Journal of Atmospheric Chemistry **8** (1989) 153–164.

Spectroscopic Measurements of Atmospheric Carbon Monoxide and Methane. 2: Seasonal Variations and Long-Term Trends

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(Received: 26 August 1987; revised: 3 November 1988)

Abstract. A spectroscopic technique for measuring CO and CH_4 contents is described and the latitudinal distributions of these gases are presented. Carbon monoxide abundance decreases southward, having two local maxima: in midlatitudes and in the tropics. The slope of latitude dependence varies according to the season of the year. The difference in CH_4 content does not exceed the accuracy of the method (±8%).

Key words. Carbon monoxide, methane, global distribution, seasonal variations, trends, spectroscopic measurements.

1. Introduction

Seasonal variations of background CO concentrations in the atmosphere of the Northern and Southern Hemispheres (NH and SH) have been widely discussed (Seiler, 1975; Dianov-Klokov and Yurganov, 1981; Seiler *et al.*, 1984). The CO maximum is found to occur in early spring, while its minimum occurs in late summer. The spring–summer decrease in the amount of CO in both hemispheres is attributed to an acceleration of CO photochemical sinks during these months (Crutzen, 1983) according to $CO + OH \rightarrow CO_2 + H$. Another mechanism contributing to the depletion of atmospheric CO is its absorption by soil bacteria (Zavarzin and Nozhenikova, 1977; Seiler, 1974).

An anthropogenic CO source seems to be a cause of the CO seasonal increase during the cold months in the NH (from October to March). No adequate mechanism has been established for the SH as yet (Seiler *et al.*, 1984).

A long-term trend of carbon monoxide was investigated by a number of authors. Measurements made by Dvoryashina *et al.* (1984) in 1970–1982 and by Khalil and Rasmussen (1984a) in 1979–1983 in the NH, indicate a certain increase in the background CO concentrations. There is also evidence of similar increase at the South Pole (Khalil and Rasmussen, 1984b). Measurements of CO concentrations at other sites of the SH (Voskresensky *et al.*, 1986; Seiler

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et al., 1984; Fraser *et al.*, 1986) have not, however, confirmed a long-term trend of CO concentration increase so far.

To reveal such a trend for carbon monoxide, an extremely variable gas, a longer observational series is required. The NH data discussed in the present paper cover an interval from 1970 to 1985 (no data are available for the years from 1977 to 1979, though). Our data indicate an increase of CO concentration at a rate of 1.5–2% per year. Measurements of CO levels in Antarctica (1977–1986) have not revealed any long-term change of the gas in the atmosphere (Voskresensky *et al.*, 1986).

Methane measurements from 1979 to 1982 by different groups of authors (e.g., Blake *et al.*, 1982; Khalil and Rasmussen, 1983) indicate an increase in CH_4 concentration at a rate of 1.3 and 1.2% per year in the Northern and Southern Hemispheres, respectively. Spectroscopic data discussed in this paper (see also Dvoryashina and Dianov-Klokov, 1986) support these observations.

The total gas content U (in atm cm) was measured by IR solar atmospheric absorption spectra. For details of the method, see Dianov-Klokov *et al.* (1989). According to that paper, one obtains, by solar spectroscopy, a mean weighted mixing ratio ($R = U/H_0$, where $H_0 = 7.9$ km, the vertical atmospheric scale). The mean weighted mixing ratio appears to be the closest to its mean value throughout the troposphere (with an accuracy of ±6%). The error of a single measurement of U is estimated as ±(8 – 10%) and the error of the mean daily quantity by 10–20 spectra is ±(4–6)%.

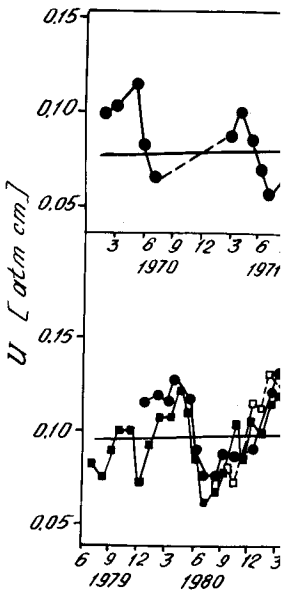

Fig. 1. Mean monthly values
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△ – the Arctic (76° N, 153° E)
Cape Meares (54° N, 125° W).
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2. Results

Northern Hemisphere

Regular measurements were carried out at the Zvenigorod station of the Institute of Atmospheric Physics (56° N, 37° E, ~200 m above sea level). The station is located 50 km westward of Moscow. The special feature of our technique (i.e. averaging throughout the atmosphere) and the prevailing winds (westerly winds, i.e. towards Moscow), permit us to consider the Zvenigorod mean monthly CO levels as background concentrations not affected by Moscow (see also Dianov-Klokov and Yurganov, 1981). About 10–20 spectra were recorded per day. (There were from a few to 10–15 working days in a month, depending on the weather conditions.) In November and December, observations are not carried out due to unfavourable weather conditions. In 1977–1979, no observations were made at all, as the facility was not in operation.

Figure 1 shows the seasonal variations of CO levels from Zvenigorod data, along with measurements from other unpolluted locations in the U.S.S.R.: each point corresponds to a CO concentration averaged for 10–15 days of observations. There is good agreement between the observations in different locations. This confirms our assumption on the background nature of the Zvenigorod data

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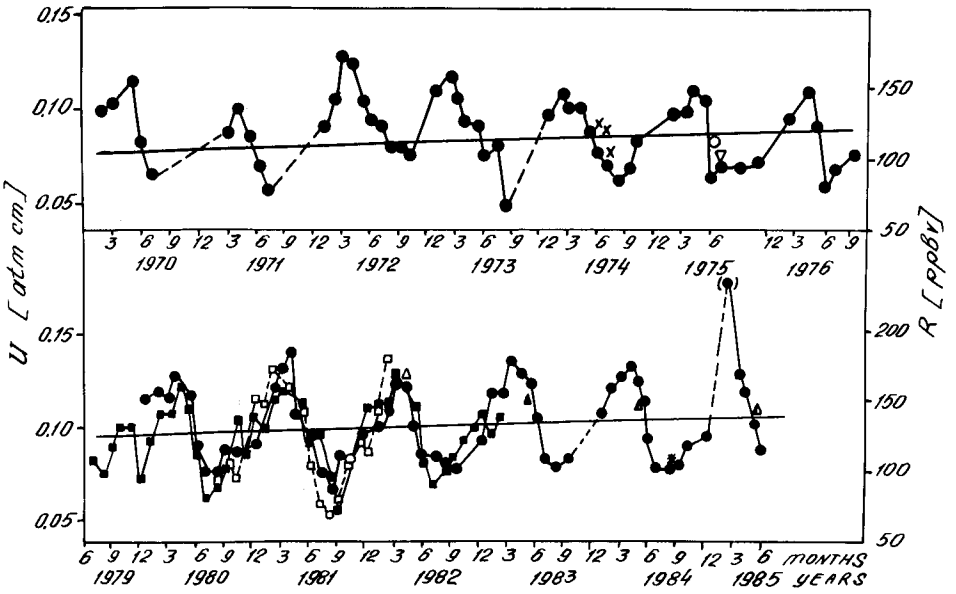

Fig. 1. Mean monthly values of the CO background concentration in the atmosphere in different years and different measurement sites. The left ordinate axis shows the total gas content (atm cm) and the right ordinate axis is the mean weighted mixing ratio (ppbv). ● – Zvenigorod (56° N, 37° E), × – West Siberia (54° N, 83° E), ○ – East Siberia (58° N, 126° E), ▽ – East Siberia (54° N, 124° E), △ – the Arctic (76° N, 153° E), ▲ – the Arctic (79° N, 95° E), ▲ – the Arctic (71° N, 178° E), ■ – Cape Meares (54° N, 125° W), □ – Point Barrow (71° N, 156° W). The last two measurements are the GC ones of Khalil and Rasmussen (1984a) and Rasmussen and Khalil (1982).

and it also testifies to the fact that, at any time, there is a spatial uniformity of the background CO level distribution over all of the U.S.S.R. Moreover, as is seen from the comparison of our data with the gas chromatography (GC) measurements of Khalil and Rasmussen (1984a) in the surface atmospheric layer at Cape Measures (45° N, 125° W) and at Point Barrow (71° N, 156° W) (Rasmussen and Khalil, 1982), our conclusion on the spatial uniformity of the background CO levels can be applied to mid and high latitudes of the NH (at least, for the spring months).

Figure 2 displays short-term (day-to-day) changes of CO abundances expressed by frequency distributions of mean daily levels measured in Zvenigorod: the absciss axis shows column amounts U and the ordinate axis shows a share of total number of days (N) in percent (dn/N), when the gas content was ranging from U to $U + dU$, where $dU = 0.05$ atm cm. To exclude seasonal variations, the analysis was made separately for a seasonal minimum (July–September: upper panel) and for a seasonal maximum (March–April: lower panel). The measurements of 1970–1976 (without the abnormal 1972, see below) and for 1980–1984, were also analyzed separately; the corresponding histograms are shown by thin (shaded area) and thick lines. In addition, mean square

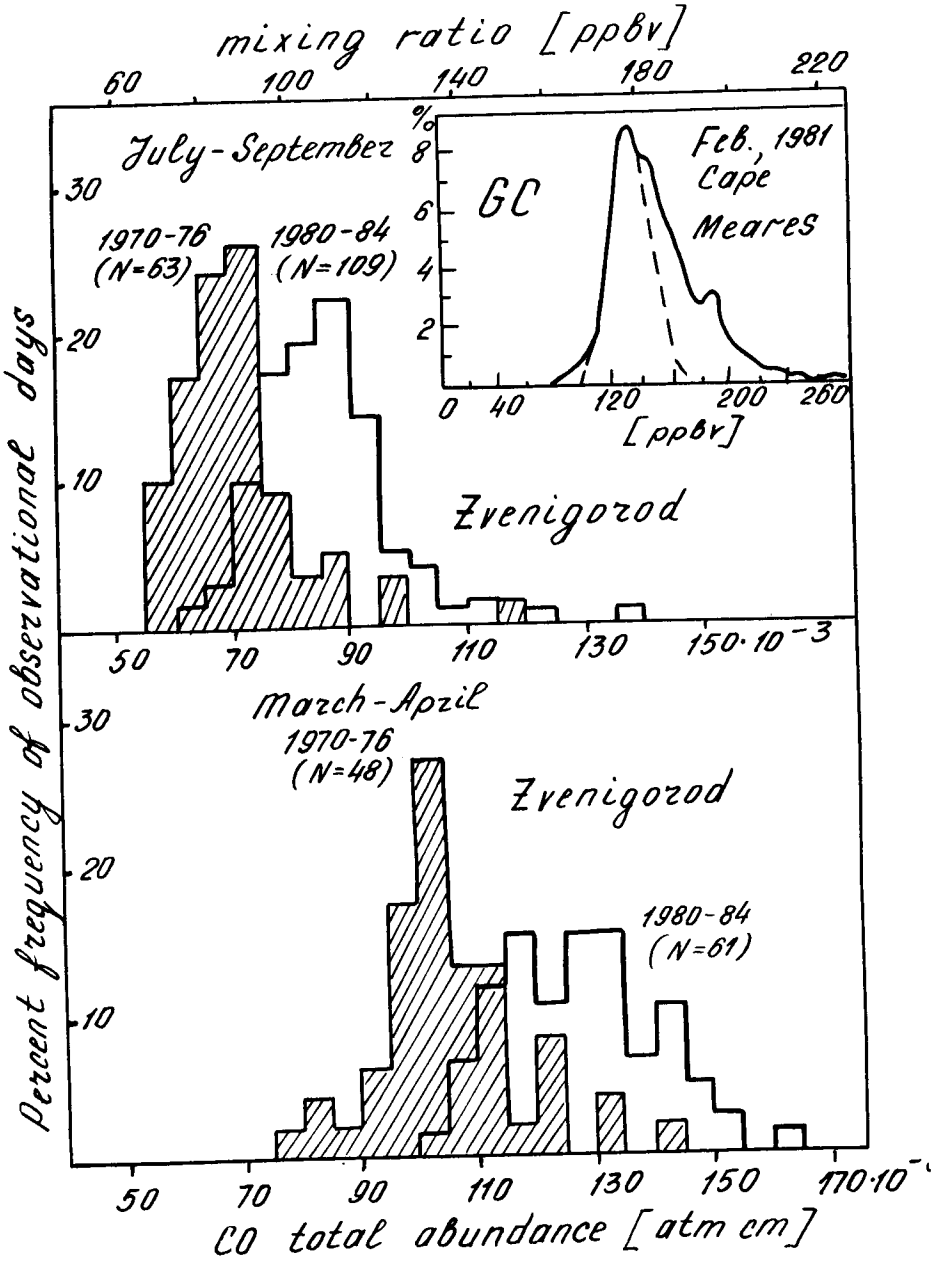

Fig. 2. Frequency distribution of mean daily CO amounts in Zvenigorod near the seasonal minimum (upper part) and near the seasonal maximum (lower part). Shaded histograms correspond to 1970–1976 (1972 excluded) nonshaded correspond to 1980–1984. The inset shows a frequency distribution of single GC measurements (Khalil and Rasmussen, 1984a).

Table I. The results of s

Period of averaging (month, year)	
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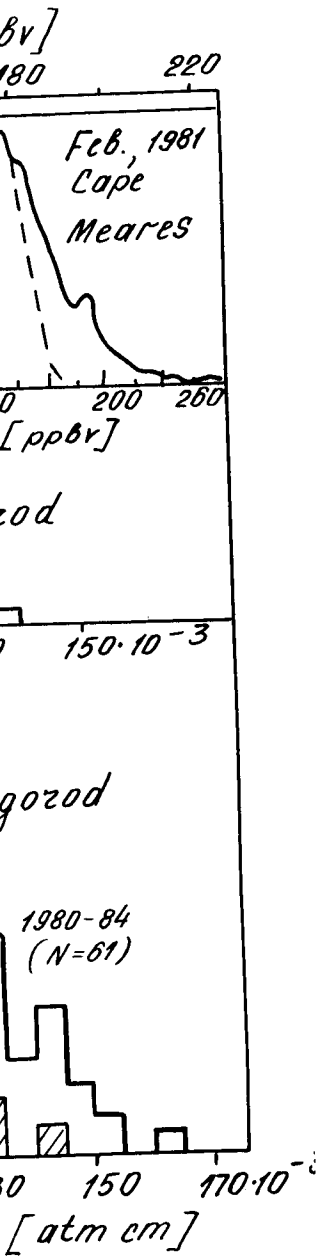

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Table I. The results of statistical treatment of CO data

Period of averaging (month, year)		Number of days	Mean content $U \times 10^3$ atm cm	rms deviation $\sigma \times 10^3$ atm cm	$\frac{\sigma}{U}$ %	$\frac{U(80-84)}{U(70-76)}$
III–IV	(1970–76)	48	106	13	12	1.21
III–IV	(1980–84)	61	128	13	10	
VII–IX	(1970–76)	63	72	11	15	1.17
VII–IX	(1980–84)	109	84	8	9	

root deviations (σ) and mean values for all four groups of observations were calculated (see Table I).

An examination of Figure 2 and Table I suggests two major inferences. First, the day to day rms deviations are within ±10%. Since the error of the daily mean value (U) is ±5–6% (see Dianov-Klokov *et al.*, 1989) the natural variability is about ±(8–10)%. The estimation is in excellent agreement with Seiler's (1984) and Khalil and Rasmussen's (1984a) estimations of the background CO mixing ratio variability. To obtain undisturbed background data, the authors of both cited works had to cut off 15–20% of the data affected by local sources, since some of them almost doubled the mean values (see, for instance, the inset in Figure 2). In our case, no data filtering was required. This underscores the advantages of total column approach in comparison to the local one.

Second, the mean CO levels in summer and winter display a 17–20% increase of mean CO values over 10 years. This trend is well seen in Figure 3, showing the CO levels averaged by seasons for different years: circles showing the values for January–April and squares for July–September. The 1972 data stand out clearly: in winter they are 3σ larger and in summer 4σ larger than the regression curve connecting all these points, except the one of 1972. (Here, σ is the rms deviation of the points from the regression curve.) Blocking high pressure systems, which seem to favour CO accumulation over the industrial European U.S.S.R. areas, were typical of the 1972 weather situation. Another example of such an anomaly is February 1985 (Figure 1) when a similar weather pattern prevailed and the monthly mean CO content appeared to be 50% higher than usual. In the summer of 1972, additional amounts of CO were accumulated due to forest fires. Besides, 1972 was also the last year before the energy crisis started and, as emphasized by Dvoryashina *et al.*, 1982, this crisis resulted in a lower consumption of fuel. Smaller rates of CO emissions in 1974–1975 might result in a decrease of CO levels in the atmosphere, as compared to 1972.

The regression lines of Figure 3 correspond to long-term growth rates (1.8 ± 0.4) and (1.7 ± 0.6)% per year for seasonal maxima and minima, respectively (1972 data were excluded and confidence intervals are given for a probability of 0.9). The correlation coefficients are $r = 0.93$ and 0.84, respectively. According to similar calculations for all the data (1972 data were included), the

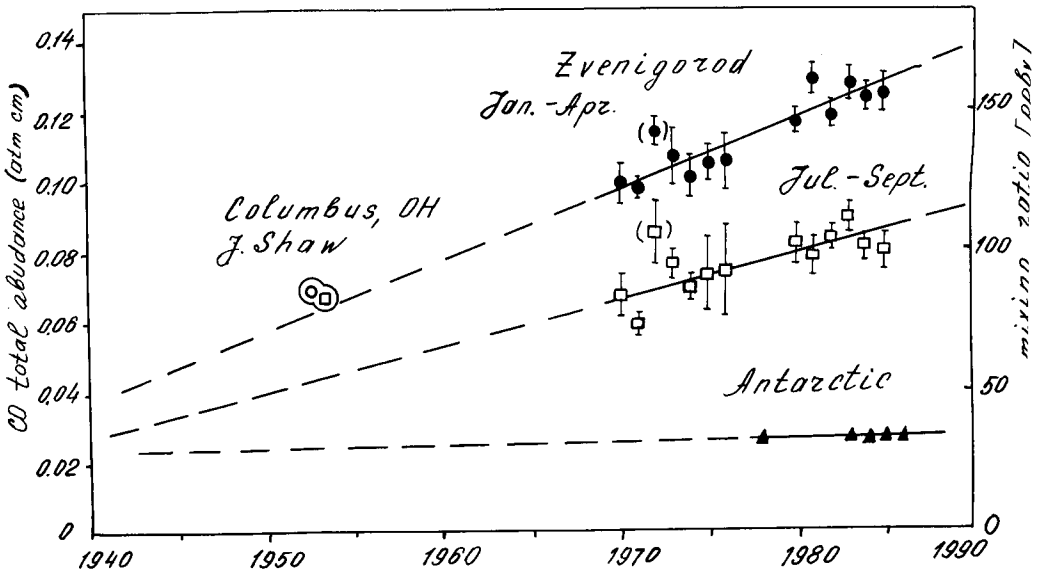

Fig. 3. CO content seasonally averaged for measurements in various years. Full circles and open squares show the mean January–April and July–September values, respectively. The same full circles and open squares in larger circles show similar spectroscopic measurements by Shaw (1958) recalculated by the authors. Triangles indicate the January–February mean values of carbon monoxide levels in Antarctica (1978, Molodezhnaya Station, 68° S, 48° E, other data belong to Mirny, 67° S, 93° E). Vertical lines are the confidence intervals for the mean value with a probability of 0.9.

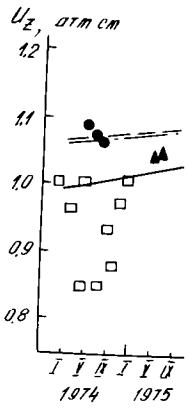

Fig. 4. Mean monthly v
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and Rasmussen (1983).

trends were lower: 1.6 ± 0.5 and $1.3 \pm 0.8\%$ per year at $r = 0.88$ and 0.66 for winters and summers, respectively.

Khalil and Rasmussen (1984a) also concluded that CO background concentrations showed a tendency to grow in the Northern Hemisphere. Their inference of the 6% yr^{-1} growth rate seems to be an overestimation, since their observation series is too short, only 3.5 years. It is worth noting that the regression line plotted by our data practically fits the points corresponding to the spectroscopic data by Shaw (1958) obtained in Columbus (Ohio, U.S.A.) in 1952–1953. The data were reprocessed by the present authors (Dianov-Klokov and Yurganov, 1981) to make them compatible (Figure 3). Similarly, the treatment of corresponding European measurements made in 1950–1951 by Benesch *et al.* (1953) and carried out by Rinsland and Levine (1985), yielded growth rates about 2% per year, which is very close to our results. Thus, the background CO concentrations in the Northern Hemisphere have grown, at least for the last 30 years, at a rate of 1.5–2% per year. There is evidence, though, that this growth has not been monotonic as periods of higher rates alternated with stable CO levels and lower rates, e.g. 1972–1976.

CH_4 measurements have been carried out at Zvenigorod Station since 1974 and expeditional measurements have been carried out in other localities in the

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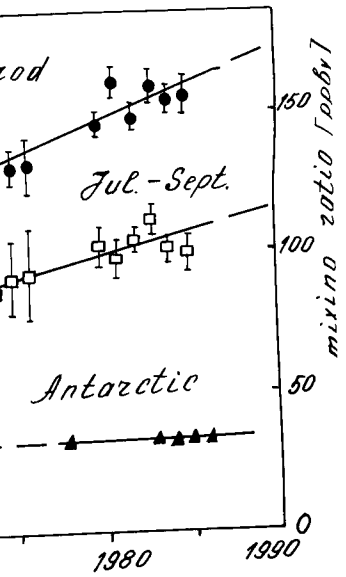

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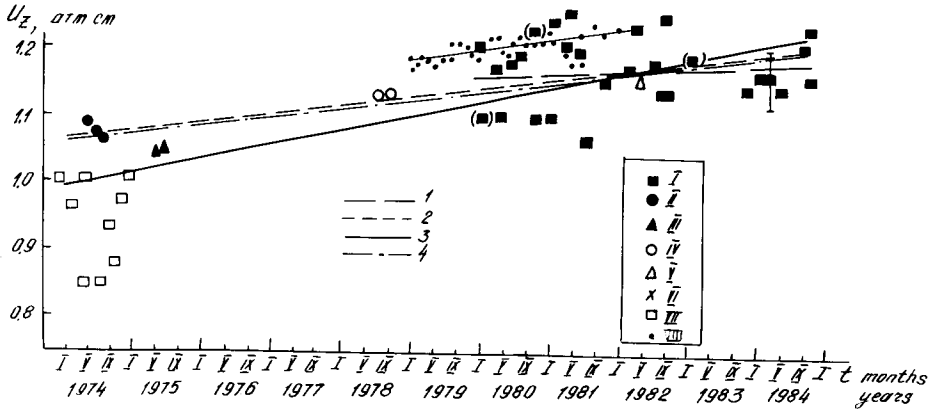

Fig. 4. Mean monthly values of the total methane content in the atmosphere in the NH (measurements from different sites). I, VII – Zvenigorod Station (56° N), II – West Siberia (54° N), III – East Siberia (58° N), IV – Cape Kaliakra (43° N, 28° E), V – the Arctic (76° N), VI – Northern Caucasus (44° N, 43° E), VIII – Cape Meares (45° N). The last set is local GC measurements by Khalil and Rasmussen (1983).

U.S.S.R. and Bulgaria. Figure 4 presents the mean monthly CH_4 values (Dvoryashina and Dianov-Klokov, 1986). The figure also shows the comparison of surface measurements by Khalil and Rasmussen (1983) recalculated for the total gas concentration, allowing a decrease of the CH_4 mixing ratio in the stratosphere.

The rms scatter of spectroscopic data amounts to ±(4–6)%, which is considerably larger than that of GC (±1%). This may be attributed to the lower accuracy of our surface-concentration measurements in comparison with GC. Absolute methane concentrations obtained by Khalil and Rasmussen (1983) differ from our data by an average of 5–6%. The cause of the difference has not been established so far.

Direct regression analysis by the least-squares method has been carried out in order to reveal a trend in spectroscopic data. Calculations have been made for four cases: (1) Zvenigorod data of 1980–1984 only (curve 1); (2) data set including all other measurements except those of Zvenigorod of 1974: I + II + III + IV + V + VI (curve 2); (3) data set consisting of I + II + III + IV + V + VI + VII (curve 3), i.e. results of all measurements; (4) data including expeditional measurements only: II + III + IV + V + VI (curve 4).

The Zvenigorod measurements of 1974 have been separated from the other data, since their validity is doubtful: the summer CH_4 content (0.85 atm cm) turned out to be 15% lower than in the autumn and winter months. The reality of such a 'pit' in CH_4 concentrations is doubtful if we compare them with almost 'normal' (1.05 atm cm) CH_4 concentrations in West Siberia during the same period (black circles in Figure 4).

Curve 3 has the largest slope (it reflects all the data, even doubtful measure-

ments of 1974): $2.0 \pm 0.4\%$ per year (the confidence level here and below corresponds to a probability of 0.9, i.e. 1.9σ), curves 2 and 4 have almost identical slopes ($1.2 \pm 0.4\%$ per year) and curve 1 (Zvenigorod, 1980–1984) has the smallest slope $0.5 \pm 1.2\%$ per year. The short period of measurements with a large data scatter involved a large error in curve slope determination in the last case. It is interesting to note, though, that at Cape Meares a stability of the mixing ratio of CH_4 in 1980–1982 was also recorded, compared with precedent years (Khalil and Rasmussen, 1983).

Thus, the most reliable portion of our measurements during 1974–1984 indicates a rise in CH_4 abundance with a rate of $1.2 \pm 0.4\%$ per year. This estimate coincides with that of Khalil and Rasmussen (1983) calculated by more accurate GC measurements, though their observation period was shorter and they were made at a single observation point.

Southern Hemisphere

The first measurements of CO and CH_4 concentrations in the atmosphere of the Antarctic continent were carried out by Yurganov *et al.* (1979) during the summer months of 1977–1978 at Molodezhnaya Station (68° S, 46° E). Since 1982, these measurements have been taken by a scientific team of the Arctic and Antarctic Research Institute during the summer months at the Mirny Observatory (67° S, 93° E) by means of common techniques (Radionov and Voskresensky, 1983). All available mean daily values of CO concentrations in the Antarctic atmosphere are shown in Figure 5. The December–January decrease

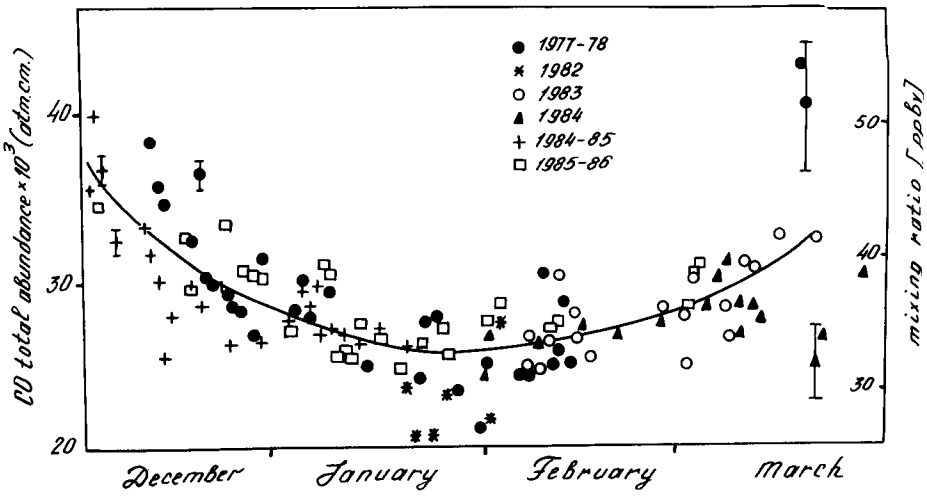

Fig. 5. Mean daily levels of carbon monoxide in Antarctica, 1977–1986 (Soviet Antarctic stations Molodezhnaya and Mirny). Vertical bars show the rms scatter of single measurements, and the solid line is the cubic spline.

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Table II. Averaged CO cont
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Period of averaging (months, days)	Years
	1977
January	
1–5	
6–10	
16–20	
21–25	
26–28	
February	
1–5	
6–10	
11–15	
December	
12–16	36.8(2)
17–21	33.5(2)
22–26	31.3(4)
27–31	28.8(4)

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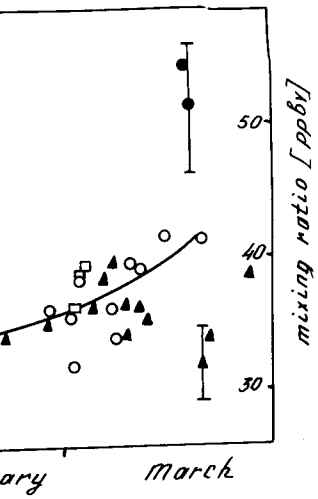

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in CO abundance is quite obvious, the minimum occurring in the end of January; the CO level starts to increase slowly in February–March. Similar pattern was recorded by Seiler *et al.* (1984) along the coast of South Africa. Summer values of the CO mixing ratio measured by us are appreciably lower than the January mean reported by Seiler *et al.* (1984) (53 ppbv). Khalil and Rasmussen (1984b) measured R to range from 36 to 46 ppbv at the South Pole in January and Fraser *et al.* (1986) showed R to be equal to 29–36 ppbv at Tasmania (41° S, 145° E) and Mawson Station (68° S, 63° E). On the one hand, these apparent discrepancies of the measured values of the tropospheric CO mixing ratio stress the importance of equipment intercalibration and, on the other hand, stimulate searches of possible inhomogeneities in the longitudinal distribution of CO concentrations in the Southern Hemisphere.

An examination of Figure 5, which shows daily CO values for an 8 year period, suggests a negligible long-term trend of CO abundance changes. To estimate the value of the trend and errors in its determination, the whole period was divided into 5 day intervals and the CO values were averaged interval by interval (Table II). Then, using the least-squares method, the rate of CO concentration changes has been determined, assuming these changes to be linear, in percentages of the CO mean concentration and per year (the last column of the table). For different pentads, the linear trend values range from –2% to +2% per year.

The trend value for the whole data set average by pentads is equal to (0.0 ± 0.6)% per year. In December, the trend is (–0.8 ± 1.1), while in January–February it is (+0.5 ± 0.6)% per year. The error is assumed to be $2\sigma_T/\sqrt{N}$, where

Table II. Averaged CO content in Antarctic atmosphere (atm cm × 10^3), trend estimates (the number of days with measurements is shown in brackets)

Period of averaging (months, days)	Years						Trend (%/y)
	1977	1978	1983	1984	1985	1986	
January							
1–5		28.0(1)			27.9(1)	27.2(1)	–0.25
6–10		29.1(3)			28.4(5)	30.7(2)	+0.30
16–20		25.0(1)			27.3(1)	25.7(2)	+0.68
21–25		25.8(2)			26.1(1)	26.2(1)	+0.18
26–28		25.5(2)				26.4(2)	+0.44
February							
1–5		23.0(2)		25.7(2)		27.8(2)	+2.22
6–10		26.5(4)	25.2(3)	26.1(1)		–	–0.50
11–15		26.0(4)	27.8(4)			27.2(2)	+0.63
December							
12–16	36.8(2)			31.7(3)			–2.00
17–21	33.5(2)			27.8(3)	31.0(2)		–1.62
22–26	31.3(4)			29.2(2)	33.5(1)		+0.20
27–31	28.8(4)			26.4(2)	30.6(3)		+0.05

σ_T is the rms deviation of the trend value in pentads, and N is the number of pentads. In addition, a regression analysis has been made for averaged January–February U values, that is, about the seasonal minimum (See Figure 3). The slope of the regression curve in this case is $+0.3 \pm 0.4\%$ per year. Thus, on the basis of our data, we can conclude that any long-term change of the CO concentration in the Antarctic atmosphere is extremely small; it was found not to exceed $\pm 0.6\%$ per year.

3. Discussion and Conclusions

The experimental results discussed in this paper clearly show the possibilities and limitations of our approach to the spectroscopic solar method. The accuracy of a single measurement of such a variable gas as carbon monoxide (± 8–10%), proved to be sufficient for the study of latitudinal, seasonal and secular variations of its atmospheric levels. The methane concentration is measured with similar accuracy, although its seasonal and latitudinal variations were found to be within the measured scatter of the values. Nevertheless, a long-term growing of the methane abundance in the atmosphere for a 10 year period is quite apparent.

Dianov-Klokov and Yurganov (1981) were the first to propose a global model of latitudinal/seasonal variations of carbon monoxide. During the last 6 years, new experimental data, discussed in this paper and that by Dianov-Klokov *et al.* (1989), were obtained. The latitudinal distribution of carbon monoxide has been updated during two recent shipboard expeditions. Nevertheless, the model of 1981 is still valid.

Gabriyelyan *et al.* (1983, 1984) showed the distribution of the total CO content in mid and polar latitudes to be uniform on the basis of field measurements. Further updating of the spatial distribution of CO will require constant monitoring by stations distributed across the hemisphere.

The carbon monoxide content in Zvenigorod (56° N, 37° E) increased in the 1970–1985 period, the rate of increase being 1.6–1.8% per year. The rate of increase of the background concentrations could be somewhat overestimated, due to Moscow effects, as shown by Dvoryashina *et al.* (1984). This overestimation would be not more than 0.2% per year. The comparison of contemporary data with the results of spectroscopic carbon monoxide measurements in Europe and the United States at the beginning of the 50's (recalculations by Dianov-Klokov and Yurganov (1981) and Rinsland and Levine (1985)) has also yielded a value of 2% per year.

Hence, the estimation of Khalil and Rasmussen (1984a), equal to about 6% per year, seems to be too large.

The rate of the background CO concentration increase in the NH in 1950–1985 seems to be, on average, 1.5–2% per year. In Antarctica, no CO increase greater than 0.6% per year in 1978–1986 was found. In this connection, there is a problem if we w
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there is a problem if we want to know the preindustrial CO level. Figure 3 shows that a backward linear data extrapolation for Zvenigorod and Antarctica would result in the intersection of all three straight lines in the 30's, when the mixing ratio was 30–40 ppbv. It is evident that the natural background levels in the NH and SH should not necessarily coincide, because of the difference between the two hemispheres (land/sea distribution, for instance). At present, the preindustrial CO level in the NH can only be roughly estimated to range from 30 to 70 ppbv. Nevertheless, even this rough estimate indicates that the modern background mixing ratio of carbon oxide has doubled or even tripled, compared to an undisturbed level.

The agreement between different estimates (different authors) for the methane secular increase, is better: it appears that during the last 30 years, its background mixing ratio in the NH increased at a rate of 1.1–1.3% per year (the present paper, Dvoryashina and Dianov-Klokov, 1986; Khalil and Rasmussen, 1983; Rinsland *et al.*, 1985). There is evidence that the methane concentration has doubled in comparison with its background level (Khalil and Rasmussen, 1982). All geophysical consequences of such an increase in the concentration of these two gases, is difficult to predict at present. In particular, it is worth noting that the hydroxyl amount depletes and the tropospheric ozone increases (Crutzen, 1983).

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