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The seasonality of CO abundance in the Southern Hemisphere

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ABSTRACT

CO mixing ratios in air have been measured continuously at Cape Point (34°21′S; 18°29′E) between 1978 and 1981. The results show a seasonal variation of the CO mixing ratios with minimum values of 53 p.p.b.v. during January/February and maximum values of 87 p.p.b.v. during September/October. Short-term variations of CO mixing ratios in clean, undisturbed air were lacking, indicating that CO is well mixed in the Southern Hemisphere at latitudes of 20–40° S and that the observed seasonal variation is not due to temporal changes of local and regional source strengths. The seasonality of CO is explained by the seasonal variation of OH and by the north–south shift of the intertropical convergence zone. The agreement of CO mixing ratios measured at Cape Point and over the Southern Atlantic in 1971/1972 indicates that the southern hemispheric CO mixing ratios cannot have changed by more than 5–10% during the last decade.

1. Introduction

The global budget and distribution of atmospheric CO have received considerable attention during recent years, for three main reasons. Firstly, CO is one of the most abundant pollutants in the troposphere with mixing ratios up to a few p.p.m.v. in polluted continental air masses. The total CO emission into the atmosphere due to anthropogenic emissions accounts for more than 600–800 million metric tons per year (Seiler, 1974; Logan et al., 1981). Secondly, photochemical oxidation of CO is the main process involved in forming tropospheric O_3 (Fishman et al., 1979). Thirdly, the reaction between CO and OH represents the dominant sink mechanism for tropospheric OH which—because of its high reaction potential—plays a central role in atmospheric chemistry.

Any change in the tropospheric CO mixing ratios, e.g., by increasing emission rates of man-made CO, will therefore lead to a change in the distribution and abundance of O_3 and OH which in turn will have a significant impact on the tropospheric cycles of a variety of trace gases such as CH_4, non-methane hydrocarbons, CH_3Cl, CH_3CCl_3, $(CH_3)_2S$ and others. Some of these gases behave like a "greenhouse-gas" so that a change in the tropospheric CO may also have climatological consequences.

Most recently, a temporal increase of tropospheric methane concentration has been observed (Rasmussen and Khalil, 1981; Blake et al., 1982; Fraser et al., 1981) which is most likely caused by anthropogenic activities, e.g., by increasing cattle population, changes in agriculturally used areas etc. (Seiler, 1984). Because of increasing rate of biomass burning (Seiler and Crutzen, 1980; Crutzen et al., 1979) and increasing industrial activities (Seiler, 1974; Logan et al., 1981) which account for approximately 40% of the total global CO production, a temporal increase in tropospheric CO abundance can also be expected.

Measurements of the global distribution of CO have been carried out repeatedly during the last 12 years by different groups (Seiler, 1974; Wilkniss et al., 1973; Heidt et al., 1980; Seiler and Fishman, 1981). However, the present data basis is still too limited to give reliable information on the possible temporal change of CO mixing ratios in the troposphere. This is particularly true for the Southern Hemisphere where CO measurements have been carried out only sporadically. To obtain a better data basis, a program on monitoring CO in air at Cape Point, South Africa, was started in 1978 in cooperation between CSIR/South Africa and the Max-Planck Institute for Chemistry, Mainz, Germany. In this paper, the first data set obtained during a 3-year observation period is presented and discussed.

2. Measurement site

CO measurements were carried out at Cape Point, the most south-westerly point of South Africa (latitude 34° S; 18° E), located at the southern end of the Cape Peninsula which is a mountainous north–south stretch of country (Fig. 1) bounded by the Atlantic Ocean in the west and False Bay in the east. The highest elevation on the Cape Peninsula is Table Mountain, directly north of Cape Point at an altitude of 916 m at its northern edge. The elevations decrease towards the south and increase again to an altitude of 245 m at the southern tip of the Peninsula where the two-room building with the measuring equipment for recording the CO mixing ratios is located.

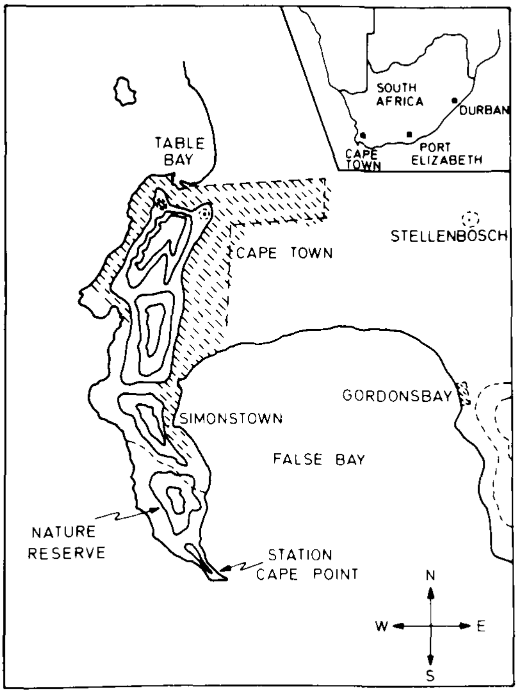

Fig. 1. Location of the measuring site, Cape Point, south of Cape Town, South Africa.

The southern part of the peninsula is a nature reserve; thus the measuring site is well protected from future urbanization and industrial activities. The nearest community is Simonstown (population about 20,000) which is approximately 19 km to the north of the station. Cape Town, at the foot of Table Mountain, is more than 40 km north of Cape Point. Automobile traffic of tourists to the nature reserve is stopped approximately 1 km north of the station. Because of prevailing southerly winds, the measuring site is shielded from these direct human interferences during most of the sampling time.

Electrical power for operating the CO instrument is drawn from the South African Railway system which runs generators near the measuring site to power the Cape Point light house. The generators supply a constant voltage of 220 V 50 Hz thus guaranteeing a regular CO record for 24 h a day. Contamination by the buildings, particularly by the exhaust gases of the Diesel engines, is avoided by running a 120 m long stainless steel tube (ID = 6 mm) from the instrument building down to the south-east slope to an altitude of 150 m above sea level or 70 m below the generator building. The air intake is approximately 2.5 m above ground which is high enough to prevent influences by CO production and destruction processes occurring at the soil surface. The flow rate through the sampling line was held constant at rates of 60–100 l h^{-1} corresponding to a residence time of the sampled air within the stainless steel tube of 2–3 min. Repeated measurements of CO in air taken directly above the building and in air drawn in through the sampling line did not show any significant differences. Interferences of the CO measurements by the relatively long sampling line can therefore be excluded.

The distribution of the wind vectors in the planetary boundary layer at Cape Point for summer and winter conditions is illustrated in Fig. 2. The frequency of the wind directions is calculated for eight selected sections and based on observations and wind data provided by the South African Meteorological Service. Following the wind rose shown in Fig. 2, the prevailing wind directions in summer are those between 90 and 270° account-

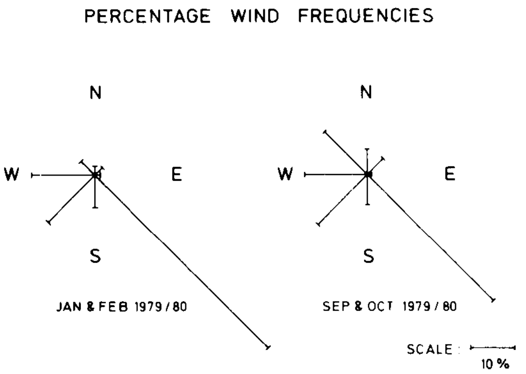

Fig. 2. Frequency of the wind vectors at Cape Point for January/February and September/October of 1978, 1979 and 1980.

ing for about 90% of the observation period. Also in winter, northerly winds, although more pronounced, do not occur during more than 20% of the time, indicating that the station at Cape Point is almost exclusively influenced by marine, unpolluted air masses. The dominant wind direction is south-east, indicative of the southern trade wind region.

3. Instrumentation

CO measurements were carried out using a CO instrument based on the mercury oxide vapor technique described by Seiler and Junge (1967) and Seiler et al. (1980). The instrument provides a continuous CO recorded with a retention time of approximately 15–20 s depending on the volume of molecular sieve used as a filter for hydrocarbons interfering with the CO measurements. The lower detection limit is less than 0.5 p.p.b.v. which is more than two orders of magnitude lower than the lowest CO value found at Cape Point during the 3-year observation period. The precision of the CO measurements at mixing ratios between 50 and 200 p.p.b. is ±1%. Perturbations by water vapor are eliminated by passing the air through two consecutive cooling traps having temperatures of 0 °C and −40 °C, respectively. The cooling traps and also the chemicals of the CO instruments are changed once a week.

The most crucial point in monitoring atmospheric trace substances over long periods covering several years is the absolute calibration and the stability of the calibration standard. Calibration of the CO instrument installed at Cape Point is carried out automatically once every 3 h using a calibration device in which a primary CO standard is diluted with CO-free synthetic air (80% N_2; 20% O_2) in two consecutive steps to mixing ratios of 50 p.p.v. and 90 p.p.v., respectively. The individual flow rates are measured using electronic flow meters and the flow rates are registerd allowing the calculation of the CO mixing ratio of the calibration gas introduced into the CO instrument.

The primary CO standard ($m = 10.7$ p.p.m.v.) is stored under high pressure (>20 bar) in a steel tank ($V = 50$ l). The stability of the CO standard was monitored for a period of 3 years before the tank was shipped to Cape Point. Tests carried out in our laboratory have shown that standards having CO mixing ratios ≥ 5 p.p.m.v. are stable as long as the pressure in the tank exceeds values of 20 bars. Below this pressure, the CO mixing ratios of the standards often change with time. To check the long-term stability of the primary standard, air samples were taken sporadically in Cape Point and sent to Mainz for analysis in our laboratory.

The CO mixing ratio of the standard used at Cape Point has been determined by comparison with the primary standard available in the laboratory in Mainz. This primary standard was prepared in 1969 and has been used for all CO measurements of this laboratory since that time. This procedure allows the comparison of all our CO data taken during the last 14 years and enables the determination of possible trends in tropospheric CO abundance.

4. Results

Fig. 3 shows a section of the CO record obtained between July 16, 1981 at 10 p.m. and July 17, 1981 at 7 a.m. The zero point of the CO instrument was measured once every 1.5 h and the calibration of the record using two calibration standards was carried out once every 3 h. The downward step of the zero point directly before the calibration is due to the higher H_2 mixing ratios of the outside air compared to that in the dilution gas (synthetic air) used in the calibration device.

The first section of the record gives an impression of the stability of the CO mixing ratios generally found in marine air masses. With

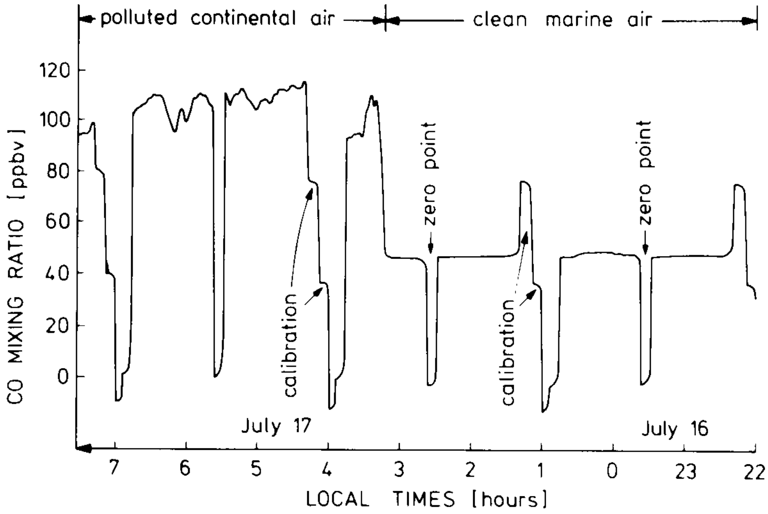

Fig. 3. Section of the original CO record obtained on July 16 and 17, 1981. Note that the time scale runs from right to left. The zero point is checked once every 1.5 h. The calibration of the instrument is repeated once every 3 h.

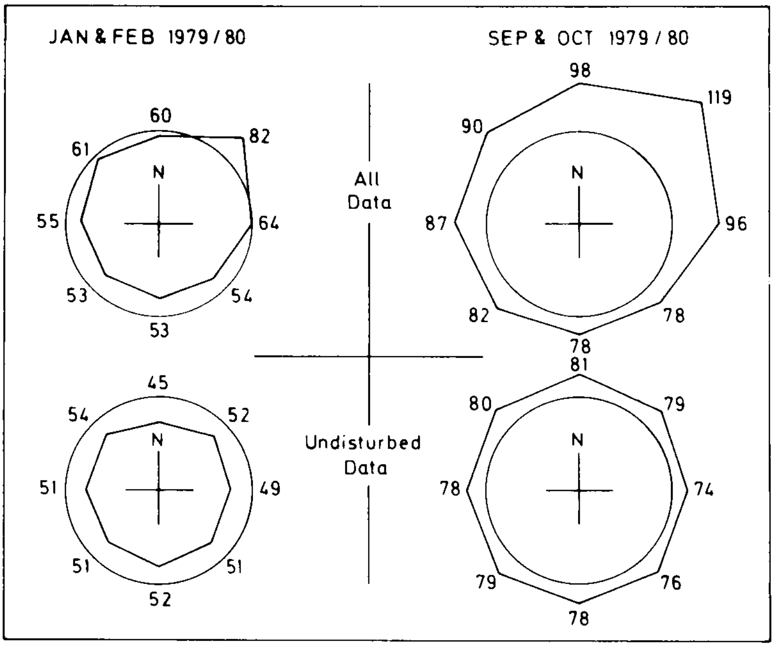

Fig. 4. Wind rose of the CO mixing ratios (p.p.b.v.) measured at Cape Point during January/February and September/October of 1978, 1979 and 1980. Figure represents CO mixing ratios averaged over the given time period and the 45° wind section. The upper part of the figure includes all CO data, the lower part neglects CO data obtained in polluted air masses.

southerly wind directions prevailing, the CO mixing ratios often stayed constant over a period of days and weeks. On a few occasions, however, the CO mixing ratios showed large variations which, in general, were accompanied by elevated CO values. An excellent example of these conditions is the second part of the CO record of Fig. 3 obtained at times after 3 a.m. when the CO mixing ratios increased erratically by more than a factor of two. These elevated CO mixing ratios combined with the large short-term variations have only been observed during short periods of several hours up to a few days and are always connected with northerly to easterly winds. During these meteorological conditions, the station was influenced by continental air masses which most likely were polluted by Cape Town and other communities located in the southernmost part of South Africa.

The pollution effect is confirmed by the observation of a high positive correlation between CO and condensation nuclei and also between CO and $CFCl_3$ measured simultaneously at Cape Point. Generally, the numbers of condensation nuclei increased dramatically from approximately 300 cm^{-3} with southerly winds to more than 7000 cm^{-3} with northerly winds. Correspondingly, the $CFCl_3$ mixing ratios increased by more than 40–50%. Periods with elevated concentrations of CO, $CFCl_3$ and condensation nuclei accompanied by large short-term variation of CO were therefore considered to be due to polluted air masses.

The influence of pollution can also be recognized from Fig. 4 showing the wind rose of the average CO mixing ratios measured in January/February and September/October of 1979 and 1980. These two periods were selected because they represent the seasons with minimum and maximum CO mixing ratios, respectively. Using all CO data obtained during these measuring periods, the CO mixing ratios show an asymmetrical distribution with higher CO values at wind directions between 280 and 90° (see upper part of Fig. 4). If we neglect the CO data showing significant short-term variations, the CO mixing ratios are independent of the wind direction (see lower part of Fig. 4). Apparently, the CO mixing ratios of unpolluted continental and marine air masses in South Africa at 30° S do not differ significantly. We have to point out, however, that the present data basis for unpolluted continental air masses measured at Cape Point is inadequate and that further measurements, particularly on the continental areas of South Africa, are urgently needed to confirm this observation.

The stability of the CO mixing ratios observed at Cape Point is illustrated in Fig. 5 showing the frequency distribution of the hourly averaged CO values measured in January/February 1979 and 1980. Data obtained in unpolluted and polluted air masses are shown by different symbols. Although the data included in Fig. 5 were obtained during 2 consecutive months and two different years with different weather conditions, the spectrum of the frequency distribution is very narrow with minimum values of 45 p.p.b.v. and maximum values of 60 p.p.b.v. Exceptions are those values observed during episodes with polluted air when the CO mixing ratios increased to values of more than 150 p.p.b.v. Using all 2784 individual data points representing hourly averages, the average CO mixing ratio for January/February is calculated to be 57 ± 18 p.p.b.v. If we omit the CO data obtained in polluted air, the number of individual data points decreases to 2360 and the average CO mixing ratio reduces to 53 ± 5 p.p.b.v. Similarly, the average CO mixing ratio observed in October/November (see Fig. 6) reduces from 86 ± 23 p.p.b.v. to 79 ± 7 p.p.b.v. when all data points are considered for unpolluted air masses. Thus, the variability of the CO mixing ratios in unpolluted air at Cape Point is less than ±10% which is surprisingly low if one considers the relatively short residence time of CO of 1 to 3 months at these latitudes. Applying the empirical relationship between the variation (σ) of the mixing ratios of a trace substance and its residence time (τ) in the troposphere.

$$\sigma \times \tau = 0.14$$

as proposed by Junge (1974) and using CO residence times in the order of 1 to 3 months, one should expect variations of the CO mixing ratios which are a factor of 4 to 10 higher than actually observed at Cape Point.

A distinct seasonal variation is observed in the CO mixing ratios which is illustrated in Fig. 7 for the time period between 1978 and 1981. Each value represents the average monthly CO mixing ratio. The seasonal variations recurred regularly during the 3-year observation period with minimum values of 50–55 p.p.b.v. from January to March which is the southern hemispheric summer/fall. The highest

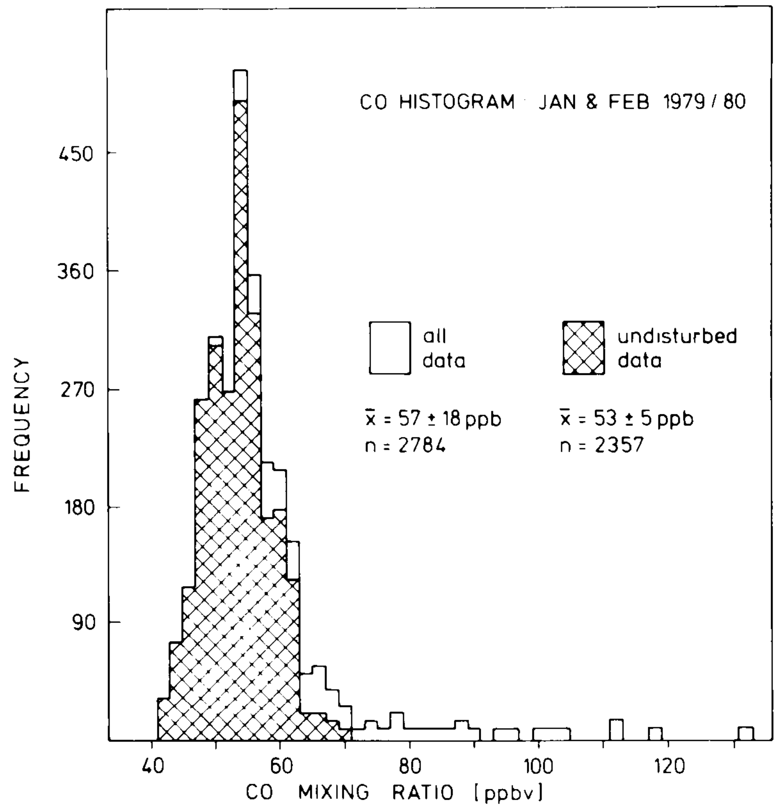

Fig. 5. Frequency distribution of hourly averaged CO values measured in January/February 1979 and 1980.

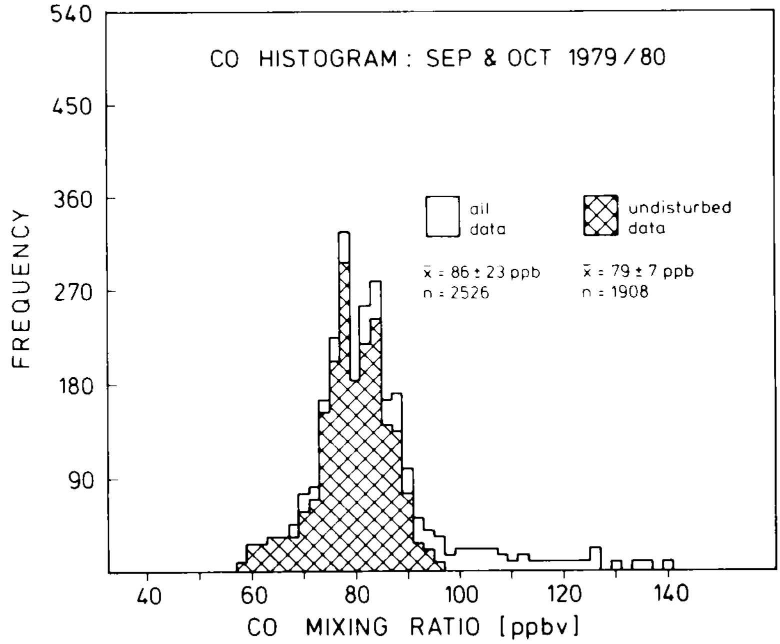

Fig. 6. Frequency distribution of hourly averaged CO values measured in September/October 1979 and 1980.

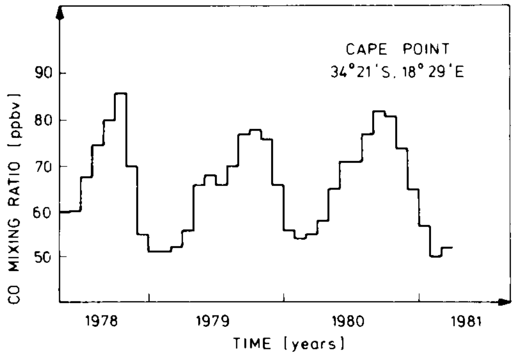

Fig. 7. Seasonal variation of the monthly average CO mixing ratios obtained from continuous CO record at Cape Point.

CO values were observed during winter/spring when the monthly average CO mixing ratios varied between 78 and 86 p.p.b.v. Interestingly, the pattern of the seasonal CO variation shows a slow increase of the CO mixing ratios from March to September and a sharp decrease from October to January which is readily reproducible during the whole observation period. Averaging the CO data obtained during the 3-year period results in a seasonal CO variation with a maximum value of 80 p.p.b.v. in spring and 53 p.p.b.v. in fall. The annually averaged CO mixing ratio accounts for 66 p.p.b.v. It is noteworthy that a similar seasonal variation has also been observed in the northern hemisphere at Mauna Loa Observatory (19.5° N), but with a phase shift of approximately 6 months (Seiler et al., 1976).

Comparable CO data sets for the southern hemisphere are rare. Seiler (1974) reported average CO mixing ratios of 50 p.p.b.v. measured during a shipboard cruise over the South Atlantic and South Pacific at 40–63° southern latitude during the period December to March 1971/1972. Further CO data were obtained by this laboratory during three cruises between Hamburg, Germany and Buenos Aires or Montevideo (30° S) which showed CO mixing ratios averaged over 20–40° southern latitudes of 83 p.p.b.v. for October 1977, 80 p.p.b.v. for November/December 1978 and 72 p.p.b.v. for October/November 1980. Seiler and Fishman (1981) reported CO values of 74 p.p.b.v. for the lower troposphere at 20–40° S. The latter values were obtained from aircraft measurements in July/August 1974 over the southern Pacific near the west coast of the South American continent and showed a constant CO distribution with altitude south of 20° S. Heidt et al. (1980) found CO values of 57 and 56 p.p.b.v. at 5 km altitude during the GAMETAG-flight over the middle of the Pacific Ocean (25–36° S) on May 7 and 11, 1978, respectively. Most recently, Crutzen et al. (1984) found CO values of 75–85 p.p.b.v. in the free troposphere above the planetary boundary layer over the South American continent at 5° S and 60° W during September. CO measurements carried out at the Antarctic station MOLODYZHNAYA using spectroscopic methods indicate CO values of 40–55 p.p.b.v. for the total troposphere during December 1977 to March 1978 (Dianov-Klokov and Yurganov, 1981). Although the CO data summarized above were obtained at different latitudes and longitudes of the southern

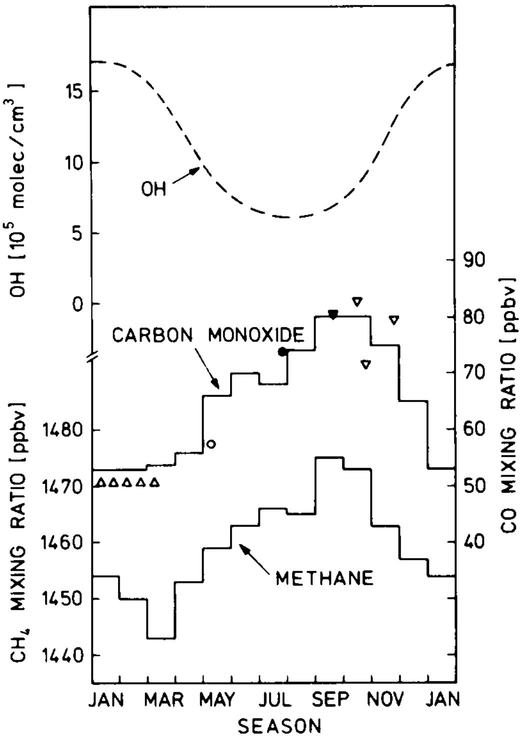

Fig. 8. Average seasonal variation of CO mixing ratios measured at Cape Point between 1978 and 1981. The figure also includes the seasonal variation of CH_4 (Fraser et al., 1981), the seasonal variation of OH (calculated from data published by Logan et al., 1981, and Crutzen, 1982) and data on individual CO measurements by Seiler, 1974, (△), by Heidt et al., 1980 (○), Seiler, unpublished values from marine expeditions (▽), Seiler and Fishman, 1981, (●) and Crutzen et al., 1984, (▼).

hemisphere and also during different years, the values agree reasonably well with the seasonal variation observed at Cape Point (see Fig. 8).

5. Discussion and conclusion

The good agreement of the CO mixing ratios obtained at Cape Point with CO mixing ratios measured by other groups in the southern hemisphere at different latitudes, longitudes and altitudes (see Fig. 8) clearly demonstrates that the observed seasonal variation is a general phenomenon for unpolluted southern hemispheric air.

CO records obtained in unpolluted air did not show short-term variations and were independent of the weather conditions, e.g., wind speed and wind direction, indicating that CO is well mixed with respect to latitude and altitude in the southern hemisphere south of 20°. The same conclusion was drawn earlier by Seiler (1974) based on a 3-month continuous CO record measured on board RS "Shackleton" over the South Atlantic Ocean at 40–63° S which showed even smaller variations of the CO mixing ratios in air. The assumption of a uniform distribution of CO in unpolluted southern hemispheric air is in agreement with the observation of almost constant CO mixing ratios over large areas of the Atlantic (Seiler, 1976) and Pacific Oceans (Wilkniss et al., 1973) and is also consistent with the observation of constant CO mixing ratios with altitude in the southern hemispheric troposphere south of 20° S (Seiler and Fishman, 1981). The lack of short-term variations of the CO mixing ratios and the short residence time of CO with values varying between 1 and 3 months also indicates that the sources and sinks responsible for the observed seasonal variation at Cape Point must be widespread and cannot be of local or regional origin.

Because of the strong seasonal variation, a temporal trend of CO mixing ratios in the southern hemispheric troposphere cannot be deduced from the 3-year CO record at Cape Point. Of great importance, therefore, are CO measurements carried out on board RS "Shackleton" over the South Atlantic which showed CO mixing ratios of 50 p.p.b.v. during an observation period between December 1971 and March 1972 (Seiler, 1974). This value compares very well with the CO value of 53 p.p.b.v. observed during the same season in 1978–1981 at Cape Point. Since both CO data sets are based on the same CO standard and were obtained from continuous records over a period of at least 2 months using the same measuring technique, we conclude that the CO mixing ratios of the southern hemispheric troposphere may not have changed by more than a few p.p.b.v. or 5–10% during the last decade.

It is most interesting that a seasonal variation has also been observed for southern hemispheric CH_4 (Fraser et al., 1981) whose pattern compares excellently with that of the CO variation. As can be seen from Fig. 8, both gases show similar concentration patterns and reach their maxima or minima at comparable time periods. The CO and CH_4 seasonal variation is anticorrelated with the seasonal variation of the 24 h average tropospheric OH number densities for the southern hemisphere and latitudes between 20 and 40° S. The OH number densities given in Fig. 8 were calculated from values taken from Logan et al. (1981) and Crutzen (1982) who have calculated the two-dimensional distribution of OH using photochemical models. According to these authors, the OH number densities are uniformly distributed with altitude in the troposphere at 20–40° S. Using a one-dimensional model, Logan et al. (1981) calculated the maximum noon value of OH for the 20–40° latitude belt to be 62×10^5 mol cm^{-3} for January and 32×10^5 mol cm^{-3} for July which corresponds to a 24-h average OH concentration of 18 and 8×10^5 mol cm^{-3}, respectively. Crutzen (1982), using a two-dimensional model, reports daytime average OH number densities of 23×10^5 mol cm^{-3} for February and 13×10^5 mol cm^{-3} for July, which, on a 24-h basis corresponds to OH values of 14×10^5 mol cm^{-3} and 5×10^5 mol cm^{-3}, respectively. Considering the great uncertainties involved in the model calculations, these figures agree well with those calculated from the data reported by Logan et al. (1981).

It should be noted that the calculated OH figures do not take into account the possible influence of aerosols and clouds on the average OH concentration, which, according to Logan et al. (1981), may cause a reduction of 23% in the average tropospheric OH number densities on a global scale. Unfortunately, the effect of clouds and aerosols on OH number densities in the 20–40° South latitude range in question is not known.

However, one would expect the actual reduction of the OH number densities in this particular region to be lower than that calculated for average global conditions since this latitude range is situated in the southern trade wind region of the southern hemisphere where cloud cover and aerosol concentration are minimal. Considering the large uncertainties involved in the model calculations of the OH number densities, use of the OH values without correction for the cloud/aerosol factor should have little influence on the interpretation of CO mixing ratios observed at Cape Point. Therefore, in this paper average OH number densities of 16 × 10^5 mol cm^{-3} for January and 6 × 10^5 mol cm^{-3} for July will be used. These OH figures result in average CO residence times of 1 and 3 months, respectively.

The positive correlation between CO and CH_4, as well as the anticorrelation between these gases and OH (see Fig. 8), suggests that the seasonal variation of CO may be due to the OH oxidation of CH_4 as the predominant CO source and the OH oxidation of CO as the main CO sink. In this case, the observed CO mixing ratios should be comparable to the steady state mixing ratios calculated from

$$m_{\mathrm{CO}} = \frac{K(\mathrm{CH_4})}{K(\mathrm{CO})}\, m_{\mathrm{CO_4}}$$

For both reactions, the currently recommended rate constants in the temperature range of 200–300 °K are $1.35 \times 10^{-3}\,(1 + P)$ cm^3 mol^{-1} s^{-1} for $K(\mathrm{CO})$ and $2.4 \times 10^{-12} \exp(-1710/T)$ cm^3 mol^{-1} s^{-1} for $K(\mathrm{CH_4})$ where P is the pressure in atmospheres (Hampson, 1980) and T is the temperature in Kelvin.

Applying the observed CH_4 mixing ratios in the southern hemisphere (Fraser et al., 1981) and using the average tropospheric temperatures for 35° S, the calculated steady state CO mixing ratios vary between 29 p.p.b.v. in January and 33 p.p.b.v. in August (Fig. 9). If we consider the possible loss of carbonaceous intermediates of the CH_4 oxidation chain such as HCHO or CH_3OOH by heterogeneous processes as quoted by Logan et al. (1981), the steady state CO mixing ratios decrease by 20% and should be in the range of 23 to 26 p.p.b.v. These values are significantly lower than the CO mixing ratios observed at Cape Point.

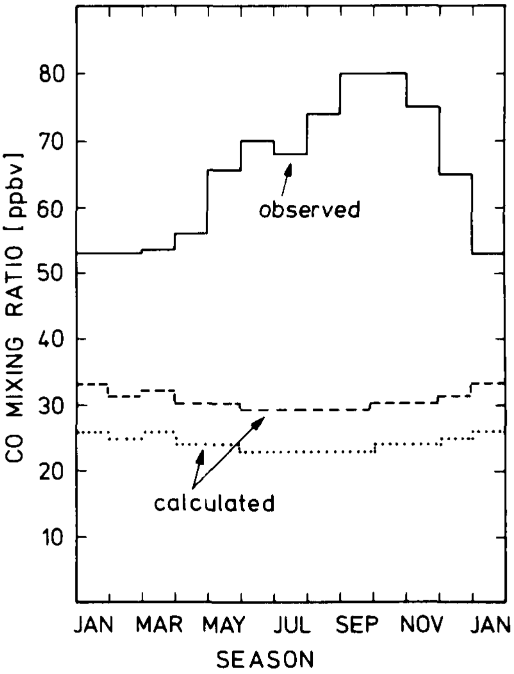

Fig. 9. Comparison between the seasonal CO variation actually observed at Cape Point (upper curve) and the calculated seasonal CO variation assuming steady state conditions between the photochemical CO oxidation and the photochemical CO production by CH_4 oxidation. The dashed curve assumes quantitative conversion of oxidized CH_4 into CO; the dotted curve assumes a 20% loss of intermediates of the CH_4 oxidation chain (e.g. HCHO, CH_3OOH).

The difference between observed and calculated CO mixing ratios and the lack of a pronounced seasonal variation of the calculated CO mixing ratios may be explained by the existence of CO sources in addition to the photochemical CO production. Potential sources of this "excess CO" are technological processes (such as automobiles, industry, home-heating), burning of biomass, photochemical oxidation of hydrocarbons as well as CO emissions by plants, CO formation in the ocean and transport of CO from the northern into the southern hemisphere by interhemispheric air mass exchange (Newell et al., 1974; Seiler, 1976; Seiler, 1978; Bauer et al., 1979; Logan et al., 1981; Crutzen and Gidel, 1983; Conrad et al., 1982). The source strengths of these processes in the southern hemisphere have recently been estimated to be 526–915 Tg yr^{-1} which exceed the photochemical

CO production of 302–405 Tg yr^{-1} by a factor of about 2 (Logan et al., 1981; Crutzen and Gidel, 1983). These given source strengths are annually averaged values. Information on the possible seasonal variation of the "excess CO" at 20–40° southern latitudes are not available but can be obtained from the difference of the photochemical CO destruction rate (i.e., reaction of CO with OH) and the photochemical CO production rate (i.e., reaction of CO by CH_4 oxidation) calculated for the different seasons. Based on CO and CH_4 data obtained at Cape Point and Cape Grim (Tasmania), respectively, and using average tropospheric temperatures as well as OH number densities (as given in Fig. 8), the potential tropospheric CO production by photochemical CH_4 oxidation at 20–40° southern latitudes is calculated to be 110×10^{-13} g cm^{-2} s^{-1} for summer conditions and 39×10^{-13} g cm^{-2} s^{-1} for winter conditions. The corresponding figures for the CO sink strengths are 177×10^{-13} g cm^{-2} s^{-1} and 107×10^{-13} g cm^{-2} s^{-1}, respectively. Subtracting these figures results in a CO production rate of the "excess CO" of about 70×10^{-13} g cm^{-2} s^{-1} which is independent of the season.

This result is unexpected since most of the CO sources of the "excess CO" are dependent on temperature, radiation intensities, and biological activities in the different ecosystems and thus should show seasonal variations. Summer maximum production rates should occur in summer for the CO emission by plants and oceans as well as for the CO production by the photochemical oxidation of natural hydrocarbons. Because of the seasonal CO variations in the northern and southern hemispheres, a variation is also expected for the transport of CO between the two hemispheres. With data on air mass exchange rates given by Newell et al. (1974) and with CO values measured in the northern hemisphere at Mauna Loa Observatory (Seiler et al., 1976) and in the southern hemisphere (see this paper), we obtain a net flux of CO into the southern hemisphere which accounts for 14×10^6 g s^{-1} in December/February, 7×10^6 g s^{-1} in March/May, 6×10^6 g s^{-1} in June/August and 3×10^6 g s^{-1} in September/November and thus again shows the maximum value during summer conditions. The CO formation by technological processes can be assumed to be independent of the season and the CO production by biomass burning should vary with wet and dry season in different regions. Summarizing the strengths of the individual CO sources, it is very likely that the integrated CO source for the southern hemisphere at 20–40° S shows a seasonal variation with maximum values during the summer period and minimum values during the winter period which is in contrast to the observed CO variation.

We therefore believe that there are still other processes influencing the absolute amount and seasonal CO variation observed at Cape Point. One possible process is the seasonal shift of the Intertropical Convergence Zone (ITCZ) showing its most northerly position in June/September and most southerly position in December/February. Fig. 10 illustrates the geographical position of the ITCZ over Africa and part of Asia (Tsuchia, 1972). During the southern hemispheric winter

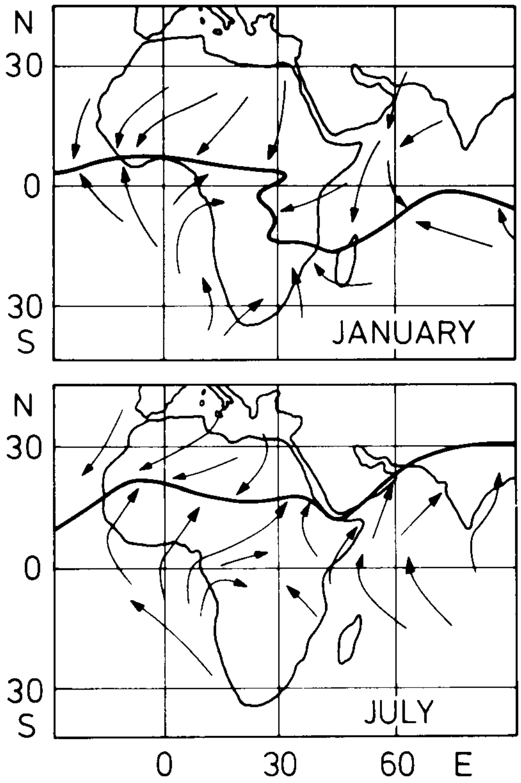

Fig. 10. Geographical position of the Intertropical Convergence Zone over Africa and Asia (after Tsuchia, 1972).

(i.e., June/September), the ITCZ is generally located north of the equator. In some cases, e.g., between 60–120° E longitudes, the ITCZ reaches 30° N so that during the winter season large parts of the East, e.g., India, share the air mass of the southern hemisphere. During the southern hemispheric summer (i.e., December/February), the ITCZ reaches the most southerly latitudes at Madagascar at 20° S. The shifting position of the ITCZ results in a strong seasonal variation on the land surface area of the southern hemisphere. Neglecting the ice-covered areas of Antarctica, the biologically active areas of the southern hemisphere vary between the seasons by more than a factor of 3 with a minimum during summer and maximum during winter conditions. Since most of the CO sources are of continental origin, the southern hemispheric CO source strength should show a similar seasonal variation with a minimum rate during summer and a maximum rate in winter which correlates very well with the observed seasonal variation of the CO mixing ratios observed at Cape Point.

Taking into account the fact that the biologically most productive areas are located near the equator and that the highest OH number densities are calculated for the tropical area, the north–south shift of the ITCZ will also have considerable impact on the abundance and distribution of a variety of other trace substances, e.g., CH_4 which are of biological origin and/or undergo photochemical production and destruction processes in the troposphere. Similarly, we also expect a seasonal variation of man's impact on the southern hemisphere since several countries with high population densities, e.g., India, Indonesia, parts of China, etc., are located in latitudes influenced by the shift of the ITCZ and thus emit their pollutants into southern hemispheric air during winter and into northern hemispheric air during summer conditions. Thus, the north–south shift of the ITCZ causes a seasonality of emission rates of a variety of trace gases having significant natural and anthropogenic sources in the tropical and subtropical regions. This seasonality of the source and sink strengths has so far not been considered in the present atmospheric chemical models.

Another process influencing the CO variation at Cape Point may be the transport within the southern hemisphere. This process is of particular importance for those stations located at latitudes south of 30° S where the land surface and thus the continental CO production is negligible. The oceanic CO source strengths, either by direct CO emission from the oceans (Conrad et al., 1982) or by CO formation of hydrocarbons emitted from the ocean (Lamontagne et al., 1974, 1975; Singh et al., 1978; Rudolph et al., 1982) are very small if compared with the total CO source strengths. Thus, the "excess CO" to balance the photochemical production and destruction of CO at 35° S must be advected from northerly latitudes. As pointed out by van Loon (1972), the cyclonic activity and thus mixing of air is more pronounced in the southern hemispheric midlatitudes during winter than during summer so that the higher CO mixing ratios from the continental tropical regions north of Cape Point should also be more efficiently transported southwards in July than in January. This effect will be intensified by the fact that the residence time of CO in January is significantly lower than in July so that a significant fraction of the CO produced in tropical areas at low latitudes is photochemically oxidized during the transport and may not reach Cape Point, particularly if one takes into account that the prevailing wind direction at this station is south-east to south-west.

Transport of CO from tropical continental regions may explain the observed seasonal variation of CO. However, transport is inconsistent with the lack of significant variations of the CO mixing ratios at Cape Point. In many cases, particularly during the southern summer conditions, the variability of the CO mixing ratios is identical with the precision of the CO instrument so that we can assume constant CO mixing ratios for periods of several weeks. During these periods, the CO mixing ratios are independent of wind speed and wind direction. If transport contributes significantly to the "excess CO" and if CO has residence times of 1–3 months in tropical regions, one should expect significant variations of CO mixing ratios of air masses reaching Cape Point, particularly because of changing weather conditions causing different pathways and transport times of the individual air masses. In addition, the air masses originate from different continental and marine areas with different CO source distributions and thus different CO mixing ratios.

The reasons for the lack of considerable variations of the CO mixing ratios at Cape Point remain unclear. One possibility might be the fact that during the summer period Cape Point is located at the northerly part of the Headley cell circulation. In this case, the air reaching Cape Point has not been in contact with continental areas for longer time periods so that the CO mixing ratios may have approached the steady state values determined by the photochemical CO destruction and production due to OH reactions with CH_4. This process would explain the lack of significant CO variations; however, it is in disagreement with the observation of CO mixing ratios of 53 p.p.b.v. which is about 2 times higher than the calculated CO mixing ratio assuming steady state conditions. It is therefore also possible that either the actual OH number densities in the southern hemisphere at 20–40° S are lower than presently estimated by Logan et al. (1981) and Crutzen (1982) or that the rate coefficient of the photochemical CO oxidation by OH might be lower than summarized by Hampson (1980), or that CO sources exist in the southern hemisphere which have not yet been identified.

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REFERENCES

Bauer, K., Seiler, W. and Giehl, H. 1979. CO Produktion Pflanzen (CO production by higher plants). *Z. Pflanzenphysiol. 94*, 219–230.

Blake, D. R., Mayer, E. W., Tyler, S. C., Makide, Y., Montagne, D. C. and Rowland, F. S. 1982. Global increase in atmospheric methane concentrations between 1978 and 1980. *Geophys. Res. Lett. 9*, 477–480.

Conrad, R., Seiler, W., Bunse, G. and Giehl, H. 1982. Carbon monoxide in seawater (Atlantic Ocean). *J. Geophys. Res. 87*, 8839–8852.

Crutzen, P. J., Heidt, L. E., Krasnec, J. P., Pollock, W. H. and Seiler, W. 1979. Biomass burning as a source of atmospheric gases CO, H_2, N_2O, CH_3Cl and COS. *Nature 282*, 253–256.

Crutzen, P. J. 1982. The global distribution of hydroxyl. In *Atmospheric chemistry* (ed. E. D. Goldberg). Dahlem Konferenzen: Springer Verlag, 313–328.

Crutzen, P. J. and Gidel, L. T. 1983. A two-dimensional photochemical model of the atmosphere II: The tropospheric budgets of the anthropogenic chlorocarbons, CO, CH_4, CH_3Cl, and the effects of various NO_x sources on the tropospheric ozone. *J. Geophys. Res. 88*, 6641–6661.

Crutzen, P. J., Delany, A. C., Greenberg, J., Haagenson, P., Heide, L., Lueb, R., Pollock, W., Seiler, W., Wartburg, A. and Zimmerman, P. 1984. Chemical observations of air composition in Brazil between the equator and 20° S during dry season. *J. Atmos. Chem.* accepted for publication.

Dianov-Klokov, V. I. and Yurganov, L. N. 1981. A spectroscopic study of the global space-time distribution of atmospheric CO. *Tellus 33*, 262–273.

Fishman, J., Solomon, S. and Crutzen, P. J. 1979. Observational and theoretical evidence in support of a significant in-situ photochemical source of tropospheric ozone. *Tellus 31*, 432–446.

Fraser, P. J., Khalil, M. A. K., Rasmussen, R. A. and Crawford, A. J. 1981. Trends of atmospheric methane in the Southern Hemisphere. *Geophys. Res. Lett. 8*, 1063–1066.

Hampson, R. F. 1980. Chemical kinetic and photochemical data sheets for atmospheric reactions. Report No. FAA-EE-80-17, US Department of Transportation, 1–490.

Heidt, L. E., Krasnec, J. P., Lueb, R. A., Pollock, W. H., Henry, B. E. and Crutzen, P. J. 1980. Latitudinal distributions of CO and CH_4 over the Pacific. *J. Geophys. Res. 85*, 7329–7336.

Junge, C. E. 1974. Residence time and variability of tropospheric trace gases. *Tellus 26*, 477–488.

Lamontagne, R. A., Swinnerton, J. W. and Linnenbom, V. J. 1974. C_1–C_4 hydrocarbons in the North and South Pacific. *Tellus 26*, 71–77.

Lamontagne, R. A., Smith, W. D. and Swinnerton, J. W. 1975. C_1–C_3 hydrocarbons and chlorophyll a concentrations in the equatorial Pacific Ocean. *Advances in Chemistry Series 147*, 163–171.

Logan, J. A., Prather, M. J., Wofsy, S. C. and McElroy, M. B. 1981. Tropospheric chemistry: A global perspective. *J. Geophys. Res. 86*, 7210–7254.

Newell, R. E., Boer, G. J. and Kidson, J. W. 1974. An estimate of the interhemispheric transfer of carbon monoxide from tropical general circulation data. *Tellus 26*, 103–107.

Rasmussen, R. A. and Khalil, M. A. K. 1981. Atmospheric methane, trends and seasonal cycles. *J. Geophys. Res. 86*, 9826–9832.

Rudolph, J., Ehhalt, D. H., Khedim, A. and Jebsen, C. 1982. Latitudinal profiles of some C_2–C_5 hydrocarbons in the clean troposphere over the Atlantic. Second symposium on the composition of the non-urban troposphere, Williamsburg, Am. Met. Soc. Boston, 284–286.

Seiler, W. 1974. The cycle of atmospheric CO. *Tellus 26*, 117–135.

Seiler, W. 1976. The CO cycle in the atmosphere, Proc. of the Intern. Conf. on Environm. Sensing and Assessment (ICESA), 1975 at Las Vegas (USA), Vol. 2, 35/4, 1–9.

Seiler, W. 1978. Influence of the biosphere on the atmospheric CO and H_2 cycles. *Environm. biogeochem. and Geomicrobiol. 3* (ed. W. Krumbein). Ann Arbor Science, 773–810.

Seiler, W. and Crutzen, P. J. 1980. Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. *Clim. Change 2*, 207–247.

Seiler, W. and Junge, C. 1967. Entwicklung eines Meßverfahrens zur Bestimmung kleiner Mengen CO. *Meteorol. Rundsch. 40*, 175–176.

Seiler, W., Giehl, H. and Ellis, H. 1976. A method for monitoring of background CO and first results of continuous CO registrations on Mauna Loa Observatory, Hawaii, WMO Special Environm. Report No. 10: Air Pollution Measurement Techniques, WMO-No 460, 31–39.

Seiler, W., Giehl, H. and Roggendorf, P. 1980. Carbon monoxide and hydrogen detection by mercury oxide/mercury vapor conversion, *Atmos. Technol. 12*, 40–45.

Seiler, W. and Fishman, J. 1981. The distribution of carbon monoxide and ozone in the free troposphere. *J. Geophys. Res. 86*, 7255–7265.

Seiler, W. 1984. Contribution of biological processes to the global budget of CH_4 in the atmosphere. *Microb. Ecol. 1984*, accepted for publication.

Singh, H. B., Salas, L. J., Shigeishi, H. and Scribner, E. 1978. Global distribution of selected halocarbons, hydrocarbons, SF_6, and N_2O. Report for EPA, grant No 8038020, 1–72.

Tsuchia, I. 1972. *Climate of Africa, World Climatography 2.* Kokon Shoin, Tokyo.

Van Loon, H. 1972. Wind in the Southern Hemisphere. In: *Meteorology of the Southern Hemisphere* (ed. C. N. Newton), *Meteorol. Monogr. 13*, 87–99.

Wilkniss, P. E., Lamontagne, R. A., Larson, R. E., Swinnerton, J. W., Dickson, C. R. and Thompson, T. 1973. Atmospheric trace gases in the Southern Hemisphere. *Nature 245*, 45–47.