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RELATIONSHIP BETWEEN SURFACE, FREE TROPOSPHERIC AND TOTAL COLUMN OZONE IN TWO CONTRASTING AREAS IN SOUTH AFRICA

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Abstract—Measurements of surface ozone in two contrasting areas of South Africa are compared with free tropospheric and Total Ozone Mapping Spectrometer (TOMS) total column ozone data. Cape Point is representative of a background monitoring station which is remote from pollution impacts, whereas the Eastern Transvaal Highveld (ETH) stations of Elandsfontein and Verkykkop are situated in an area of intense urban and industrial activity. At Cape Point the diurnal cycle in surface ozone is small, the seasonal cycle shows a winter maximum and a summer minimum. In contrast, the ETH stations show a spring maximum in surface ozone with evidence of a summer enhancement. Comparison with Cape Point data suggests that photochemical ozone production accounts for about 50% of the background value. Seasonal variations in total ozone are consistent over the whole of South Africa, indicating a cycle which is independent of varying surface ozone concentrations. The spring maximum in free tropospheric ozone (up to 12 km) over the interior of South Africa is thought to be due to long-range transport of biomass burn products from latitudes to the north, rather than the extension of a localised surface photochemical influence through the troposphere.

Key word index: Ozone, surface and total, urban/industrial contribution, stratospheric injection, TOMS data.

INTRODUCTION

Most of the ozone is found in the stratosphere between 15 and 50 km, peaking at a height of 25 km. Concentrations in the stratosphere are around 10,000 ppbv compared with a few tens ppbv in the troposphere (NRC, 1991). The tropospheric contribution to the total column ozone is of the order of 10–15% (Fishman *et al.*, 1990). However, the distribution of tropospheric ozone is not homogeneous, varying with latitude from less than 7% of the total vertical column in the tropics, 9% in the mid-latitudes, and about 10% in the polar regions (Bojkov, 1985).

One way in which to understand the relationship between ozone in the troposphere and the stratosphere is to compare the surface, free troposphere and stratospheric ozone concentrations on various time scales ranging from hours to years. If, for example, large phase differences exist in the ozone seasonal cycles between the stratosphere and the troposphere, it suggests a loose coupling between ozone in the two parts of the atmosphere (Oltmans and Komhyr, 1976).

The objective of this paper is to explore the relationship between surface, free tropospheric and total column ozone (in the absence of stratospheric ozone data) for two contrasting areas in South Africa. Cape Point is selected as representative of a clean unpolluted environment and two stations in the Eastern Transvaal Highveld (ETH) are chosen to represent a relatively polluted urban/industrial environment.

DATA

The following data were used in this paper.

Surface ozone data

Measurements of surface ozone from three stations in South Africa were used in this study. The first is Cape Point, where background ozone measurements have been made since 1982 as part of a co-operative venture between the Council for Scientific and Industrial Research (CSIR) and the Fraunhofer Institute for Atmospheric Environmental Research (IFU) in Germany. The station is located at the Cape of Good Hope (34°21′S; 18°29′E) at an altitude of 210 m above sea level (ASL). It is ideally suited as a background monitoring station as it is removed from direct pollution impacts and because air masses which reach the station are mainly of oceanic origin. The other two stations of Elandsfontein and Verkykkop are situated in the ETH, which is an area of intense urban and industrial activity and the main coal producing region of South Africa. Here 80% of the country's electricity is generated by coal-fired power stations (Tyson *et al.*, 1988). Elandsfontein (26°15′S; 29°25′E) is situated

centrally in the ETH at an altitude (1742 m ASL) equivalent to that of the general terrain. Verkykkop (27°18′S; 29°53′E) is situated 130 km to the south–east at an altitude of 2047 m, some 300 m above the general terrain (Tyson *et al.*, 1988). The data were supplied by Eskom.

Ozone measurements at Cape Point are made by a Dasibi (Model 1008 PC) analyser. The principle of this operation is based on ultraviolet absorption (254 nm wavelength) of the ozone molecule (Brunke and Allen, 1985). The ETH stations use the Dasibi Model 1008 RS, Thermo Electron Model 49 and the Monitor Labs Model 8810 interchangeably. All instruments are calibrated against a standard by an accredited agency and are fully compatible with EPA requirements (Turner, 1993). At Cape Point and the ETH stations the data are archived as hourly mean values in parts per billion by volume (ppbv). Thereafter, daily and monthly means were estimated. Data for the period 1988–1991 were used. At Cape Point the data are filtered to take account of the influence of local and regional pollution and to differentiate the true background values. The procedure is described in Scheel *et al.* (1990). In all cases the filtered or background data are used in this study unless otherwise indicated.

Total ozone data

Total Ozone Mapping Spectrometer (TOMS) data which are measured by the Nimbus 7 satellite have been used in this study. Daily data for the period 1988–1991 were obtained on CD-ROM from the National Space Science Data Center (NSSDC) in the United States. Version 6 TOMS data, which have been corrected for a negative drift due to the degradation in the reflectivity of the aluminium diffuser plate on the TOMS instrument, have been utilized. Data resolution is 1° latitude by 1.25° longitude and readings have been extracted from single cells within which each of the surface stations lie. The data are measured in Dobson Units (DU) where 1000 DU are equivalent to 1 cm of ozone at 1000 hPa.

SURFACE OZONE CHARACTERISTICS

The diurnal cycle in surface ozone at Elandsfontein and Verkykkop is characterised by a minimum in the morning and a maximum in the afternoon (Fig. 1a). The strong diurnal cycle at the ETH stations is typical of that generally found in polluted environments (Oltmans, 1981). It reflects the relationship between the buildup of ozone precursor gases in the early morning and the subsequent photochemical formation of ozone. The steady depletion of near-surface ozone at night occurs through physical adsorption at the ground and/or chemical destruction (Helas *et al.*, 1987; Helas, 1993). The diurnal pattern is seasonally consistent, but higher night-time ozone values are evident in winter than in summer (Fig. 1b). This difference is most likely related to seasonal contrasts in the occurrence of nocturnal temperature inversions which are prevalent in the interior of South Africa. Frequencies of night-time surface inversions at the nearby station of Pretoria range from over 80% in winter to about 40% in summer (Tyson *et al.*, 1976). The inversions would prevent mixing of air from higher levels, simultaneously trapping ozone within the inversion layer. With the breakup of the surface inversion after sunrise, near-surface ozone mixing ratios increase.

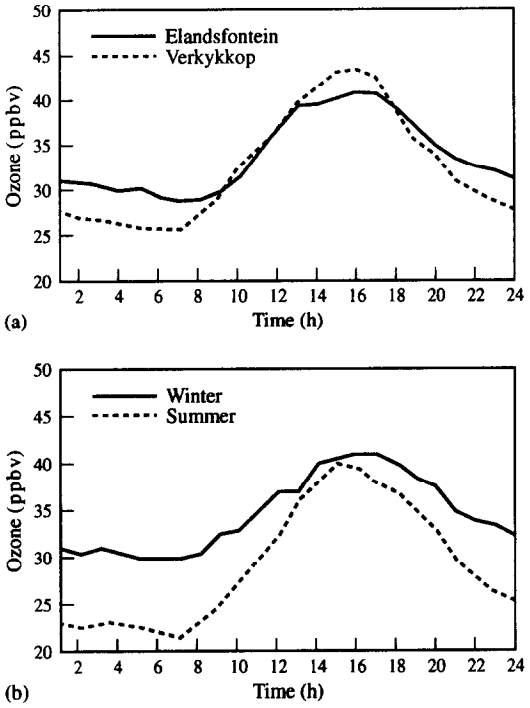

Fig. 1. (a) Mean annual diurnal variation in surface ozone (ppbv) at Eastern Transvaal Highveld (ETH) stations for the period 1988–1991 (b) mean winter (June to August) and summer (December to February) diurnal variation in surface ozone (ppbv) at Elandsfontein for 1991.

In contrast to this, the clean air site of Cape Point exhibits a weak diurnal cycle (Fig. 2). Here the amplitude of the mean monthly diurnal wave is no more than 2 ppbv. The diurnal cycle is also seasonally consistent reflecting the absence of a seasonal inversion control. Inversion frequencies at Cape Town are between 40 and 50% throughout the year (Tyson *et al.*, 1976).

Similar contrasts between the two areas are observed in the seasonal ozone patterns. At Cape Point the winter maximum (approx. 28 ppbv) occurs between May and July and the summer minimum (approx. 13–14 ppbv) falls in December or January (Fig. 3). The ETH stations display different seasonal cycles. Peak values, in excess of 40 ppbv occur in spring, usually in September, but values generally lie above 35 ppbv between July and December (Fig. 4). An exception occurs in March 1990 at Elandsfontein

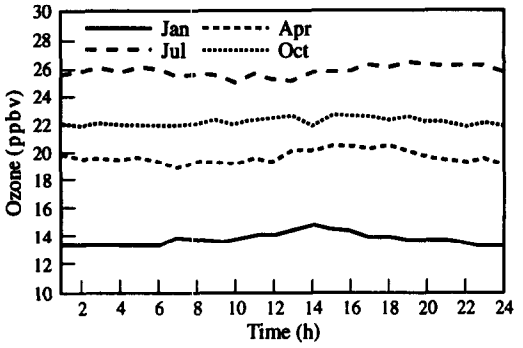

Fig. 2. Mean diurnal variation in surface ozone (ppbv) at Cape Point for the period 1988–1991.

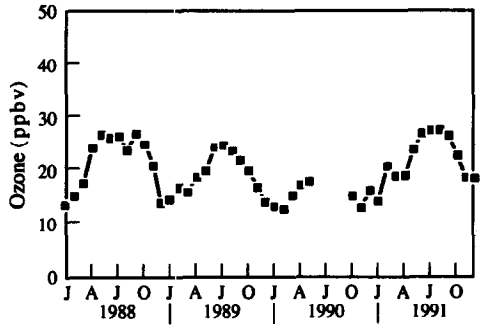

Fig. 3. Mean monthly surface ozone values (ppbv) at Cape Point over the period 1988–1991. Data are missing between June–September 1990.

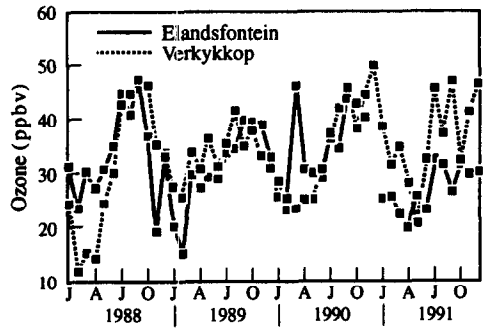

Fig. 4. Mean monthly surface ozone values (ppbv) at Verkykkop and Elandsfontein over the period 1988–1991.

when an anomalously high mean monthly value of 46.3 ppbv is recorded. No explanation could be discerned from the data at hand. Differences in the magnitude of ozone concentration between the two ETH stations indicate that local factors are important and suggest photochemical influences.

Many clean air sites, remote from the effects of industrial activity, typically depict a winter ozone maximum and a summer minimum, for example Cape Grim in Tasmania (Logan, 1985; Elsworth *et al.*, 1988). This pattern of seasonal change is consistent with the injection of stratospheric ozone-rich air into the troposphere, which is most effective in the late winter and spring months (Danielsen, 1968; Danielsen and Mohnen, 1977; Mahlman and Moxim, 1978) and has been cited by many authors as the source of tropospheric ozone at these locations (Oltmans, 1981; Logan, 1985; Scheel *et al.*, 1990). It should be noted, however, that this is not the only process governing the seasonal cycle of surface ozone. Fishman *et al.* (1979) have drawn attention to the mechanism of photochemical ozone destruction which, assuming low NO_x levels, would be greatest at the time of maximum solar ultra-violet radiation in summer. In the absence of NO_x measurements at Cape Point, these ideas could not be tested. Also, in the marine environment, methyl iodide released from the ocean may provide an additional sink for ozone (Chemeides and Davis, 1980). Indeed, Oltmans and Levy (1994) analysed a number of locations which run from 14°S to 90°S, and their seasonal surface ozone cycles all show a winter maximum and summer minimum. However, it is noted that not all clean air sites display the winter maximum and summer minimum pattern. Oltmans and Levy (1994) have shown that at some mid-latitude and subtropical sites in the Northern Hemisphere there is a distinct spring maximum and a late summer or autumn minimum.

The broad summer maximum in surface ozone evident at the ETH stations reflects the greater availability of sunshine in the summer months and is indicative of photochemical production of ozone associated with anthropogenic emission of NO_x, CO and hydrocarbons from fossil-fuel combustion. Heavily populated and industrialised regions of the United States are characterised by a broad summer maximum in surface ozone which persists from spring into summer (March to August) (Logan, 1985). Typical average spring and summer concentrations in the eastern United States are between 30 and 50 ppbv. While the summer enhancement is indicative of photochemical ozone production in urban/industralised areas, the spring maximum is also present in some remote sites in the Northern Hemisphere mid-latitudes and subtropics (Oltmans and Levy, 1994), and is most likely related to stratospheric–tropospheric injection.

Figure 5 shows mean monthly values averaged over the 4-year period together with standard deviation bars for the three stations. The greater variability observed at the ETH stations is consistent with the photochemical origin of ozone, which varies as a function of the production of precursor gases and their accumulation due to varying meteorological conditions.

We next compare the mean monthly values between Cape Point and ETH in order to obtain an estimate of ozone production due to photochemical sources. We assume Cape Point data to be representative of baseline ozone conditions in the whole South

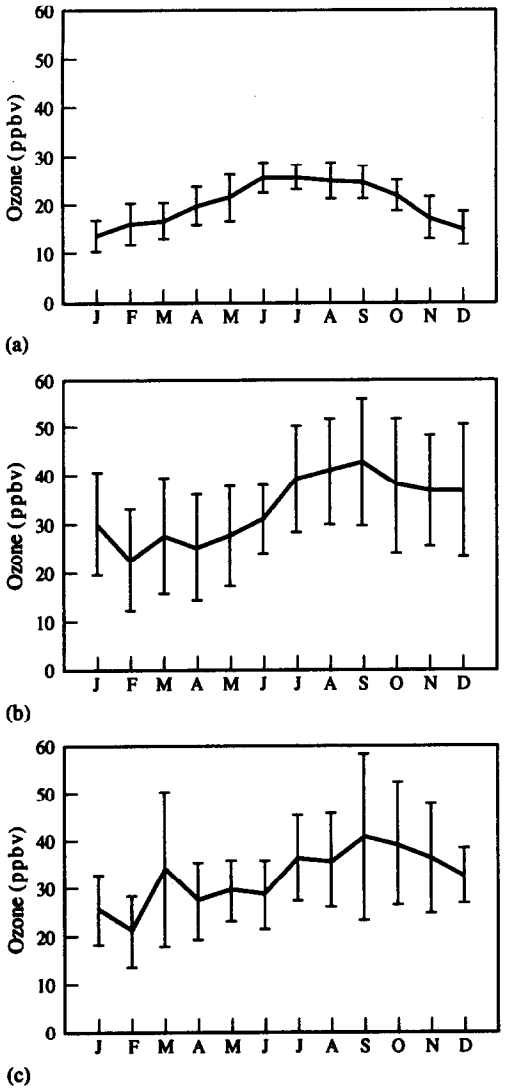

Fig. 5. Mean monthly (1988–1991) surface ozone (ppbv) at (a) Cape Point, (b) Verkykkop and (c) Elandsfontein. The bars represent the standard deviations.

African region. It is recognised that baseline conditions at the ETH stations may differ because of elevation differences. Cape Point data may also not be entirely free of the influence of biomass burning as has been noted by Scheel *et al.* (1994) who suggested that the slightly elevated ozone levels between August and November could be due to biomass burning, as evidenced by the high CO values at this time. In the absence of any means of quantifying these effects at this stage, a first estimate of ozone production due to photochemical sources is made by subtracting the Cape Point data from the ETH data (Fig. 6). The differences range from about 8 ppbv in autumn to 15–20 ppbv between July and January, and account for approximately 50% of the surface ozone present in the ETH. It is worth noting that the enhancement is characterised by a broad maximum which extends

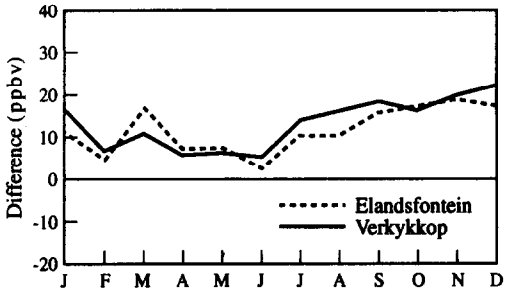

Fig. 6. Mean monthly difference in surface ozone (ppbv) between ETH stations and the background Cape Point station.

from late winter into summer, consistent with the seasonal pattern of photochemical ozone production due to anthropogenic influences.

FREE TROPOSPHERIC OZONE CHARACTERISTICS

Logan (1985) has shown the extent to which photochemical influences extend through the lower to mid-troposphere by examining seasonal variations of ozone at a number of standard pressure levels above the surface. In the polluted environments of Europe and North America, the seasonal peaks at 700 and 500 hPa are in phase with that at the surface (i.e. summer maximum), indicative of a ground-based source of ozone. At 300 hPa, however, the maximum occurs in spring (March to May), resembling the seasonal cycle of the lower stratosphere (Oltmans, 1981).

Little information about the vertical distribution of ozone over South Africa is available. Zunckel (1992) and Zunckel *et al.* (1992) have discussed trends in the vertical distribution of ozone at Pretoria, based on a comparison of ozone concentrations in nine standard Umkehr layers for a historic background period (1965–1968) and a more recent period (1990–1991). The recent data were recorded at Irene, which is situated some 20 km south of the centre of Pretoria but still highly urbanised, whereas the earlier data were recorded in Pretoria at a time when anthropogenic influences were far less. For example, registered motor vehicles in Pretoria numbered approximately 100,000 in 1966, compared with 360,000 in 1988. Furthermore, national electricity production was around 40 TWh in 1965 and 160 TWh in 1990. According to Zunckel (1992), the growth of NO_x sources since the 1960s as indicated by these statistics, must imply an increase in the photochemical production of ozone.

There is evidence of a marked increase in tropospheric ozone between the two periods which is attributed to photochemical ozone production from industrial and urban sources. Comparison between the seasonal distribution of ozone in the lowest two layers (up to 12 km ASL) between the two periods shows a spring maximum, except in earlier period

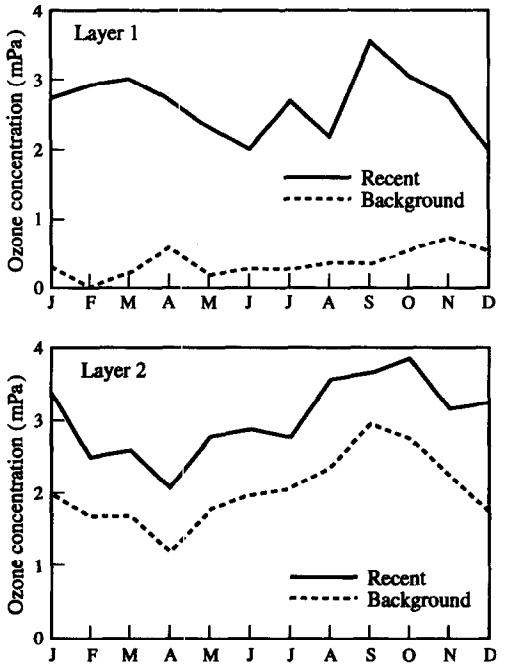

Fig. 7. Comparisons between mean monthly ozone concentrations (mPa) at Pretoria in layer 1 (surface to 6 km) and layer 2 (6–12 km) for a background period (1965–1968) and a recent period (1990–1991) (redrawn from data in Zunckel, 1992).

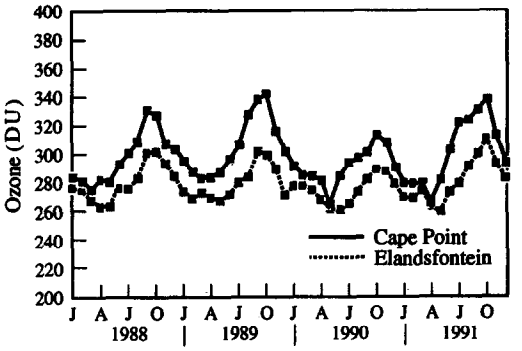

Fig. 8. Mean monthly (1988–1991) variations in TOMS total ozone (DU) for grid squares corresponding to locations of Cape Point and Elandsfontein.

Table 1. Relationship between mean monthly TOMS total ozone and surface ozone for Elandsfontein, Verkykkop and Cape Point (1987–1991)

	Elandsfontein	Verkykkop	Cape Point
r	0.42	0.42	0.38
r^2	17.20%	17.89%	14.28%

Significant at 95% confidence level.

layer 1 data, when values differed little from month to month (Fig. 7).

TOTAL OZONE CHARACTERISTICS

Seasonal variations in total ozone over South Africa have been discussed in a number of papers (e.g. Diab *et al.*, 1992). All refer to the distinct annual cycle, with a spring-time maximum in September or October, whereafter values decline during the summer months to reach a minimum around May. There is a latitudinal dependence in annual range. The southernmost stations of Cape Town and Port Elizabeth exhibit greater ranges than the more northerly located stations such as Bloemfontein and Pretoria. It is generally thought that this spring-time maximum is a reflection of the strengthening of the mid-latitude ozone ridge due to transport away from equatorial regions in the stratosphere in the austral spring. Seasonal variations in total ozone for the period 1988–1991 and corresponding to the locations of the surface based ozone stations show a similar pattern (Fig. 8).

RELATIONSHIP BETWEEN SURFACE, FREE TROPOSPHERIC AND TOTAL OZONE

The seasonal pattern in total ozone is consistent over the whole of South Africa, indicating a cycle which is independent of varying surface ozone contributions. Indeed, the expected poor relationship between surface and total ozone is demonstrated statistically by results presented in Table 1. Correlation coefficients between mean monthly TOMS total ozone and surface ozone range from 0.38 at Cape Point to 0.42 at both Verkykkop and Elandsfontein. Although the results are statistically significant at the 95% level, less than 20% of the variance in total ozone is accounted for by surface ozone variations. On a daily basis the relationships are weaker as is evidenced by even lower correlation coefficients.

Although the seasonal cycle in surface ozone at ETH stations and the seasonal cycle in ozone in the first two tropospheric layers (up to 12 km) at Irene are in phase, both showing a spring maximum, it is not possible to conclude that this is a local surface photochemical influence extending through the troposphere. One would expect the summer enhancement to be better developed in the lower layer than the second layer, if localised ground level sources were responsible. This is not the case as is shown in Fig. 7. Some other explanation for the free tropospheric spring maximum should be sought. The influence of biomass burning which is prevalent to the north of these latitudes and which peaks during this period is the most likely cause. There are indications of long-range transport of biomass burn products in elevated layers above the surface (Garstang, 1993).

Above the troposphere, between 12 and 30 km, maximum ozone is reached in winter (Zunckel, 1992),

consistent with stratospheric–tropospheric (S–T) injection theory. At higher altitudes, an October maximum is present, which probably accounts for the total ozone October maximum. The greatest seasonal variability is found in the 12–18 km layer.

CONCLUSIONS

The relationships between surface, free tropospheric and total ozone have been explored for two contrasting areas in South Africa, viz. Cape Point and the ETH. Cape Point is typical of a remote background site, where the diurnal cycle in surface ozone is small and the seasonal cycle shows a winter maximum most likely produced through S–T injection. The summer minimum is thought to be due to low NO_x values which provide a photochemical sink for ozone. In contrast, the ETH sites show a spring maximum in surface ozone, with evidence of a summer enhancement, indicative of photochemical ozone production. Comparison with Cape Point data suggests that photochemical ozone production accounts for about 50% of the background value.

A comparison of the vertical distribution of ozone at Pretoria between a historic background period (1965–1968) and a more recent period (1990–1991) showed that there has been a marked increase in tropospheric ozone levels.

Seasonal variations in total ozone are consistent over the whole of South Africa, indicating a cycle which is independent of varying surface ozone concentrations. This was confirmed statistically by testing the relationship between total and surface ozone. It was found that less than 20% of the variance in total ozone is accounted for by surface ozone variations. Although the seasonal cycles in surface ozone at the ETH stations and the seasonal cycle in free tropospheric ozone (up to 12 km) at Irene are in phase, it could not be concluded from this analysis that this is due to the extension of a localised surface photochemical influence through the troposphere. Long-range transport of biomass burn products from latitudes to the north was suggested.

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