# GASEOUS COMPOSITION OF THE ATMOSPHERE AND ITS VARIATION

**G.S. Golitsyn, V.N. Aref'ev, E.I. Grechko, A.N. Gruzdev, N.F. Elanskii, A.S. Elokhov, and V.K. Semenov**

*Institute of Atmospheric Physics, Russian Academy of Sciences, Moscow*
*Institute of Experimental Meteorology, Obninsk*
*Scientific and Production Corporation "Taifun," Obninsk*
*Kirghiz State University, " ishkek*
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*Gaseous composition of the atmosphere is an important factor determining the radiation balance on the Earth's surface and the Earth's climate. It is monitored by different means including a ramified ground-based observational network. Observations of the pollutants playing a leading role in climate formation were carried out at the stations Zvenigorod, Kislovodsk, and Issyk-Kul' of the former USSR. Data of long standing observations of the* $O_3$, $NO_2$, CO, $CH_4$, $CO_2$, *and* $H_2O$ *contents in the atmosphere and atmospheric transparency are presented and analyzed in the paper. Main peculiarities of their long-term variations have been established. Evaluated trends of* CO, $CH_4$, *and* $CO_2$ *variations are toward the steady increase of their contents in the atmosphere. The contributions of various factors determining the variation of the atmospheric composition are examined including anthropogenic and natural sources and sinks of pollution.*

## INTRODUCTION

Long-term observations of gaseous components and aerosols playing a leading role in climate formation yield information needed for estimating the variation of the atmospheric composition. Only this information provides a basis for predicting the future state of the Earth's climate and possible consequences of its change.[1]

At present, the Global Atmospheric Watch System (GAWS) is used to monitor the content of the key atmospheric climatic components and the physical-chemical parameters of the atmosphere. It incorporates the Background Air Pollution Monitoring Network and the Global Ozone Network that came into operation in the 1960 and 1950's, respectively.[2] Such Networks provide an insight into many peculiarities and reasons for variation of the chemical atmospheric composition and estimation of trends of individual components. A definite contribution to the operation of global networks comes from the stations located in the territory of the former USSR. These stations also can be divided into two networks, namely, the Background Air Pollution Monitoring Network and the Ozone Network. However, these stations are equipped, as a rule, with less accurate devices in comparison with the GAWS and their capabilities are severely limited.[3] So, the M-124 filter ozonometers rank considerably below the Dobson and Brewer ozonometers in their accuracy. They fail to measure the vertical ozone profiles with the use of the reversal effect.

Ozonesondes are not sent aloft at the Ozone Network. In addition, the number of stations is sharply decreased and the quality of experimental data is decreased too in recent years in the states of the former USSR due to total crisis.

The World Meteorological Organization, other international organizations, and some countries make their efforts to develop the monitoring network. First of all, these efforts are directed toward full coverage of Asia with stations and creation of reference stations that are capable of measuring the concentration of the largest possible number of pollutants including not only their surface concentration, but also their vertical profiles in the entire troposphere and the stratosphere.

In the states of the former USSR, there are only several stations that satisfy the requirements of the GAWS standards. Among them are three stations that could be considered as reference ones, namely, the stations Kislovodsk and Zvenigorod of the Institute of Atmospheric Physics of the RAS and the station Issyk-Kul' of the Kirghiz State University and the Institute of Experimental Meteorology.[4,5] The longest-term and most qualitative series of observational data on climatically active pollutants were obtained at these stations.

Here, we present mainly the results of these observations. To describe the spatial distribution of pollutants, we also present results of individual observations performed in the other regions.

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## MEASUREMENTS

The station Zvenigorod (200 m above sea level and 55.42°N, 36.47°E) is located to the southwest of Moscow at a distance of 50 km in a rural region. The effect of urban surroundings is not so strong, because west winds prevail in this region.[1]

The high-mountain station Kislovodsk (2070 m above sea level and 43.73°N, 42.66°E) is located on a plateau in the foothills of the Bol'shoi Kavkaz to the south of the Kislovodsk health resort at a distance of 18 km. There are no noticeable sources of atmospheric pollutants in the neighborhood of the station.[4]

The high-mountain station Issyk-Kul' (1650 m above sea level and 42.63°N, 76.98°E) is located on the shore of Lake Issyk-Kul' in a rural region. Here, industrial sources of pollution have practically no effect on the experimental results.[5]

Observations of a large number of chemically active and trace components of the atmosphere producing the greenhouse effect were performed at these stations. Table I lists regularly or continuously measured atmospheric components used to estimate long-term variations of their concentration. Results of analysis of long-term series of data on individual components are given below.

*TABLE I. Pollutants measured at scientific stations and year of the regular measurement start.*

| Station | Pollutant | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $O_3$ | $NO_2$ | CO | $CO_2$ | $CH_4$ | $H_2O$ | $[O_3]$ | UV-B |
| Zvenigorod | – | 1990 | 1970 | 1990 | 1972 | 1974 | – | – |
| Kislovodsk | 1979 | 1979 | 1993 | – | – | 1993 | 1989 | 1993 |
| Issyk-Kul' | 1980 | 1980 | – | 1980 | – | 1980 | – | – |

## OZONE

The total ozone content (TOC) in the atmospheric column has been measured at the station Kislovodsk since 1979. At first, measurements were carried out with the use of a special spectral device developed at the Institute of Atmospheric Physics (IAP). Since 1987, the measurements have been performed with the use of the Brewer spectrophotometer No. 43 (Fig. 1). Both devices were regularly calibrated and their readings yielded a homogeneous data series.[4]

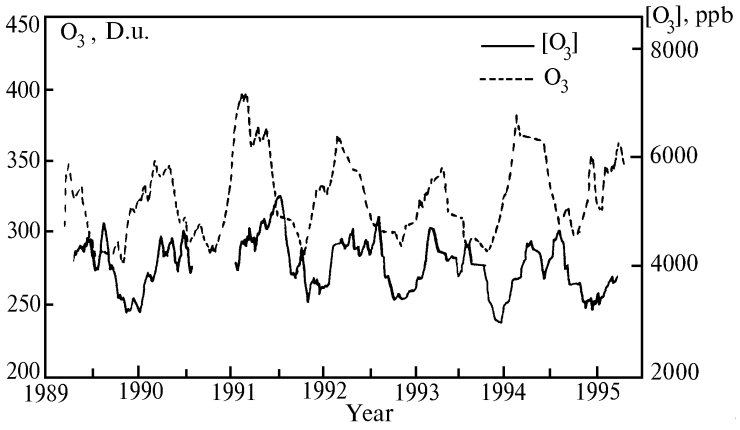


*FIG. 1. Surface ozone concentration and total ozone content (averaged over 21 measurements) from the data of observations at the station Kislovodsk.*

The TOC also has been measured at the station Issyk-Kul' with a spectral device, calibrated against the national standard,[5] since 1980.

According to the experimental data, the TOC was decreased in 1980–1990, with the rate of decrease of about 1.4 D.u. (Dobson units) per year. The rate of the decrease was higher in 1990–1993 and the ozone content reached its minimum. The same decrease of the TOC was observed nearly at all the stations of the Ozone Network located at high and middle latitudes of the northern hemisphere, with the highest rate of decrease in winter–spring. In the next two years, the ozone content was somewhat increased. Ozone nearly recovered its average level in 1995. However, winter–spring anomaly of ozone behavior became more pronounced for Eastern Siberia. There the total ozone content in March decreased by 40% in comparison with its average level. This suggests a possible development of an ozone hole above Eastern Siberia.[6]

Contrary to the TOC, whose value is primarily determined by stratospheric ozone, the surface ozone concentration in the northern hemisphere $[O_3]$, on average, has been increased in recent decades.

In some regions of Western Europe and the U.S.A. the rate of increase reached 1% per year.[7] High levels of the surface ozone concentration (SOC) have already had an adverse effect on population, crop, and environment. National economy of many countries suffers heavy loss.[8]

Efforts made by developed countries toward the development of the Ozone Network led to the conclusion that the rate of ozone change varied from region to region and was primarily determined by the pollution of the atmosphere with nitrogen oxides and hydrocarbons.[7,8]

In March of 1989, a start was made on regular measurements of the ozone concentration at the station Kislovodsk. They solve two problems. First, the data obtained at this station are representative of the ozone variability typical of the free atmosphere not only on regional, but also on global scale. Second, they provide a possibility to select the effect of dynamic processes on the ozone regime in an unpolluted region.

The measurements were performed during day and night with the Dasibi 1008 AN device.[9] The average-annual ozone concentration was 39 ppb (see Fig. 1). The maximum values of concentration were recorded in summer, while the minimum ones - in winter.

Seasonal and daily ozone variations there were much less pronounced in comparison with the rural plain regions and the more so with industrial regions. Elucidation of the mechanism of diurnal ozone variation was an important result. It was governed by mountain–valley circulation and photochemical ozone destruction for low concentration of nitrogen oxides and enhanced solar activity. The estimated trend of the average-annual ozone concentration was (−1.2) ppb for 1989–1995, which corresponded to the 0.5% rate of ozone concentration decrease per year. This result shows the reverse tendency of variation of the ozone concentration in comparison with plain regions of Eastern Europe. Unfortunately, we could not estimate the ozone variations in any other region of our country due to the lack of the network of tropospheric ozone monitoring in Russia.

Occasional ozone measurements were performed in different regions. In particular, a comprehensive study of the ozone vertical profiles was performed in the Atlantic and the Weddell Sea.[10] In unpolluted remote oceanic regions, the photochemical processes resulted in ozone destruction in the bright sunlight as they did under high-mountain conditions. The diurnal and seasonal variations of ozone were also small there. For weak illuminance of the sea surface (typical of the Weddell Sea), the photochemical processes were weakly pronounced. They had practically no effect on the temporal ozone behavior in the surface layer. Among dynamic processes, advection of air from continents and vertical mixing in the troposphere played dominant roles.[10]

Radically different ozone behavior was observed in Moscow.[11] Individual runs of measurements of ozone and other gases were performed in different seasons. It was found that the ozone concentration in urban surroundings was much lower than in the rural ones. Ozone destruction was primarily caused by its reaction with nitrogen oxide (NO), exhausted in the atmosphere by motor engines and emitted by industrial enterprises. A quasistationary state, close to the state of photochemical equilibrium set up in the daytime between ozone and nitrogen oxide in the air basin above Moscow, was found to be established according to our studies. It turned out that such equilibrium held within the limits of experimental error under conditions of weak illumination (in fall and winter and in the presence of cloudiness in spring and summer). This testifies that the rate of reactions of hydrocarbon oxidation is much lower in polluted urban air than in relatively clear rural air. That is, an abundance of hydrocarbons, emitted into the atmosphere in Moscow, leaves it practically without destruction. Obviously efficient transformation of pollutants occurs in the urban plume in which high and ecologically hazardous values of the ozone concentration may be observed.

## NITROGEN DIOXIDE

Regular measurements of the total $NO_2$ content and vertical profiles of the $NO_2$ concentration in the atmosphere were performed at the stations Zvenigorod, Kislovodsk, and Issyk-Kul'. Individual series of observations were performed in the Antarctic and the Atlantic.[4,5,12–15]

### A. Observations at the station Zvenigorod

Measurements of the $NO_2$ content were based on recording of the spectral intensity of the scattered solar radiation in the zenith in the wavelength range 435–450 nm with the MDR-23 monochromator. The measurements were performed in the twilight at solar zenith angles varying from 84 to 96°. The $NO_2$ content for a slant path was estimated from the recorded spectrum by the differential $NO_2$ absorption considering the absorption by $O_3$, single molecular and aerosol scattering, and the Ring effect. The $NO_2$ masses were calculated for a spherical model of the atmosphere scattering the solar radiation to determine the total $NO_2$ content and the vertical profiles of the $NO_2$ concentration. In the calculations, the photochemical model of the diurnal behavior of $NO_2$ was used. The vertical profile of the $NO_2$ concentration was estimated for layers 5 km thick and for a thin atmospheric surface layer. It was determined by the inverse-problem method with the use of the modified method proposed by Elokhov and Gruzdev[15] and analogous to the method by McKenzie et al.[16]

The $NO_2$ content has been regularly measured since March of 1990. Figure 2 shows the behavior of sliding ten-day average values of the total $NO_2$ content from the data of morning and evening measurements performed from March of 1990 to February of 1996. The total $NO_2$ content was determined as a sum of $NO_2$ content in the layers above 10 km. It is seen from Fig. 2 that it undergoes variations in a wide range of temporal scales. The annual behavior of $NO_2$ with the summer maximum and the winter minimum, caused primarily by photochemical processes (see the review of related papers in Ref. 14) and typical of non-tropical latitudes of the northern hemisphere, was prevalent. An excess of morning values of $NO_2$ content over evening ones was representative of the diurnal behavior of stratospheric $NO_2$ typical of mid-latitudes. Day-to-day variations of $NO_2$ were caused by synoptic processes.

In addition, substantial year-to-year variability of the $NO_2$ content in the stratosphere is seen from Fig. 2. In 1992, the sharp decrease of the total $NO_2$ content was observed. It reached 40% in spring and summer of 1992 in comparison with the corresponding values of the total $NO_2$ content in 1991. The same decrease was observed by other authors elsewhere.[14,15] It was assumed to be partly due to heterogeneous chemical processes, in which the volcanic aerosols were involved formed after the eruption of Pinatubo Volcano in summer of 1991. By 1993 and 1994, the total $NO_2$ content in the stratosphere was partly restored; however, it had not yet reached the level of 1991. A slower rate of the increase of the total $NO_2$ content in 1993–1994 should be pointed out in comparison with 1992–1993.

Figure 3 shows the spatiotemporal distribution of the average monthly values of the $NO_2$ concentration in the atmosphere over Zvenigorod in 1991–1994 obtained by way of interpolation of the values of $NO_2$ content in 5-km layers. In calculation of the $NO_2$ content in 1992, nearly tenfold increase of the aerosol content in the volcanic aerosol layer centered at an altitude of about 20 km was considered.[15] The decrease of the $NO_2$ content in 1992 and its subsequent partial recovery in 1993 and 1994 are clearly seen from Fig. 3 at various altitudes in the stratosphere.

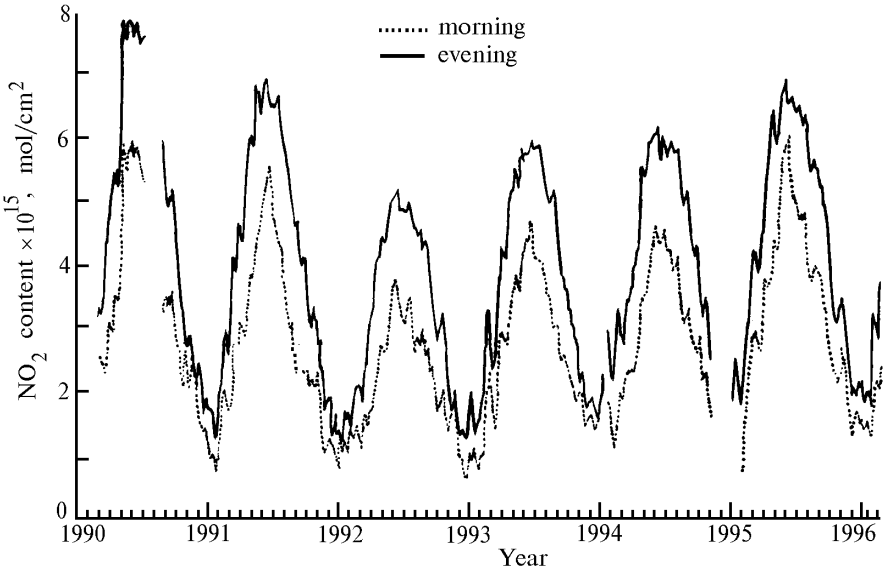


*FIG. 2. Sliding ten-day average values of the total* $NO_2$ *content in the stratosphere at the station Zvenigorod.*

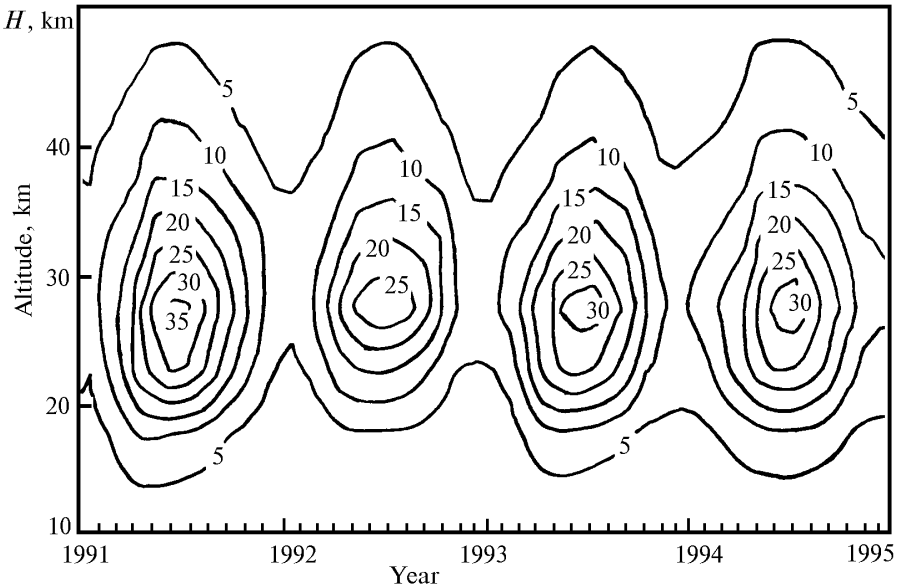


*FIG. 3. Spatiotemporal behavior of the average monthly* $NO_2$ *concentration from the data of measurements at the station Zvenigorod in 1991–1994. The numbers adjacent to the curves indicate the concentration* × 10 mol/cm.

To distinguish the decrease of the $NO_2$ content and its vertical structure, the deviations of the running average monthly values of the $NO_2$ content in the 5-km layers from their averages for four years (1991–1994) were calculated. Figure 4 shows the spatiotemporal distribution of the monthly deviations normalized to the average monthly values of the total $NO_2$ content in the atmosphere for four years. Isolines shown in Fig. 4 are constructed by way of interpolation between the values at the centers of the 5-km layers. The figures adjacent to these isolines indicate the percentage of variation of the total $NO_2$ content in the 5-km layers normalized to the total $NO_2$ content in the stratosphere.

The sharp decrease of the $NO_2$ content in the lower stratosphere in 1992 is clearly seen from Fig. 4. The $NO_2$ content in the layer 20–25 km was decreased by 6–7% in spring–summer of 1992 in comparison with the total $NO_2$ content in the stratosphere. It is also important to note that the first indications of the decrease of the $NO_2$ content in the stratosphere became pronounced already in fall of 1991 (considering that negative deviations of the $NO_2$ content analogous to those shown in Fig. 4 but calculated from the unperturbed distribution of $NO_2$ manifest themselves earlier than in Fig. 4).

Returning to the problem of year-to-year variability of $NO_2$, we note a large increase in the total $NO_2$ content in the stratosphere in 1994–1995. As a result, the total $NO_2$ content in 1995 reached the values observed in 1991 (see Fig. 2). Considering that the rate of the increase of the $NO_2$ content for the preceding year (1993–1994) was much less, we can draw a conclusion that the increase of the $NO_2$ content in 1995, as well as its decrease in 1991 (in comparison with 1990) was at least partly caused by its natural variability in the chemically unperturbed stratosphere.

In addition to the $NO_2$ content in the stratosphere, the $NO_2$ content in the troposphere was also measured at the station Zvenigorod. Figures 5*a* and *b* show the average monthly values of the $NO_2$ content in a thin surface layer, in the layer 0–5 km (without surface $NO_2$), and in the layer 5–10 km from the data of morning and evening measurements from March of 1990 to February of 1996. The tropospheric $NO_2$ content has clearly pronounced diurnal behavior, day-to-day variability, annual behavior, and year-to-year variability. The highest values of the tropospheric $NO_2$ content were observed during periods of tropospheric pollution that were most often encountered in winter.[15] As seen from Fig. 5, the $NO_2$ content in the surface layer was commonly higher in the evening than in the morning and was representative of local peculiarities of $NO_2$ production during the day. The $NO_2$ content in the layer 0–5 km was commonly higher in the morning than in the evening, which is probably connected with different solar ray paths (in the morning, solar rays were propagated above Moscow with its environs characterized by an enhanced level of tropospheric pollution by nitrogen oxides).

Periods with high level of tropospheric pollution by nitrogen dioxide were followed by periods of the clear air troposphere 5–10 days long from October to March, that is, they have temporal scale typical of the synoptic processes. Therefore, it is natural to assume that high values of the tropospheric $NO_2$ content over Zvenigorod from fall to spring are connected with pollutant transport.

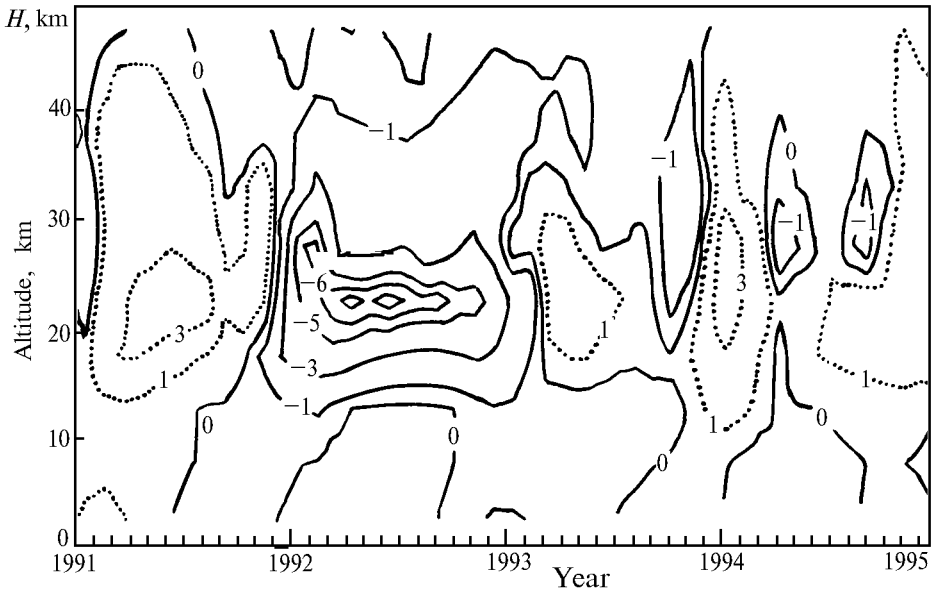


*FIG. 4. Deviations (in %) of the average monthly values of the* $NO_2$ *concentration in the* 5-km *thick layers from their average for four years normalized to the total* $NO_2$ *content in the stratosphere derived from the data of measurements at the station Zvenigorod in 1991–1994.*

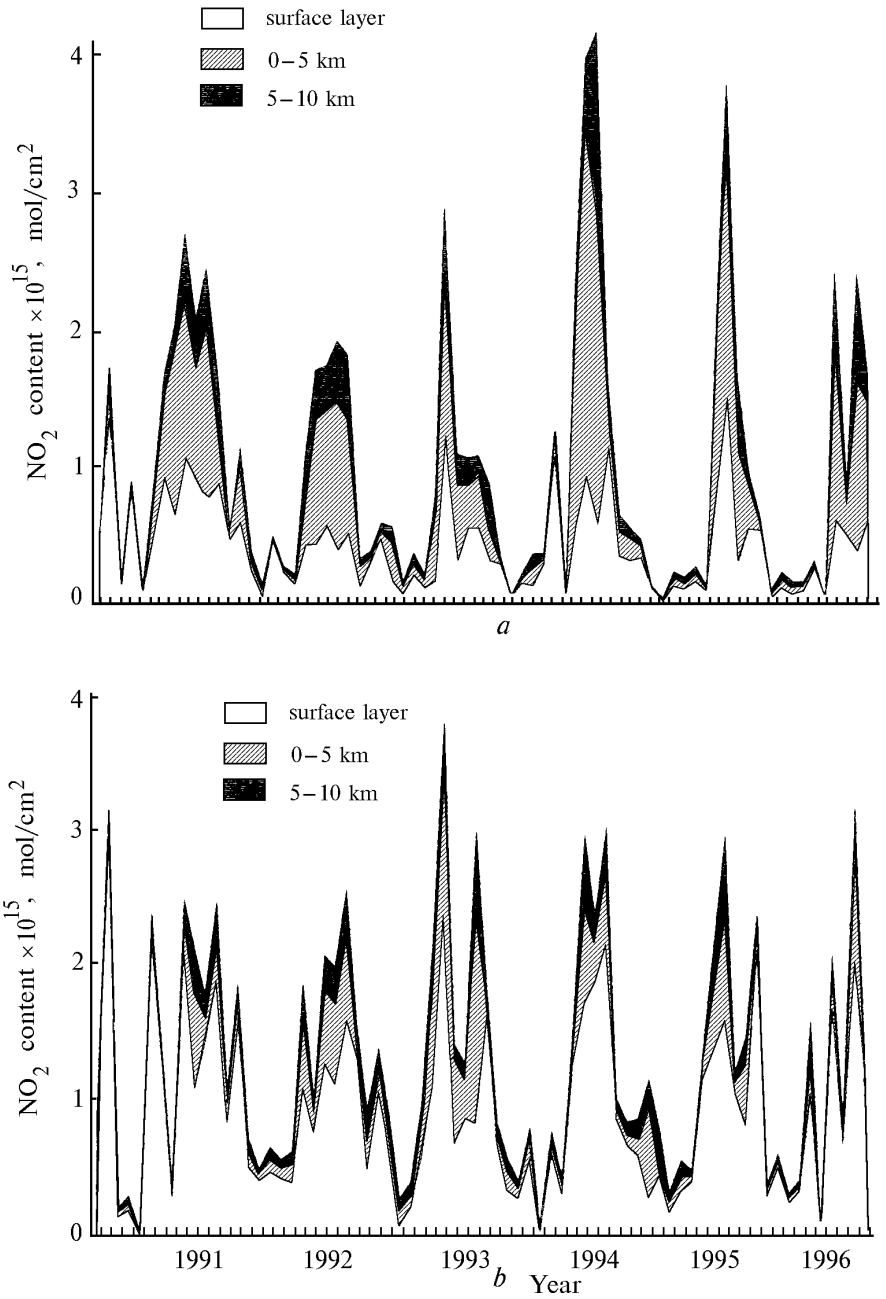


*FIG. 5. Average monthly* $NO_2$ *content in the surface layer, in the layer* 0–5 km *(without surface value of* $NO_2$*), and in the layer* 5–10 km *during six years from the data of morning (a) and evening (b) measurements at the station Zvenigorod.*

### B. $NO_2$ in the Antarctic and the Atlantic

Here, we present some results of measuring the $NO_2$ content from aboard the scientific-research vessel *Akademik Fedorov* during its mission to the Antarctic and back in late 1989. In addition to the results of analysis of the temporal variability of $NO_2$ obtained at the station Zvenigorod, measurements in the Antarctic and the Atlantic show some peculiarities of the spatial variability of $NO_2$.

Figure 6 shows the values of the total $NO_2$ content derived from the data of morning and evening measurements in the Weddell Sea (Eastern Antarctic) in September–October of 1989 when the ship sailed slowly in the 62–66°N latitude belt. The temperature at an altitude of 20 km from data of radiosonde measurements is also shown in this figure. First of all, we note large day-to-day variations of the total $NO_2$ content, being well correlated with temperature variations. Seasonal behavior is seen to be neutral in Fig. 6 (cf. with that in Fig. 2 for

March–April). The minimum values of the total $NO_2$ content, observed at the end of September, were typical of the period of the ozone hole over the Antarctic,[12] whereas at mid-latitudes of the northern hemisphere they were observed in winter (see Fig. 2). The variations of the total $NO_2$ content shown in Fig. 6 were connected with evolution (displacement and deformation) of the stratospheric circumpolar vortex.

Figure 7 shows latitudinal distribution of the total stratospheric $NO_2$ content and of the total tropospheric $NO_2$ content (in the 0–10 km layer) derived from measurements in the Atlantic in November – early December of 1989. Larger values of the total stratospheric $NO_2$ content were observed in the southern hemisphere (SH) in comparison with the northern hemisphere (NH). This is representative of the seasonal deviations of $NO_2$, with the maximum $NO_2$ content in summer (cf. with latitudinal distribution of the total $NO_2$ content in other seasons[13,14]).

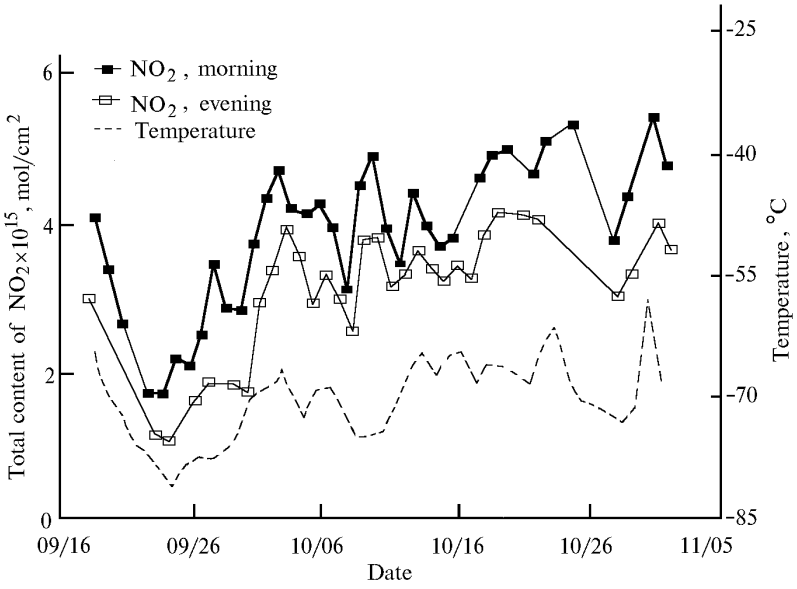


*FIG. 6. Total* $NO_2$ *content and the air temperature at an altitude of* 20 km *from the data of measurements in the Weddell Sea in September–October of 1989.*

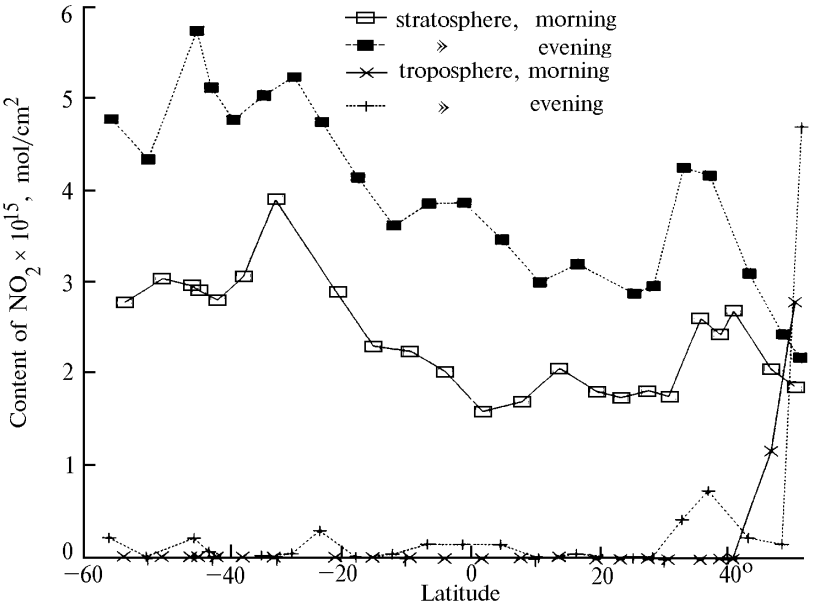


*FIG. 7. Latitudinal distribution of the total stratospheric* $NO_2$ *content and of the tropospheric* $NO_2$ *content (in the layer* 0–10 km*) in the Atlantic from the data of morning and evening measurements.*

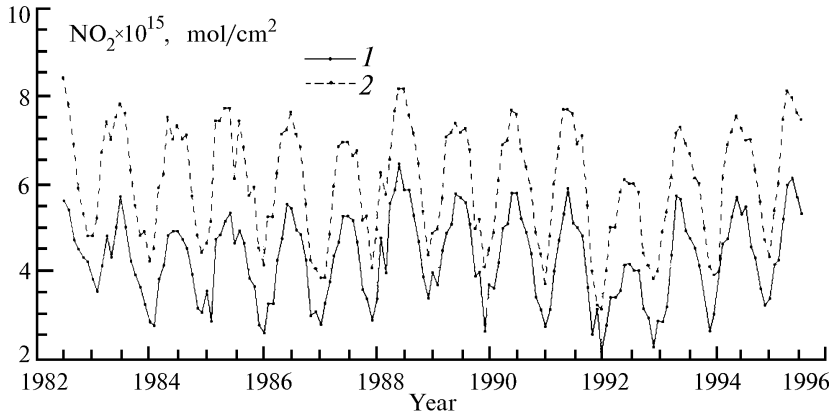


*FIG. 8. Average monthly values of* $NO_2$ *content from the data of observations at the station Issyk-Kul'.*

The fine structure of the longitudinal distribution of the stratospheric $NO_2$ is caused by circulation processes.

The maximum $NO_2$ content was recorded at subtropical latitudes of the NH to the north of the subtropical jet. The same behavior was observed in May of 1988 by Elokhov and Gruzdev.[13]

The background tropospheric $NO_2$ content over the Atlantic was very low (Fig. 7). However, there were six maximums in the latitudinal distribution of the total tropospheric $NO_2$ derived from the data of evening measurements. Five of them, along with the sole maximum in morning run of measurements, may be explained by the proximity of continents. Two maximums in the SH at 55 and 45°S were observed when the vessel approached Southern America (the sun was above the continent when evening measurements were performed). The maximum at 25°S was recorded when the vessel traversed Rio de Janeiro and the maximum at 35°N – when the vessel traversed the Strait of Gibraltar, where shipping routes converge. Very high values of the total tropospheric $NO_2$ content were recorded in the English Channel (50°N). Obviously, they were caused by a high level of the tropospheric pollution above Europe and England.

An interesting and important peculiarity of the tropospheric $NO_2$ content seen from Fig. 7 is its weak but steady evening maximum in the equatorial belt. Two reasons for the occurrence of this maximum may be given, namely, the increase of the tropospheric $NO_2$ content by the evening due to first, the air exchange between the stratosphere and troposphere as a result of convection in the intratropical zone of convergence and second, generation of $NO_2$ in the lightning accompanying the evolution of convective cloudiness. An analysis of the vertical profiles of the tropospheric $NO_2$ content above the equatorial belt shows that it is insignificant in a thin layer adjacent to the water surface and approximately equal for the layers 0–5 and 5–10 km. Thus, we cannot decide between these hypotheses.

### C. Observations at the stations Kislovodsk and Issyk-Kul'

Longer-term series of $NO_2$ observations were performed at the stations Kislovodsk and Issyk-Kul' (see Table I). At the first station, the $NO_x$ content was derived from the measurements of the direct solar radiation and at the second station – from scattered solar radiation measured in the zenith in the visible spectral range. Observational data (Fig. 8) and analyses of the long-term variability of the pollutant were presented in Elanskii et al.[4] and Aref'ev et al.[5] A salient feature of the $NO_2$ behavior was the sharp decrease of its content in 1991–1992. It was decreased by 30–40% by the end of 1992. Thus, the anomaly was observed at all stations. It gives us estimates of the magnitude and character of the effect of the volcanic eruption on the stratospheric composition.

#### *Carbon oxide*

Carbon oxide is a key trace gas of the troposphere. Its equilibrium content to a considerable degree determines the OH concentration, which in its turn is a sink for $NO_x$, $H_2S$, DHS, and other pollutants in the troposphere. Carbon oxide produces the greenhouse effect. Its radiative impact is comparable to that of F-11. Thus, monitoring of the background CO content is an important problem of tropospheric chemistry.

The spectrometric method was used for measuring the CO content. It is based on recording of solar radiation transmitted through the atmosphere in spectral ranges in which absorption lines of CO are presented. The relation of the measurable characteristics with the column gas content was determined by way of mathematical modeling of the atmospheric transmission by the line-by-line method with the use of spectroscopic data bases, specifications of measuring devices, and meteorological conditions.[17] In comparison with local methods, the spectroscopic method allowed us to eliminate the effect of local anthropogenic and natural sources of pollution when the accuracy

of individual measurement was 3–5%. Field spectrophotometers equipped with a solar tracking system and a spectral recording and processing system[18] were used to perform the measurements.

Measurements of the CO content were started at the station Zvenigorod in 1970. The longest-term series of data were obtained. Figure 9 shows the average monthly values of the CO content. Carbon oxide undergoes seasonal variations with the spring maximum (in March-April) and the fall maximum (in September). The amplitude of seasonal variations was 50%. Deviations of the running monthly values of CO from their average for 1970–1994 are shown at the bottom of this figure. A common positive trend in the behavior of the CO content is vividly seen.

The data of measuring the CO content for winter–spring and summer-fall are shown in Fig. 10. On average, the CO content has been increased in winter–spring in the last 25 years by 0.7% per year and in summer–fall by 1% per year. At the same time, whereas in 1970–1985 the rate of the CO increase was 1.9 and 1.8%, respectively, in the last decade a trend has become pronounced toward its slower increase in summer–fall (0.5% per year) and even toward the occurrence of a negative trend in winter–pring (–0.2% per year). The same trend was established elsewhere[19] not only for CO, but also for methane.

At present, two possible reasons for the slower CO trend are discussed. The first reason is associated with the decreased amount of CO due to the use of internal combustion engines with reduced CO exhausts as well as with less intensive development of virgin land in savanna when large areas covered with dry grass are set on fire to clear the land for cultivation. The second reason is associated with the stratospheric ozone depletion. In this case, the amount of the UV radiation, actively influencing tropospheric hydroxyl production, increases. As a result, the increase of the OH content, considering that the reaction between OH and CO is the main sink for CO, leads to fast removal of this gas from the troposphere through its transformation into carbon dioxide and water vapor.

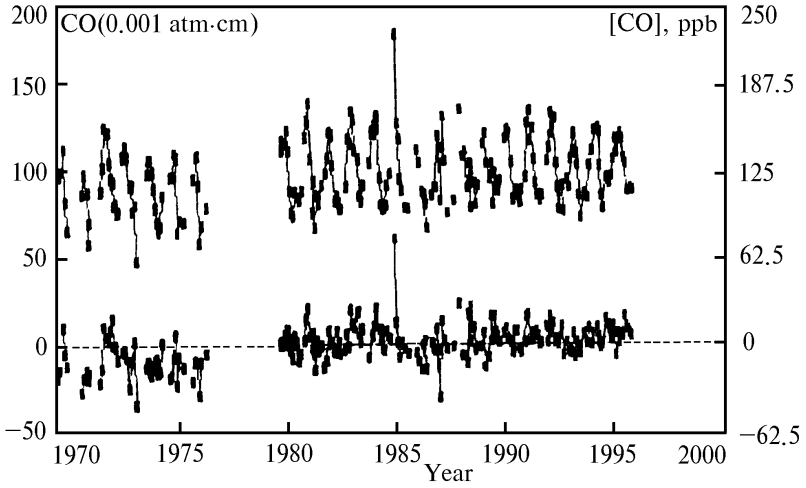


*FIG. 9. Average monthly values of* CO *content at the station Zvenigorod and deviations (*ΔCO*) from their average for 1970–1994.*

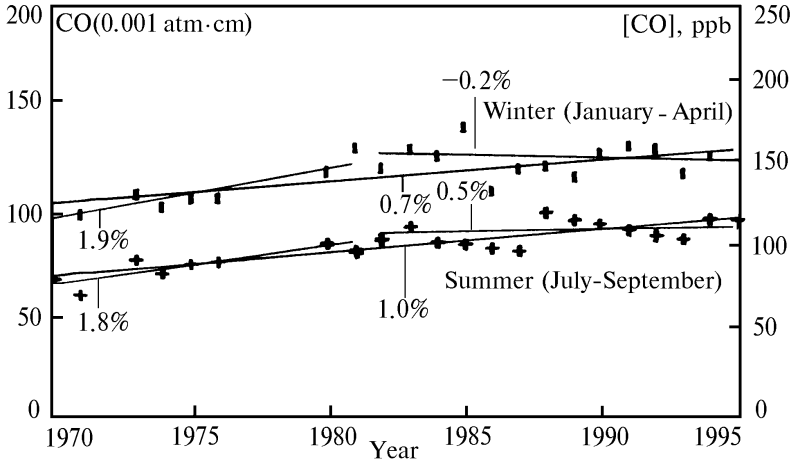


*FIG. 10. Long-term trends of the* CO *content observed at the station Zvenigorod for different seasons.*

Further observation will demonstrate how stable are the trends of the CO increase established in the last decade.

*Methane*

The data of measuring the methane content in the atmosphere at the station Zvenigorod are shown in Fig. 11. The measurements were started in 1974. A trend is seen toward the methane increase by 0.5% per year. At the same time, in 1974–1987 the methane content increased by 1% per year. The rate of the increase of the methane content measured by Bekki et al.[19] and McManus et al.[21] was 0.5–1%.

*Carbon dioxide*

The spectroscopic method based on measuring the solar radiation absorption at a wavelength of 2.06 μm was used for monitoring of the $CO_2$ concentration in the atmosphere. The spectral resolution of a spectrophotometer was 3 $cm^{-1}$. The $CO_2$ content was determined by way of comparison of the measured radiation absorption with its calculated values. Calculation procedure was identical to that used for measuring CO.

The data of measuring $CO_2$ content at the station Issyk-Kul' are shown in Fig. 12. Seasonal variations of $CO_2$ concentration during the year are representative of the seasonal variations of $CO_2$ exchange between the biota and the atmosphere. The maximum $CO_2$ variations were recorded in spring (in May), whereas the minimum ones – in fall (in September).

The amplitude of seasonal variations in 1980–1982 was 6–8 ppm. In 1982–1986, it was increased up to 11 ppm and in 1987 it reached its maximum (24 ppm). In succeeding years the amplitude was decreased down to 6–8 ppm. Average-annual values of the $CO_2$ concentration, recorded at the station Issyk-Kul' in 1981–1995, confirmed the global increase of the $CO_2$ content in the atmosphere.

In 1980–1988, the $CO_2$ increase coincides, on average, with that recorded at the other stations of background monitoring.

In 1990–1994 (with the exception of 1992), the average-annual values of concentration remained practically unchanged. Only in 1995, the $CO_2$ increase became pronounced again.

The trend of $CO_2$ concentration, estimated in the linear approximation, was 2.2 ppm/year. The annual $CO_2$ concentration, calculated for $CO_2$ emission borrowed from Ref. 20 for 1980–1988, practically coincided with the measured one. The standard deviation of calculated values from experimental ones was 1.5%. Recent data on $CO_2$ emission are lacking or unreliable.

*Water vapor*

Observations are performed at the station Issyk-Kul' by the spectroscopic method described above. The same device and spectral band as for measuring $CO_2$ are used.

Average monthly values of $H_2O$ content are shown in Fig. 12*b*. The minimum $H_2O$ content was observed in winter (0.3–0.6 g/$cm^2$) and the maximum – in summer (2.3–2.8 g/$cm^2$). Average amplitude of seasonal variations was 1.9 g/$cm^{-2}$.

To estimate long-term variations and trend of the $H_2O$ content, sliding averaging was performed over twelve months. In 1981–1985, the $H_2O$ content decreased from 1.4 to 1.0 g/$cm^2$ and then it increased steadily. The coefficient of correlation between the smoothed values of $H_2O$ content and the corresponding smoothed surface temperatures was 0.7.

The estimated rate of the linear $CO_2$ increase for the measurement period was 0.18 g/$cm^2$ per year or about 1% per year.

The aerosol plays an important role in the Earth's climatic system. It is involved in the radiation balance. In addition, it is involved in heterogeneous atmospheric processes being responsible, in particular, for such anomalies as ozone holes.

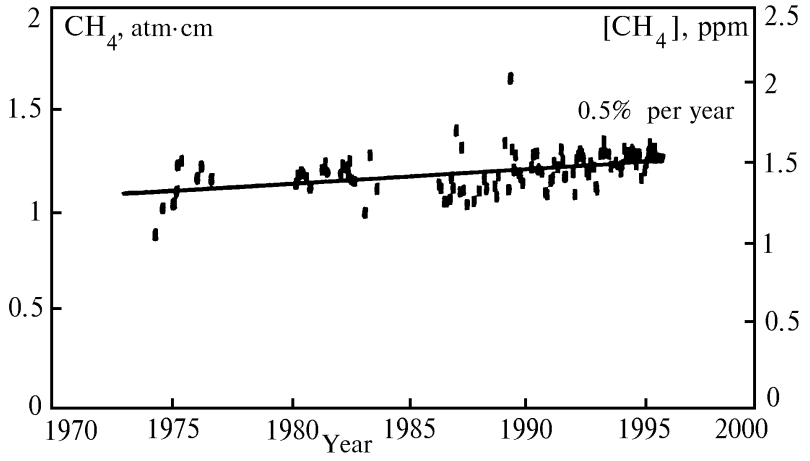


*FIG. 11. Long-term trend of the methane content observed at the station Zvenigorod.*

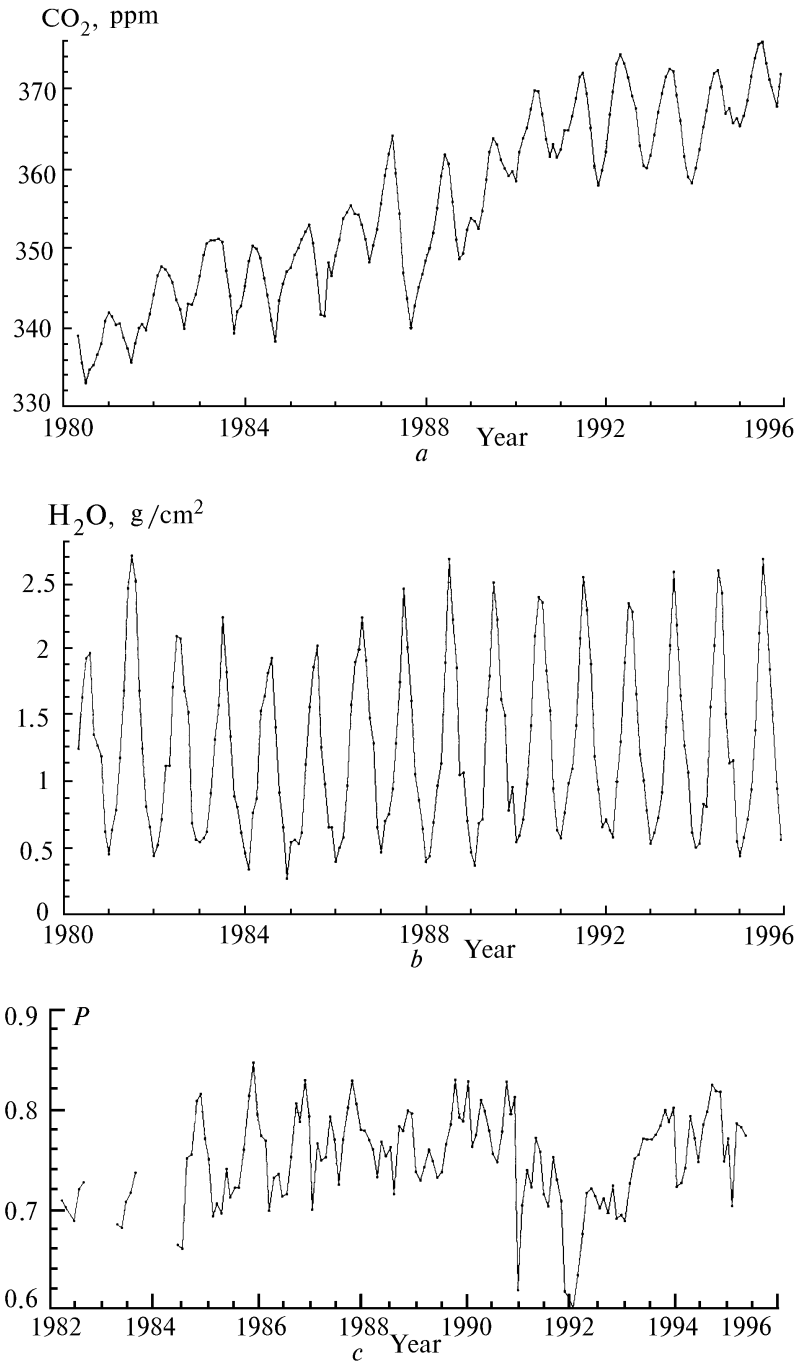


*FIG. 12. Average monthly values of the* $CO_2$ *(a) and* $H_2O$ *(b) concentration and atmospheric transparency (c) from the data of observations at the station Issyk-Kul'.*

*Atmospheric transparency (aerosol)*

Aerosol plays an important role in the Earth's climatic system. It is involved in the radiation balance. In addition, it is involved in heterogeneous atmospheric processes being responsible, in particular, for such anomalies as ozone holes. Regular observations of the atmospheric transparency and of the aerosol optical thickness are performed at the station Issyk-Kul'. The long-term variations of transparency were established from the observational data (Fig. 12*c*). In particular, its marked decrease in the latter part of 1991–1992 is seen from the figure. The decrease was due to the volcanic aerosols emitted in the atmosphere during the eruption of Volcano Pinatubo. Simultaneous observations of ozone and nitrogen dioxide showed that their reduced contents were observed synchronously with the increased stratospheric aerosol concentration. The amplitude of recorded variations confirms the observed contents of gases and aerosol, theoretical

estimates of the efficiency of heterogeneous processes, and their possible roles in the formation of $O_3$ and $NO_2$ anomalies in polar regions.

## EVALUATION OF SOURCES AND SINKS

Variations of the content of pollutants in the atmosphere are caused by the action of their sources and sinks. In this section we present some results of investigations performed at the Institute of Atmospheric Physics (IAP) of the Russian Academy of Sciences.

Intense sources of an important gas producing the greenhouse effect – methane – are leaks in gas-supply pipes and stations of gas pressure reduction. Natural gas is 98% methane. The amount of $CH_4$ discharged into the atmosphere was experimentally investigated at the gas pressure reduction stations located in the Moscow Region. We used the method of dynamic modeling and the trace gas method.

The essence of the dynamic modeling method is retrieval of the gas source strength from the measured field of $CH_4$ concentration nearly the source. Air samples were taken leeward simultaneously at different distances from the station in the experiment. Then the $CH_4$ concentration was determined with a gas chromatograph. In the experiment, we also measured the meteorological parameters including the wind velocity and the parameters describing the boundary layer stratification and the cloud type. The Pasquill-Gifford theory of concentration distribution over a plume was employed to solve the inverse problem.

The trace gas method harnesses any trace gas that has no natural sources. In this case, $SF_6$ was used. A calibrated source of $SF_6$ was placed near the $CH_4$ source. The values of concentration of these two gases were measured leeward in plumes of $SF_6$ and $CH_4$ gases at large distances (several hundreds of meters). Considering that plumes of these gases overlap, the amount of examined gas discharged into the atmosphere through leaks can be estimated from the relation

$$Q_{CH_4} = Q_{SF_6}\, C_{CH_4} / C_{SF_6} ,$$

where $Q$ is the amount of gas discharged into the atmosphere and $C$ is its concentration.

The amount of $CH_4$ discharged into the atmosphere through leaks was measured at three pressure reduction stations located in the vicinity of Moscow. The gas pressure was reduced from 20 to 4 atm at these stations. As a result, the measurements performed by two different methods demonstrated satisfactory agreement (within 50%). It was found that from 0.002 to 0.4% of throughout capacity of gas-supply pipes was lost through leaks. These estimates are of the same order of magnitude as those obtained for American stations.[21]

Investigation of ozone sources and sinks shows that ozone is most intensively produced in moderately polluted air over rural regions (at the station Zvenigorod, for example). Its sources are photochemical reactions with nitrogen oxides, CO, $CH_4$, and other volatile hydrocarbons. Ozone is formed in the light reaction and its concentration increases during the day reaching its maximum in the afternoon. The rate of ozone production reaches 5–10 ppb/h.

In a large city (investigations were carried out in Moscow) with high level of pollution the rate of $O_3$ production was much lower.[11] Even in summer, being most favorable for the ozone generation, it did not exceed, on average, 3–5 ppb/h. In fall and winter the photochemical ozone generation was small and practically vanished in the presence of thick clouds. This is because by day ozone in the urban surroundings is at the state close to that of photochemical equilibrium with nitrogen oxides $NO_x$. This state might be disturbed through the reaction with the products of hydrocarbons oxidation. However, hydrocarbons leave the urban air basin practically undisturbed due to low level of the OH concentration. This result is of great importance for elucidation of mechanisms of air pollution and change of the photochemical state of the urban air.[11]

For low values of the $NO_x$ concentration (less than 0.01 ppb) ozone destruction takes place by day instead of generation. This is the case of mountain regions and remote oceanic areas. Thus, the daytime minimum observed at the station Kislovodsk is indicative of an active ozone sink in the bright sunlight. The brighter is the sunlight, the stronger is the sink.[9]

The second important ozone sink in the surface air layer is dry sedimentation of ozone on the underlying surface. The rate of sedimentation was estimated for moderately clear air of rural regions and for the urban air. These measurements were performed for the first time in our country.[23,24] The rate of the $O_3$ sink was determined by the turbulent ozone flow near the surface. A hemiluminescent gas analyzer with response time in the range 0.3–0.4 s was specially developed for its measuring. Synchronous measurements of $O_3$, wind velocity components, and temperature were performed at the scientific station of the IAP in Tsimlyansk (the Rostov Region) in summer and at the center of Moscow in April for stable temperature stratification.

It was shown that the direction and the velocity of vertical flows of gaseous pollutants as well as the temperature can be reliably estimated by the pulsation method in urban surroundings in spite of inhomogeneous conditions. This conclusion was based on the results of comparison of the correlation coefficients for the vertical velocity $w$, temperature $T$, and pollutant concentration in natural and urban surroundings. The comparison also indicated that the amplitudes of $CO_2$ and $O_3$ variations in urban surroundings were 2–3 times higher those that of natural variations above a steppe.[24]

The ozone flow above the steppe in summer was always directed downward and decreased from day to night. Its average daily value was about 0.5 $\mu g/m^2 \cdot s$. The coefficient of ozone correlation with the

temperature reached (−0.7) in the daytime and (+0.5) at night.

In the city, the vertical $O_3$ and $CO_2$ flows at an altitude of 8 m were close to zero. A negative correlation[24] was found between $CO_2$ and $O_3$. The coefficient of correlation reached −0.5 (observations in April of 1994).

## CONCLUSION

Development of the informational data base provides the basis for the study of the variations of the atmospheric gaseous composition and its possible consequences on the climate. This calls for extended network of regular observations and increased number of the pollutants being monitored and the atmospheric meteorological parameters. Further increase of the measurement accuracy and attachment of our measuring devices to the Global Observational Network are also of great importance. Considering severe financial problems, we obviously have to restrict ourselves to the maintenance of continuous measurements at existing stations and the performance of field experiments in the regions with anomalous variations of the pollutant content. Long-term observations of the pollutants yield information about their transport, transformation, sources, and sinks. Detailed mathematical models are required to assimilate and to use efficiently the obtained information. Consideration of heterogeneous processes substantially increases the reliability of numerical estimates of possible consequences of anthropogenic effect on the environment. Development of numerical modeling in combination with high-quality long-term series of data on the atmospheric composition and its physical-chemical properties makes it possible to increase the reliability of the estimates of possible changes of the atmosphere and climate and their possible consequences for people.

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