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Surface Ozone Concentration Measurements at the Kislovodsk High-Altitude Scientific Station: Temporal Variations and Trends

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Abstract—Observational data on the surface ozone concentration between 1989 and 1998 obtained at the Kislovodsk high-altitude scientific station (KVNS) of the Oboukhov Institute of Atmospheric Physics, Russian Academy of Sciences, are presented. Characteristic features of the temporal variability of the surface ozone concentration are studied. By and large, ozone variations at the KVNS are significantly smaller than those at other European high-altitude stations due to cleaner air and weaker flows of polluted air from the atmospheric boundary layer to the free troposphere. From year to year, daily and seasonal variations have a regular structure that is almost exactly reproduced. Over the observation period, the trend in the ozone concentration is equal to -1.75 ±0.40% per year. At nighttime (01:00-05:00, local time), when the station is in the free troposphere with no fog or heavy precipitation, the trend is equal to -1.45 ± 0.35% per year.

INTRODUCTION

The ozone content in the troposphere is substantially influenced by human activity. Atmospheric emissions of nitrogen oxides (NOx), carbon oxides (CO and CO_2), methane (CH_4), and different organic compounds promote ozone formation in polluted air and increase the ozone concentration in the troposphere as a whole [1—3]. Since ozone is the strongest oxidant and a greenhouse gas, an increase in its content in the atmosphere has an adverse effect on living matter and climate [4].

The nonuniform arrangement of pollution sources on the earth's surface and high spatial and temporal variability of atmospheric transport and photochemical transformation of trace gases lead to a rather complicated pattern of space-time ozone content variability over the troposphere and, especially, over the atmospheric surface layer [5]. A clear demonstration of this variability is a significant difference in ozone trends varying from positive to negative values within a limited region such as Europe [6, 7].

High-altitude stations located more than 1500 m above sea level are of special importance in the ozone network. The data obtained at these stations are only slightly influenced by anthropogenic processes and primarily contain information on regional and global states of the troposphere [8-12]. At the same, complex relief results in some peculiarities in the temporal behavior of ozone concentration. At such stations, vertical air transport, which is responsible for the exchange between the stratosphere and the troposphere and between the atmospheric boundary layer (ABL) and the free troposphere, is rather intense [9-13]. However, in the vicinity of such stations, due to the small content of minor species that react with ozone, its photochemical destruction and formation is depressed, and the ozone concentration is not as variable as it is over plains. The ozone variations are usually regular. Therefore, at high-altitude stations, the correlation between these variations and specific dynamic and photochemical processes can be revealed more easily. Thus, there are possibilities for obtaining significant estimates of the long-term ozone variability in the corresponding regions and latitudinal belts and also for refining the notions of the nature and mechanisms of these processes.

In the world network, there are about fifteen long-functioning high-altitude stations that are surrounded by air of the free troposphere most of the time; the majority are located in central Europe and in the United States, and the rest on islands and in Antarctica [4-8]. The Kislovodsk high-altitude scientific station (KVNS) of the Oboukhov Institute of Atmospheric Physics (IFA) is located in the North Caucasus on the Shadzhatmaz Plateau (2070 m above sea level), 18 km south of the town of Kislovodsk, in the alpine grassland zone. An extensive area of the Caucasian State Preserve, with no population and no economic activity, is located south of the station,. The Shadzhatmaz Plateau is characterized by stable weather with a high frequency of cloudless days and high atmospheric transparency. For this reason, the Main Astronomical Observatory of the

Table 1. Monthly mean heights of the atmospheric boundary layer (//) and frequencies of occurrence of the tropical tropopause *(N)'*, both are computed for the period from April 1989 to March 1990 on the basis of aerological sounding at the Minvody station

Month	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	March
H, km *N*, %	1.5 0	1.65 8	1.75 18	1.8 89	1.75 78	1.6 33	1.5 14	1.35 2	1.35 0	13 5	1.25 0	1.35 17

Russian Academy of Sciences set up the Solar Station here for regular observations.

The KVNS and the Solar Station use electric power to heat their buildings. In the nearest surroundings, there are only minor sources of pollutants. In the town of Kislovodsk, which is a health resort, vehicular traffic is the dominant source of pollution. The town is situated 800-900 m above sea level. The observation site (43.9° N, 42.7° E, 890 m above sea level) is located on its southern outskirts, in the Recreation Park. Here, continuous measurements of the ozone concentration and episodic measurements of the NOx, CO and aerosol concentrations are performed to control the contents of pollutants that might be transported to the KVNS by uphill north winds. However, since the town of Kislovodsk is situated in a valley oriented from the west-north-west to the east-south-east, such winds are not prevailing in the local uphill-downhill air circulation.

Among the world -network of high-altitude stations, the KVNS occupies a special place. In fact, it is the only continental station in the Northern Hemisphere that is located in a region where there are no significant anthropogenic or natural sources of ozone precursors and where moderate climatic conditions do not promote photochemical processes in the environment. Against the background of small ozone variations associated with stable local dynamic processes, we can identify weak long-term ozone variations and estimate the contribution of the long-range transport of ozone and its precursors. Another quality of the station is also determined by its location on a plateau on the gentle northern side of the Caucasus far (no closer than 45 km) from the Main Caucasian Ridge. Since the north sides of the mountains are warmed up only slightly by the sun, the regional uphill-downhill air circulation is not intense, and air flows coming into the space over the station from outside are only slightly turbulent. Combined observations at these two sites allow monitoring of the regional air transport and the photochemical formation and decomposition of ozone in the lower troposphere. Most of the time, the KVNS is surrounded by air of the free troposphere. Table 1 lists the mean heights of the upper level of the planetary boundary layer obtained from the data of sounding performed in 1989-1990 at the town of Minevody (60 km north of the KVNS).

The aim of this work is to obtain information on the daily, day-to-day, seasonal, and long-term ozone variations typical of the lower troposphere and to identify the main factors determining these variations.

OBSERVATIONS

The ozone concentration has been measured at the KVNS since March 1989. During this entire period, the measurements have been performed with a Dasibi 1008-AH gas analyzer. It automatically takes into account changes in pressure and temperature. The sensitivity of the instrument is 1 ppb (by volume), and the absolute measurement error is 1-2 ppb. The measurement interval is 10 s. The response time (0-95%) is 50 s. Air is sampled at a height of 3 m above the ground and is pumped into the instrument through a teflon tube 3.5 m long.

We regularly checked the instrument against the Dasibi 1008-AH and Dasibi 1008-RS gas analyzers used at other stations of the IFA and in the International TROICA experiments [15, 16]. All these instruments were regularly calibrated with two ozone generators: GP-024 and the generator built into the Dasibi 1008-RS instrument. A distinctive feature of the instrument installed at the KVNS is its operational reliability. During the entire observation period, the readings of the instrument were corrected as a result of checks and calibrations by no more than a few percent. Upon changing the halogen lamp or the "zero" filter used for ozone destruction, the correction was of particular importance.

A Dasibi-1003 gas analyzer was installed at the town of Kislovodsk. This instrument has no device for taking pressure and temperature variations into account. Therefore, meteorological parameters were measured simultaneously with the measurements performed with this instrument. Every several months, the operational reliability of the instrument was checked against the Dasibi 1008-AH gas analyzer. For each check, we brought the latter instrument from the KVNS.

At the KVNS, in addition to the surface ozone content (SOC), we daily measured the UV spectra of solar radiation and the total contents and vertical profiles of atmospheric ozone, carbon monoxide (CO), and nitrogen dioxide (NO_2) and episodically measured the surface concentrations of NO, NO_2, some other minor gases, and aerosol [17]. The meteorological data necessary for the analysis and interpretation of observational data were obtained from the Meteorological station of the Russian Hydrometeorological Service located on the Shadzhatmaz Plateau.

The program of O_3 monitoring involves continuous round-the-clock measurements with short interruptions

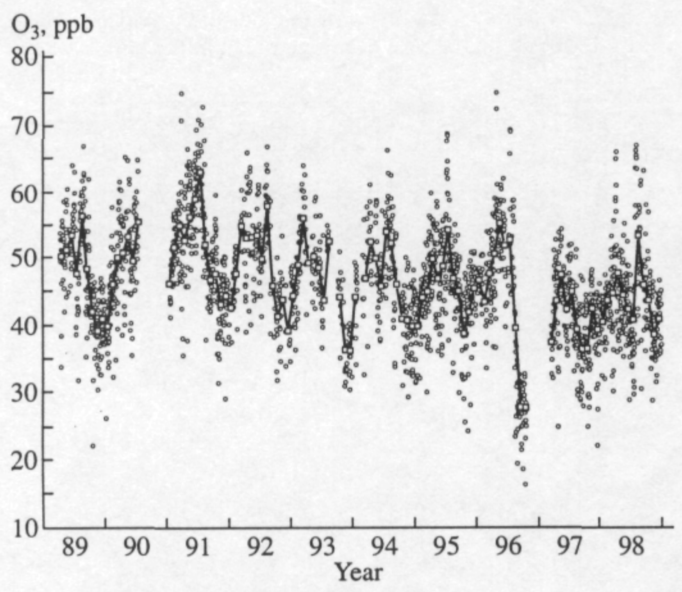

Fig. 1. Monthly and daily mean ozone concentrations observed at the KVNS.

(once every few days), the latter for preventive maintenance and changes of some details and filters. In the case of highly unfavorable natural events, such as thunderstorms, rainfalls, and heavy snowfalls with fitful wind, measurements were also stopped for a time. By and large, this program was implemented. However, rather long downtimes sometimes occurred; they could be caused by station deenergization, instrument malfunctions, and some other unforeseen events.

RESULTS AND DISCUSSION

Observational Data

The data recording frequency was equal to 10 s^{-1}. For processing, we used observational data in the form of a series of 1 -min mean values. Taking into account the response time characteristic of the instrument, we can consider these values to be mutually independent. We analyzed the results in the form of series of the 10-min, hourly, daily, and monthly mean values. The daily means were computed if the observation period was no shorter than 12 h per day. The accuracy of the daily means was usually rather high due to very small daily ozone variations. To study the detailed structure of temporal ozone variability and to estimate the effect of the uphill-downhill air circulation, we computed two series of the means: for the nighttime from 1:00 to 5:00 and for the daytime from 10:00 to 14:00 (local time).

Figure 1 presents the daily and monthly mean ozone concentrations for the ten-year observation period from 1989 to 1998. Two long interruptions, in 1990 and 1996-1997, were associated with eliminating instrument faults and with transporting the instrument to Moscow for calibration. In the 1996/1997 fall-winter season, during the period of a prolonged dramatic decrease in the ozone concentration, we compared the instrument operating at the station with the Dasibi-1008 RS instrument calibrated by the manufacturer in the spring of 1996. Both of these instruments registered this unusual depletion of ozone.

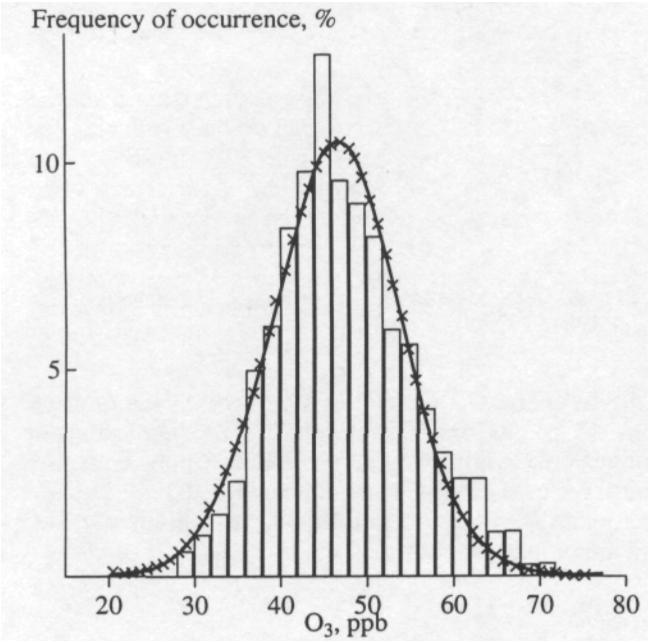

Fig. 2. Distribution and its Gaussian approximation for the frequency of occurrence of the daily mean ozone concentration averaged over four years, 1991, 1992, 1995, and 1998.

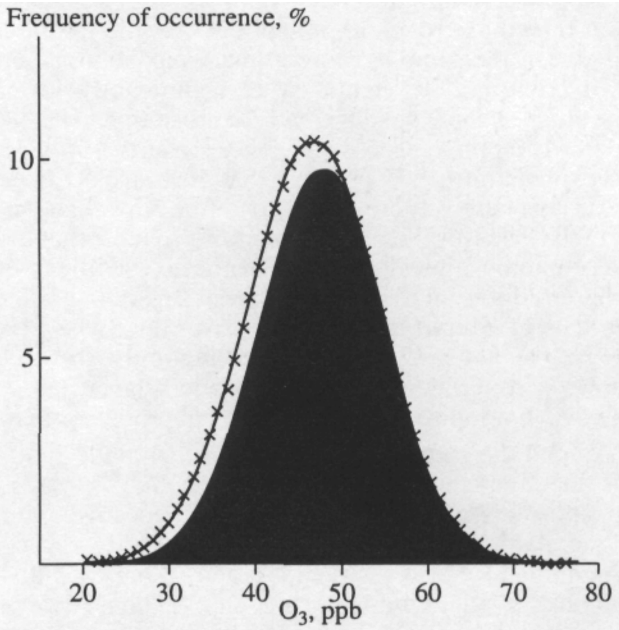

Fig. 3. Smoothed distribution of the frequency of occurrence of the 03 daily mean concentration computed on the basis of measurements in a four-year period (1991, 1992, 1995, and 1998) for the total data set (undashed area) and for the data measured only at an air humidity less than 85% in the absence of fog and precipitation (dashed area).

The main characteristics of SOC temporal variability for the entire observation period are given in Table 2. The range of ozone variation is not wide. For ten years, the minimum and maximum hourly mean values are 16.3 and 74.8 ppb, respectively. Thus, the range of SOC variation observed at the KVNS is significantly narrower than that observed at other high-altitude stations [18-23, 26].

Frequency of Occurrence

Figure 2 shows the frequency of occurrence of the daily mean SOCs observed for four years (1991, 1992, 1995, and 1998) characterized by the least frequent interruptions between observations. The principal features of this distribution are its proximity to a normal one, with a small shift toward the range of high SOC values, and also the total absence of both very low (below 23 ppb) and very high (over 75 ppb) SOC values. Most frequently, an SOC value ranging from 44 to 45 ppb was observed. The Gaussian distribution approximating the observational results has a maximum at 46-47 ppb.

A comparison of this distribution with analogous distributions [7, 18] obtained since 1978 at the Zugspitze (2962 m above sea level) and Wank (1780 m above sea level) alpine stations gives the following - results. For the above-mentioned years, the mean SOC values at the KVNS were very close to the values of 49-51 ppb measured at the Zugspitze station and coincided almost exactly with the values of 46-48 ppb measured at the Wank station. For the same years, at the KVNS, the minimum SOC values were somewhat lower than those (over 30 ppb) at the Zugspitze station and almost the same as those at the Wank station, and the maximum SOC values were significantly lower than those at the Zugspitze and Wank stations (85-90 and 90-100 ppb, respectively). These results may have two explanations. It is possible that air transport from the stratosphere is more intense over the Alps than that over the Caucasus; however, it is most probable that the rate of photochemical ozone formation is significantly higher in Alpine air than that in Caucasian air. In particular, data of aircraft measurements over the Swiss Plateau [12] testify to O_3 and NO_2 arriving in the free troposphere from the atmospheric boundary layer and to an active development of photochemical processes in it.

Among the meteorological factors that could influence the frequency distribution of the SOC are fog, rain, and snowfalls. To estimate this influence, we used the standard measurements of the humidity at the Shadzhatmaz meteorological station. We excluded from our consideration the ozone data relating to periods when the humidity exceeded 85%. In Fig. 3, we present the smoothed frequency distributions computed for the same four-year periods as in Fig. 2, ignoring the data obtained under conditions of precipitation and fog. It is seen that the principal changes in the form of the frequency distribution, namely, a significant decrease in the frequency, is characteristic of the SOCs ranging from 23 to 50 ppb. However, the median criterion changes only slightly, by no more than 2 ppb. Thus, the weather factor has no significance for explaining the differences between observational data obtained at the Alpine stations and at the KVNS.

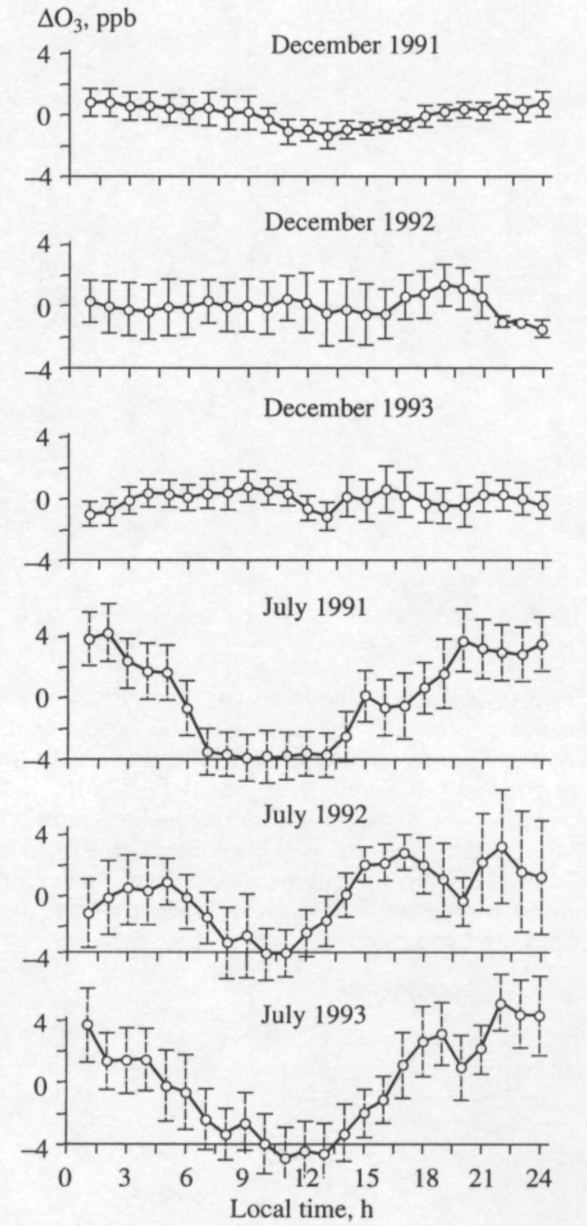

Fig. 4. Daily variation of the ozone concentration for December and July 1991–1993.

Daily Variation

The characteristic features of the daily variation of the SOC at the KVNS are a noon minimum and a seasonally dependent shift of the maximum toward the evening or night hours (Fig. 4). Such a form of SOC

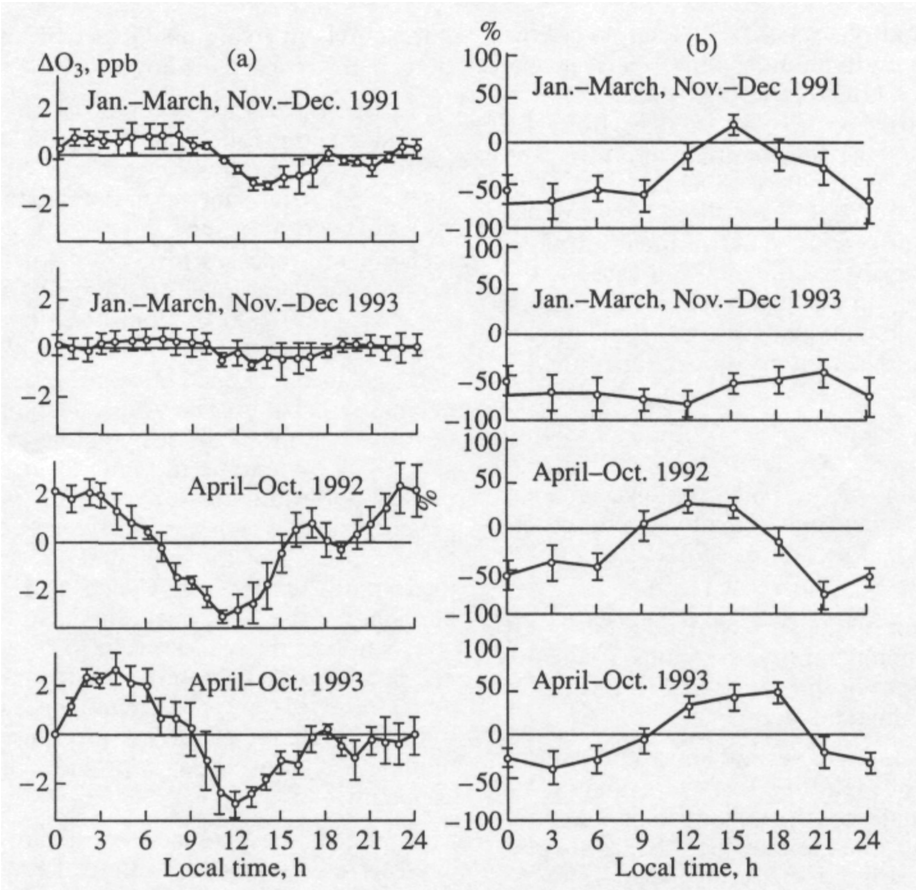

Fig. 5. (a) Daily variation of the ozone concentration and (b) balance between the uphill and downhill air flows computed on the basis of the standard meteorological observations performed in the cold periods of 1991 and 1993 and in the warm periods of 1992 and 1993.

daily variation is almost opposite to the one characteristic of mountain stations surrounded by somewhat polluted air, for example, stations located in western areas of the United States [8] and in Greece [19] and also for plain stations.

In [14], we showed that a number of specific features in the daily SOC variation observed at the KVNS could be caused by uphill-downhill air circulation. In the lower troposphere, the ozone concentration increases with height, except when ozone is actively

Table 2. Variability of the hourly mean ozone concentration for the observation period 1989-1998

Year	Ozone concentration, ppb							
	minimum	5%	25%	median mean	mean	75%	95%	maximum
1989	22.2	38.3	41.6	46.4	47.4	53.1	57.9	66.9
1990	26.2	39.0	44.0	49.2	48.7	53.9	57.8	65.3
1991	29.1	42.5	46.2	51.3	51.9	56.9	62.6	74.8
1992	31.8	39.3	44.6	51.0	49.8	54.5	60.0	66.9
1993	30.4	36.2	41.6	47.5	46.8	52.4	56.1	64.1
1994	29.3	36.7	41.0	46.3	46.4	52.5	56.4	66.3
1995	24.3	37.3	41.7	45.6	45.6	49.5	53.4	68.8
1996	16.3	26.8	33.6	46.7	44.2	53.2	57.2	74.8
1997	22.2	33.5	37.4	41.6	41.1	45.4	48.3	54.4
1998	28.8	36.1	39.5	43.1	43.9	46.8	52.6	67.1

generated in the atmospheric surface layer. As follows from [20,21], in the midlatitudinal atmospheric layer at heights from 1 to 3 km, the vertical gradient of the ozone concentration is positive and ranges from 4 to 6 ppb/km during the year. Such a gradient allows us to qualitatively explain the daytime SOC decrease at the KVNS by the effect of uphill air flow. However, the extension of the data set and the use of the information from the Kislovodsk observational site located within the urban air flowing up along the valley led us to the undoubted conclusion that the daily SOC variation had a fine regular structure caused by joint action of the following factors.

(1) Photochemical processes. Within the atmo spheric boundary layer, they lead to a daytime SOC increase characteristic of the plain stations, whereas, within the free troposphere and under the condition that the N0^ concentration does not exceed 10-20 ppt, they can lead to a daytime SOC decrease [1-3].

(2) Dry deposition on the surface. Under the condi tions of nighttime temperature inversions frequently observed at the bottom of the valley and rifts the SOC sometimes reduces almost to zero.

(3) Turbulent mixing. For several hours after sunrise and the destruction of nighttime surface inversion, tur bulent mixing equalizes the ozone concentration throughout the entire thickness of the ABL. This phe nomenon results in some decrease in the morning O_3 concentration at the station near the upper boundary of the ABL. The process of turbulent mixing can lead to the stable transport of O_3, NO_2, and other minor species into the free troposphere. This transport is most intense in the afternoon. According to [12], in summer, the O_3 flow intensity over the Swiss Plateau and Hong Kong runs as high as about 8 x 10~^{3} and 11 x 10^{-3} mmol/(s m^2), respectively. As a result, even in the free troposphere, the afternoon maximum in the regional O_3 concentra tion is sometimes observed in the case of occurrence of intense sources of ozone precursors.

(4) Local mountain-valley circulation. In the vicin ity of the KVNS, the mountain-valley circulation is complicated. The main uphill-downhill air flow deter mined by an increase in the height of the massif toward the Main Caucasian Ridge is imposed by the small-scale air flows caused by heating of the sunward valley slopes. On warm sunny days, as noon approaches and the upper boundary of the ABL ascends to the KVNS (see Table 1), the polluted plain air may be transported to the station. It should be noted that the entire region of the Kavminevody is a specially protected resort zone with no developed industry. Therefore, the atmosphere is significantly less polluted over this region than over European Russia and the more so than over western and central Europe.

(5) Upward convective transport of polluted air within the ABL and into the free troposphere. Such transport is accompanied by active photochemical interactions in rising air flows and less active interactions in descending air flows.

In warm seasons, when all these factors are most significant, the following processes seem to be most probable for explaining daily SOC variations (see Figs. 4, 5). After sunrise, in the free troposphere at low N0x concentrations and intense UV illumination, photochemical processes result in a small decrease in the ozone concentration. Turbulent mixing and air flows ascending 400-500 m along the slopes of the quickly warming canyon of the Khasaut River also lead to a decrease in the ozone concentration. The cause of this decrease is an almost complete decomposition of ozone near the bottom of the canyon due to nighttime inversions. The monotonic morning decrease in the SOC at the KVNS terminates at about 9:00, when the free-troposphere ozone-rich air fills the space around the station as a result of the extended upward air flow along the foothills of the North Caucasus. However, when the boundary of the ABL rises above the KVNS, the ozone concentration decreases again. By noon, vertical mixing, similarly to the uphill wind from the canyon, leads to the filling of the space around the station by air of the lower ABL characterized by a decreased ozone concentration. A similar effect is provided by convective air transport.

By noon, the extended uphill flow transports polluted air masses from the valley of Kavminvody toward the KVNS. At high temperatures, intense solar illumination, and high concentrations of NO_X and volatile organic compounds, ozone is generated in upward air flows. In the afternoon, the ozone concentration gradually increases until the intensity of solar illumination begins to decrease. By 18:00, as the illumination intensity falls, ozone generation slows down, and the downhill flow intensifies. These processes lead to the displacement of the ABL air by the free-troposphere air. By 22:00, the ozone concentration level characteristic of the free troposphere is reestablished. From Figs. 4 and 5, it is seen that the daily ozone variation at the KVNS is smaller than that at the Alpine stations where, by around noon, instead of decreasing to a minimum value, the ozone concentration, on the contrary, increases to a maximum value exceeding the basic level by several ppb [7, 18]. This peculiarity means that, in the Alps, the process of ozone formation at heights up to 3 km is more intense than that at the KVNS in connection with a higher concentration of pollutants and probably with a more intense mountain-valley circulation.

In cold seasons, this scheme continues to work, but all processes are less intense (Figs. 5, 6). In addition, during cold seasons, the KVNS is in the free troposphere most of the time. As a result, regular daily variations are small or absent. It should be noted that the KVNS weather peculiarities, first of all, the variability of the large-scale atmospheric circulation, introduce some changes to the regular structure of the daily vari-

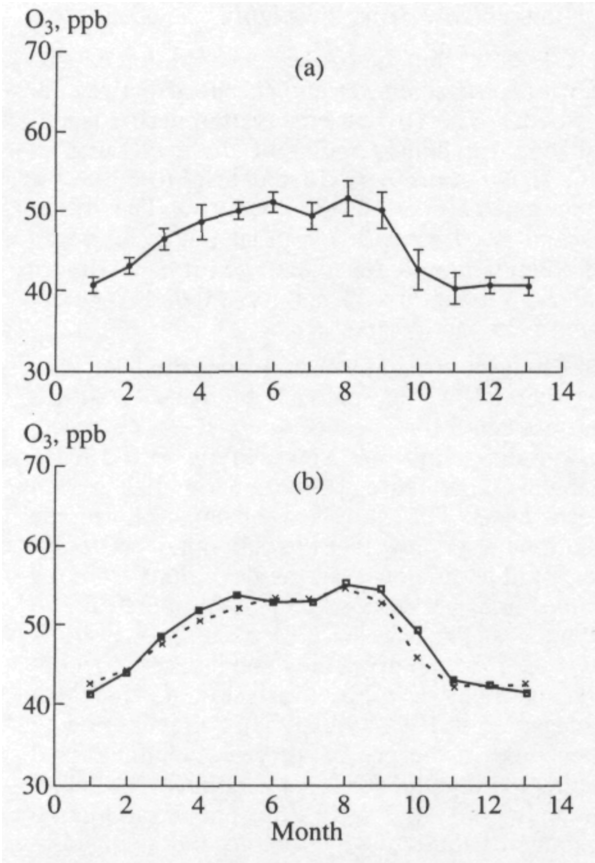

Fig. 6. Seasonal variation of the ozone concentration averaged (a) over the total data set and (b) over the nighttime data only (/) throughout the entire observation period and (2) throughout the period without 1991 and 1996, when anomalous data were obtained.

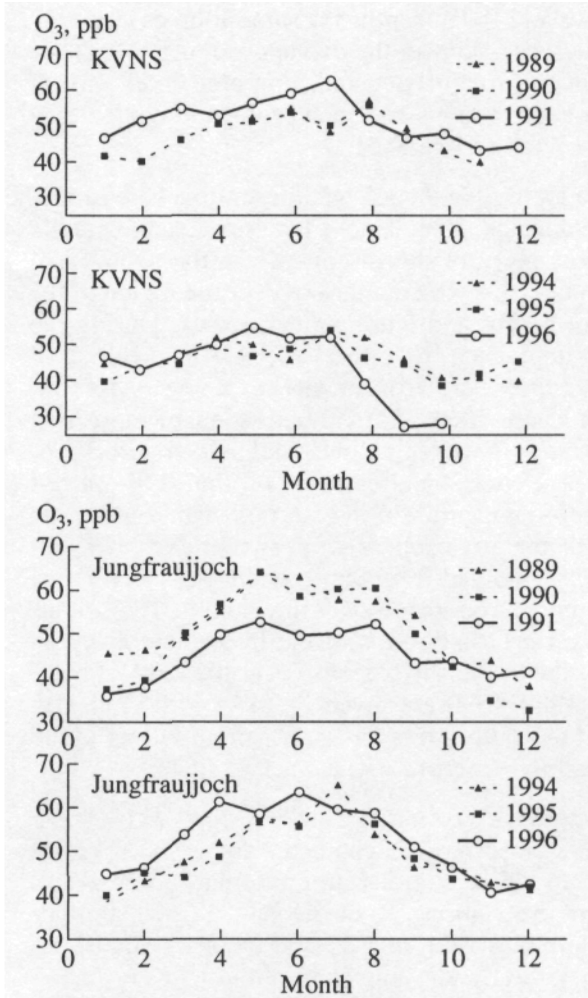

Fig. 7. Anomalous ozone concentrations observed at the KVNS and at the Jungfraujjoch station [7] for 1991 and 1996 in comparison with those for two years preceding 1991 and 1996.

ation of the ozone concentration at this station. Figure 5 gives daily ozone variations for the cold and warm seasons of 1991-1993 and also the daily variation for the index of the local mountain-valley circulation. This index is computed as the three-hour balance of the uphill and downhill air flows along the foothills of the North Caucasus and is expressed in percent. From this figure, it is seen that, in the cold season of 1993, due to the weather conditions, the uphill flow was virtually undeveloped, and the ozone concentration was nearly constant in the course of the day. In the same period of 1991, the mountain-valley circulation was more intense, and daily ozone variations were more clearly pronounced.

A delay in intensification of the uphill flow along the foothills of the North Caucasus in the warm period of 1993 in comparison with that of 1992 led to the delay in daily ozone variations observed in 1993 in comparison with those observed in 1992. In 1991, when the air temperature and ozone concentration were unusually high for several months, a deviation from the mean daily variation, namely, a more prolonged daytime minimum, was also noted (Fig. 4). This example and many other similar examples identifying relations between the dynamic regime and changes in the ozone concentration confirm and clearly illustrate the scheme explaining the ozone daily variation described above.

Seasonal Variations

In Fig. 6, the seasonal behavior of the ozone concentration at the KVNS averaged over 1989-1998 is presented. For the periods October-December and May-August, low and high concentrations, respectively, are revealed. The seasonal behavior is characterized by the occurrence of two maxima: in April-May and July-August. Such seasonal behavior is typical of high-altitude stations and is hardly observed at all at plain stations [4, 18, 23]. It is influenced by two sources of tropospheric ozone, namely, by photochemical generation and transport from the stratosphere, which are most intense in middle latitudes in July and March-April, respectively [24]. Evidently, the same sources influence the annual variations in the ozone concentration at sea level, but the irregularity and temporal variability of anthropogenic actions and meteorological characteristics mask such an influence.

In the vicinity of the KVNS, the stratosphere-troposphere exchange depends to a large extent on whether the discontinuity of the tropopause in the subtropical high frontal zone, which migrates over the region of the station in spring and late summer, exists. During the summer migration, the effects of high insolation and intense stratosphere-troposphere exchange superimpose on each other. Possibly, this superimposition explains a peculiarity in the seasonal behavior in Fig. 6, namely, a clearer manifestation of the July-August maximum compared to the spring maximum. The activity of the stratosphere-troposphere exchange can be indirectly judged from the frequency of occurrence of the tropical tropopause over the KVNS. The sounding data on the distribution of the frequency of occurrence for the tropical tropopause over the town of Minvody in 1989-1990 are given in Table 1. It is clearly seen that the distribution has a maximum falling in the period of July-August.

.The seasonal ozone variations observed at the KVNS are close in their character and value to those observed at alpine stations. In particular, at the Wank and Zugspitze stations, as at the KVNS, two summer maxima are observed, in May and in July [18, 23]. At all three stations, the annual minimum in the ozone concentration is observed in October-November. The absolute values in these minima are very close to each other and are equal to 40.3, 40.8, and 38.4 ppb at the KVNS, Zugspitze, and Wank stations, respectively. In the summer maximum, the differences between the values measured at the KVNS and the values measured at the Zugspitze and Wank Alpine stations are not large and are equal to 7.7 and 4.3 ppb, respectively. However, these differences are of a fundamental nature. They confirm our assumption that, in summer, the rate of photochemical ozone generation in the Alpine region is, as a rule, higher than that in the North Caucasus. This assumption is also supported by a close relation between the excess ozone content and the concentrations of anthropogenic NOy, SO_2, and CO in the atmosphere [18, 23].

At nighttime, when the stations are in the free troposphere (Fig. 6b), the differences between the maximum values obtained at the KVNS and at the Zugspitze and Wank Alpine stations decrease to 5.0 and 2.5 ppb, respectively. If the anomalous data obtained at the KVNS in 1991 and 1996 are not included in the comparison, these differences are still smaller: 4.5 and 2.0 ppb, respectively.

Long-Term Variability

Figure 1 shows that the ozone concentration experiences not only seasonal variations, but also irregular long-term ones. The 10-year observation period is sufficiently long for consideration of these changes as trends. Over the entire period from 1989 to 1998, the ozone content decreased significantly. The mean annual trend is -1.75 ± 0.40%. The multiyear mean monthly trend is month-dependent; i.e., it is maximum for August-October and is not identified for winter months.

Over a long period in 1991 and from the latter half of 1996 to early 1997, anomalously high and low levels of ozone concentration, respectively, were observed. These anomalies contribute significantly to the trend value. However, the causes of these anomalies are not sufficiently clear. The multiyear observations at the alpine stations also show that the data obtained during these years are anomalous, but the deviations from the mean values are of the opposite sign compared to the data obtained at the KVNS. This peculiarity is illustrated by Fig. 7, which gives the annual ozone concentration behavior at the Jungfraujjoch station [7] and the KVNS measured in 1991 and 1996 in comparison with those measured in the preceding years, characterized by a stable annual behavior. This peculiarity indicates the influence of the large-scale atmospheric circulation on the ozone distribution in the regions under consideration. In 1991, the atmospheric circulation led to prolonged periods of stable transport of warm air enriched by Mediterranean and North African air to European Russia and of cold and humid North Atlantic air with a relatively low ozone concentration to central Europe. All other factors determining the photochemical formation and vertical transport of ozone are also dependent on the intensity of zonal and meridional air transport.

The strong decrease in the ozone concentration observed at the KVNS in the latter half of 1996 and early in 1997 is more difficult to explain. We can only note that, in 1996, anomalously high ozone concentrations were observed at the Jungfraujjoch station [7] and, by analogy with 1991, associate these deviations, which are opposite to those observed at the KVNS, with the effect of large-scale circulation. However, at present, the available information is not sufficient for such a conclusion. Therefore, it is of interest to analyze the nighttime data obtained at high-altitude stations surrounded by free-troposphere air minimally influenced by local and regional factors.

Table 3 lists the nighttime ozone concentration trends estimated on the basis of data obtained for 1:00-5:00 local time in different months in the absence of fog and heavy precipitation. Over the 1989-1999 observation period, the annual trend of the nighttime ozone concentration was equal to -1.45 ± 0.35%. The computation of such a trend with neglect of the anomalously low concentrations measured in the period from August 1996 to March 1997 gives a value of-0.85 ± 0.30%. We

Table 3. Annual trends of the nighttime ozone concentrations measured from 1:00 to 5:00 local time in the absence of fog and intense precipitation for each month over the ten-year period from 1989 to 1998

Month	Annual trend, % per year	Annual trend, % per year without data for Aug.-Oct. 1996 and March 1997
Jan.	0.12 ±1.02	0.12 ±1.02
Feb.	-0.14 ±0.69	-0.14 ±0.69
March	-2.61 ±1.16	-1.57 ±0.86
April	-0.87 ± 0.69	-0.87 ± 0.69
May	-1.52 ±0.58	-1.52 ±0.58
June	-1.62 ±0.90	-1.62 ±0.90
July	-1.07 ±0.71	-1.07 + 0.71
Aug.	-2.35 ± 1.32	-1.18 + 0.80
Sept.	-2.26 ±1.71	-1.21 ±0.69
Oct.	-2.27 ±1.48	-1.36 ±0.93
Nov.	0.11 ±0.62	0.11 ±0.62
Dec.	0.32 ±1.29	0.32 ±1.29

believe that, for the Caucasian region, the nighttime trends are most representative for estimating the long-term ozone behavior in the free troposphere. The annual trends vary significantly from month to month. If the anomalous data are not taken into account, they range from near-zero values for November-February to 1.5-1.6% per year for May and June. These trends differ significantly from the corresponding values obtained at the Alpine stations [7], where the ozone concentration was increasing over a prolonged period in the 1980s and 1990s. However, the data obtained at individual stations have some peculiarities. Thus, at the Zugspitze station, over the period from 1982 to 1999, the ozone concentration increased almost linearly with an annual trend of 1.48 ± 0.5% per year. At the Wank station, over the period from 1984 to 1996, the ozone concentration increased very slightly and, over the last four years, it has decreased [7-18]. The trend at the Jungfraujjoch station is positive, with heightened values for October, December, and February [7].

In the free troposphere over central Europe, for the entire prolonged period from 1970 to 1996, an increase in the ozone concentration is observed with ozonezondes [22]. However, over the last portion of this period, from 1980 to 1996, no trend is observed [22]. For the same period, ozonezonde measurements over the eastern United States and Canada at the Edmonton and Goose stations located at a latitude of 53° N give clearly pronounced negative annual trends of-0.35 and -0.75% per year, respectively, for an 800-hPa level. In contrast, over the period from 1980 to 1996, ozonezonde measurements over a number of Japanese stations give a significant positive annual trend ranging from 0.2 to 1.0% per year [22] at the same height level. Thus, for the last 15-20 years, a zonal character of long-term variations becomes noticeable; namely, the atmospheric ozone concentration increases over central Europe and Japan and decreases over the United States, the Caucasus, and Canada. This peculiarity in the spatial distribution of ozone variability and also the opposite anomalies in central Europe and the Caucasus cannot be explained by any regional or global changes in tropospheric pollution. Most likely, these phenomena are caused by long-term variations in the wave character of the large-scale atmospheric circulation. In particular, in [25], it is shown that such variations reveal themselves in the location of high frontal zones and in the spatial distribution of the total ozone content.

CONCLUSIONS

It is evident that the KVNS is able to occupy a prominent place in the system of surface-ozone monitoring. It is located in a region with a stable climate and with no active natural or anthropogenic sources of ozone precursors. In addition, in this region, the mountain-valley circulation is not intense and thus the transport of pollutants from lower atmospheric levels is not significant. Therefore, the KVNS is characterized by the smallest seasonal variations in the ozone regime in comparison with those characteristic of the stations in the same latitudinal belt and by a stable daily variation in the ozone concentration with a noon minimum and a minor or negligible daytime rate of ozone formation. The station is located most of the time over the atmospheric boundary layer, and therefore its data on atmospheric parameters characterize the atmospheric state not only in the Caucasian region but also on a global scale.

Unlike alpine stations, at the KVNS, a significant negative trend in the SOC is observed. In addition, at the station, some long-term anomalies in the ozone concentration are alternating in time. These phenomena give us grounds to suppose that long-term ozone variations are closely associated with the variability of the large-scale atmospheric circulation.

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REFERENCES

1. Crutzen, P.J. and Zimmermann, P.H., The Changing Photochemistry of the Troposphere, *Tellus A, B,* 1991, vol. 43, pp. 136-151.

2. Wang, Y., Jacob, D.J., and Logan, J.A., Global Simulation of Tropospheric O3-NO^-Hydrocarbon Chemistry: 3. Origin of Tropospheric Ozone and Effect of Nonmethane Hydrocarbons, *J. Geophys. Res.,* 1998, vol. 103, pp. 10757-10767.
3. Lelieveld, J. and Dentener, F.J., What Controls Tropospheric Ozone, *J. Geophys. Res.,* vol. 105, pp. 3531-3551.
4. Scientific Assessment of Ozone Depletion: 1998, *WMO Global Ozone Research and Monitoring Project Report,* Geneva, 1999, no. 44.
5. Oltmans, S.J. and Levy II, H., Surface Ozone Measurements from a Global Network, *Atmos. Environ.,* 1994, vol. 28, pp. 9-24.
6. Low, P.S., Kelly, P.M., and Davies, T.D., Variations in Surface Ozone Trends over Europe, *Geophys. Res. Lett.,* 1992, vol. 19, pp. 1117-1120.
7. Tropospheric Ozone Research-2, *EUROTRAC Annual Report 1998,* Munich, 1999.
8. Kley, D., Geiss, H., and Mohnen, V.A., Tropospheric Ozone at Elevated Sites and Precursor Emissions in the United States and Europe, *Atmos. Environ.,* 1994, vol. 28, pp. 149-158.
9. Danielsen, E.F., Stratospheric-Tropospheric Exchange Based on Radioactivity, Ozone and Potential Vorticity, *J. Atmos. ScL,* 1968, vol. 25, pp. 502-518.
"10. Shapiro, M.A., Turbulent Mixing within Tropopause Folds As a Mechanism for the Exchange of Chemical Constituents between the Stratosphere and Troposphere, *J. Atmos. ScL,* 1980, vol. 37, pp. 994-1004.
11. Frost, G.J., Trainer, M., Allwine, G., *el al.,* Photochemical Ozone Production in the Rural Southeastern United States during the 1990 Rural Oxidants in the Southern Environment (ROSE) Program, *J. Geophys. Res.,* 1998, vol. 103, pp. 22491-22508.
12. Lehning, M., Richner, H., and Kok, G.L., Transport of Air Pollutants from the Boundary Layer to the Free Troposphere over Complex Terrain, *Phys. Chem. Earth,* 1998, vol. 23, pp. 667-672.
13. Cooper, O.R. and Moody, J.L., Meteorological Controls on Ozone at an Elevated Eastern United States Regional Background Monitoring Site, *J. Geophys. Res.,* 2000, vol. 105, pp. 6855-6869.
14. Elanskii, N.F. and Senik, I.A., Surface Ozone Concentration Measurements at the Kislovodsk High-Altitude Scientific Station: Seasonal and Diurnal Variations, *Izv. Akad. Nauk, Fiz. Atmos. Okeana,* 1995, vol. 31, no. 2, pp. 251-259.
15. Crutzen, P.I., Golitsyn, G.S., Elanskii, N.F., Brenninkmeijer, C.A.M., Scharffe, D., Belikov, IB., and Elokhov, A.S., Trace Gas Measurements over Russia Using a Railroad Laboratory, *Dokl. Akad. Nauk,* 1996, vol. 350, no. 6, pp. 819-823.
16. Elanskii, N.F. and Markova, T.A., Diurnal Variations in the Surface Ozone Concentration from Measurements Taken at a Research Rail Car along the Trans-Siberian Railroad, *Int. Conf. on Atmospheric Aerosol Physics Devoted to the 85th Birthday ofG.V. Rosenberg,* 1999, pp. 437-442.
17. Elanskii, N.F., Arabov, A.Ya., Elokhov, A.S., Makarov, O.V., Savastyuk, V.V., and Senik, I.A., Observations of Atmospheric Trace Gases and UV Radiation at the Kislovodsk High-Altitude Scientific Station, *Izv. Akad. Nauk, Fiz.. Atmos. Okeana,* 1995, vol. 31, no. 1, pp. 10-19.
18. Scheel Aresrkoug, H., Geiss, H., *et al,* On the Spatial Distribution and Seasonal Variation of Lower-Troposphere Ozone over Europe, *J. Atmos. Chem.,* 1997, vol. 28, pp. 11-28.
19. Glavas, S., Surface Ozone and NO^ Concentrations at a High Altitude Mediterranean Site, Greece, *Atmos. Environ.,* 1999, vol. 33, pp. 3813-3820.
20. Fortiun, J.P.F. and Kelder, H., An Ozone Climatology Based on Ozonesonde and Satellite Measurements, *J. Geophys. Res.,* 1998, vol. 103, pp. 31709-31734.
21. Lawrence, M.G., Crutzen, P.J., Rasch, P.J., Eaton, B.E., and Mahowald, N.M., A Model for Studies of Tropospheric Photochemistry: Description, Global Distributions, and Evaluation, *J. Geophys. Res.,* 1999, vol. 104, pp.26245-26277.
22. Logan, J.A.,Megretskaia, I.A..Miller, A.J., *et al.,* Trends in the Vertical Distribution of Ozone: A Comparison of Two Analyses of Ozonesonde Data, *J. Geophys. Res.,* 1999, vol. 104, pp. 26373-26399.
23. Scheel, H.E., Sladkovic, R., and Kanter, H.-J., Ozone Variations at the Zugspitze (2962 m a.s.l.) during 1996-1997, *Proc. EUROTRAC Symp. 1998,* Borrel, P.M. and Borrell, P., Eds., Southampton: WITPRES, 1999, pp. 264-268.
24. Appenzeller, C., Holten, Y.R., and Rosenlof, K.H., Seasonal Variation of Mass Transport across the Tropopause, *J. Geophys. Res.,* 1996, vol. 101, pp. 15071-15078.
25. Elansky, N.F., Arefev, V.N., and Grechko, E.I., Some Peculiarities and Possible Causes of Long-Term Changes of the Trace Gases Amount over the Former USSR, *Eastern Europe and Global Change,* Ghazi, A., Mathy, P., and Zerefos, C., Eds., Halkidiki, Greece, 1997, pp. 173-184.
26. *Tropospheric Ozone Research-2: Annual Report 1999,* Munich, 2001.

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