



PERGAMON



Atmospheric Environment 35 (2001) 777–786

ATMOSPHERIC
ENVIRONMENT

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Trace gas variations at Cape Point, South Africa, during May 1997 following a regional biomass burning episode

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Received 8 November 1999; accepted 24 April 2000

Abstract

During the continuous monitoring of atmospheric parameters at the station Cape Point (34°S, 18°E), a smoke plume originating from a controlled fire of 30-yr-old fynbos was observed on 6 May 1997. For this episode, which was associated with a nocturnal inversion and offshore airflow, atmospheric parameters (solar radiation and meteorological data) were considered and the levels of various trace gases compared with those measured at Cape Point in maritime air. Concentration maxima in the morning of 6 May for CO₂, CO, CH₄ and O₃ amounted to 370.3 ppm, 491 ppb, 1730 ppb and 47 ppb, respectively, whilst the mixing ratios of several halocarbons (F-11, F-12, F-113, CCl₄ and CH₃CCl₃) remained at background levels. In the case of CO, the maritime background level for this period was exceeded by a factor of 9.8. Differences in ozone levels of up to 5 ppb between air intakes at 4 and 30 m above the station (located at 230 m above sea level) indicated stratification of the air advected to Cape Point during the plume event. Aerosols within the smoke plume caused the signal of global solar radiation and UV-A to be attenuated from 52.4 to 13.0 mW cm⁻² and from 2.3 to 1.3 mW cm⁻², respectively, 5 h after the trace gases had reached their maxima. Emission ratios (ERs) calculated for CO and CH₄ relative to CO₂ mixing ratios amounted to 0.042 and 0.0040, respectively, representing one of the first results for fires involving fynbos. The CO ER is somewhat lower than those given in the literature for African savanna fires (average ER = 0.048), whilst for CH₄ the ER falls within the range of ERs reported for the flaming (0.0030) and smouldering phases (0.0055) of savanna fires. Non-methane hydrocarbon (NMHC) data obtained from a grab sample collected during the plume event were compared to background levels. The highest ERs (Δ NMHC/ Δ CH₄) have been obtained for the C₂–C₃ hydrocarbons (e.g. ethene at 229.3 ppt ppb⁻¹), whilst the C₄–C₇ hydrocarbons were characterised by the lowest ERs (e.g. *n*-hexane at 1.0 and *n*-pentane at 0.8 ppt ppb⁻¹). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Carbon monoxide; Methane; Ozone; Emission ratios; Biomass burning

1. Introduction

As one of the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) baseline stations, Cape Point (34°S, 18°E) is operated as a remote

monitoring site in the mid-latitudes of the southern hemisphere. At the station atmospheric trace gas data, representative of clean maritime air masses, are collected. Long-term measurements have been conducted at Cape Point since the end of the 1970s (Brunke and Allen, 1988; Brunke et al., 1990; Scheel et al., 1990; Brunke and Scheel, 1995). At times continental air, often influenced by local and/or regional pollution, is encountered at Cape Point (Brunke and Scheel, 1998). The related data are flagged and separated from the baseline data set, which is utilised for the determination of long-term trends as well as for

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the determination of seasonal variations of CO, O₃ and CH₄. However, certain pollution events are of air-chemical interest and warrant further investigation.

One such case has been a fire involving essentially Cape fynbos (indigenous shrub land comprising heath, protea and others), whose smoke plume passed over Cape Point during the night and morning of 6 May 1997. The primary intention of this paper is to present trace gas variations related to the biomass burning event as well as emission ratios of CO₂, CO, CH₄ and several non-methane hydrocarbons (NMHCs) prevalent in the smoke plume. The motivation for this study lies in the fact that the fire in the Villiersdorp district (southwestern Cape) presented an ideal situation for studying the trace gas emissions from a typical fynbos fire by sampling directly (several kilometres down flow) air from the plume at the Cape Point monitoring station. This happens to be the first study of its kind involving fynbos vegetation, which constitutes a major part of the vegetation of the Western Cape Province.

The results obtained here are compared to those obtained during intensive studies such as the SAFARI-92 field campaign for savanna fires (Lindesay et al., 1996 and references therein). The SAFARI-92 campaign as well as previous studies (Crutzen et al., 1979; Seiler and Crutzen, 1980; Greenberg and Zimmerman, 1984; Logan and Kirchoff, 1986; Fishman et al., 1991; Levine, 1991) have shown that biomass burning is a major source of CO, CH₄, NMHCs, CO₂ and O₃. In particular, the emitted CO, CH₄ and NMHCs can exert a significant influence on the chemical processes in the troposphere on both regional and global scales. For example, they affect the ambient levels of the hydroxyl (OH) radical, which, on a global scale, determines the atmospheric lifetime of a number of trace gases (Fehsenfeld et al., 1992; Jenkins et al., 1997).

2. The burning event

As part of their mountain catchment management strategy, Cape Nature Conservation authorities initiated a controlled burn on 5 May 1997, which started around 09:00 (local time) at the southwestern side of the Theewaterskloofdam, Nuweberg region, Villiersdorp district (34°05'S; 19°07'E). The Nuweberg region lies 66 km to the northeast from Cape Point (Fig. 1). A total area of 1000 ha comprising essentially 30-yr-old fynbos was burnt by Cape Nature Conservation. On the same day, a secondary burn was carried out by private landowners on a section of the Riviersonderend catchment within the same area. The material burnt comprised a 4–5 km strip of river reeds (palmiet type) as well as 50 ha of old pine plantation (dead and standing). However, the 30-yr-old fynbos region constituted about 95% of the total area burnt and can be considered as the primary source of the

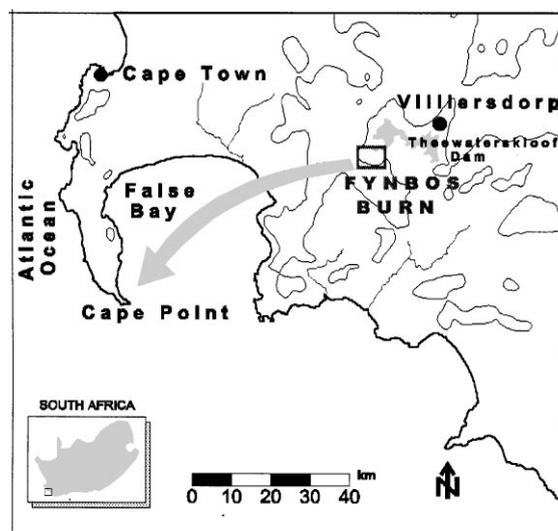


Fig. 1. Locality map indicating area of biomass burns and plume transport towards the Cape Point monitoring site.

smoke plume emitted from the fires (Mark Gentle, Cape Nature Conservation, personal communication). When reference in this study is made to the Theewaterskloofdam fynbos burn, it automatically implies that about 5% of the burnt biomass was not fynbos. The combined effects of the two fires, together with unique meteorological conditions (Section 4.1) were such that the fynbos smoke plume was still visible about 100 km to the southwest of the source two days later.

Fynbos is a term describing the sclerophyllous shrub land vegetation indigenous to the southwestern Cape Province of South Africa (Van Wilgen, 1985). The natural vegetation in this area belongs to Acocks veld types 69 and 70 (false Macchia), which occur in undeveloped mountain areas such as the Nuweberg region (Acocks, 1953). These two veld types are collectively known as mountain fynbos (Van Wilgen and Burgan, 1984). Whilst fire is a natural feature of the fynbos ecosystem (Kruger, 1977; Van Wilgen, 1982), most of the active management of conservation areas, such as the one described in this study, involves the periodic use of controlled burns (Kruger, 1982).

3. Experimental procedures

Continuous measurements of tropospheric trace gases, such as CO, CH₄, CO₂, O₃ and halocarbons, are being made at Cape Point as part of the station's WMO/GAW commitments. The analytical techniques used have been described elsewhere (Brunke et al., 1990; Scheel et al., 1990; Brunke and Scheel, 1995). The air to be analysed is drawn by means of metal bellows pumps through stainless

steel and Teflon tubing (4 and 6 mm internal diameter, respectively) attached to a 30 m high aluminium mast. At the end of 1996, a 4 m high mast consisting of glass tubing (50 mm ID) was installed on the instrument deck to supplement the O₃ measurements already made from the 30 m high mast (Brunke and Scheel, 1995). A high-volume fan draws the air through the glass tubing at a rate of 2 m³ min⁻¹ to minimise any possible O₃ loss due to wall reactions. The 4 and 30 m high air intakes represent altitudes of 234 and 260 m above sea level, respectively.

Besides the in situ measurements, flask samples are being collected for the analysis of NMHCs. Stainless-steel canisters are filled with ambient air under baseline conditions at a frequency of about 1–2 samples per month. They are sent to the Fraunhofer Institute in Garmisch, Germany, where they are being analysed for a suite of NMHCs using gas chromatography (GC) techniques (Matuska et al., 1986; Habram et al., 1998). Analyses usually take place within a period of two weeks after sampling. In addition to basic meteorological measurements (wind, pressure, temperature and humidity), solar radiation measurements are also performed. Global and diffuse radiation measurements are carried out by means of LICOL pyranometers, whilst UV-A (290–385 nm) is being recorded with an Eppley UV radiometer, which was calibrated by its manufacturer six months previously (November 1996). Two PC data logging systems are operative at Cape Point, gathering GC peaks and the other analogue voltage signals (e.g. meteorological parameters, O₃ and CO₂). In the latter case, data are available as 2 min averages. For the GC data, sampling intervals vary from 12 min (CO and CH₄) to 60 min (halocarbons).

4. Results and discussion

4.1. Meteorology, halocarbons and solar radiation

Due to offshore airflow and a nocturnal inversion over the southwestern Cape, the plume from the fynbos burn, described above, was observed at Cape Point during the night and morning of 6 May 1997. Two staff members of the station, who arrived there early on 6 May, also noticed a white to light brown coloured smoke plume. This plume, which substantially reduced the visibility, covered the whole area of the southern Cape Peninsula, stretching far afield across the sea. Some ash fall-out was seen around the station and a distinct, intense smell of burnt bush was noticeable as well. Ten-day isentropic back trajectories calculated by NOAA CMDL (Boulder, Colorado) (for details see Harris and Kahl, 1990) showed that on 5 May air moved in over the sub-continent from the southwest for a distance of about 300 km, then reversed its direction and passed over the fynbos fire region before it arrived at Cape Point from a northeasterly

direction. The arrow in Fig. 1 indicates the general air-flow path deduced from the above considerations. For the first 30 km the air flowed over mountainous terrain followed by a seaside resort (Gordon's Bay) and then across the sea (False Bay) before reaching Cape Point.

Another feature, which prevented the plume from the fynbos burn to be dispersed and diluted, was the occurrence of a nocturnal inversion over the Cape Peninsula during the night of 5 May. Data from a midnight radio sonde, launched at Cape Town international airport (46 km to the northeast of Cape Point), indicated a temperature inversion (lapse rate: 1.45°C per 100 m) at approximately 790 m above sea level (Fig. 2). The inversion also coincided with low-velocity winds (2.1 m s⁻¹ at 08:00; 6 May) as opposed to strong winds (22.7 m s⁻¹ at 19:00) on the previous day (Fig. 3). The wind direction recorded at Cape Point during the early hours of 6 May was from the northeast (Fig. 3), in agreement with the direction indicated by the trajectories. In addition, the decrease in relative humidity (RH) at the station from 85% (02:00 local time) to 30% (06:00) and its increase to 85% again at 15:00 is indicative of the passage of a dry continental air mass (Fig. 3). This offshore airflow, characterised by higher than normal temperatures for this time of the day, was not in phase with the usual diurnal cycle. The associated minimum of RH was lower than could be explained by the mere temperature change. Coinciding with the RH minimum and temperature maximum was a pressure low. The barometric pressure decreased by 5.2 hPa from 995.9 hPa on 5 May (11:00) to a minimum of 990.7 hPa on 6 May (05:00). Thereafter, it rose again to 995.6 hPa (24:00) the same day. As shown below, the occurrence of the highest CO, CO₂ and CH₄ levels observed at Cape Point on the 6th also took place shortly after 06:00 (Section 4.2).

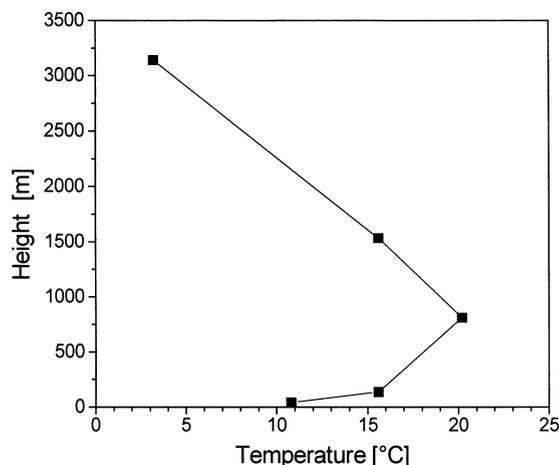


Fig. 2. Temperature profile above Cape Town international airport on 5 May 1997 (23:00).

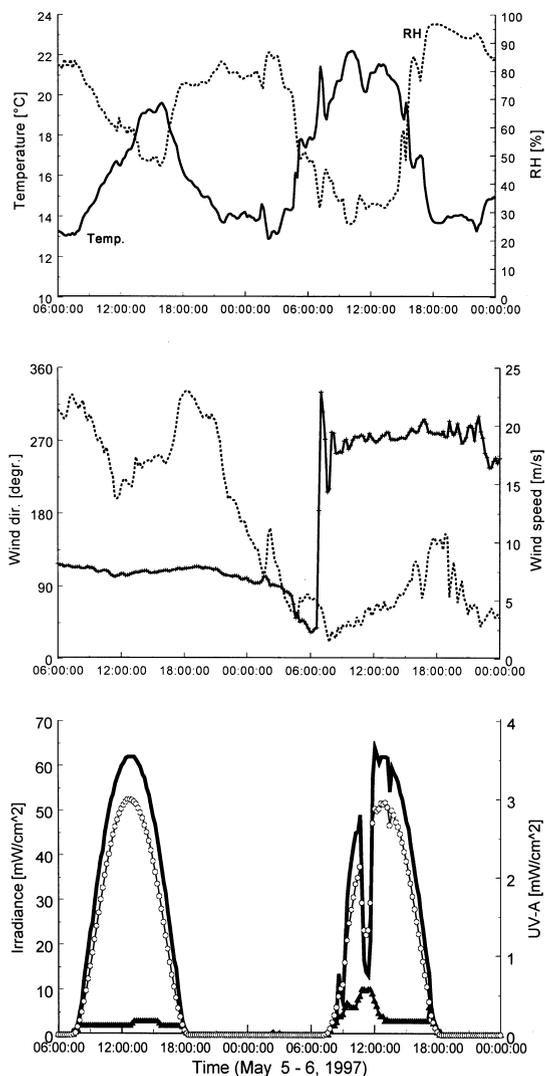


Fig. 3. Cape Point time series plot (5–6 May 1997) showing temperature, relative humidity, wind direction, wind speed as well as solar radiation in terms of total (solid line) and diffuse (triangles) irradiance and UV-A (open circles). The individual traces represent 12 min averages.

The prevailing conditions, as described, were such that they channelled emissions from the fynbos burn (which occurred at an approximate elevation of 788 m, still below the inversion layer) directly towards Cape Point 66 km away. The airflow reaching Cape Point under these conditions was practically free of contamination from the greater Cape Town industrial area. This is substantiated by the low variability and baseline levels of several halocarbon species, such as Freon-12 (CF_2Cl_2) and methyl chloroform (CH_3CCl_3) (Table 1), which can be sensitive indicators of anthropogenic pollution (Brunke and Allen, 1988). Observations over the past few

years have confirmed that urban pollution events occasionally experienced at Cape Point can be identified by means of significantly increased halocarbon values. Although halocarbon data are unavailable from 10:00 (6 May) onwards due to laboratory calibration experiments, which were, unfortunately, performed without realising the significance of this fynbos burn at that time, the actual measurements did cover the period of interest (02:48 till 09:36) during which the other trace species experienced maximum concentrations (Section 4.2).

On 6 May, the skies above the Western Cape were quite clear and sunny, with the exception of the region covered by the plume. Measurements of global and UV-A radiation showed periods during which the sunlight was strongly attenuated at Cape Point (Fig. 3) – a phenomenon not observed on days with moderate cloud cover. The most spectacular attenuation of solar radiation occurred between 10:40 and 11:50, which is about 5 h after the concentration maxima of several trace gases were observed (next section). Global radiation decreased from a value of 52.4 mW cm^{-2} (10:40) to a minimum of 13.0 mW cm^{-2} at 11:12. Diffuse radiation, in contrast, showed elevated levels amounting to 10 mW cm^{-2} at that time. This represents an increase by a factor of 2.3 relative to the previous day, when clear-sky conditions prevailed. In the case of UV-A, the signal decreased from 2.3 mW cm^{-2} at 10:40 to a minimum of 1.3 mW cm^{-2} at 11:12. However, when the period of significant absorption (10:00 till 13:00) is ignored, a comparison between the diurnal cycles of 6 May with that of the previous day shows good agreement, differing by an average value of merely 0.024 mW cm^{-2} (0.8% of the daily maximum). This implies that the turbidity per se, which was observed around the station for most of the day, was not the primary reason for causing global radiation and UV-A to be attenuated so strongly between 10:40 and 11:50. The reason for this significant reduction in sunlight is not clear, especially in view of the haziness, which prevailed practically throughout the greater part of the day in correspondence with the passage of the dry air mass as indicated by the RH data (02:00–15:00) on 6 May. It is therefore assumed that the aerosol loading within the smoke plume – not discernible to the human eye – reached its peak at the time of maximum attenuation of solar radiation (10:40 till 11:50). By the same token, it seems likely that the concomitant increase in diffuse radiation is related to an increase in light scattering from the aerosol particles at that time.

4.2. Variations of CO , CH_4 , CO_2 and O_3

Time series plots for CO , CO_2 , CH_4 and O_3 (5–6 May 1997), each having a temporal resolution of 12 min, are presented in Fig. 4. The entire pollution event at Cape Point lasted from 17:00 on 5 May until about midnight of the following day. CO , CH_4 and CO_2 showed highly

Table 1

Cape Point halocarbon data: from 09:00 of 5 May to 09:00 of 6 May (mixing ratios given in ppt)

	CFC1 ₃ (F-11)	CF ₂ Cl ₂ (F-12)	CCl ₂ FCClF ₂ (F-113)	CH ₃ CCl ₃	CCl ₄
Mean	266.8	527.7	86.5	80.5	105.4
SD	0.7	0.9	1.7	0.9	0.4

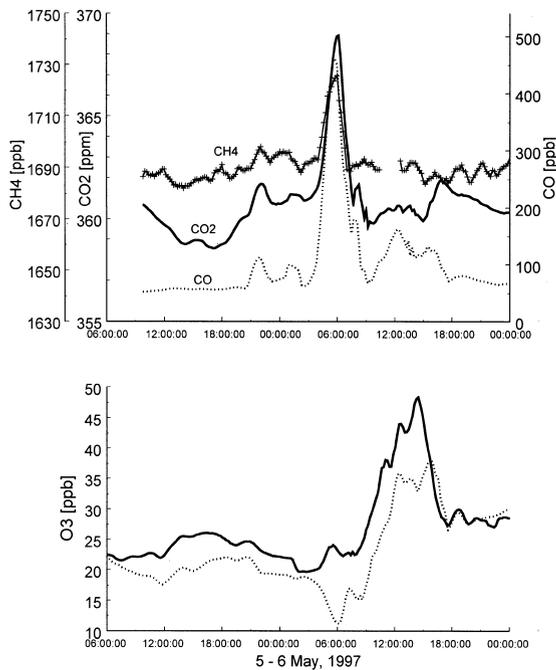


Fig. 4. Cape Point time series plot (5–6 May 1997) showing CO, CO₂, CH₄ and O₃. For O₃ the two lines represent different sampling heights. Solid line: 4 m, dotted line: 30 m above the station.

elevated concentrations over the same 7-h period as well as reaching peak concentrations concurrently on 6 May. Table 2 presents a comparison between background levels for CO, CH₄, CO₂ and O₃ (first week in May) with the maximum values recorded during the fynbos plume event as observed at Cape Point. The CO maximum amounted to 491 ppb, which is 9.8 times its background level of 50 ppb. The other gases (CH₄, CO₂ and O₃) showed smaller increases in mixing ratio relative to their background levels. However, compared to normally observed variations of CO₂ and CH₄, these increases are also remarkably high.

Noteworthy differences in O₃ mixing ratios (Fig. 4) were observed between the heights of 4 and 30 m above the station. This is in contrast to observations made under baseline conditions when O₃ values from the two intakes generally agree within 1–2 ppb. During the latter

half of 4 May and early hours of 5 May, for instance, the average difference in O₃ mixing ratios between the two air intakes was less than 1 ppb. This difference falls within the range of analytical uncertainty and indicates that differences due to instrumentation and/or air intake systems were insignificant. However, from about 07:00 (5 May) onwards, the O₃ levels at the two heights started to diverge. This lasted until about 18:00 on 6 May, when the O₃ difference between the two heights became negligible again (Fig. 4). During the period of maximum difference between the two heights (from 12:00 of 5 May to 15:00 of 6 May), the average O₃ level was 25.0 ± 4.4 ppb at 4 m above the station and 19.7 ± 3.9 ppb at 30 m. Short-term differences up to 12.2 ppb have been observed.

A slight O₃ minimum (19.6 ppb) was recorded for the 4 m air intake at 03:00, whilst for the 30 m air intake the minimum was much more pronounced (10.5 ppb) and occurred 3 h later (06:00). A shorter time shift was observed for the O₃ maxima. Air sampled at 4 m above the station revealed a maximum (47.6 ppb) at 14:36, whilst O₃ in air from the 30 m intake peaked (38.2 ppb) about 1 h later (15:48; cf. Fig. 4). Although the time lag between distinct ozone variations in the air at the two heights is variable, there exists remarkable agreement in the fine structure. Cross-correlation analysis of the two data sets yielded maximum correlation ($r = 0.82$) for a time lag of 84 min. Taken together, these results point to small-scale inhomogeneity within the air column. This suggests that the air mass derived from the burn formed a wedge-shaped front with the upper layers being shifted forward relative to those closer to surface. Such a profile could have developed as the air moved across the Hottentots Holland Mountains (Fig. 1) causing the air at higher altitudes to flow somewhat faster, whilst the air at lower altitudes lagged behind due to topographical obstruction.

The O₃ concentrations shown in Fig. 4 reflect processes of both O₃ loss and O₃ production in polluted air. During the night and early hours of 6 May, while the concentrations of CO, CO₂ and CH₄ were reaching their maximum, the O₃ level measured at the 30 m air intake decreased to its minimum (10.5 ppb at 06:00). Generally, the nighttime loss of O₃ under these conditions could have been due to chemical destruction, notably NO titration, and heterogeneous reactions. However, the ozone

Table 2
Cape Point CO, CH₄, CO₂ and O₃ data: background and 6 May 1997

	CO (ppb)	CH ₄ (ppb)	CO ₂ (ppm)	O ₃ (ppb)
Maximum value on 6 May	491	1730	370.3	47
Background value for first week in May 1997	50	1683	358.4	25
Excess concentration above background	441	47	11.9	22

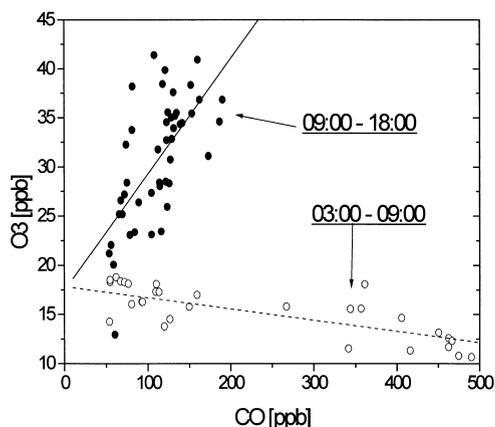


Fig. 5. Variations of O₃ (30 m air intake) versus CO for two different time periods during 6 May 1997. For $\Delta O_3/\Delta CO$, linear regression yielded slope values of -0.011 and $+0.12$.

concentrations being lower at 30 m above the station than at 4 m (Fig. 4) suggest that surface deposition was playing a minor role. After sunrise, the O₃ levels increased sharply, probably a result of photochemical reactions within the remaining pollution plume. As time progressed, the air mass gradually moved towards the east causing the pollution plume to diminish in intensity over Cape Point. The O₃ maximum observed at the 4 m mast was about 22 ppb above the average background (25 ppb O₃ for that time of the year). This is minimal in view of the anomalous O₃ levels, typically in excess of 80 ppb, reported from other biomass burning events (Fishman et al., 1991; Olson et al., 1996). Since the air mass which contained the highest trace gas mixing ratios (CO > 450 ppb) had already passed the station when photochemical activity was still absent (before sunrise), it is very likely that most of the O₃ generated within the fynbos smoke plume occurred further downwind towards the east of Cape Point. This is substantiated by the relationship of O₃/CO for two relevant time intervals (Fig. 5). In view of the high CO concentrations, the ozone loss was very small. Linear regression yielded a small negative slope value of -0.011 (Fig. 5). In contrast, from regression on the data from the period of obvious ozone production, a slope of 0.12 ppb O₃ per ppb CO was obtained (Fig. 5). This is still a small number in compari-

son with the $\Delta O_3/\Delta CO$ ratios (around 0.3) observed during episodes of urban pollution at Cape Point (Brunke and Scheel, 1998).

4.3. Emission ratios for CO and CH₄

Since absolute mixing ratios of trace gases within smoke plumes are a function of the degree of dilution within the plume, they are of little significance when comparing trace gas releases from different fires. Use is hence made of the concept of the emission ratio, ER (Andreae et al., 1996; Hao et al., 1996; Lacaux et al., 1996; Cofer III et al., 1996; Le Canut et al., 1996), which is defined as follows:

$$ER = \frac{([Y]_{\text{smoke}} - [Y]_{\text{background}})/([X]_{\text{smoke}} - [X]_{\text{background}})}{[X]_{\text{smoke}} - [X]_{\text{background}}} = \Delta Y/\Delta X,$$

where Y is the mixing ratio of trace gas of interest and X is the mixing ratio of reference gas (e.g. CO₂ or CH₄). In this study, ERs on a molar basis have been calculated by means of linear regression for the relationships $\Delta CO/\Delta CO_2$ and $\Delta CH_4/\Delta CO_2$ observed for the elevated trace gas levels during the morning hours of 6 May (Fig. 6). For the NMHCs the values from the single sample were put into relation with the average CH₄ and CO₂ values over 1 h bracketing the time of sampling (09:00).

For $\Delta CO/\Delta CO_2$ an average value of 0.042 ± 0.002 was calculated (95% confidence interval: 0.037–0.046). During the SAFARI-92 campaign, $\Delta CO/\Delta CO_2$ typically ranged from 0.03 to 0.08 (Table 3) with an average of 0.057 (Le Canut et al., 1996). In detail, Le Canut and co-workers found $\Delta CO/\Delta CO_2$ values of 0.064 for grasslands (fertile as well as infertile), 0.053 for Dambos (seasonally flooded saucer-like depressions, 50 m to 5 km in diameter) and 0.048 for savannas. One of the lowest ER values recorded (0.018) was that for sugar-cane fires (Table 3). When compared to the SAFARI-92 results, the $\Delta CO/\Delta CO_2$ value obtained here falls within the lower end of the scale, being marginally lower than the one (0.048) reported for African savanna fires (Table 3).

Similar calculations for $\Delta CH_4/\Delta CO_2$ yielded an ER of 0.0040 ± 0.0004 (95% confidence interval: 0.0032–0.0047). Cofer III et al. (1996) presented $\Delta CH_4/\Delta CO_2$ ratios for different ecosystems studied during the SAFARI-92

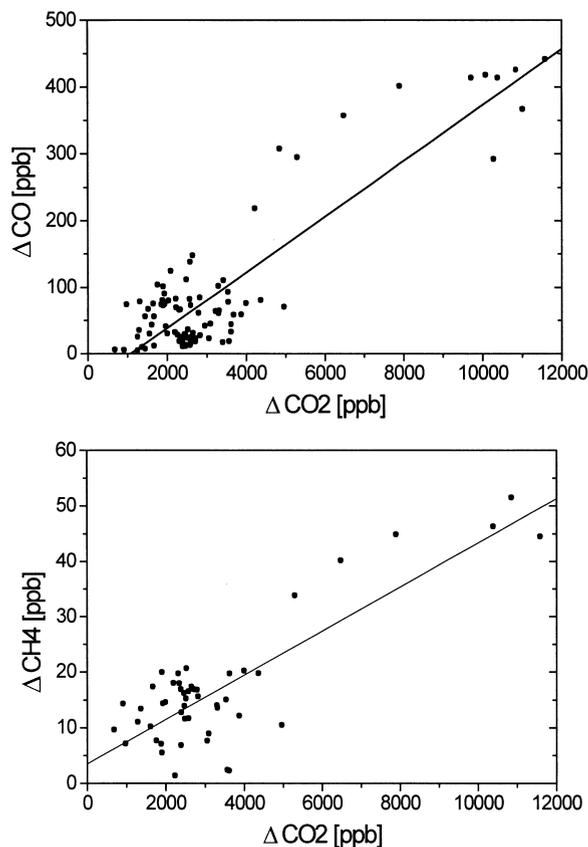


Fig. 6. ΔCO versus ΔCO_2 and ΔCH_4 versus ΔCO_2 for 5–6 May 1997. Upper plot: Slope of regression = 0.042, $N = 93$, $r^2 = 0.79$. Lower plot: Slope of regression = 0.004, $N = 50$, $r^2 = 0.70$.

campaign. They found a substantial difference between flaming and smouldering phases of fires. The smouldering phase ERs ranged from 0.0036 for wetlands, through 0.0055 (savannas) to 0.0122 for boreal regions (Table 3). The value for the fynbos burn considered here (0.004; cf. Fig. 6) falls well within the range observed for the flaming (0.0030) and smouldering phases (0.0055) of savanna fires (Cofer III et al., 1996). Low ERs are indicative of a high level of oxidation and hence efficient combustion (Cofer III et al., 1996) that normally prevails when burning biomass is well aerated and has a high surface area per unit mass, such as grasses and fynbos.

4.4. Non-methane hydrocarbons (concentrations and emission ratios)

NMHC species have been determined in six Cape Point grab samples collected under background conditions during the period from January until June 1997. In addition, a single grab sample was collected on 6 May at 09:00 (one day after the fynbos fire) at a time when the

Table 3
Emission ratios: CO and CH₄ with respect to CO₂

Campaign/ecosystem	$\Delta\text{CO}/\Delta\text{CO}_2$	$\Delta\text{CH}_4/\Delta\text{CO}_2$
SAFARI-92 ^a	0.030–0.080	
Grasslands ^a	0.064 ± 0.009	
Dambos ^a	0.053 ± 0.019	
Savannas ^{a,b,c}	0.048 ± 0.025	0.0055 ± 0.0022
Fynbos (this study)	0.042 ± 0.002	0.0040 ± 0.0004
Sugar cane ^d	0.018 ± 0.002	
Wetlands ^{b,c}		0.0036 ± 0.0013
Boreal regions ^{b,c}		0.0122 ± 0.0029

^aLe Canut et al. (1996).

^bFor smouldering phase.

^cCofer III et al. (1996).

^dAndreae et al. (1996).

smoke plume passed over the measuring site. NMHC data from half a year (6 samples) were selected to provide a suitable background reference level (maritime air) against which the data from 6 May could be compared (Table 4). Since the 09:00 flask sample was collected 3 h after the observed trace gas concentration maxima, the NMHC values reported here will probably not reflect the highest levels in the plume. Nonetheless, the $\Delta\text{NMHC}/\Delta\text{CH}_4$ values are meaningful, since concurrent measurements were still taken during the pollution event, for which we assume constant ERs. At the time of grab sample collection, the excess CH₄ and CO₂ levels above background amounted to 9.1 ppb and 1.74 ppm, respectively. These values were used to calculate the ERs.

As evident from Table 4, there is a prominent increase in almost all the NMHC compounds measured during the fynbos burn relative to the Cape Point maritime background. Ethene (2244 ppt) and ethyne (1074 ppt) showed particularly high mixing ratios in the 6 May sample. Following the C₂ aliphatic compounds, propene, *iso*-butene, and 1-butene had the highest mixing ratios in the C₃ and C₄ classes, respectively. Furthermore, the measurements indicate that for the C₂–C₄ aliphatic hydrocarbons, the unsaturated species were emitted in larger quantities. Emissions of these unsaturated compounds are of particular interest, because they are photochemically more reactive than their saturated counterparts. Of the aromatic compounds, benzene (250 ppt) and toluene (100 ppt) mixing ratios were 4–5 times higher than under baseline conditions. An additional characteristic feature of biomass burning is the relatively high level of isoprene (5–6 times the maritime background) that was recorded for the fynbos burn (Table 4). Isoprene is a common NMHC generally emitted along with the monoterpenes by many plants.

Non-methane hydrocarbon ERs, referenced to both CH₄ and CO₂, are summarised in Table 4. The $\Delta\text{NMHC}/\Delta\text{CH}_4$ ERs were selected for comparison, since

Table 4

Summary and comparison of non-methane hydrocarbon data: Cape Point (January–July 1997); Fynbos fire (6 May 1997) and SAFARI-92 (October 1992)

NMHC species	Carbon class	Cape Point marine air (Jan–July 1997)		Cape Point, 6 May 1997	Emission ratios		
		Mean value ^a (ppt)	SD (ppt)	Value (ppt)	($\Delta\text{NMHC}/\Delta\text{CH}_4$) SAFARI-92 (1992) ^b (ppt ppb ⁻¹)	Cape Point, 6 May (ppt ppb ⁻¹)	($\Delta\text{NMHC}/\Delta\text{CO}_2$) Cape Point, 6 May (ppt ppm ⁻¹)
Ethane	C ₂	350	75	778	74	47.0	246.0
Ethene	C ₂	157	43	2244	230	229.3	1199.4
Ethyne	C ₂	62	32	1074	73	111.2	581.6
Propane	C ₃	67	7	128	19	6.7	35.1
Propene	C ₃	72	24	399	68	35.9	188.0
<i>i</i> -Butane	C ₄	19	6	25	1.1	0.7	3.4
<i>n</i> -Butane	C ₄	29	9	61	3.4	3.5	18.4
1-Butene	C ₄	24	6	75		5.6	29.3
<i>iso</i> -Butene	C ₄	52	5	78	17 ^c	2.9	14.9
<i>cis</i> -Butene	C ₄	6	1	6	2.1	0.0	0.0
Isoprene	C ₅	14	4	92		8.6	44.8
<i>n</i> -Pentane	C ₅	16	3	23	3.3	0.8	4.0
<i>n</i> -Hexane	C ₆	5	3	14	0.9	1.0	5.2
Benzene	C ₆	45	26	250	20.6	22.5	117.8
Toluene	C ₇	23	18	100	10.2	8.5	44.3

^aThe calculated mean value was for six background samples.

^bHao et al. (1996).

^cThe combined ER for *iso*- and 1-butene is given for comparative purposes.

they were predominantly considered in the literature dealing with biomass burning in Africa. Emission ratios obtained during the SAFARI-92 campaign (Hao et al., 1996) indicate a rather good agreement with the 6 May data reported here, with the exception of ethyne, ethane and propene. Fig. 7 illustrates the correspondence between the two data sets. The C₂–C₃ compounds showed the highest absolute values and emission ratios (>47 ppt ppb⁻¹), with those for the C₄–C₇ species, such as *n*-hexane, *i*-butane, *iso*-butene and isoprene, ranging between 1.0 and 0.8 ppt ppb⁻¹, respectively. This is in agreement with the findings of Koppmann et al. (1997) that the emissions of NMHCs from biomass burning, with the exception of benzene and toluene, decrease with the number of carbon atoms in the aliphatic chain. The ER for ethyne within the fynbos plume exceeds that for savanna burns (SAFARI-92) by 1.5, whilst ethane and propene are merely half the value measured for savanna fires. Although this observation is tentative (one sample), the positive deviation of ethyne from the 1:1 line (Fig. 7) on the one hand and the negative deviation of both ethane and propene (similar magnitude) on the other may be significant. It could for instance reflect differences in fire type due to higher CO/CO₂ combustion within fynbos. However, this point needs to be substantiated in the future.

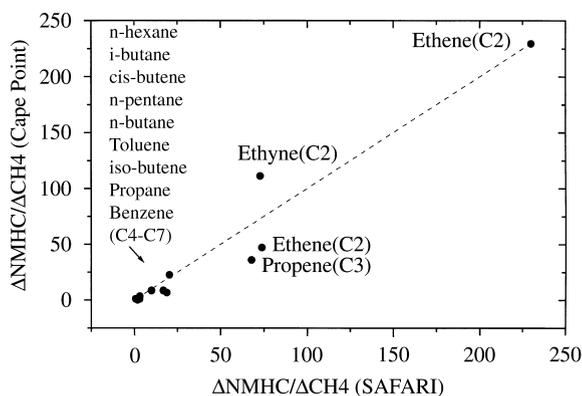


Fig. 7. Emission ratios $\Delta\text{NMHC}/\Delta\text{CH}_4$: Cape Point, fynbos (this work) versus SAFARI-92 (data from Hao et al., 1996). The straight line represents a 1:1 correspondence of the data pairs.

The NMHC ERs for benzene and toluene in this study (21.6 and 8.6) compare well with ratios obtained by Hao et al. (1996) in the SAFARI-92 campaign (20.6 and 10.2). This result strongly suggests no major input from industrial sources of the greater Cape Town area, as has also been shown by the halocarbon data. In the case of contributions from industrially polluted air, the respective benzene and toluene ratios would have differed significantly

from the SAFARI-92 observations. Furthermore, the components *iso*-octane and *n*-octane, which are common in South African automotive fuels, were not detectable in the flask sample taken on 6 May 1997. The close agreement found in NMHC ERs between the fynbos burn and those reported for savanna regions (SAFARI-92) (Fig. 7) suggests that the mechanisms responsible for producing C₂–C₆ trace gas emissions during combustion are similar for both ecosystems and that the fynbos burn might hence be classified as being of the ‘savanna type’.

5. Summary and conclusions

The smoke plume from a burning of 30-yr-old Cape fynbos vegetation (also comprising about 5% non-fynbos), which moved over Cape Point on 6 May 1997, yielded variations of several atmospheric parameters. It also provided the opportunity for assessing various important emission ratios (ER). Trace gas mixing ratios were compared to data observed at Cape Point during baseline conditions and to ERs from other biomass burning episodes reported in the literature.

The maximum aerosol loading within the smoke plume succeeded the trace gas maximum 5 h later and lasted for more than 1 h. It attenuated the global radiation signal to about 25% and that for UV-A to about 57% of the previous day’s level. The ratios $\Delta\text{CO}/\Delta\text{CO}_2$ and $\Delta\text{CH}_4/\Delta\text{CO}_2$ (0.042 and 0.0040, respectively) determined for the maximum trace gas concentrations during the morning hours of 6 May are one of the first results for fires involving fynbos plants, which are indigenous to the southwestern Cape. The relatively low $\Delta\text{CO}/\Delta\text{CO}_2$ ratio of the fynbos burn (0.042) is indicative of efficient combustion. Comparisons with other types of biomass fires have shown that this value falls within the range defined by savanna fires (ER = 0.048) on the high side and sugar-cane fires (ER = 0.018) on the low side.

Although the $\Delta\text{CO}/\Delta\text{CO}_2$ ratio indicates that the fynbos fire was characterised by a high level of oxidation, approaching that of sugar-cane fires, the $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratio (0.0040) obtained here suggests that the fynbos burn is indeed comparable in its trace gas emissions to those of savanna fires as reported for the SAFARI-92 campaign. The value falls between the ones for flaming (ER = 0.0030) and for smouldering phases (ER = 0.0055) of savanna fires. Likewise, ERs obtained for NMHC in relation to CH₄ (unfortunately only based on one sample) have shown remarkable agreement with the results obtained from savanna fires, especially for ethene (229.3 ppt ppb⁻¹), benzene (22.5 ppt ppb⁻¹), and toluene (8.5 ppt ppb⁻¹) but not for ethyne, ethane, and propene. The dominant region of biomass burning in Africa falls within the tropics and sub-tropics. Nonetheless, the southwestern Cape frequently experiences extensive mountain fires (involving primarily fynbos), especially

during the dry summer months (Van Wilgen, 1982, 1985; Van Wilgen and Burgan, 1984). The contribution made by such fires to the budgets of CO, CH₄, CO₂ and NMHCs, and thus to the hydroxyl concentration in this region, exceeds the scope of this study and still needs to be assessed.

Acknowledgements

Special thanks go to J.M. Harris (NOAA CMDL) for having made available 10-d isentropic back trajectories for Cape Point. We are also indebted to the chemical section of the Fraunhofer Institute in Garmisch for analysing the Cape Point flask samples. Furthermore, we would like to express our gratitude towards E. Mabile for technical support and assistance with processing of the raw data.

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