistance in the preparation of diagrams. The SAWS operators, N.A. Phahlane and D. Esterhyse, and the SHADOZ project (http://croc.gsfc.nasa.gov/shadoz) are acknowledged. AMT acknowledges support of the NASA Atmospheric Chemistry Modeling and Analysis Program (ACMAP) and the TOMS project.

References

Abeyasekera, A., An analysis of operating characteristics of surveys in developing and transition countries: survey costs, design effects and non-sampling errors, United Nations Statistics Division. http://milleniumindicators.un.org/unsd/Hhsurveys/ch18draft.pdf

Baldy, S., G. Ancellet, M. Besssafi, A. Badr, D. Lan Sun Luk, D., Field observations of the vertical distribution of tropospheric ozone at the island of Reunion (southern tropics), *J. Geophys. Res., 101* (D19), 23835-23849, 1996.

Baray, J. L., G. Ancellet, F.G. Taupin, M. Bessafi, S. Baldy, P. Keckhut, Subtropical tropopause break as a possible stratospheric source of ozone in the tropical troposphere, *J. Atmos. and Sol. Terres. Phy., 60*, 27 – 36, 1998.

Barsby, J., R.D. Diab, Total ozone and synoptic weather relationships over southern Africa and surrounding oceans, *J. Geophys. Res., 100* (D2), 3023-3032, 1995.

Cahoon, D.R., B.J. Stocks, J.S. Levine, W.R. Cofer III, K.P. O'Neill, Seasonal distribution of African savanna fires, *Nature, 359*, 812 – 815, 1992.

Combrink, J., R.D. Diab, F. Sokolic, F., Stratospheric-tropospheric exchange over South Africa: a case study, Proceedings of XVIII Quadrennial Ozone Symposium, L'Aquila, Italy, 335-338, 1998.

Cosjin, C., P.D. Tyson, Stable discontinuities in the atmosphere over South Africa, *S. Afr. J. of Sci., 92*, 381 – 386, 1996.

Cros, B., D. Nganga, A. Minga, J. Fishman, V. Brackett, Distribution of tropospheric ozone at Brazzaville, Congo, determined from ozonesonde measurements, *J. of Geophys. Res., 97* (D12), 12869 – 12875, 1992.

DeCaria, A. J., K.E. Pickering, G.L. Stenchikov, J.R. Scala, J. R., J.L. Stith, J. E. Dye, B.A. Ridley, and P. Laroche, A cloud-scale model study of lightning-generated NO_X in an individual thunderstorm during STERAO–A, *J. Geophys. Res., 105* (D9), 11601 – 11616, 2000.

Diab, R.D., J. Barsby, J., G. Bodeker, M.W.J. Scourfield, M. Barker, L.F. Salter, Satellite observations of stratospheric ozone above South Africa, *S. Afr. Geogr. J., 74*, 13-18, 1992.

Diab, R.D., A.M. Thompson, M. Zunckel, G.J.R. Coetzee, J. Combrink, G.E. Bodeker, J. Fishman, F. Sokolic, D.P. McNamara, C.B. Archer, D. Nganga, Vertical ozone distribution over southern Africa and adjacent oceans during SAFARI-92, *J. Geophys. Res., 101* (D19), 23823-23833, 1996a.

Diab, R.D., M.R. Jury, J. Combrink, F. Sokolic, A comparison of anticyclone and trough influences on the vertical distribution of ozone and meteorological conditions during SAFARI –92, *J. of Geophys. Res., 101* (D19), 23809 – 23821, 1996b.

Diab, R.D., M. Bessafi, F. Taupin, T. Randriambelo, Ozone transport off the east coast of southern Africa, Proceedings of XVIII Quadrennial Ozone Symposium, L'Aquila, Italy, 343-346, 1998.

Diab, R.D., A. Raghanundan, A. M. Thompson, V. Thouret, Classification of tropospheric ozone profiles over Johannesburg based on MOZAIC aircraft data, *Atmos. Chem. and Phy.*, *3*, 1-11, 2003.

Fishman, J., K. Fakhruzzaman, B. Cros, D. Nganga, Identification of widespread pollution in the Southern Hemisphere deduced from satellite analyses, *Science, 252,* 1693-1696, 1991.

Fujiwara, M., K. Kita, T. Ogawa, Stratosphere-troposphere exchange of ozone associated with the equatorial Kelvin waves as observed with ozonesonde and rawinsondes, *J. Geophys. Res., 103* (D12), 19173 – 19182, 1998.

Fujiwara, M., K. Kita, T. Ogawa, S. Kawakami, T. Sana, N. Komala, S. Saraspriya, A. Suripto, Tropospheric ozone enhancements during the Indonesian forest fire events in 1994 and in 1997 as revealed by ground-based observations, *Geophys. Res. Letters*, *26* (16), 2417-2420, 1999.

Fujiwara, M., K. Kita, T. Ogawa, S. Kawakami, T. Sana, N. Komala, S. Saraspriya, A. Suripto, Seasonal variation of tropospheric ozone in Indonesia revealed by 5-year ground based observations, *J. Geophys. Res.*, *105* (D2), 1879 – 1888, 2000.

Garstang, M., P.D. Tyson, R. Swap, M. Edwards, P. Kallberg, J.A. Lindesay, Horizontal and vertical transport of air over Southern Africa, *J. Geophys. Res., 101* (D19), 23721-23736, 1996.

Gouget, H., Case study of a tropopause fold and of subsequent mixing in the subtropics of the Southern Hemisphere, *Atmos. Environ.*, *34*, 2653 – 2658, 1999.

Helas, G., M.O. Andreae, G. Schebeske, P. Le Canut, P., SA'ARI-94: a preliminary view of results, *S. Afr. J. Sci.*, 91, 360-362, 1995.

Hudson, R.D., A.D. Frolov, M.F. Andrade, M.B. Follette, The total ozone field separated into meteorological regimes. Part I: Defining the regimes, *J. Atmos. Sci., 60,* 1669-1677.

JacobD.J., B.G. Heikes, S-M. Fan, J.A. Logan, D.L. Mauzerall, J.D. Bradshaw, H.B. Singh, G.L. Gregory, R.W. Talbot, D.R. Blake, G.W. Sachse, Origin of ozone and NO_x in the tropical troposphere: A photochemical analysis of aircraft observations over the South Atlantic basin, *J. Geophys. Res., 101* (101), 24235-24250, 10.1029/96JD000336, 1996.

Kirchhoff, V.W.J.H., R.A. Barnes, A.L. Torres, Ozone climatology at Natal, Brazil from in situ ozonesonde data, *J. Geophys. Res., 96* (D6), 10899 – 10909, 1991.

Kirkman, G.A., S.J. Piketh, M.O. Andreae, H.J. Annegarn, G. Helas, Distribution of aerosols, ozone and carbon monoxide over southern Africa, *S. Afr. J. of Sci., 96*, 423-431, 2000.

Komala, N., S. Saraaspriya, K. Kita, T. Ogawa, Tropospheric ozone behaviour observed in Indonesia, *Atmos. Environ., 30* (10/11), 1851 – 1856, 1996.

Marufu, L., F. Dentener, J. Lelieveld, M.O. Andreae, G. Helas, Photochemistry of the African troposphere: Influence of biomass-burning emissions, *J. Geophys. Res., 105* (D11), 14513-14530, 2000.

National State of the Environment Report, 1998, Department of Environmental Affairs and Tourism, Pretoria, http://www.ngo.grida.no/soesa/

Nganga, D., A. Minga, B. Cros, C. B. Biona, J. Fishman, W.B. Grant, The vertical distribution of ozone measurements at Brazzaville, Congo, during TRACE-A, *J. Geophys. Res.*, *101* (D19), 24095 – 24103, 1996.

Pickering, K.E., A.M. Thompson, R.R. Dickerson, W.T. Luke, D.P. McNamara, J.P. Greenberg, P.R. Zimmerman, Model calculations of tropospheric ozone production potential following observed convective events, *J. Geophys. Res.*, *95* (D9), 14049-14062, 1990.

Pickering, K., A.M. Thompson, W-K. Tao, T. Kucsera, Upper tropospheric ozone production following mesoscale convection during STEP/EMEX, *J. Geophys. Res.*, *98* (D5), 8737 – 8749, 1993.

Pickering, K.E., A.M. Thompson, Y. Wang, W-K. Tao, D.P. McNamara, V.W.J.H. Kirchhoff, B.G. Heikes, G.W. Sachse, J.D. Bradshaw, G.L. Gregory, D.R. Blake, Convective transport of biomass burning emissions over Brazil during Trace-A, *J. Geophys. Res.*, *101*, 23993-24012, 1996.

Piketh, S.J., R.J. Swap, W. Maenhaut, H.J. Annegarn, P. Formenti, Chemical evidence of long-range atmospheric transport over southern Africa, *J. Geophys. Res.*, *107* (D24), 4817, doi:10.1029/2002JD002056, 2002.

Poulida, O., R.R. Dickerson, A. Heymsfield, Stratosphere-troposphere exchange in a midlatitude mesoscale convective complex, *J. Geophys. Res.*, *101* (D3), 6823 – 6836, 1996.

Ramsay, L., In Search of Representative Vertical Ozone Profiles for Johannesburg: A Statistical Perspective, Unpub. BSc Hons dissertation, University of Natal, Durban, 2003.

Ramsay, L., R.D. Diab, V. Thouret, A comparison of cluster analysis techniques to classify vertical ozone profiles, In preparation, 2004.

Statistics South Africa, Census 2001, http://www.statssa.gov.za, 2001.

Swap. R.J., H.J. Annegarn, J.T. Suttles, M.D. King, S. Platnick, J.L. Privette, R.J. Scholes, Africa burning: a thematic analysis of the Southern African regional Science Initiative (SAFARI 2000), *J. Geophys. Res., 108* (D13), 8465, doi:10.1029/2003JD003747,2003a.

Swap, R.J., Szuba, T.A., Garstang, M., Annegarn, H.J., Marufu, L., Piketh, S.J., Spatial and temporal assessment of sources contributing to the annual austral spring mid-tropospheric ozone maxima over the tropical South Atlantic, *Global Change Biology, 9,* 336-345, 2003b.

Taljaard, J.J., The mean circulation in the lower troposphere over southern Africa, *S. Afr. Geogr. J.*, *35*, 33-45, 1953.

Taljaard, J.J., Synoptic meteorology of the Southern Hemisphere, In Newton, C.W. (ed.), *Meteorology of the Southern Hemisphere,* Meteorological Monographs, *35*, 139-213, 1972.

Taupin, F.G., M. Bessafi, S. Baldy, P.J. Bremaud, Tropospheric ozone above the southwestern Indian Ocean is strongly linked to dynamical conditions prevailing in the tropics, *J. Geophys. Res., 104* (D7), 8057-8066.

Thompson, A.M., R.D. Diab, G.E. Bodeker, M. Zunckel, G.J.R. Coetzee, C.B. Archer, D.P. McNamara, K.E. Pickering, J. Combrink, J. Fishman, D. Nganga, Ozone over southern Africa during SAFARI-92/TRACE-A, *J. Geophys. Res., 101* (D19), 23793-23807, 1996.

Thompson, A.M., J.C. Witte, M.T. Freiman, N.A. Phahlane, G.J.R Coetzee, Lusaka, Zambia, during SAFARI-2000: convergence of local and imported ozone pollution, *Geophys. Res. Letters, 29* (20), 37-1 – 37-2, 2002.

Thompson, A.M. *et al.*, Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2000 tropical ozone climatology: 1. comparison with TOMS and ground-based measurements, *J. Geophys. Res., 108*, 8238:doi:10.129/2001JD000967, 2003a.

Thompson, A.M., J.C. Witte, S.J. Oltmans, F.J. Schmidlin, J.A., Logan, M. Fujiwara, V.W.J.H. Kirchhoff, F. Posny, G,J.R. Coetzee, B. Hoegger, S. Kawakami, T. Ogawa, J.P.F. Fortuin, H.M. Kelder, Southern Hemisphere Additional Ozonesondes (SHADOZ) 1998-2000 tropical ozone climatology: 2. tropospheric variability and the zonal wave-one, *J. Geophys. Res. 108*, 8241, doi:10.129/2002JD002241, 2003b.

Tyson, P.D., R.A. Preston-Whyte, R.D. Diab, Towards an inversion climatology of Southern Africa : Part I, Surface inversions, *S. Afr. Geogr. J., 58*, 151-163, 1976.

Tyson, P.D., M. Garstang, R. Swap, Large-scale recirculation of air over southern Africa, *J. Appl. Meteo., 35,* 2218 – 2235, 1996.

Tyson, P.D., M. Garstang, A. M. Thompson, R.D. Diab, E.V. Browell, P.C. D'Abreton, Correspondence between ozone measurements, transport and production of ozone over south central Africa, *J. Geophys. Res., 102* (D9), 10623-10636, 1997.

Tyson, P.D., R.A. Preston-Whyte, *The Weather and Climate of Southern Africa*, Oxford University Press, Cape Town, 2000.

Zunckel, M., M.W.J. Scourfield, R.D. Diab, Vertical distribution of ozone above Pretoria from 1965 to 1968, *S. Afr. J. of Sci., 88*, 217 – 220, 1992.

Figure Captions

1. Schematic representation of meteorological processes affecting tropospheric ozone over sub-equatorial Africa. Industrial, biomass burning and biogenic sources of ozone precursors are also shown. The locations of Johannesburg, Irene and Lusaka are represented by "J", "I" and "L" respectively.

2. Monthly variations in TTO (DU) at Irene for the periods 1990-1994 and 1998-2002

3. Monthly variations in integrated ozone (DU) in 2 km layers above the surface at Irene for the periods 1990-1994 and 1998-2002

4. Contour of Irene mixing ratios during the SHADOZ period, 1998-2002. Mean Mixing ratios at 0.25 km altitude were used

5. Mean annual and mean seasonal tropospheric ozone profiles at Irene for the periods 1990-1994 and 1998-2002

6. Composite plots of seasonal ozone profiles at Irene for (a) 1990-1994 and (b) 1998-2002

7. Time-vs-altitude curtain of ozone mixing ratio (in ppbv) over Irene below 20 km, based on 0.25 km averages. Years 1999-2002 are illustrated

8. Time sequence of ozone profiles at Irene for the period 1-11 September 2000

9. Mean ozone profiles (dark line) and individual profiles for four groups resulting from a cluster analysis at Irene (1998-2002) (after Ramsay, 2003)

10. Comparison between background and 'most polluted' profiles at Irene, with percentage enhancements at particular altitudes indicated on the right hand side

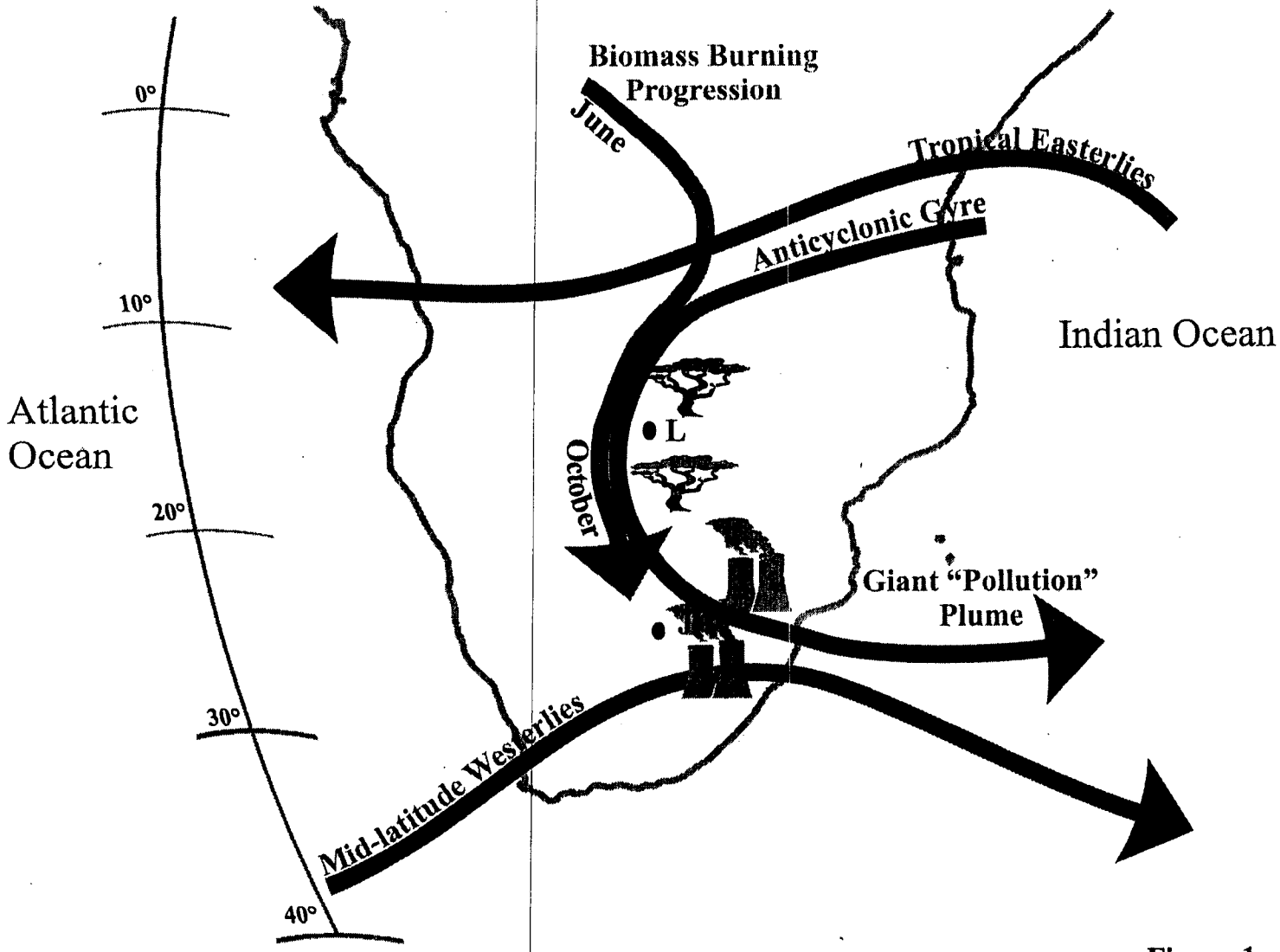

Biomass Burning
Progression
June
October
Tropical Easterlies
Anticyclonic Gyre
Indian Ocean
Atlantic
Ocean
L
Giant "Pollution"
Plume
Mid-latitude Westerlies
0°
10°
20°
30°
40°

Figure 1

Figure 2

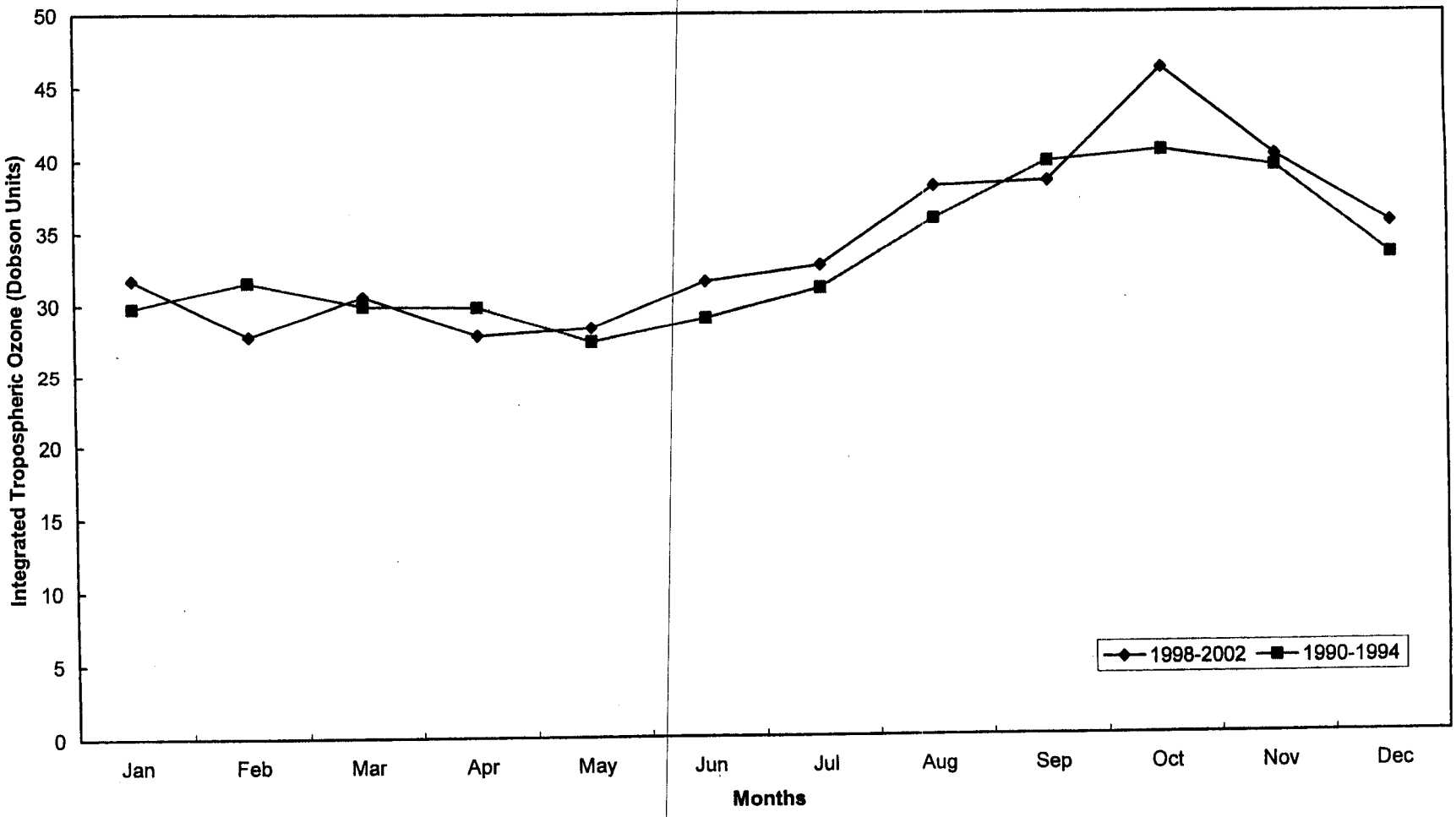
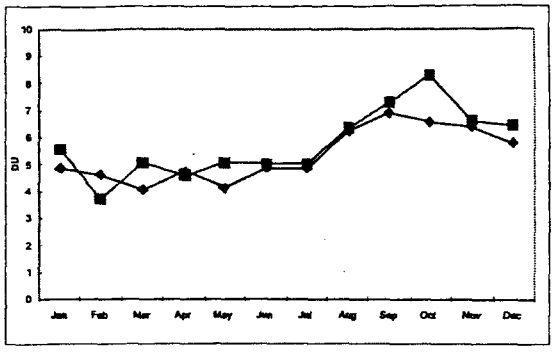

Integrated Tropospheric Ozone (Dobson Units)
50
45
40
35
30
25
20
15
10
5
0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Months
1998-2002
1990-1994

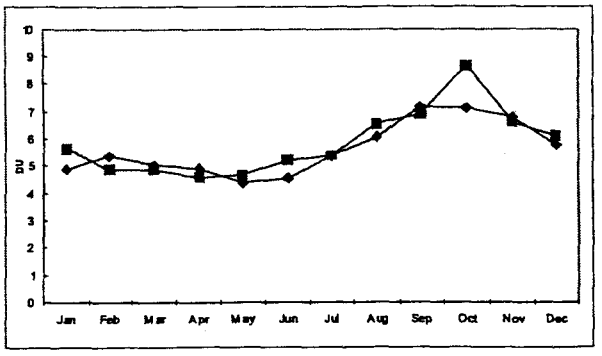
Figure 3

Blue: 1990 to 1994
Purple: shadoz (1998-2002)

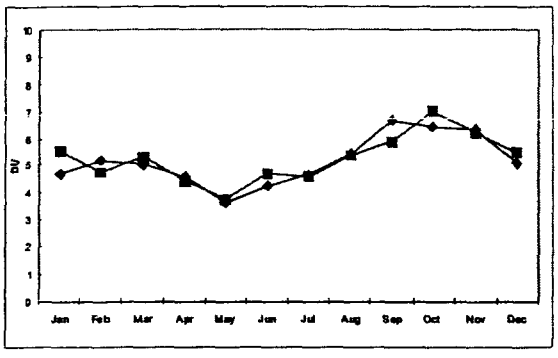
Surface 2 km



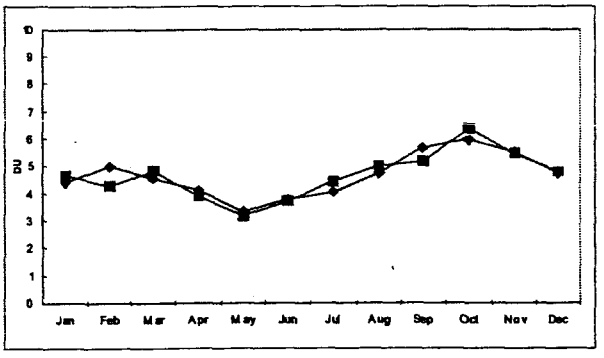
2 -4



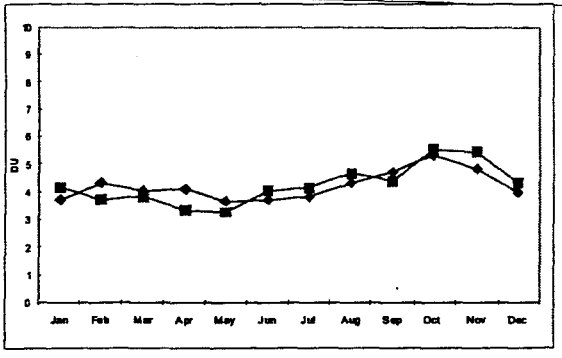
4 - 6



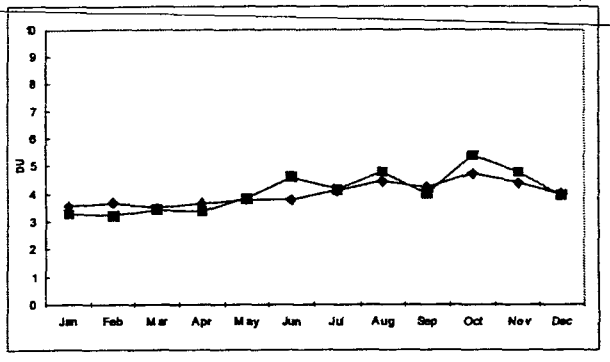
6 -8



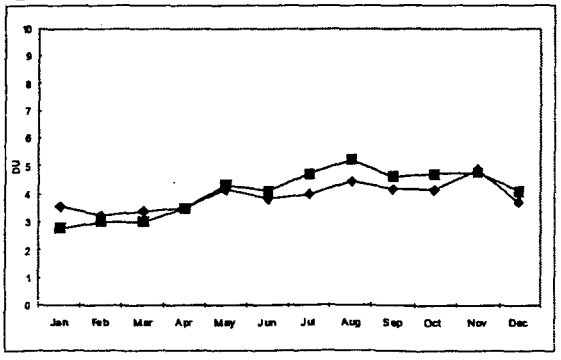
8 - 10



10 12



12 -14



14 16

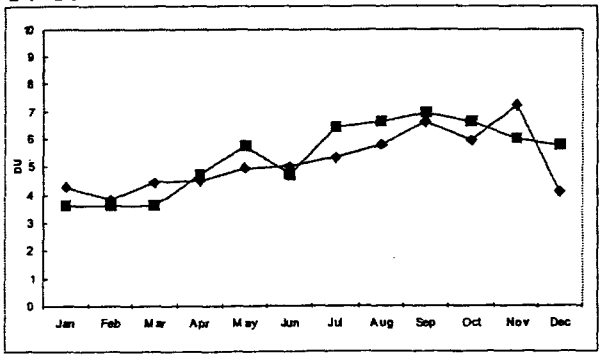
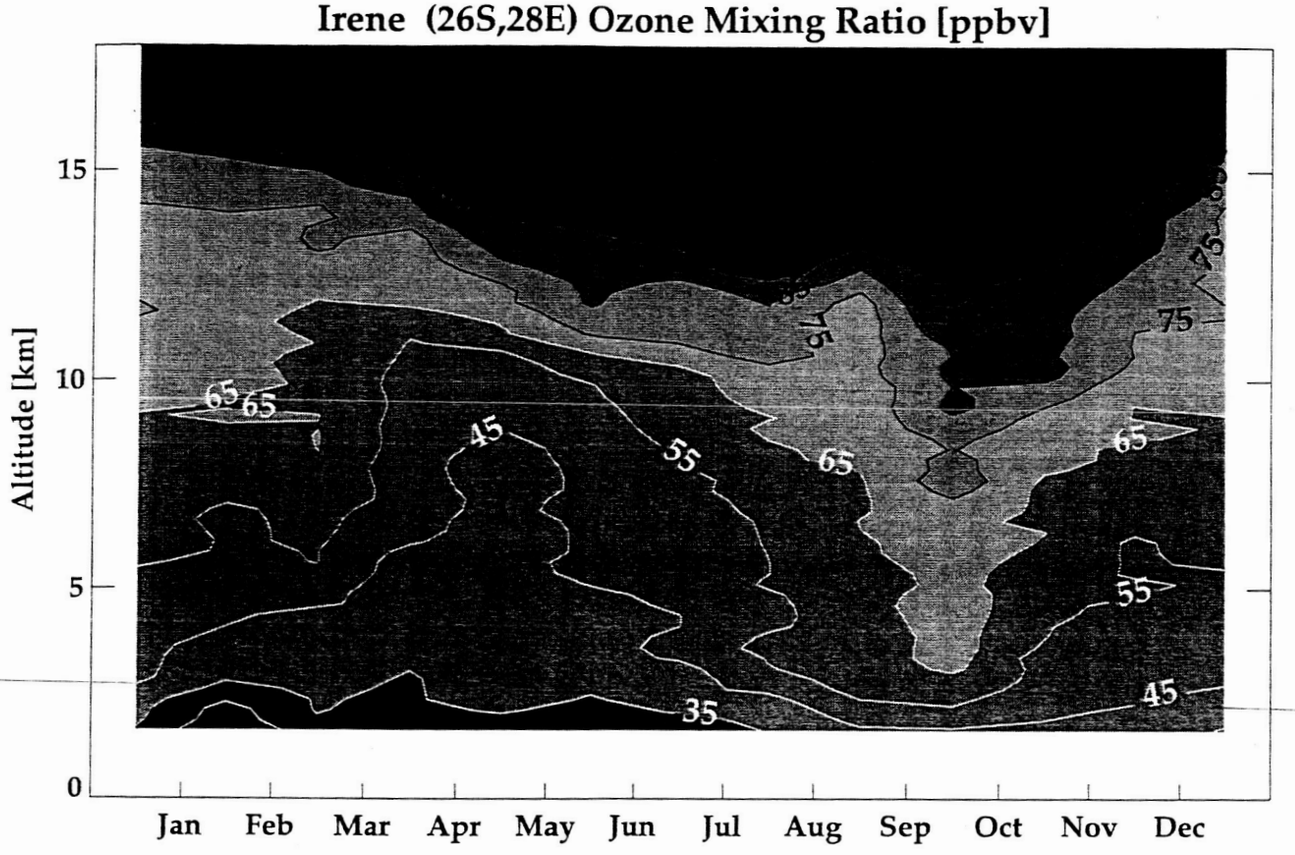


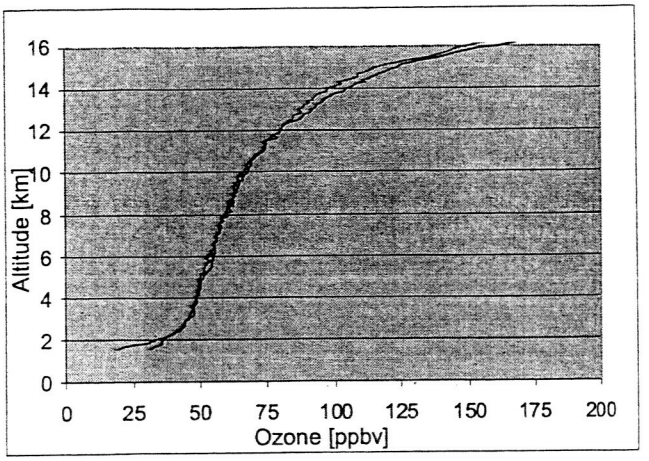
Figure 4


Irene (26S,28E) Ozone Mixing Ratio [ppbv]
Altitude [km]
15
10
5
0
75
75
65
65
45
55
65
65
55
45
35
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec
Monthly X-sections including years 1998-2002

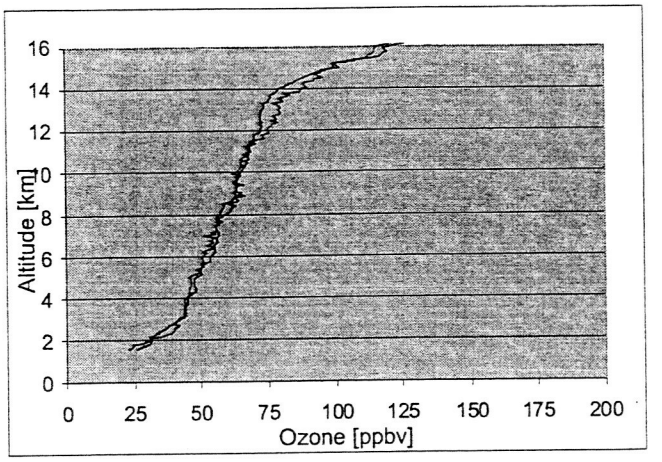
4

Figure 5

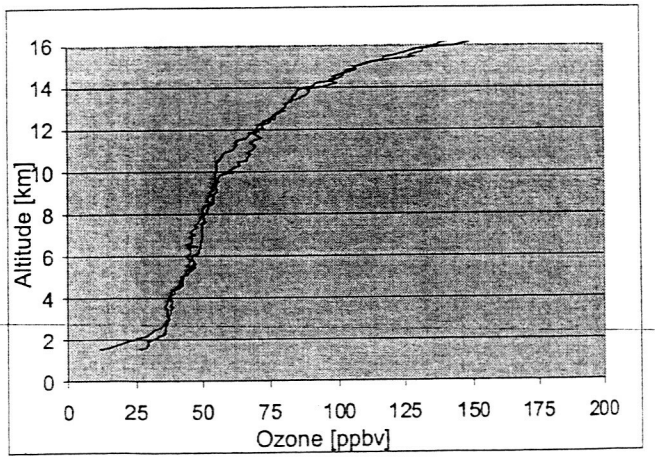
Annual



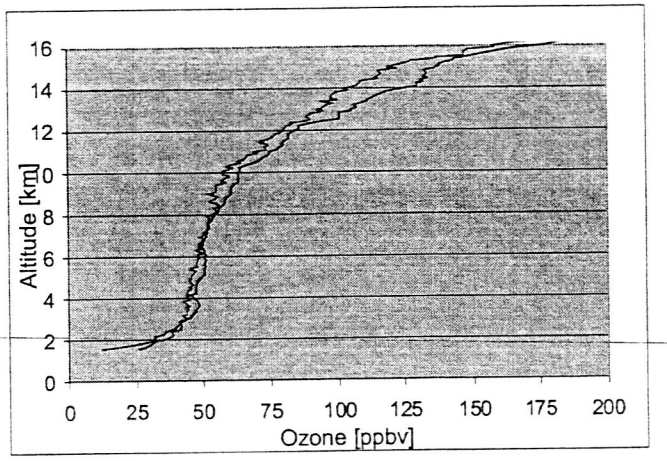
Summer DJF



Autumn MAM



Winter JJA



Spring SON

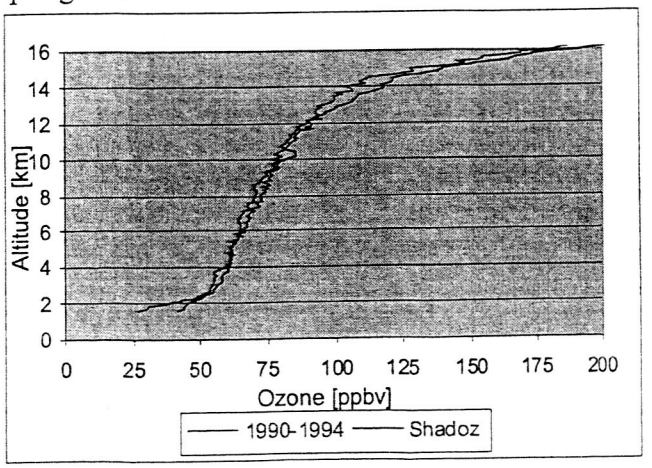
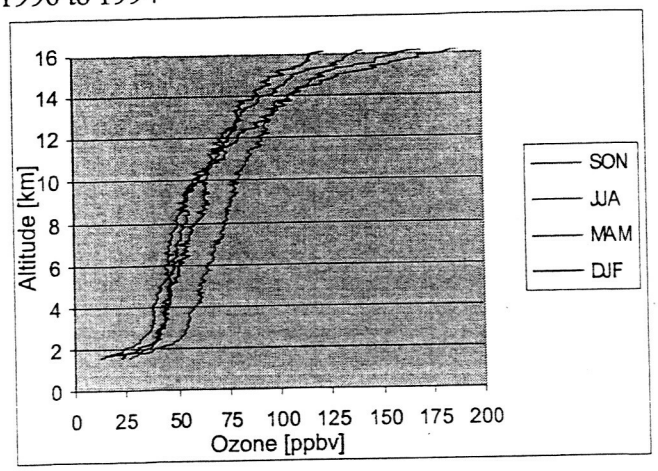
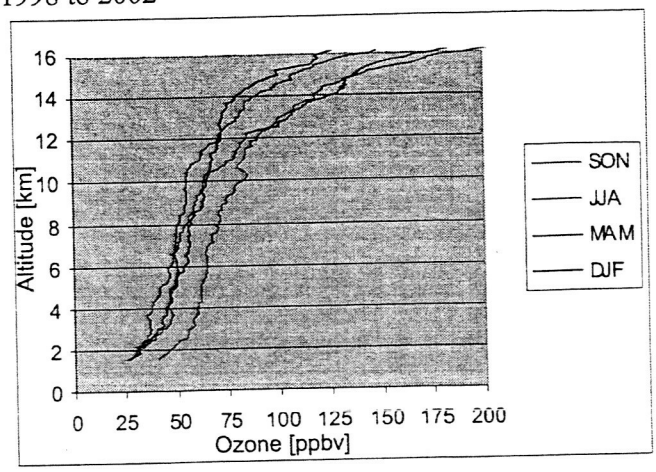


Figure 6

1990 to 1994



1998 to 2002



Irene Y99-Y02 Data - 0.25km Bins

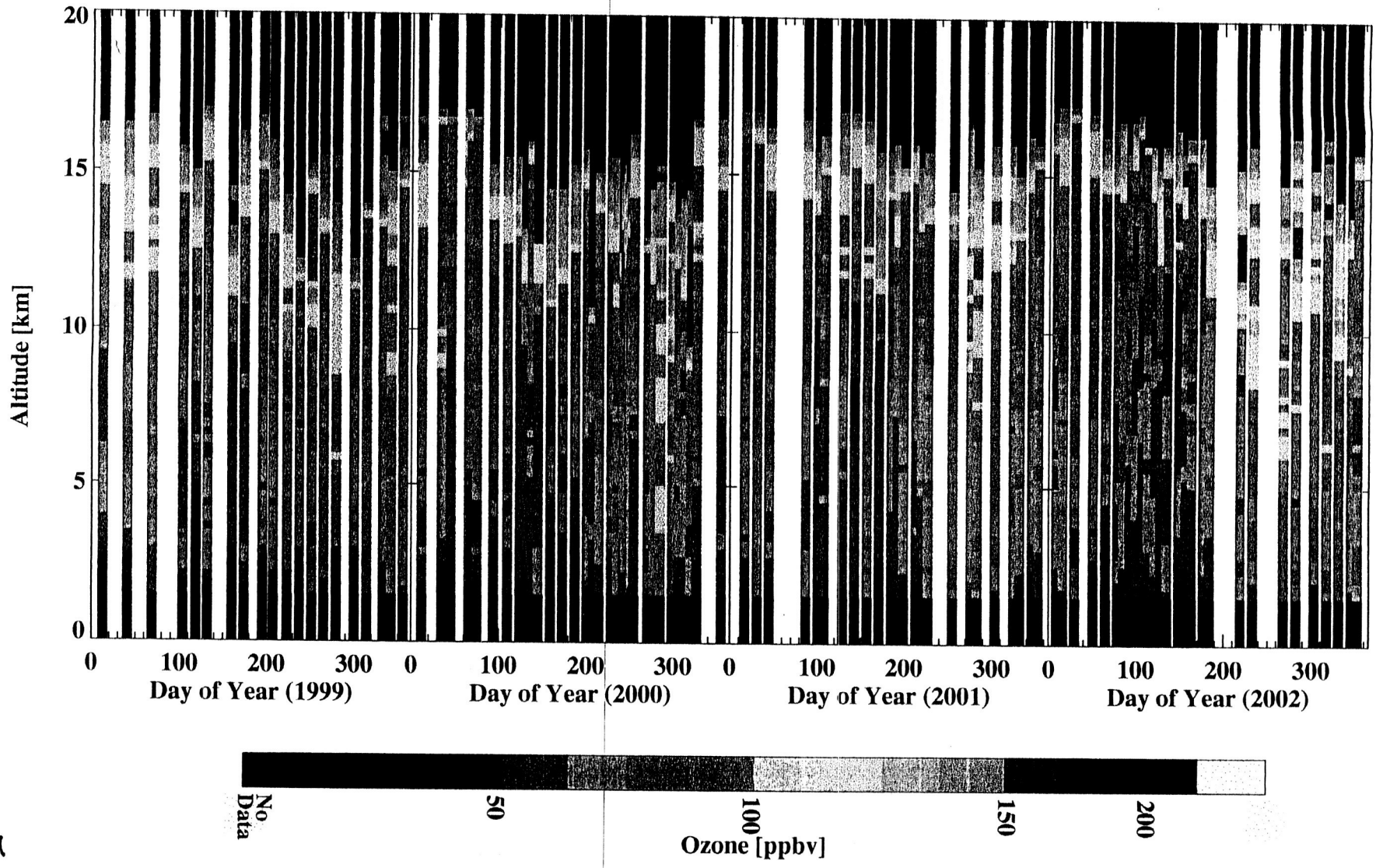
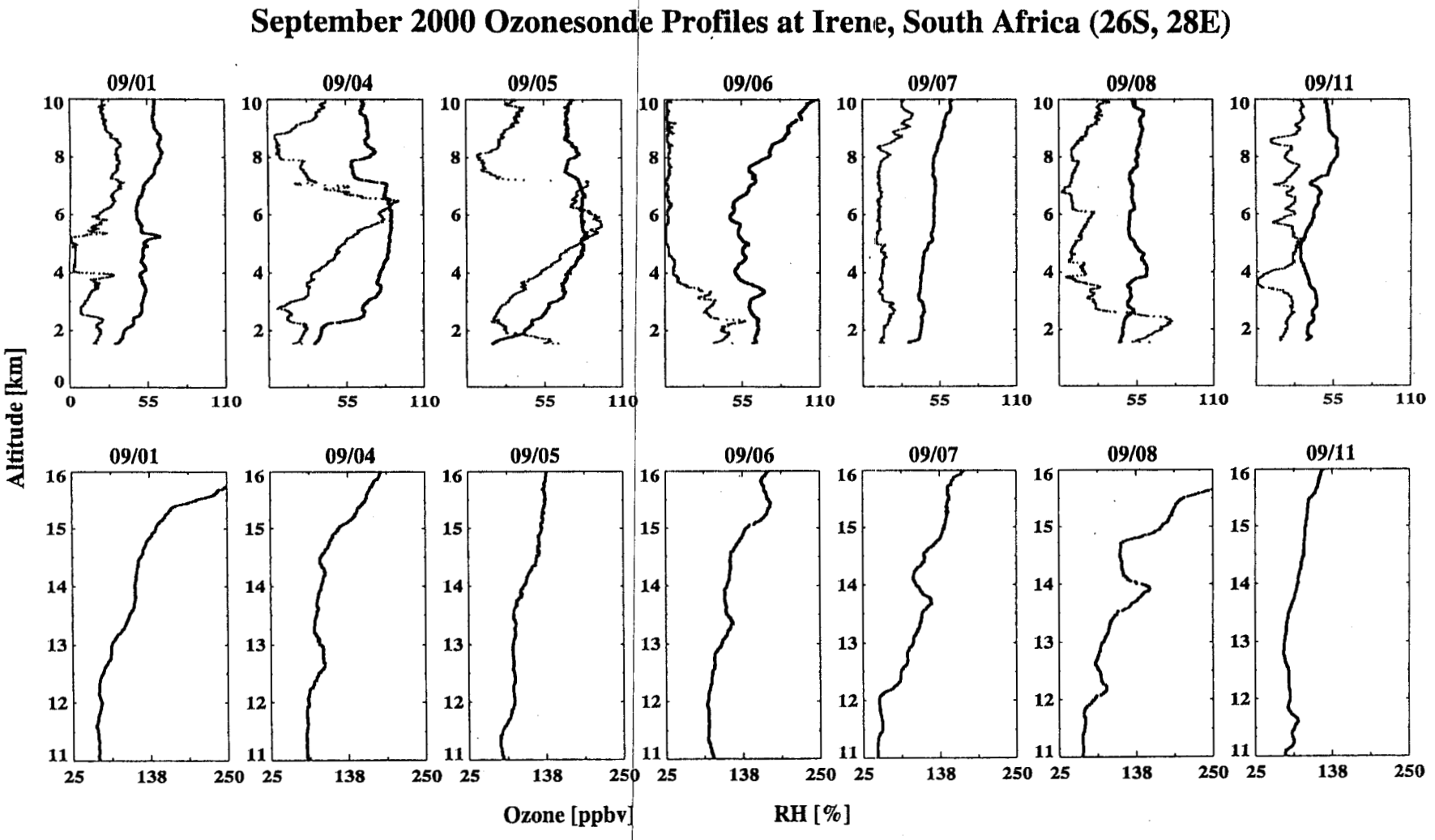


Fig 1

Figure 8


September 2000 Ozonesonde Profiles at Irene, South Africa (26S, 28E)
09/01
09/04
09/05
09/06
09/07
09/08
09/11
Altitude [km]
Ozone [ppbv]
RH [%]

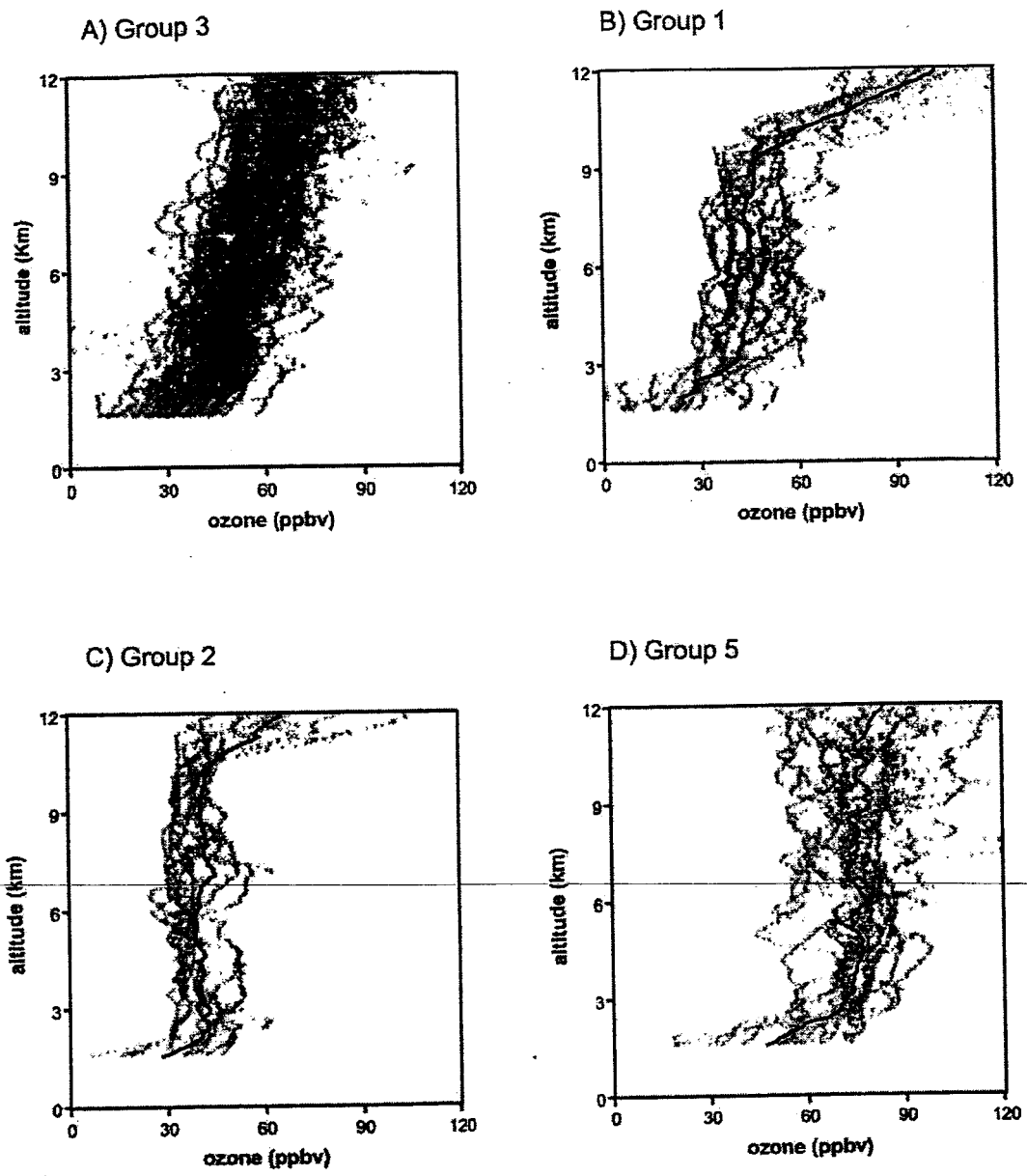

A) Group 3
B) Group 1
C) Group 2
D) Group 5
altitude (Km)
altitude (km)
ozone (ppbv)
0
3
6
9
12
30
60
90
120

Figure 9

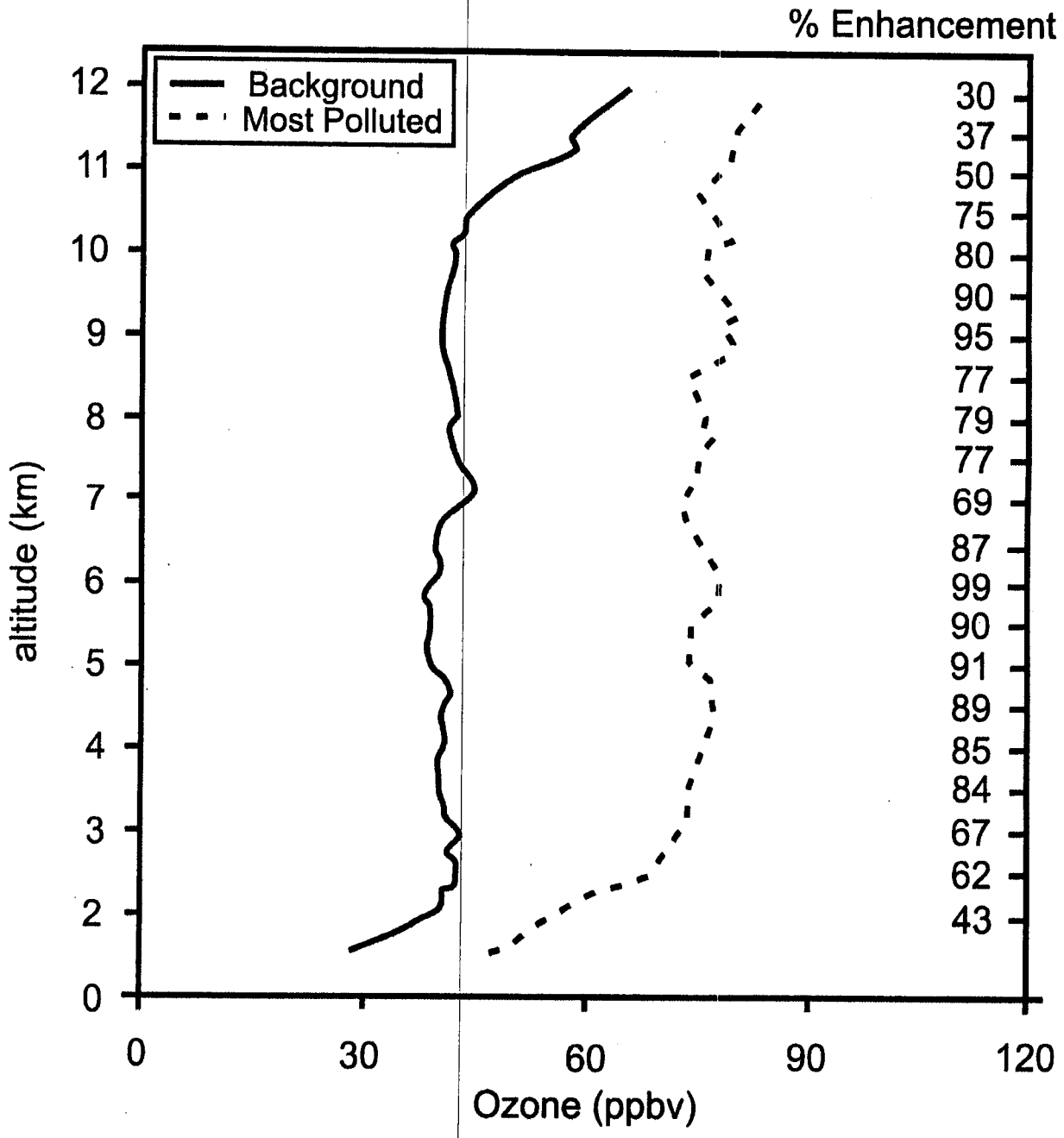

% Enhancement
Background
Most Polluted
altitude (km)
0
2
3
4
5
6
7
8
9
10
11
12
30
37
50
75
80
90
95
77
79
77
69
87
99
90
91
89
85
84
67
62
43
0
30
60
90
120
Ozone (ppbv)

Fig 19