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Surface ozone over southern Africa: synthesis of monitoring results during the Cross border Air Pollution Impact Assessment project

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Abstract

Measurements of surface ozone in the southern African region are limited to a few active and passive monitoring sites. Over the region, the mean surface ozone concentrations exhibit strong seasonal and diurnal variations. The seasonal maximum generally occurs in the spring months from August to November and the minimum occurs in December and January. With the exception of Cape Point, a strong diurnal variation is observed at all sites. Ozone concentrations increase from a minimum near sunrise to a maximum in the afternoon, then decrease again to the early morning minimum. The highest ozone concentrations occur over Botswana and the Mpumalanga highveld. In both regions the springtime maximum is between 40 and 60 ppb, but reached more than 90 ppb as a mean in October 2000. In these two regions the monthly minimum is between 20 and 30 ppb. The mean daytime ozone concentrations in Botswana and on the highveld reach 40 ppb as early as 10:00 and remain above this level for up to 10 h. At the background stations at Cape Point, in Namibia and areas adjacent to the highveld the maximum concentrations are between 20 and 30 ppb with minimums between 10 and 20 ppb. In the Cross border Air Pollution Impact Assessment project, CAPIA, a threshold value of 40 ppb is used to assess the potential risk of damage to maize by ozone. Measured data show that this threshold is exceeded over Botswana and on the South African highveld.

Keywords: Ozone; Botswana; South Africa; Zimbabwe; Zambia; CAPIA; Cape Point

1. Introduction

Ozone in the lower troposphere forms through the reaction between oxides of nitrogen (NO_x) and volatile organic compounds (VOC) in sunlight. High ozone concentrations near the earth's surface are associated with negative health impacts (Lippman, 1989), and can

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result in damage to vegetation (Emberson et al., 2001), and be harmful to materials (Lee et al., 1996; Massey, 1999). In southern Africa anthropogenic sources of NO_x occur throughout the region (Fleming and van der Merwe, 2002) and also result from soil emission (Levine et al., 1996). VOC emissions occur throughout the region from vegetation (Greenberg et al., 2003; Harley et al., 2003), and from anthropogenic activities (Fleming and van der Merwe, 2002). Biomass burning is also a major source of trace gases and particulates (Scholes et al., 1996; Helas and Pienaar, 1996). The region lies in sub-tropical and temperate latitudes with high levels of sunshine, suggesting ozone may readily form in the presence of the precursor gases.

Some studies have provided information on ozone concentrations in the lower troposphere, but very little information is available on ground level ozone concentrations over southern Africa. Using balloon-borne ozonesonde during the SAFARI-92 campaign, Thompson et al. (1996) and Diab et al. (1996) reported ozone concentrations to increase with height from approximately 20 ppb near the surface to 50 ppb or more at 700 m AGL at Pretoria (South Africa) and Etosha National Park (Namibia). Meixner and Helas (1994) found a similar pattern at the Victoria Falls (Zimbabwe) during SAFARI-92. Airborne measurements during SA'ARI-94 showed ozone concentrations to increase from 30 ppb near the surface to 50 ppb at a height of 3 km over the Alexander Bay on the Namibian coast (Helas et al., 1995).

Lacaux et al. (1993) reported surface ozone concentrations between 30 and 40 ppb in central Africa during 1983 and 1988. Combrink et al. (1995) showed surface ozone concentrations to range between 25 and 50 ppb at two stations in South Africa. During the period 1991–1993 a network of ozone monitoring stations was in operation in the eastern highlands of Zimbabwe (Jonnalagadda et al., 2001). At these sites, the mean annual surface ozone concentrations ranged between 37 and 49 ppb, with a mean standard deviation of about 11 ppb. In addition to these studies, there are a few ongoing ozone-monitoring initiatives in southern Africa. These include monitoring by local metropolitan councils in urban areas, measurements in rural and industrial environments and at so-called background stations.

This paper focuses on surface ozone monitoring outside urban areas during the period 1999–2001. The intention is to describe surface ozone characteristics in the southern African region during a period that coincides with the Cross border Air Pollution Impact Assessment project (CAPIA, 2002).

2. Monitoring sites and measurement type

During 1999–2001 surface ozone monitoring was conducted in four countries in southern Africa, namely Botswana, Namibia and South Africa, using both continuous and passive sampling techniques. The monitoring stations are listed in Table 1 together with explanatory notes on the sampling technique, the instrumentation and the monitoring period. The relative position of these sites is illustrated in Fig. 1.

Surface ozone measurements have been made at South Africa's Cape Point Global Atmosphere Watch (GAW) station since 1983 (Scheel et al., 1994; Combrink et al., 1995; Brunke and Scheel, 1998; Oltmans et al., 1998). Monitoring is done with a TEI 49 UV O_3 instrument, which analyses the air drawn in through a 4 m high glass tube ventilated by means of a high-volume fan. The data are recorded as 1-min averages, which in turn are compiled to yield half-hourly, daily and monthly averages. An external zero test as well as a span check are performed once every day. The calibration of the instrument is tied to the GAW ozone reference scale through three audits, involving O_3 intercomparisons, which were performed by the GAW O_3 calibration centre (EMPA, http://www.empa.ch/gaw) since 1995. Cape Point surface ozone data have been submitted to the World Data Centre for Greenhouse Gases (WDCGG) in Tokyo on an annual basis.

Table 1
Surface ozone-monitoring sites in southern Africa

Country	Site	Sampling type	Latitude (S)/Longitude (E)	
Botswana	Maun	Continuous	19° 58′	23° 24′
Namibia	Etosha	Passive	19° 09′	15° 49′
South Africa	Bosjesspruit	Continuous	26° 32′	29° 14′
	Cape Point	Continuous & Passive	34° 21′	18° 29′
	Amersfoort	Continuous & Passive	27° 00′	29° 51′
	Elandsfontein	Passive	26° 10′	28° 11′
	Ben MacDhui	Passive	30° 38′	27° 57′
	Palmer	Passive	25° 31′	30° 03′
	Louis Trichardt	Passive	23° 03′	29° 54′
	Skukuza	Passive	24° 59′	31° 35′

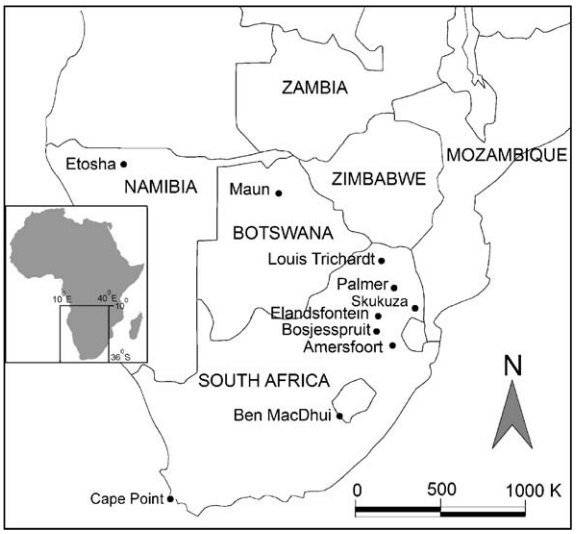

Fig. 1. The southern African region, indication the relative position of the ozone passive and continuous monitoring sites.

On South Africa's industrialised Mpumalanga highveld, surface ozone is monitored at three stations. A number of coal-fired power stations, foundries and a large petrochemical industry are located on the highveld. Bosjesspruit (Fig. 1) is located approximately 5 km from the Secunda industrial complex and Amersfoort is approximately 90 km to the southeast of Secunda and is located near the eastern escarpment, on the edge of the highveld. Continuous monitoring is undertaken at Bojesspruit with a Monitor Labs 9810 analyser and at Amersfoort with an API 400A analyser, both using UV adsorption. Zero and span tests are done every 2 weeks and a full dynamic gas calibration is performed every 3 months by the National Metrology Laboratory.

In Botswana, surface ozone has been monitored at Maun (Fig. 1) since July 1999. Maun is a small town of approximately 44 000 inhabitants in a largely rural environment near the Okavango Swamps. Northeasterly winds prevail approximately 70% of the time. The ozone monitor is located upwind of Maun in order to measure ozone concentrations that are not strongly influenced by urban activities. The area is well vegetated with mopani and acacia trees in thick grassy savanna.

At Maun ozone is monitored on a continuous basis with a Horiba APOA 360 analyser, using UV absorption. The continuous measurements are used to calculate hourly averages. Routine zero, span, step and diurnal calibration tests are performed and the instrument is calibrated every three months. From when monitoring commenced to the end of 2001 the data recovery varied from more than 90% in eight months, to zero data return in other months.

Five air quality stations are operated within the DEBITS (Deposition of Biogeochemically Important Trace Species) program of IGAC (International Global Atmospheric Chemistry) in southern Africa where monthly average background concentrations of key pollutants are monitored, including ozone. These sites are remote and are removed from any direct anthropogenic influences. Monitoring is conducted at Etosha National Park in Namibia, and in South Africa at Cape Point, at the high-altitude site on Ben McDhui, at Elandsfontein, Amersfoort and Palmer on the Mpumalanga highveld and near the South African border with Zimbabwe at Louis Trichardt (Fig. 1).

Monitoring at the DEBITS sites is done by means of passive samplers that are tested extensively within DEBITS and WMO programmes (Dhammapala, 1996; Carmichael, 1997; Carmichael et al., 2003). Passive samplers are based on chemical and physical processes. The rate at which gaseous pollutants in ambient air diffuse into the sampler is controlled by the diffusion coefficients of the respective gases. In theory, inside the sampler the gases impinge on a paper disk that has been impregnated with a chemical that reacts very specifically with the gas of interest and so quantitatively traps the pollutant. The Atmospheric Chemistry Research Group (ACRG) at the North-West University (Potchefstroom Campus) does the sampler analysis and results are submitted routinely to DEBITS.

3. Results

3.1. Botswana

Monthly average ozone concentrations at Maun for 1999 to 2001 show a marked seasonal variation with maximum concentrations occurring from spring to early summer, August to November, in all years (Fig. 2). During this period the average ozone concentration generally exceeds 40 ppb. In other months the average concentration is somewhat lower. The observed spring time ozone maximum (August–October) does not coincide with the observer seasonal cycle in biomass burning in southern Africa being most active between May and September, peaking in July. Silva et al. (2003) report a total burned area of about 340 000 km^2 in southern Africa in July 2000, decreasing to less than 150 000 km^2 in September and to about 40 000 km^2 in October. In the Maun area alone more than 3.6 million ha of savanna burnt in the period between 1999 and 2001. Rather, the observed ozone maximum coincides with the onset of summer rains and the associated spring growth in vegetation and nitrogen emissions from soil wetting.

The diurnal variation is also pronounced at Maun (Fig. 2). Here the mean of the hourly average concentrations for July 1999 to October 2001 show the concentration to increase from about 30 ppb before

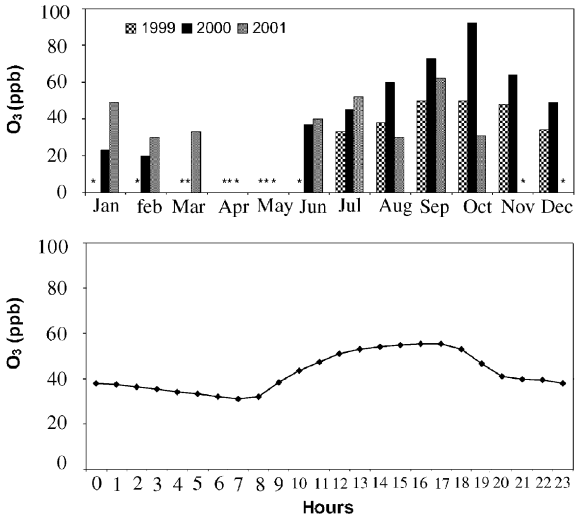

Fig. 2. Mean monthly ozone concentration in ppb at Maun for 1999–2001 (top) where crosses indicate missing data and mean hourly concentrations in ppb in 1999–2001 (bottom).

sunrise to an average maximum of about 55 ppb at 15:00. There after the concentration decreases rapidly to sunset at about 19:00, it is followed by a more gradual decrease to the minimum at sunrise. The average concentration is above 40 ppb for about 11 h.

3.2. Namibia

The monthly surface ozone concentrations at Etosha during the period June 2000–May 2002 range between a maximum of 30 ppb in October 2000 and August 2001 to a minimum of about 11 ppb in March 2001, and in the summer months from October 2001 to January 2002 (Fig. 3). The mean concentration during this period is 17 ppb. Similar to Maun, a seasonal variation is evident with the maximum occurring in the spring and the minimum during the summer. During the SAFARI-92 campaign, Thompson et al. (1996) and Diab et al. (1996) reported surface ozone concentrations of approximately 20 ppb using ozonesondes, increasing with height to 50 ppb or more at about 3000 m AGL.

3.3. South Africa

Trace gas data collected at Cape Point are primarily of maritime origin due to the dominance of winds from the SE–W quadrant, which advect air from the S–W Atlantic region to the measuring site. At times northerly air also reaches Cape Point with a continental and often anthropogenic influence from the City of Cape Town. Such pollution events tend to enhance O_3 levels at Cape Point during the summer months due to photochemical production, whilst suppressing O_3 concentrations in winter in response to ozone titration by nitrogen oxides (Brunke and Scheel, 1998). When long-term trends and seasonality under baseline conditions are determined, only data that have passed statistical filtering criteria are used. This applies to surface ozone as well as to the other trace gases measured at Cape Point.

Since the 1990s, the Cape Point O_3 data have shown a small but steady increase of 0.4 ppb yr^{-1} (Labuschagne et al., 2001). The minimum ozone concentration for the 3 years at Cape Point (range: 14–17 ppb) occurs during January/February and the maximum (range: 31–32 ppb) during July–September, constituting peak-to-peak values, which vary between 14 and 18 ppb O_3 (Fig. 4). In 2000, the minimum value occurred in February and not in January due to O_3 production brought about by unusual bush fires, which occurred in the Western Cape. Overall, the seasonal cycle is fairly repetitive from year to year and typical for the background Southern Hemispheric marine troposphere. Summer and winter months are characterized by different O_3 levels as well as varying degrees of data variability.

The composite diurnal cycles (1999–2001) depict the "all data" as well as two background data sets based on a percentile (PF) filtering technique and a ^{222}Rn selection criterion (Fig. 4). The latter technique, which is marginally stricter than the PF method, selects O_3 data on the basis of $^{222}Rn < 150$ mBq m^{-3} thereby providing an even higher degree of maritime data.

The all data set gives rise to a diurnal cycle showing minima between 06:00 and 08:00 and maxima at about 15:00 with an average peak-to-peak value of 4 ppb. It is suggested that this cycle to some extent reflects anthropogenic processes from the greater Cape Town area involving oxides of nitrogen, which lead to photochemical O_3 production during the day and O_3 titration at night. Moreover, ozone loss due to dry deposition might also play a role. In contrast, both the PF data as well as the ^{222}Rn filtered data, which essentially exclude continental/urban influences, give rise to a much smaller diurnal cycle (amplitude < 1 ppb O_3) maximizing between 12:00 and 15:00. This is in accordance with a low NO_x environment.

Results obtained from passive samples collected at Cape Point do not discriminate between background and polluted episodes and hence reflect "all data". For the period June 2000–May 2002 these samples have shown O_3 levels ranging between 33 ppb (June 2000) to 12 ppb (December 2000) (Fig. 3). As with the active sampling, the peak values occur in the winter between May and July and the minimum values occur in mid-summer, December and January. The average ozone concentration provided by the passive sampling for the period is 24 ppb in fair agreement with the in situ measurements.

Marked seasonal and diurnal ozone variations are also evident over the Mpumalanga highveld. The spring

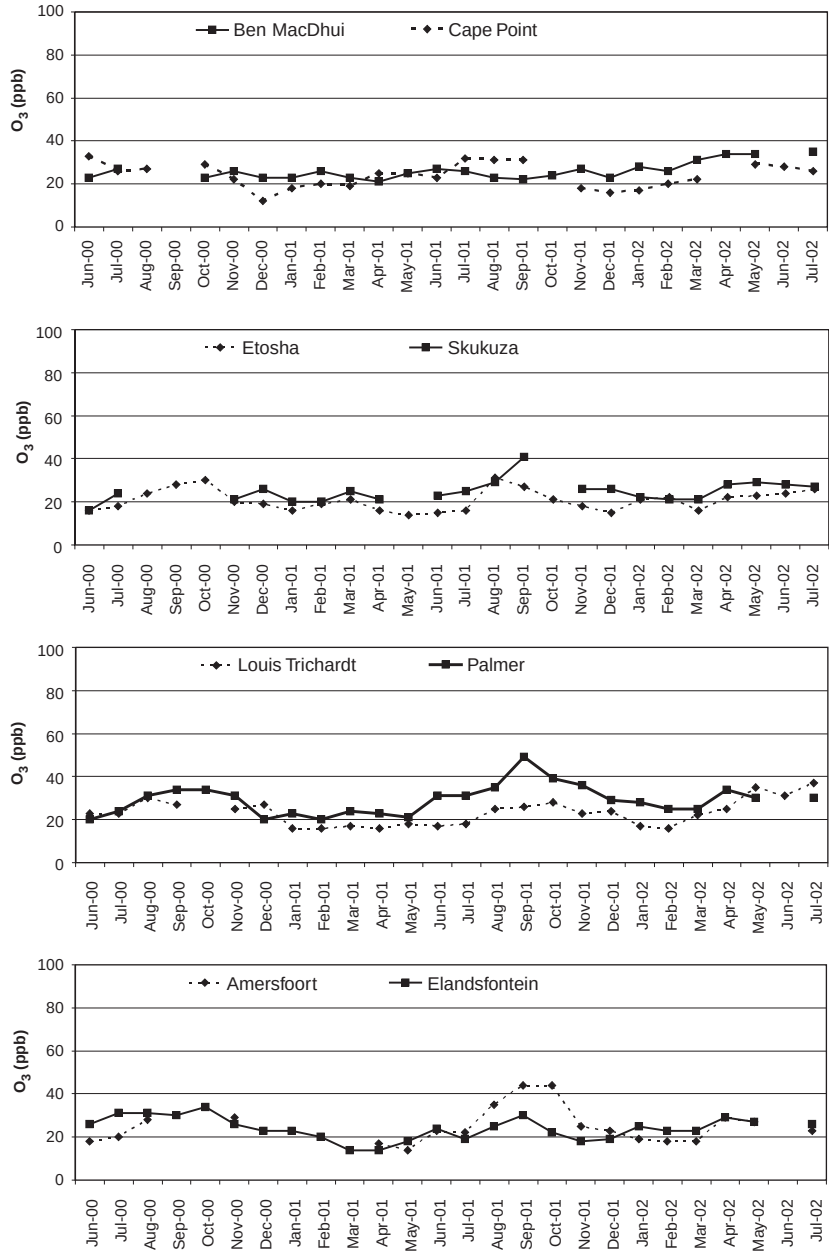

Fig. 3. Mean monthly ozone concentrations in ppb at the DEBITS sites for June 2000–May 2002 for the South African highveld (top) and the background sites (bottom).

and early summer maximum between August and October is observed at Bosjesspruit and at Amersfoort. As with Maun, this may be partly due to the regional scale trend in biomass burning. It may also be attributed to the region scale meteorology. The dominant winter anticyclone is responsible for pronounced thermally stable layers in the lower troposphere where accumulation and recirculation occur. The diurnal variation at these two stations is similar to that observed at Maun, increasing from a minimum near sunrise to maximum values in the early afternoon, and then decreasing steadily (Fig. 5). The mean hourly concentrations exceed 40 ppb at Amersfoort for approximately 7 h from about 10:00 until 17:00. The mean hourly ozone concentrations at Bosjesspruit approach this threshold in the middle of the day. Ozone concentrations are consistently higher at Amersfoort than at Bosjesspruit. With dominant northwesterly winds both sites are downwind

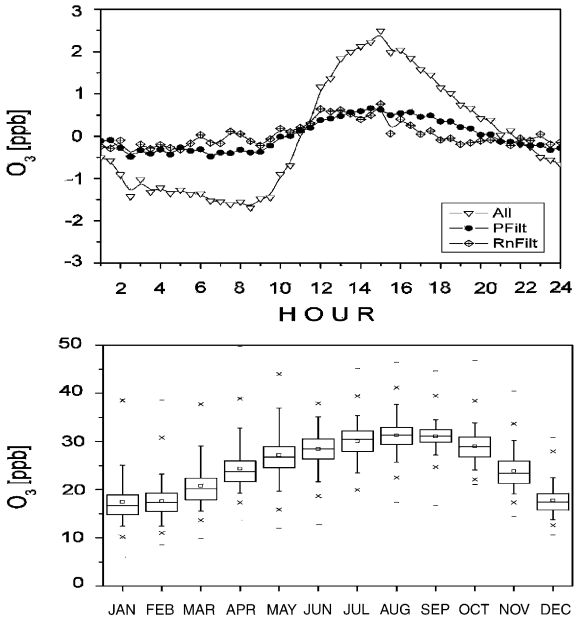

Fig. 4. Top: Monthly O_3 statistics at Cape Point based on half-hourly averages for all data from 1999–2001. The 25th and 75th percentiles determine the box; the whiskers indicate the 5th and 95th percentiles. Squares are the arithmetic mean and the crosses the 1st and 99th percentile. Bottom: Average diurnal variations (1999–2001) of O_3 at Cape Point as calculated from individual data points normalized to the respective daily mean and smoothed by 3-h moving averages. The triangles represent the all data set, the solid circles the statistically filtered (PF) data, and the diamonds the data filtered according to $^{222}Rn < 150\,mBq\,m^{-3}$.

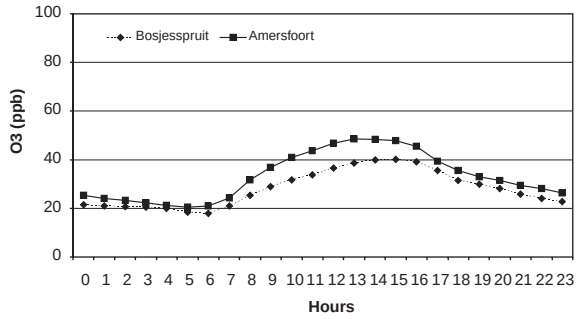

Fig. 5. Mean hourly ozone concentration in ppb at Bosjesspruit for July to December 2000 for all months in 2001 and at Amersfoort for August to December 2001.

of the precursor source area. Ozone has not had time to form at the closer located Bosjesspruit station compared with Amersfoort some 50 km further downwind.

The passive sampling programme at Amersfoort has not been as continuous as elsewhere with some data missing during the period June 2000–May 2002. Nevertheless, the springtime maximum shown by the active sampling in Fig. 5 is clearly seen in the passive data in the spring (September 2002) and early summer (November 2002) with lower concentrations during the rest of the year (Fig. 3). Due to the gaps in the passive data it is not meaningful to compare these with the active sampler as was done for Cape Point. At Palmer the spring time maximum is also clearly evident, reaching monthly average concentrations of more than 30 ppb in 2001 and more than 40 ppb in 2002. The highest ozone monthly average concentrations do not occur at Elandsfontein which is located closest to the industrial activity, but at Palmer which is located some 100 km from the main source region. The mean monthly ozone concentration near the source area at both Elandsfontein and Amersfoort is 25 ppb compared with the mean concentration of 29 ppb for the passive sampling period at Palmer. Skukuza is located below the escarpment and away from the direct influence of industrial sources. Here the annual average concentration is 25 ppb and the monthly average concentrations compare with the other background stations (Fig. 3). Biomass burning also influences the observed seasonal cycle at Skukuza.

The seasonal trend in ozone concentration of a maximum in spring that is observed at all stations in southern Africa other than Cape Point is also evident in the spring of 2000 and 2001 at Louis Trichardt, reaching mean monthly concentrations of 30 and 26 ppb, respectively. The monthly maximum of 34 ppb, however, occurs in May 2002 with the lowest values of about 14 ppb occurring in April and May 2002. At Ben MacDhui, the high-altitude station, ozone concentration ranges between 10 ppb in January 2002 to more than 30 ppb in April and May 2002. These are similar to concentrations measured at the other background sites, namely Etosha and Cape Point. The mean monthly ozone concentrations from the passive samplers at Louis Trichardt and Ben MacDhui are 23 and 24 ppb, respectively.

Dhammapala (1996) have compared mean monthly ozone concentrations measured with passive samplers at Elandsfontein and Cape Point with active sampling at the two stations. At Cape Point 48 months of data were compared, while 24 months of data were used at Elandsfontein. At Cape Point the mean monthly concentrations range between 12 and 33 ppb and passive and active sampling correlated with a coefficient of 0.7. At Elandsfontein the concentration range is greater, ranging from similar low concentrations to maximum values that exceed 40 ppb. Here a correlation coefficient of 0.8 was observed. The weaker correlation at Cape Point may be due to the fact that the inlets of the active and passive samplers are not at the same height. Ozone is not collected directly by the passive sampler, but rather by the overall oxidation potential which is proportional to the ozone concentration. An empirical

ratio of approximately 1:0.8 exists between ozone monitored with active and passive samplers and the reported passive sampler data are corrected by this factor. The ratio can be ascribed to wall effects in the passive sampler that results in ozone losses inside the sampler.

4. Discussion

The location of the various background monitoring sites in southern Africa allows a broad classification of the monitoring sites. Cape Point is a background site that is primarily influenced by maritime air masses and may therefore be classified as a background-maritime site. Etosha, Ben MacDhui, Skukuza and possibly Louis Trichardt are also background sites, but are influenced by air masses with continental origins. These may therefore be classified as background-continental sites. Maun is well removed from any direct anthropogenic sources, but is strongly influenced by biomass burning. The remainder of the sites are located on the industrialised South African highveld.

Anthropogenic emissions of ozone precursors resulting from transportation, domestic fuel burning, industry and mining occur throughout the southern African region. They are, however, dominated by the industrial and mining activities on the South African highveld and the Zambian copper belt (Fleming and van der Merwe, 2002), where emission occurs on a continuous basis. Greenberg et al. (2003) and Harley et al. (2003) showed that biogenic emissions of hydrocarbons from southern African vegetation are significant sources of these important ozone precursors. Most biogenic emissions are dependent on the solar cycle and the availability of moisture. As a result, they vary with season and time of the day, being higher in summer than winter and higher during the day than at night. Biogenic emissions also vary spatially and are typically higher in the more moist tropics and subtropics than in temperate latitudes, and higher in the moist eastern coastal areas than on the relatively dry interior plateau. In addition, biomass burning has been shown by Levine et al. (1996) and Silva et al. (2002) to be a major source of gases and aerosols in the southern African atmosphere. Biomass burning is seasonal and occurs almost exclusively during the winter and into spring, from July to September (Silva et al., 2002).

The synoptic scale meteorology of southern Africa is largely influenced by the semi-permanent mid-latitude high-pressure systems. The circulation is anticyclonic and subsident. The atmosphere is also characterised by a number of semi-permanent absolutely stable layers (Cosijn and Tyson, 1996). Pollutants are commonly trapped between these layers where they accumulate and may be transported great distances from the source, often recirculating over the source area (Tyson et al., 1996; Garstang et al., 1996). This situation provides an ideal environment and the time necessary for the formation of ozone.

Over southern Africa, the mean surface ozone concentrations exhibit strong seasonal and diurnal variations. At all sites—other than Cape Point—the seasonal maximum occurs in the spring months from August to October and sometimes extends into the early summer, due to biomass burning at this time of the year. The minimum occurs in December and January. In contrast, maritime air masses advected at Cape Point originate primarily from the SW Atlantic Ocean (NOAA CMDL back trajectories) and as such do not reflect the influences of biomass burning from Central Africa. The observed ozone seasonal cycle is therefore largely driven by the solar cycle within this low NO_x environment, giving rise to a winter maximum (July). In contrast, Etosha and Skukuza may be regarded as background stations that are mostly influenced by air masses of continental origin, or that have been modified by continental effects. As a result, the observed ozone at these two sites may be influenced more strongly by biomass burning and the annual maximum is shifted towards spring (September), coinciding with the observed peak in burning (Silva et al., 2003).

The highest hourly ozone concentrations occur over Botswana and the Mpumalanga highveld. In both regions the springtime maximum is between 40 and 60 ppb, but reached more than 90 ppb as a mean in October 2000. In these two regions, the monthly minimum is between 20 and 30 ppb. The mean daytime ozone concentrations at Maun and on the highveld reach 40 ppb as early as 10:00 and remain above this level for up to 10 h. At the background stations of Cape Point, Etosha and Louis Trichardt the maximum concentration is between 20 and 30 ppb and the minimums range between 10 and 20 ppb. Jonnalagadda et al. (2001) reported surface ozone concentrations over eastern Zimbabwe during the period 1991–1993 where they ranged between 37 and 49 ppb. From the results of the current and earlier work an area of relatively high ozone concentrations covering Botswana, Zimbabwe and the northeastern parts of South Africa is suggested.

A clear diurnal variation is observed at all sites with continuous monitoring with concentration increasing from a minimum near sunrise to a maximum in the afternoon, after which concentrations decrease again to the early morning minimum. At Maun and the two sites on the South African highveld, Bosjesspruit and Amersfoort, the daily range is marked, reaching 20–30 ppb (Figs. 2 and 5). The daily range at Cape Point for maritime air is considerably smaller at less than 1 ppb (Fig. 4). The observed diurnal variation in the surface ozone is primarily attributed to the photochemical process and the diurnal variation in the solar

cycle. The atmospheric chemistry of tropospheric ozone formation is complex. It is initiated by the photodissociation of NO_2 by solar radiation to form oxygen atoms, and subsequent reactions of these with hydrocarbons to form ozone in chain reactions (National Research Council, 1991).

5. Conclusion

Even though southern Africa is a region with numerous sources of ozone precursors and presents ideal conditions for the formation of ozone, measurements of surface ozone are limited to a few continuous monitoring and passive sampling monitoring sites. Surface ozone concentrations exhibit strong seasonal and diurnal variations with the maximum occurring in the months from August to November and the minimum in December and January. A strong diurnal variation also occurs with surface ozone concentrations increasing from a minimum near sunrise to a maximum in the afternoon, then decreasing again to the early morning minimum. The highest ozone concentrations occur over Botswana and the Mpumalanga highveld. In both regions the hourly springtime maximum is between 40 and 60 ppb, but reached more than 90 ppb as a mean in October 2000. In these two regions the mean monthly minimum is between 20 and 30 ppb. The mean daytime ozone concentrations in Botswana and on the highveld reach 40 ppb as early as 10:00 and remain above this level for up to 10 h. At the background stations at Cape Point, in Namibia and areas adjacent to the highveld the maximum hourly concentration is between 20 and 30 ppb with minimums between 10 and 20 ppb.

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