

Some Soviet measurements of trace gases

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ABSTRACT

Results of Soviet measurements during the last two decades are reported for various trace gases in the atmosphere. They are either greenhouse gases, such as carbon dioxide, methane, ozone in the atmospheric surface layer, CFSs, or gases which enter the ozone cycle or react with hydroxyl, the key cleansing agent of the atmosphere. The latter are total ozone itself, carbon monoxide and nitrogen dioxide. Measurements of CO₂ started on a regular basis in 1980 in the Tyan Shan Mountains. Together with the general trend, this mid-continent station reveals considerable inter-annual variability and large annual amplitude. Measurements of CH₄ and CO reveal trends of about 1 % yr⁻¹ for the Northern Hemisphere. Measurements of CO in the Arctic show concentrations close to those in the mid-latitudes. The NO₂ content has been measured since 1979 in the Caucasus and is the longest time series. Total ozone, surface O₃ and total NO₂ were also measured in 1986 to 1988 in Antarctica. The results show some features of total ozone for the period of filling-up the ozone hole. The surface ozone levels in Antarctica are on the average about half of the values for similar latitudes in the Northern Hemisphere. The largest inter-day surface ozone variations are caused by synoptic processes, while in the synoptically quiet period, they are smaller and influenced by the slope katabatic wind. Finally, a brief mention is presented of the findings by Isidorov of some halocarbons in volcanic gases which may reach up to 10% of the anthropogenic source of CFCs.

1. Introduction

Measurement records of the atmospheric trace gas concentrations in the USSR are often not well-known outside the country for a variety of reasons: not many specialists know Russian and follow Russian literature even if it is translated into English, an insufficient number of people from the USSR come to international conferences etc. At the same time, the results of Soviet measurements form a substantial part of the picture of the changing atmosphere (Golitsyn, 1985) and without them, the situation would be poorer than it really is. The gases that will be considered here are carbon dioxide, carbon monoxide, methane, ethane, nitrogen oxides, ozone in the stratosphere and troposphere as measured on a permanent basis at various stations within the Soviet Union and on field expeditions in the Arctic, Antarctica and on oceanographic vessels. These gases are interesting either as greenhouse gases, sinks for hydroxyl, OH, which is the main cleansing agent in the atmosphere, or important in the ozone cycle.

The feature of most measurements is that they are made with spectroscopic methods using both direct sunlight and scattered from the zenith, thereby measuring the atmospheric column total content. Besides spectroscopic information, one should also use the profiles of temperature, pressure, humidity, etc., to infer from the absorption feature the content of the gas in question. Details of experimental procedures and errors will be discussed below.

It should be noted that for comparability of our results with local measurements, the total column content is expressed in the form of a volume mixing ratio averaged through the total column (CO₂, CH₄) or through the troposphere (C₂H₆, CO).

2. Trace gases

2.1. Carbon dioxide

The first measurements of the CO₂ content on a regular basis started in 1980 near Lake Issyk-Kul

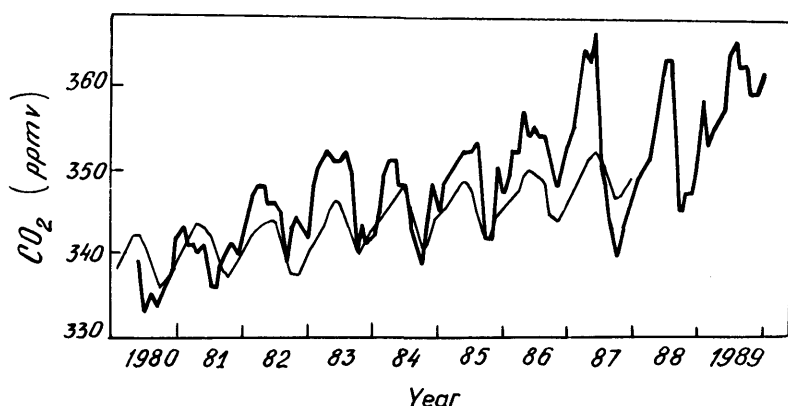


Fig. 1. CO₂ monthly mean concentrations measured at Issyk-Kul, after Arefyev et al. (1990)-thick line. The thin line is for Mauna Loa.

in the Tyan-Shan Mountains. The station with coordinates 42.6°N, 77°E is at an elevation of 1609 m.

The carbon dioxide total column content is retrieved from solar absorption spectra recorded with a spectral resolution of about 5 cm⁻¹ in the 2.06 μm (2ν₁ + ν₃) CO₂ absorption band region. The method is based on mean transmittance determination. Random error of the daily means does

not exceed ±2% (or ±6 ppmv) (Arefyev et al., 1990). Fig. 1 is from that paper and it is unique in the sense that it represents a mid-continent station for Eurasia. The thick line represents monthly averages. The annual means and the trend are in agreement with the Mauna Loa record, but there are interesting peculiarities. The amplitude of the annual cycle is larger and increasing towards the end of the decade. There is a noticeable inter-

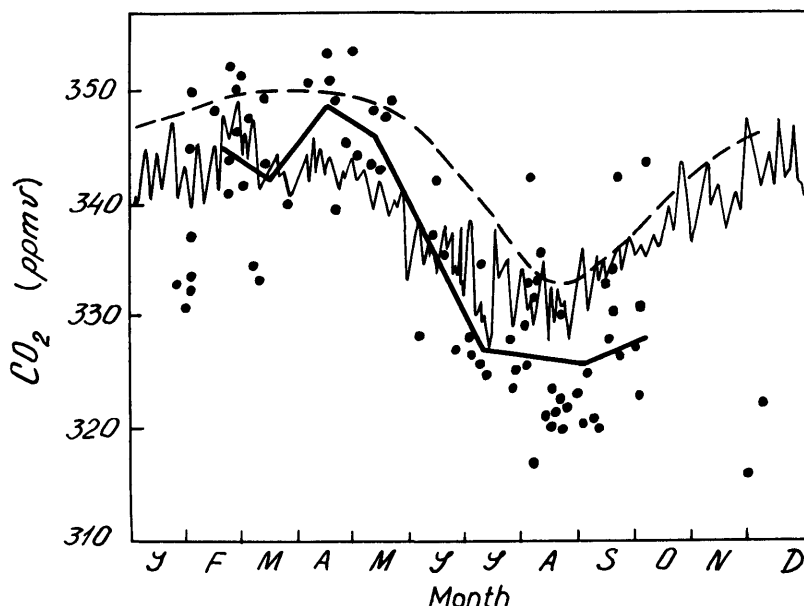


Fig. 2. Daily mean (dots) and monthly mean (thick solid line) CO₂ concentrations measured in Zvenigorod 1983–84, after Pugachev et al. (1985). The broken line is for Cold Bay, 1983, Alaska, and the thin solid line for Mt. Cimone, Italy.

annual variability in the shape of the seasonal behaviour such as the amplitude and position of the maxima and minima, etc.

Similar conclusions may be obtained from the results of Pugachev et al. (1985), who made measurements in 1983–1984 in Moscow and at the Zvenigorod Station of the Institute of Atmospheric Physics, 50 km west of Moscow. On average, the results at these two places differ only by a few percent, being slightly higher in the city than outside.

In this case, the non-linear least squares, NLLS, technique has been used to retrieve the column content from a 2.06 μm CO_2 band of the solar spectra recorded with spectral resolution of 0.25 cm^{-1} . The random error was about $\pm 2\%$ ($\pm 6\text{ ppmv}$). The results in Fig. 2 are taken from the paper above. The points represent daily mean, the thick solid line monthly averages, the thin solid line corresponds to the local measurements made at Mt. Cimone (44°N , 11°E) in the Apennines in Italy and the broken line is for Cold Bay, Alaska (55°N , 163°W). Again, for plain level mid-continental Moscow, the amplitude of the seasonal cycle is larger.

2.2. Carbon monoxide

Carbon monoxide is a species measured since 1970 at the Institute of Atmospheric Physics and its records in Moscow and Zvenigorod evidently cover the longest time period, in the literature.

Total CO content is retrieved from the measurements of equivalent half-width of the $\text{CO } \nu_1$ band R3 line, centered at 2158.3 cm^{-1} ($4.63\text{ }\mu\text{m}$). Spectra are recorded with a resolution of 0.2 cm^{-1} . The vertical volume mixing ratio profile is assumed constant up to 10 km, exponentially decreasing in the stratosphere. The total RMS error of a daily mean is about $\pm 10\%$. For more method and measurement details, see Dianov-Klovov et al. (1989).

The results for this gas up to 1984 were published by Dianov-Klovov et al. (1989) and by Dianov-Klovov and Yurganov (1981). In Fig. 3, we present our results for the next five years, and old results by Benesch et al. (1953) and Shaw (1958) from the early 1950s. The old results fit in quite nicely in the overall picture. The trends for winter and summer differ somewhat. The other feature which could be significant is the levelling off during the last 5–6 years.

Besides Zvenigorod, the CO content has also been measured extensively in the Arctic and in Antarctica (Radinov and Voskresensky, 1983) and during several oceanographic cruises. These measurements together with others (Seiler et al., 1984; Bogdanov et al., 1979) make it possible to construct a seasonal-zonal distribution of CO in the atmosphere (apart from the general increase). Such a distribution is illustrated in Fig. 4. Due to a strong anthropogenic component in the CO build-up and the residence time in the atmosphere

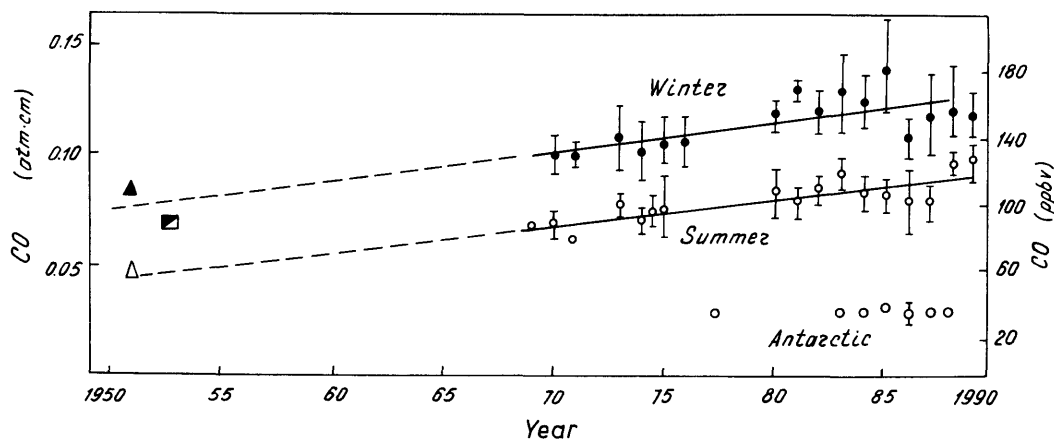


Fig. 3. CO concentrations. The upper curve is for winter and the lower curve for summer. Triangles are due to Benesch et al. (1953) and the 1953 point is due to Shaw (1958).

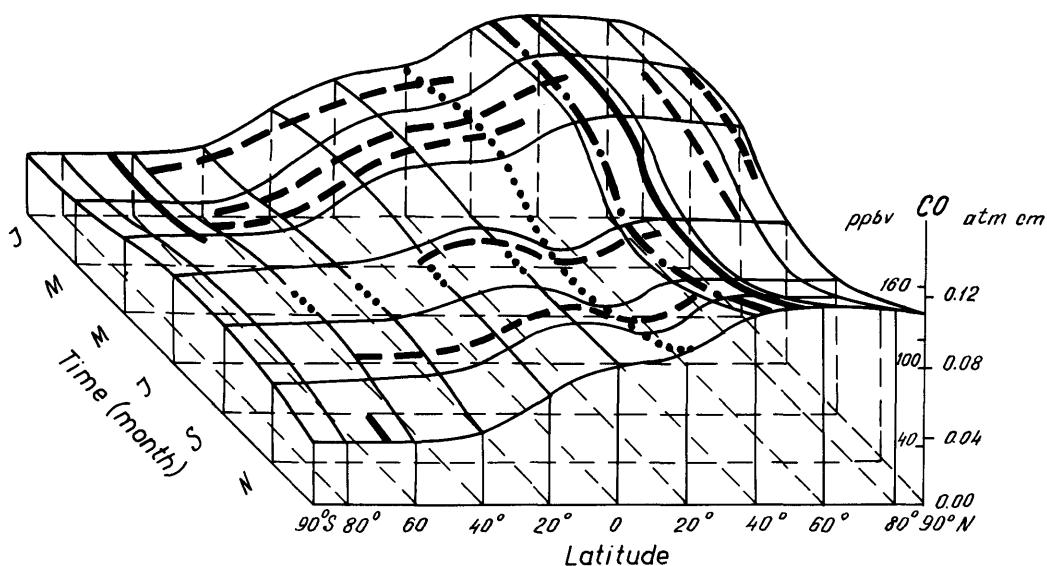


Fig. 4. Model for latitude distribution of the total content of CO. The thick solid lines are from our data for Zvenigorod and the Antarctic Continent; the thick broken lines from the results of our sea and Arctic expeditions; the thick dotted lines from the data of Seiler (1976) and Seiler et al. (1977); the dot-dash line from the results of Bogdanov et al. (1979).

of only a few months, there is a strong meridional gradient in its content. The recently discovered important feature of the CO distribution is that in the Arctic, where we have measured CO for a number of years at various places, its concentration is about the same as in the middle latitudes

of the Northern Hemisphere. Due to the above-mentioned peculiarities of the CO cycle in the atmosphere, the distribution could be very patchy, especially in the tropics where there are sources due to biomass burning (Newell et al., 1989) comparable with that from transport and industry. It is

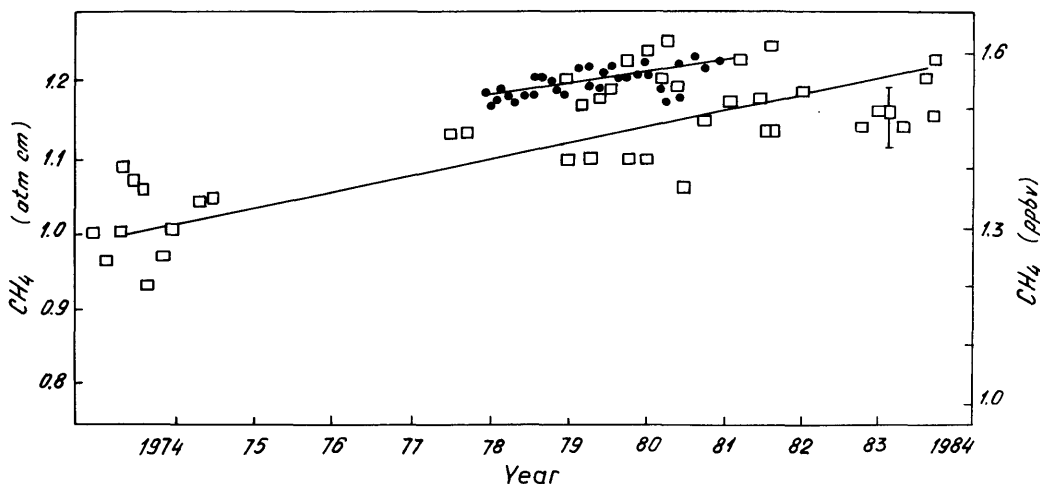


Fig. 5. The methane content for Zvenigorod (hollow squares) and local concentrations after Khalil and Rasmussen (1984) (dots).

worth mentioning that one of us (Grechko, 1987) during two cruises in the Atlantic in 1981 and 1983 also observed substantial amounts of CO in tropical latitudes (not ascribed to the burning).

2.3. Methane

We have measured the methane content in the atmosphere since 1974, first in Zvenigorod and later at various other places (Dianov-Klokov et al., 1989; Gabrielyan et al., 1983). For measurements of CH₄, the ν_1 band P2 line centered at 2998.9 cm⁻¹ (3.33 mcm) is used. The method and accuracy are the same as for CO content retrievals (Dianov-Klokov et al., 1989).

The results of the measurements in Zvenigorod are presented in Fig. 5, where hollow squares are monthly mean values. The dots correspond to measurements by Khalil and Rasmussen (1984). The general trend for the decade 1974–1984 is 1.5% per year in Zvenigorod, but for the last 5–7 years, the growth is considerably slower. Khalil and Rasmussen's measurements were performed using a chromatograph and show considerably less scatter. The difference in the CH₄ content between the Northern and Southern Hemispheres is within error bars of our measurements ($\pm 8\%$), but the results of measurements in Antarctica seem to indicate lower levels compared to the Northern Hemisphere data (Radionov and Voskresensky, 1983).

Due to the large greenhouse efficiency of methane (about 20 times more per molecule than CO₂) and its importance for many reactions in the atmosphere, methane has attracted more and more attention in recent years. Its sources and sinks are not yet well understood and new measurements of the gas and its fluxes are needed both at high and low latitudes, such as the eddy flux measurements of carbon dioxide (Volkov et al., 1986, 1989).

2.4. Ethane

One of us (NSP) started to measure ethane (C₂H₆) in 1989 in Zvenigorod. For C₂H₆ measurements, the ν_7 band Q₃⁺ subbranch centered at 2976.8 cm⁻¹ (3.36 mcm) is used. Column content is retrieved by means of the NLLS method from spectra recorded with a spectral resolution of 0.07 cm⁻¹. We estimate the accuracy of our data (daily mean) to be around $\pm 8\%$ with a precision of about 10%. The relatively low accuracy is due to the high noise level in the recorded spectra (Pugachev and Bessonov, 1990).

Ethane and other hydrocarbons are very important components in tropospheric chemistry (sinks for OH). The present tropospheric concentrations are of the order of tenths of ppb, making them unimportant as greenhouse gases. The ethane content shows a substantial seasonal course (see Fig. 6). The short period of measurements does

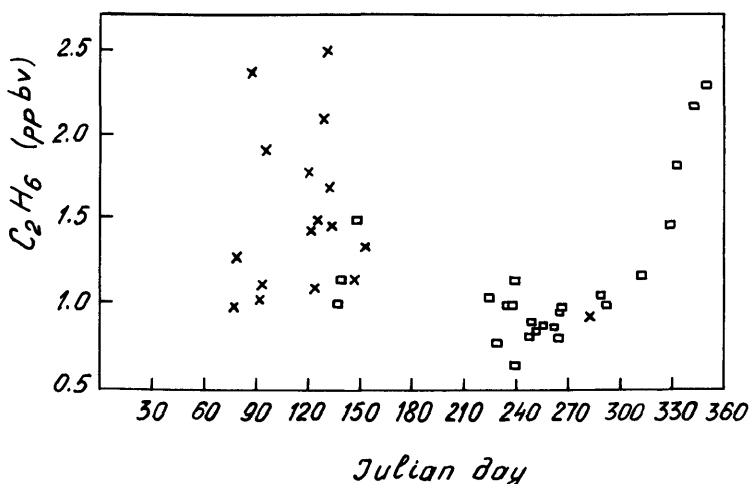


Fig. 6. Daily mean ethane concentrations measured in 1989–1990 at Zvenigorod; squares–1989, crosses–1990 (from Pugachev and Bessonov, 1990).

not allow us to draw conclusions concerning the representativeness of this seasonal course. The wide spring spread of points could possibly be explained by a strong meridional gradient of ethane (Blake and Rowland, 1986) and unstable atmospheric circulation in the spring.

Some measurements of acetylene (C_2H_2) have also been started (Pugachev and Bessonov, 1990).

2.5. Nitrous oxide

Similarly to CO and CH_4 , a spectroscopic method was used to measure N_2O (Gabrielyan et al., 1983), but the number of measurements is considerably less than for CO or CH_4 because of greater difficulties in extracting the N_2O content. Our mean value of measurements before 1982 is 292 ± 12 ppb. Because of large scatter of the data, reduction relative to dry air has not been made and

no statistically significant trend can be determined. The mean value seems to be lower than the estimated value for the period around 1980, about 300 ppb, but this value is related to near surface values and ours is the column content. For this and other reasons, we do not expect a full coincidence of these results.

3. Ozone and NO_2 total column content

At the Institute of Atmospheric Physics (IAP), scientific station Kislovodsk ($43.7^\circ N$, $42.7^\circ E$, 2070 m above mean sea level), ozone measurements have been carried out since 1979. Up to 1989, the measurements were made with the IAP special instrument. The method is based on the standard Dobson method (Elansky et al., 1986a).

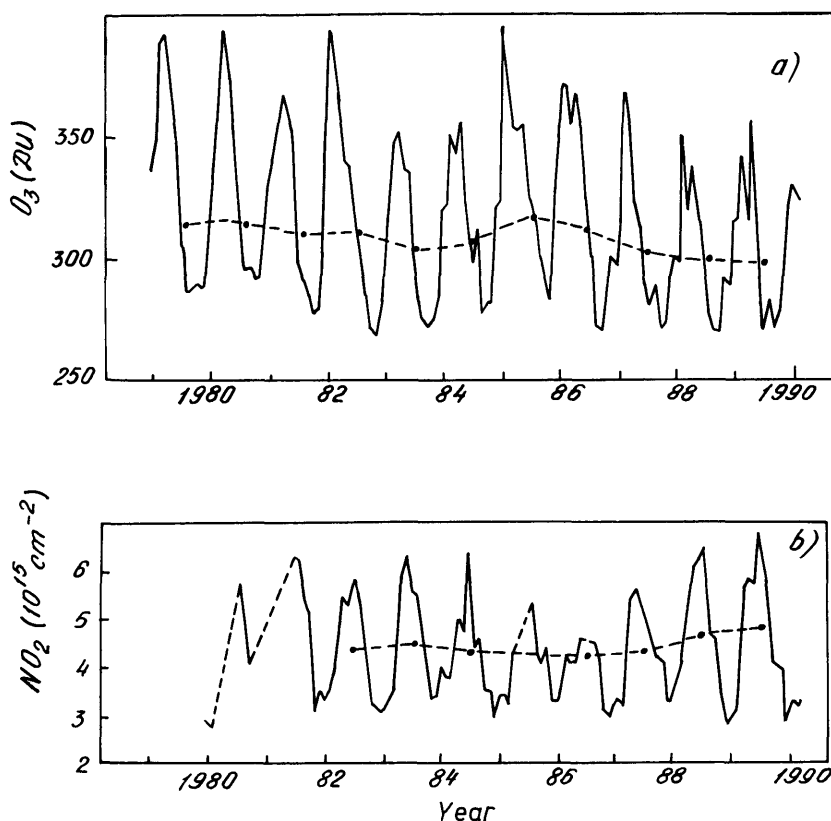


Fig. 7. Ozone and NO_2 total column content above Kislovodsk station; solid curve-monthly mean, dash-and-point curve-annual mean.

This device was calibrated in 1987 by a Dobson No. 108 spectrophotometer. In 1989, the Brewer No. 43 device was mounted at Kislovodsk and now these two instruments operate simultaneously. The Brewer spectrometer was calibrated in August 1990 by the Canadian Atmospheric Environment Service mobile etalon and its data are published in "Ozone Data for the World".

Intercomparison of the Brewer and IAP instrument data shows that the IAP data were systematically 2% lower than the Brewer data; the random standard difference of daily means is also about 2%. Thus, the set of total ozone content (TOC) data presented in Fig. 7a may be used for analysis of TOC temporal variations.

The seasonal course of TOC above Kislovodsk is presented in Fig. 8. For comparison, the mean TOC seasonal variations for the period 1960–1989 and averaged over latitudinal (30°N – 40°N and 40°N – 50°N) bands are also presented in the figure. Taking into account the 2% systematic shift and the fact that the station is at 2070 m and therefore does not include the 0–2 km layer (corresponding to about 2% of the TOC), the data are in reasonable agreement. The decrease of

TOC between July and October may be attributed to the continental Normand–Dobson effect.

It can be seen from Fig. 7a that since 1986, there has been a negative trend of TOC annual mean. This trend is due to a strong decrease of TOC during the spring/summer period (see also the Brewer data in Fig. 8).

Measurements of the NO_2 column content were started at Kislovodsk in 1979. The location of the station is suitable for such measurements, as it is far from anthropogenic NO_x sources. All data presented here have been obtained by the same spectral instrument and retrieved by the same method. The method is based on the measurements of the intensity of direct solar radiation at 5 wavelengths within the 430–445 nm region (Elansky et al., 1986a). The observations are made just after sunrise or before sunset at solar zenith angle 78° – 87° . Each morning and evening set contains 40–60 individual measurements. The standard deviation within each set depends on the atmospheric stability. Under the best conditions, it is about $2 \cdot 10^{15}$ molecules cm^{-2} , corresponding to a standard error of the set mean of $0.4 \cdot 10^{15}$ molecules cm^{-2} .

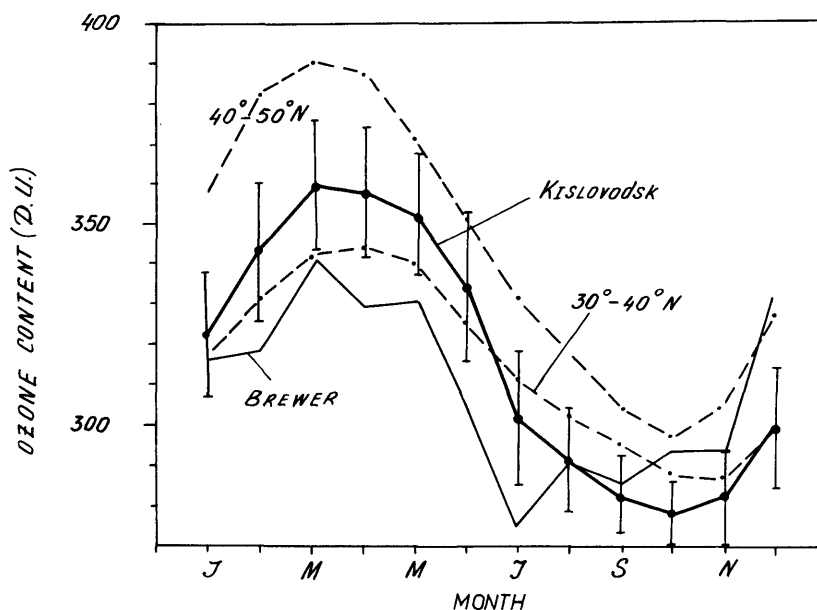


Fig. 8. Ozone total column content mean season courses. For more details, see the text. Vertical bars indicate standard deviations of monthly means during the measurement period (1979–1989).

The standard error of the data presented is on the average less than $0.7 \cdot 10^{15}$ molecules cm^{-2} . Data with an error exceeding $1 \cdot 10^{15}$ molecules cm^{-2} have not been included in the daily averages.

We estimate the systematic error of our measurement to be 40%. The main cause of such low accuracy is uncertainty of NO_2 spectroscopic parameters. The full set of measurements covering the time period from 1979 to 1984 is published by Elansky et al. (1986a). The monthly mean values are presented in Fig. 7b. Gaps correspond to months with less than 5 days of measurements. Standard deviation of NO_2 content within a single month varies from 10% in August to 30% in December.

The "direct sun" method has several advantages over that based on the zenith sky measurements: (i) it provides us with NO_2 content in the total column of the atmosphere above the point of observation; (ii) it has low sensitivity to variations of the NO_2 vertical profile, the stratospheric aerosol content and the molecular multiple scattering. For these reasons, the data for NO_2 could be used for analysis of long-period variations. The main shortcoming of the "direct sun" method is its dependence on cloudless weather.

The annual mean NO_2 content is presented in Fig. 7b. There is a detectable increase of NO_2 after 1987. Analogous to the ozone trend (see Fig. 7a), this increase is due to a significant deviation from mean spring and summer data. Possibly, it may result from 11-year period variations of the intensity of solar radiation. For more details, see Elansky et al. (1991). Several NO_2 measurements have also been made from aircraft (Elansky et al., 1986b; Elokhov et al., 1988).

3.1. Ozone surface concentration

The role tropospheric ozone plays in atmospheric photochemistry make regular concentration measurements very urgent. At some stations, long-term trends, both positive and negative, have been detected (Oltmans et al., 1989). As the ozone concentrations is strongly influenced by different atmospheric pollutants, measurements for climatic monitoring should be carried out at remote stations.

At the Kislovodsk station, regular measurements of surface ozone concentration were started in April 1989. A Dasibi 1008-AH analyzer with detection limit of 1 ppb was used. The monthly

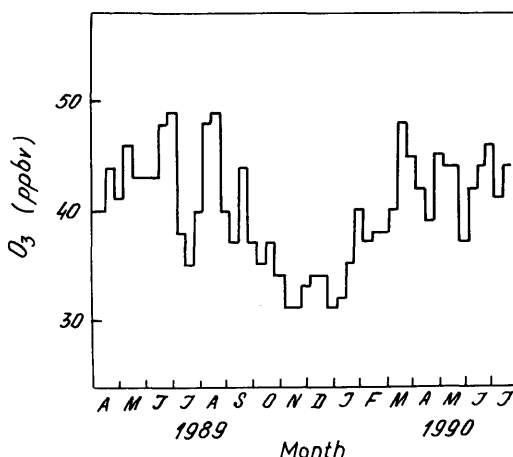


Fig. 9. Monthly mean surface ozone concentrations (Kislovodsk station).

mean values are presented in Fig. 9. Absolute values and seasonal variations are in reasonable agreement with those observed at a mountain station in Germany (Reiter et al., 1987). There is no substantial local pollution at Kislovodsk. This fact is consistent with the high reproducibility of the ozone mean daily course (Fig. 10). It differs significantly from the daily course registered in lower plain stations by the existence of a minimum at noon. This and other features may be related to a mountain ridge circulation of air and to a reduced photochemical formation of ozone at

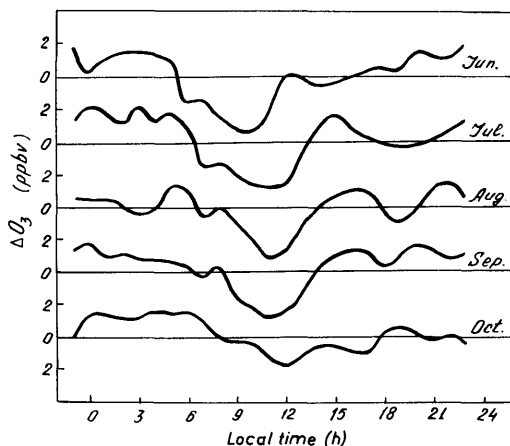


Fig. 10. Ozone surface concentration. Mean daily courses (deviations from monthly mean; Kislovodsk).

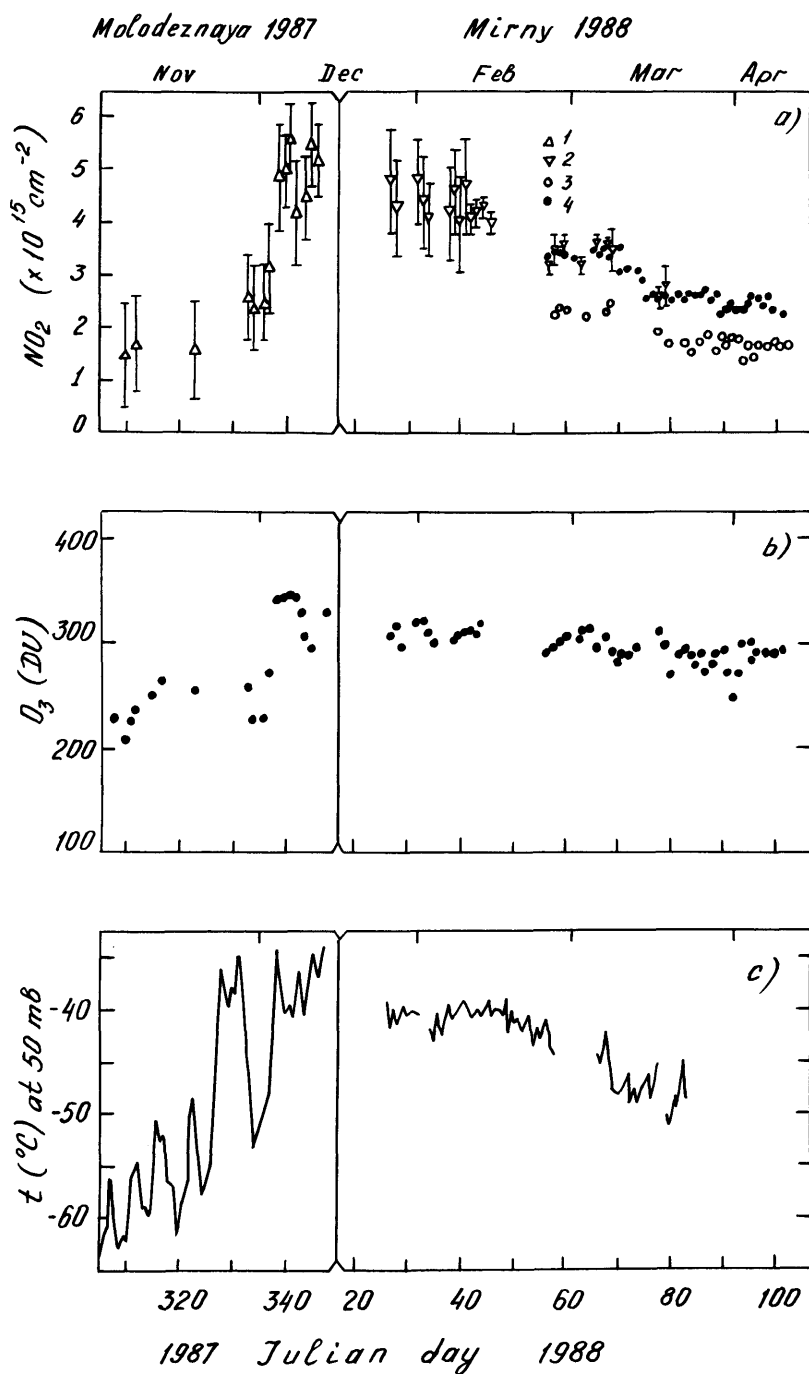


Fig. 11. Results of measurements at the Antarctic Stations (Molodezhnaya-left and Mirny-right): (a) NO_2 content: 1-morning; 2-evening, measurements using sun; 3-morning; 4-evening, measurements using zenith scattering of the solar radiation; (b) total ozone content in Dobson units; (c) temperature at level 50 mb after Gruzdev and Elokhov (1991).

higher elevations (more than 2 km) during daytime. Summertime NO_x daily mean concentrations measured by an AC-30M analyzer do not exceed 2 ppb.

3.2. Measurements of ozone and nitrogen dioxide in Antarctica

The measurements were carried out in November 1987 to April 1988. They include measurements of TOC, NO_2 total content, ozone concentration in the atmospheric surface layer at Mirny (66°33'S, 99°01'E) and Molodezhnaya (67°40'S, 45°50'E) and also during the flight Mirny–Vostok–Mirny at altitudes 30–50 m on 8 February 1988. Some preliminary results were presented by Gruzdev and Elokhov (1991). Here we summarize the results. Measurements of NO_2 were made with both the direct sun and zenith sky methods. For NO_2 measurements by direct sun radiation, the method similar to that of Solomon et al. (1987) was used. The results are shown in Fig. 11. The vertical bars indicate the random errors of the NO_2 measurements by the direct sun, while the random errors of the total ozone measurements are too small to be shown in the figure (the relative random errors here are less than 1%).

The total ozone and NO_2 content was observed over Molodezhnaya in November–December 1987 and over Mirny February–April 1988. During the first period, an irregular increase of TOC is observed from about 200 to 340 DU (Dobson Units) (see Fig. 11b). The “ozone hole” is filling up (the minimum of TOC was reached one month earlier). Alongside with this process, the stratosphere is warming (Fig. 11c) and an increase of the nitrogen dioxide content from $1.5 \cdot 10^{15} \text{ cm}^{-2}$ up to over $5 \cdot 10^{15} \text{ cm}^{-2}$ is observed. The increase in NO_2 and ozone levels is explained by the stratospheric circulation in the South polar region.

During the summer-autumn period (the right-hand parts of Fig. 11), a slow decrease of TOC is observed with daily variations due to synoptic processes. The average value for February–April is 295 DU. The NO_2 content is also decreasing, reflecting its typical seasonal course with maximum in the summer. Comparison of the morning and evening values of the nitrogen dioxide content shows (Fig. 11a) that the latter are systematically some 30% higher than the former. This reflects changes in NO_2 from day to night due to transformation of NO_x to N_2O_2 during the night with subsequent increase in NO_2 during the day as a result of photodissociation of N_2O_5 .

Measurements of the surface ozone concentration using a Dasibi AH-1008 gas analyzer (the precision is 1 ppb) reveal that it is lower than in the middle and high latitudes of the Northern Hemisphere. The results for Molodezhnaya and Mirny are presented in Fig. 12. The observed concentrations are within 10–25 ppb, only about half of what is characteristic for the Northern Hemisphere.

The seasonal variation of the surface ozone concentration in Antarctica is characterized by the winter maximum and summer minimum, which are different from the seasonal variation in the middle latitudes of the Northern Hemisphere. This is probably related to a larger intensity of dynamical processes in winter, which causes enhanced exchange between stratosphere and troposphere in the middle latitudes of the Southern Hemisphere, with subsequent ozone transfer into the lower troposphere and surface layer of the polar region.

The surface ozone concentration (SOC) has variations up to 10 ppb connected with synoptic processes. There is no statistically significant daily variation. In a synoptically quiet period, February 1988, at Mirny, the time variations of SOC are

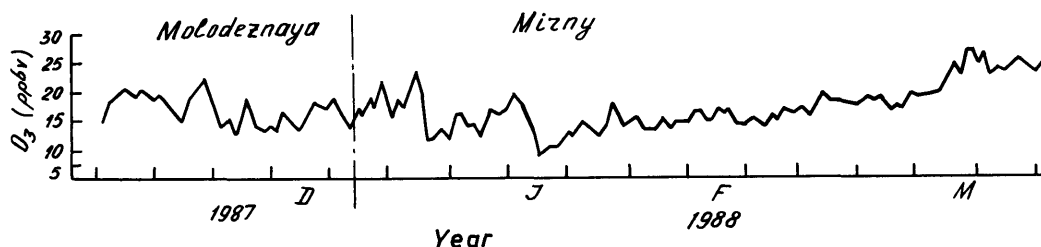


Fig. 12. Daily mean surface ozone concentration at Molodezhnaya and Mirny after Gruzdev and Elokhov (1991).

small and depend on the regime of the slope katabatic wind. An increase of the katabatic wind component in the surface wind leads to enhanced ozone concentrations.

Surface ozone measurements were also performed during the flight of the aircraft IL 14 at altitudes 30–50 m over the Antarctic plateau on 8 February 1988. As far as we know, such measurements have never been performed before. The flight route was Mirny–Vostok–Mirny and took place in a synoptically quiet period. The spatial (latitudinal) surface ozone distribution was very homogeneous at the level 13–15 ppbv with some tendency to increase towards the Vostok station (78°28'S, 106°48'E, H = 3500 m). Such a direction of the latitudinal ozone gradient gives additional support to the katabatic wind causing the surface ozone variations in synoptically quiet periods.

4. Chlorofluorocarbons

The measurements of these gases started rather recently as part of the USA–USSR Agreement on Protection of the Environment. The measurements made in Estonia and during several oceanographic

cruises have not revealed anything unexpected, but the real sensation is the discovery by Isidorov (1990) and by Isidorov et al. (1990) of several halocarbons in the volcanic gases. The gas chromatographic analysis allowed the detection of CFCl_3 (F11), CF_2Cl_2 (F12) and CCl_4 . Preliminary estimates show that the volcanic source may contribute up to 8–10% of the anthropogenic source. As the volcanic source is operating on a geological time scale, it evidently poses the problem of natural sinks for halocarbons and the steady state natural level of their atmospheric concentrations. The anthropogenic source is, at least, an order of magnitude greater than the volcanic one, so this new source does not in any sense undermine the Montreal Protocol and the necessity to phase out the production of CFCs.

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