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## MEASUREMENTS OF LOWER TROPOSPHERIC OZONE AT MID-LATITUDES OF THE NORTHERN AND SOUTHERN HEMISPHERE

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### ABSTRACT

Ground-based measurements of ozone have been carried out at three stations in the German alps (47°N, 11°E, altitudes 740, 1776 and 2962 m a.s.l.) as well as at the coastal station Cape Point (34°S, 18°E). For the mountain sites (at 1776 and 2962 m), trend calculations based on monthly means have yielded O<sub>3</sub> growth rates of 0.8 and 0.9 ppbv yr<sup>-1</sup>, respectively, over the period 1978-91. Seasonally differentiated data sets have yielded higher rates for summer than for winter. The impact of near-ground photochemical O<sub>3</sub> production on the observed O<sub>3</sub> concentration is shown. No significant long-term O<sub>3</sub> trend has been observed at 740 m (valley floor) as well as at the southern hemispheric station Cape Point. Evidence exists for a close relationship between the amplitude variations of the annual cycles of O<sub>3</sub> and CO at Cape Point.

### 1. INTRODUCTION

The existence of a long-term rising trend of lower tropospheric ozone over large parts of the Northern Hemisphere seems to be evident (Penkett, 1991 and references therein). However, the observed growth rates differ considerably among the different sites of observation (see e.g. Low et al., 1992), which is at least partly due to specific characteristics of the individual locations, such as influences from local meteorology. It is assumed that enhanced photochemical ozone production in the lower troposphere is responsible for the increase in O<sub>3</sub> observed during the last decades (Logan, 1985). For the Southern Hemisphere, long-term O<sub>3</sub> records are only available from a few sites. At none of these sites has a significant increase in O<sub>3</sub> been observed. For Antarctica even a decrease in O<sub>3</sub> has been reported (Schnell et al., 1991).

We report here on in-situ measurements of ozone performed at three neighboring stations in the German alps (47°N, 11°E) as well as at a coastal station in the south-eastern part of Africa (34°S, 18°E). The alpine sites are located at elevations of 740 m a.s.l. (station Garmisch, on the floor of the valley), 1776 m a.s.l. (station Wank, ca. 1100 m above ground) and 2962 m a.s.l. (station Zugspitze, ca. 2200 m above ground). Details of the alpine sites and the O<sub>3</sub> measurements have been described by Reiter et al. (1987). Information on geographic location and instrumentation of the coastal station Cape Point has been given by Seiler et al. (1984) and Brunke et al. (1990).

### 2. NORTHERN HEMISPHERIC RESULTS

Figure 1 shows the monthly means of ozone for Zugspitze together with trend estimates. The time series is composed of seasonal variations, pronounced interannual variability, and a long-term trend. The rates of increase were highest during the period 1978-82. Thereafter the increase in O<sub>3</sub> was considerably slower. This is assumed to be at least partly related to changes in meteorological conditions, in particular to periods of enhanced cloudiness. The average growth rate for the period 1978-91 amounts to 0.9 ppbv yr<sup>-1</sup>. A time series of similar shape and comparable trend has been obtained for the station Wank (growth rate 0.8 ppbv yr<sup>-1</sup>). Near the ground, at Garmisch, no trend is indicated. Similar to Zugspitze (cf. Fig. 1) interannual variations with a period of 4 - 5 years are also present in the time series of the two lower-laying stations. The ozone concentrations observed on the floor of the valley are the result of source and sink relations that are strongly influenced by local meteorology. This is evidenced by Figure 2, where the average diurnal cycles for the individual stations are shown.

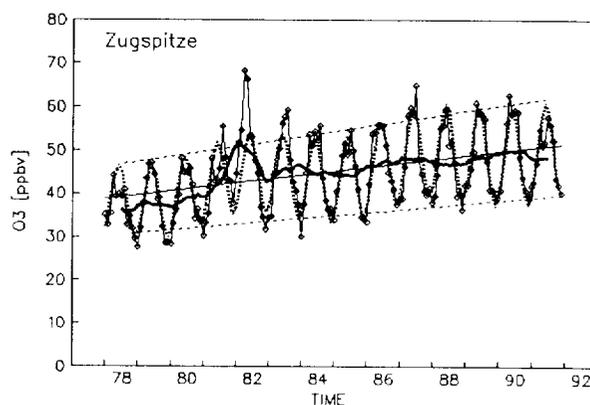


Fig. 1. Monthly mean values of O<sub>3</sub> at Zugspitze and 12-month moving averages (thick curve) together with trend estimates. The slope of the straight solid line corresponds to an average growth rate (1978-91) of 0.92 ppbv yr<sup>-1</sup>. The non-linear regression function (dotted line) indicates an increase in seasonal amplitudes with growth rates of 1.2 and 0.7 ppbv yr<sup>-1</sup> obtained for the summer maxima and winter minima, respectively (slope of dashed lines).

In contrast to the valley, at the station Zugspitze local influence on the diurnal shape of ozone is only observed during spring and summer. For most of the time, the O<sub>3</sub> concentrations at this site can thus be regarded as representative of ozone levels characteristic of the lower free troposphere.

A temporal increase in the seasonal amplitudes is expected as a consequence of the seasonal dependence of photochemical ozone production. In order to test whether such an increase was reflected by the monthly means, a non-linear regression function with a linear gain term for the amplitudes was applied to the data. The resulting least squares fit has indicated an increase in seasonal amplitudes (peak-to-peak) of 4.6 ppbv over the whole time period. Moreover, for Zugspitze the calculations have suggested an average cycling time of 5.6 years for the interannual variations.

For a more detailed study of the impact of lower tropospheric photochemical O<sub>3</sub> production at the mountain sites, trend estimates have been performed on seasonally differentiated percentiles (5th, 25th, 50th (=median), 75th, and 95th) using linear regression. Figure 3 summarizes the results. Under conditions of enhanced photochemical O<sub>3</sub> production, i.e. is for spring and summer, the high ozone concentrations, as characterized by the 95th percentiles, have been increasing at a rate which is nearly twice the rate of the low concentrations. Accordingly, the rate of increase estimated for high summer concentrations is considerably greater than the rate determined for high winter concentrations (Fig. 3).

In Figure 4 the seasonal variations of O<sub>3</sub> at Zugspitze are depicted. The maximum of the seasonal cycle is observed in spring, which is in agreement with observations reported from other European locations (cf. Logan, 1985). For the first half of the measuring period, the seasonal amplitude is smaller than for the second half. From a different approach this confirms the above finding that the amplitudes of the annual cycle have been increasing due to enhanced concentrations in spring and summer.

The strong impact of solar radiation and thus of photochemistry on the ozone concentrations can be seen from Figure 5. Daily maxima have been classified according to the relative sunshine duration (RSD). Under conditions of cloudy sky (RSD < 1 % of the time), the annual cycles at the mountain stations show similar levels.

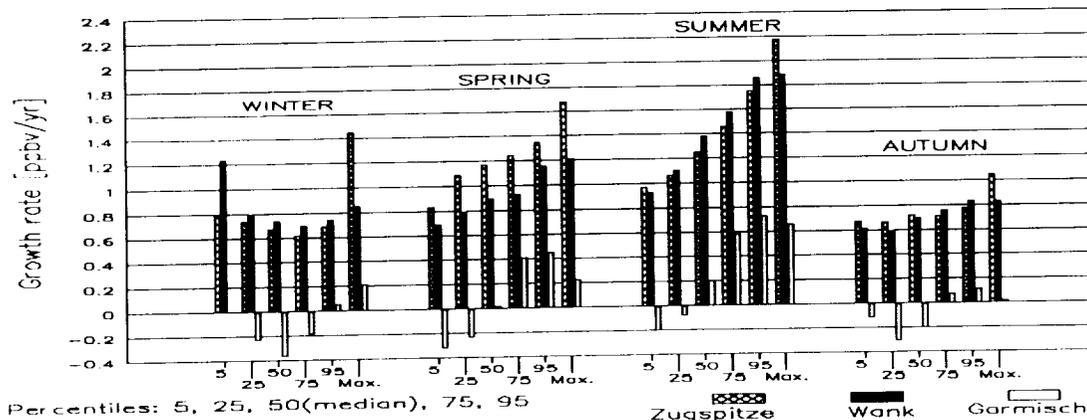


Fig. 3. Ozone trend (1978-90) at the mountain sites (Zugspitze, Wank) as a function of season and statistical parameters. For Garmisch (floor of the valley) none of the rates shown by the bars is statistically significant.

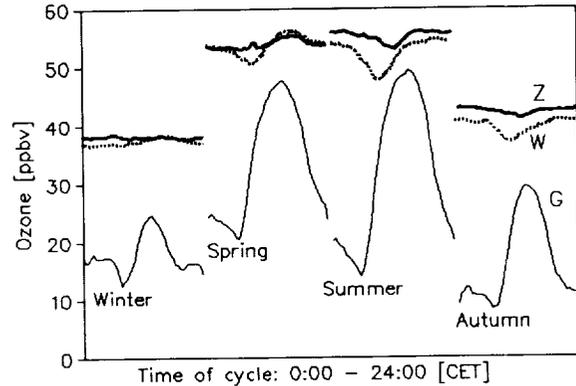


Fig. 2. Average diurnal cycle of O<sub>3</sub> (1986-88) at the stations Garmisch, Wank, and Zugspitze for the different seasons.

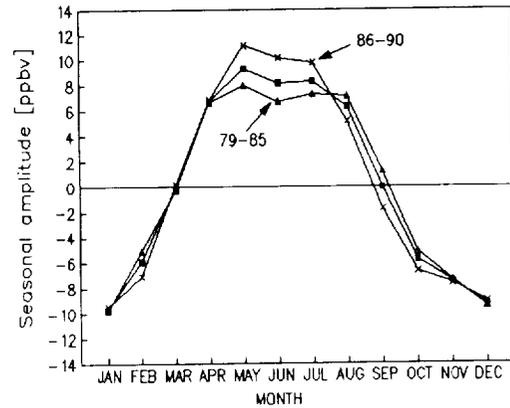


Fig. 4. Average seasonal variations (calculated from the difference between monthly mean value and 12-month moving average) of O<sub>3</sub> at Zugspitze for different time periods (79-90; 79-85 and 86-90).

Peak ozone levels in the valley (at Garmisch) are lower by about 12 ppbv. In contrast, under conditions of intense solar radiation (RSD > 80 %), the peak of the distribution for Garmisch even surpasses the one for Zugspitze, which reflects a significant contribution from locally produced ozone. For RSD > 80 %, however, highest O<sub>3</sub> concentrations are observed at Wank, i.e. at an elevation of about 1000 m above ground. This supports the finding from model calculations (McKeen et al., 1989) that optimum conditions for photochemical ozone production can be expected around this altitude.

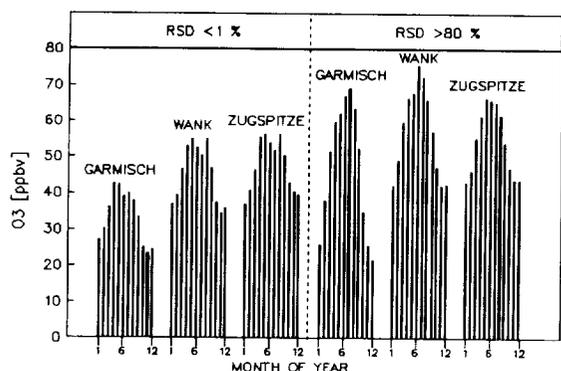


Fig. 5. Average annual distributions of daily O<sub>3</sub> maxima (1978-91) for low and high relative sunshine duration (RSD < 1 % and > 80 %).

### 3. SOUTHERN HEMISPHERIC RESULTS

The time series of O<sub>3</sub> at Cape Point as given by the monthly means (Oct. 82 - Dec 91) is shown in Figure 6. The shape is characterized by both seasonal cycling and great interannual variability. Maximum O<sub>3</sub> concentrations occur in austral winter (July) and minima in summer (January). The annual means of O<sub>3</sub> center around 21 ppbv with average seasonal amplitudes of about ±7 ppbv. So far, the monthly means do not indicate any long-term trend of O<sub>3</sub> at Cape Point. This is confirmed when the monthly means for the individual seasons are considered separately. However, in view of the strong interannual variability and the severe data gaps, the results obtained so far should be regarded as preliminary.

In Figure 7 the average annual cycle of ozone is shown. As is generally assumed for these southern latitudes, the cycle of surface ozone is mainly controlled by two types of processes, i.e. stratosphere/troposphere exchange (Liu et al., 1980) as well as photochemical ozone destruction (Fishman et al., 1979). The latter process, which is closely related to the annual cycle of solar UV radiation (Fig. 7), is assumed to lead to the O<sub>3</sub> minima observed around January. In contrast to the rather symmetric shape of the UV cycle, the ozone distribution with its maximum in July shows a slight shoulder between August and November.

The ozone distribution thus suggests that additional processes might contribute to its shape. One such process could possibly be biomass burning. This seems to be implicated by the following findings: Firstly, carbon monoxide, which has been measured at Cape Point since 1978 (Seiler et al., 1984; Brunke et al., 1990), shows an annual

distribution with a maximum around September/October (Fig. 7). The CO maximum thus coincides with the shoulder observed in the O<sub>3</sub> distribution during austral spring. After various interpretations have been put forward to explain the annual cycle of CO (Khalil and Rasmussen, 1984; Seiler et al., 1984; Fraser et al., 1986), recent publications have largely attributed the occurrence of the CO maximum to biomass burning (Heintzenberg and Bigg, 1990; Fishman et al., 1991, and reference therein). Secondly, Fishman et al. (1991), who studied upper tropospheric ozone from satellite data, have shown that ozone which originates from biomass burning also displays annual cycling with increasing concentrations from July to November. According to the results presented by Fishman et al. (1991), the rise of integrated O<sub>3</sub> in the troposphere over Cape Point partly parallels the shape of the CO distribution observed at ground-level, but is not in phase with the surface ozone observed at Cape Point (maximum in July). We thus speculate that the seasonal increase in ozone in the upper troposphere, which originates from biomass burning, does put its mark on the distribution of surface O<sub>3</sub> at Cape Point during the months August to November.

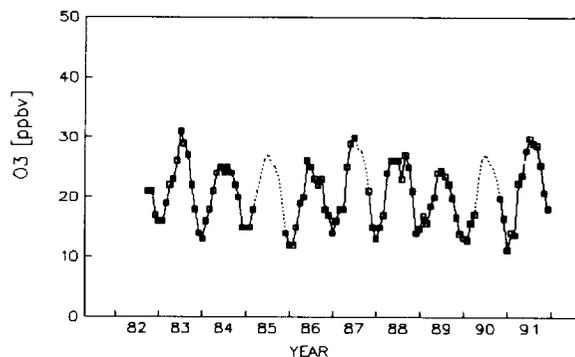


Fig. 6. Monthly means of O<sub>3</sub> as obtained for Cape Point (34°S, 18°E) between Oct. 82 and Dec. 91. Periods of data loss, which are due to instrumental failures, have been interpolated by values from the average annual cycle (dotted line).

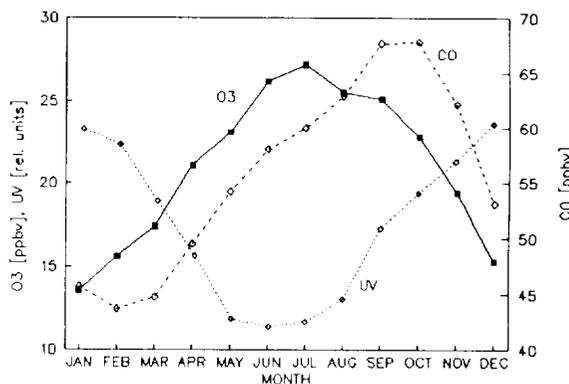


Fig. 7. Average annual cycles of O<sub>3</sub> (1983-91), UV radiation (1989-91) and CO (1979-91) at Cape Point.

At Cape Point, the annual peak-to-peak amplitudes of O<sub>3</sub> and CO (Fig. 8) show a close relationship (correlation coefficient of 0.9). This result has not yet been analyzed in detail; nonetheless it seems to support the view of either partly common sources or partly common transport mechanisms for O<sub>3</sub> and CO. Interestingly, the highest amplitudes were observed for El-Niño years, when among others the tropical meteorology and thus transport processes are strongly affected. Such a possible impact of El-Niño events on trace gas levels observed at Cape Point seems to merit further attention when more data are available.

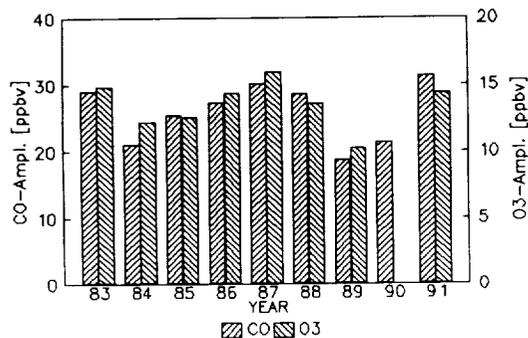


Fig. 8. Comparison between the annual peak-to-peak amplitudes of O<sub>3</sub> and CO at Cape Point. The data yield a correlation coefficient of 0.9.

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