Izvestiya, Atmospheric and Oceanic Physics, Vol. 41, No. 1, 2005, pp. 67–79. Translated from Izvestiya AN. Fizika Atmosfery i Okeana, Vol. 41, No. 1, 2005, pp. 78–91.

Main Patterns of the Temporal Variability of Surface Ozone in the Region of the Town of Kislovodsk at 870 and 2070 m above Sea Level

I. A. Senik*, N. F. Elansky*, I. B. Belikov*, L. V. Lisitsyna*, V. V. Galaktionov, and Z. V. Kortunova*****

**Oboukhov Institute of Atmospheric Physics, Russian Academy of Sciences, Pyzhevskii per. 3, Moscow, 119017 Russia*

e-mail: elansky@ifaran.ru

***Central Aerological Observatory, ul. Pervomaiskaya 3, Dolgoprudnyi, Moscow oblast, 141700 Russia*

****State Research Institute of Balneology, Ministry of Public Health of the Russian Federation, pr. Kirova 30, Pyatigorsk, Stavropol krai, 357500 Russia*

Received September 22, 2003; in final form, May 13, 2004

Abstract—Surface ozone concentrations measured simultaneously at the Kislovodsk high-altitude scientific station (KVNS) (2070 m above sea level) and at the town of Kislovodsk (870 m above sea level), located 18 km away from the station, are analyzed. The main patterns of ozone behavior at these sites over the observation period are revealed. Combined expedition measurements allowed a comprehensive description of the possible photochemical and dynamic mechanisms of daily variations in ozone at Kislovodsk. The surface ozone concentrations and their variations observed at Kislovodsk and the KVNS correspond to moderately polluted urban regions and background alpine regions, respectively. Analysis of the interannual variability has allowed us to evaluate the intensity of air exchange between the two observation sites and to infer that the surface ozone concentration at the KVNS depends only slightly on anthropogenic factors and, therefore, yields information mainly on the state of the regional and global troposphere.

1. INTRODUCTION

Ozone, as a powerful oxidizing agent, plays a central role in the photochemical transformation of atmospheric pollutants and, as a greenhouse gas, significantly influences the thermal conditions of the Earth's surface. The ozone concentration in the lower troposphere, especially in the atmospheric surface layer, varies widely depending on photochemical processes, horizontal advection, intrusions of stratospheric air, vertical mixing, dry and humid deposition, etc [1–4]. At high-altitude stations located above the planetary boundary layer (PBL), anthropogenic factors manifest themselves only slightly. Therefore, such stations give information relating mainly to the state of the regional and global troposphere. Obtaining such information is an important problem of environmental monitoring. Mountains introduce some specific features to ozone variability. At high-altitude stations, vertical transport of air is rather intense and provides the air exchange between the stratosphere and troposphere and between the atmospheric boundary layer (ABL) and the free troposphere. The air exchange depends on local topographic features. Therefore, the atmosphere of different mountain regions is influenced differently by local pollutants. Most of the stations are located on mountain tops or steep slopes in the immediate vicinity of populated valleys (for example, Niwot Ridge (Colorado, USA) [1], Jungfraujoch (Sweden) [2], Peloponnese (Greece) [3], and Alpe Motta and Passo S. Marco (Italy) [4]). The pollutants transported as a result of the daytime uphill–downhill atmospheric circulation significantly influence the ozone concentration over these stations.

Unlike the stations mentioned above, the Kislovodsk high-altitude scientific station (KVNS) of the Oboukhov Institute of Atmospheric Physics, Russian Academy of Sciences, is located on a plateau. In the vicinity of the KVNS, there are no significant sources of pollutants. Kislovodsk, the town nearest to the KVNS, is located 18 km away and 1200 m below (Fig. 1). In 1998, instrumentation for monitoring the surface ozone concentration (SOC) was installed in a park on the outskirts of Kislovodsk.

The simultaneous SOC measurements at Kislovodsk and at the KVNS allow us to assess the effect of urban pollutants on the ozone situation at the KVNS and to discriminate the regional component in the measured values. This work is the first to present the main patterns of the SOC temporal variability observed by us at Kislovodsk in the period from 1998 to 2001 and to refine the mechanisms of forming the SOC level and its

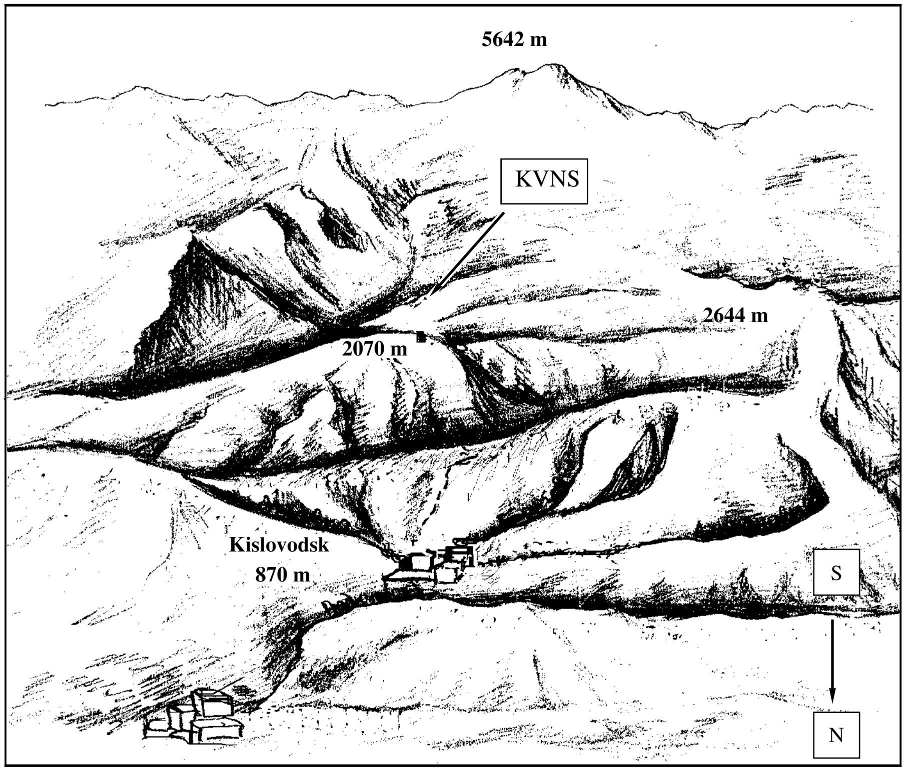

Fig. 1. Map of the region of location of the Kislovodsk high-altitude scientific station (KVNS) and the town of Kislovodsk.

variations that were revealed at the KVNS from the data obtained at this station for the previous ten years.

2. INSTRUMENTATION

At the KVNS, SOC measurements have been performed since 1989 with a Dasibi 1008-AH gas analyzer described in [5]. Air was taken at a height of 3 m above the ground level. At Kislovodsk, SOC measurements were performed from August 1998 to February 2001 (Fig. 2). The Dasibi 1003-AH gas analyzer was installed at the meteorological site of the clinic of the State Research Institute of Balneology. Air was taken at a height of 10 m above the ground level. An air sampler was installed at the end of a 7-m Teflon tube extended up to the level of the building's roof at a distance of 3 m from the wall.

The instruments installed at the KVNS and Kislovodsk represent different modifications of Dasibi gas analyzers. Both instruments record the absolute concentrations of ozone. The Dasibi 1008-AH instrument records the concentrations in ppb corrected for ambient temperatures and pressures. The Dasibi 1003-AH instrument records the data with no correction; therefore, its readings were corrected during data processing. The ambient temperature and pressure were measured at the meteorological site.

The performance specifications of these instruments were as follows: the sensitivity was 1 ppb, the absolute measurement error was 1–2 ppb, the measurement interval was 10 s, and the response time (0–95%) was 50 s. The data obtained at the KVNS represent a series of values recorded every minute. The data recorded at the town were sequentially averaged to the hourly means, because air temperatures and pressures used for data correction were measured at 1-h intervals. The Dasibi 1008-AH instrument no. 4565 was calibrated by the manufacturer against a standard benchmark instrument; in addition, it has been verified at regular intervals against the Dasibi 1008-RS benchmark instrument and the European ENV 03-41M Standard no. 1298. The operation of the Dasibi 1008-AH instrument no. 4565 was recognized to be stable, and it was used as a standard for verification of the Dasibi 1003-AH instrument.

At the KVNS, the instrument operates on a 24-h basis with its switching off once every ten days for routine inspections or in bad weather (heavy rain, dense fog). At the town, measurements were less regular; there were periods with interruptions of 5 to 12 h a day or even of several days.

We also use the data of combined measurements of tropospheric gaseous and aerosol pollutants and meteorological parameters in the Kavkazskie Mineral'nye Vody (Kavminvody) region. These data were obtained within the framework of the International TROICA

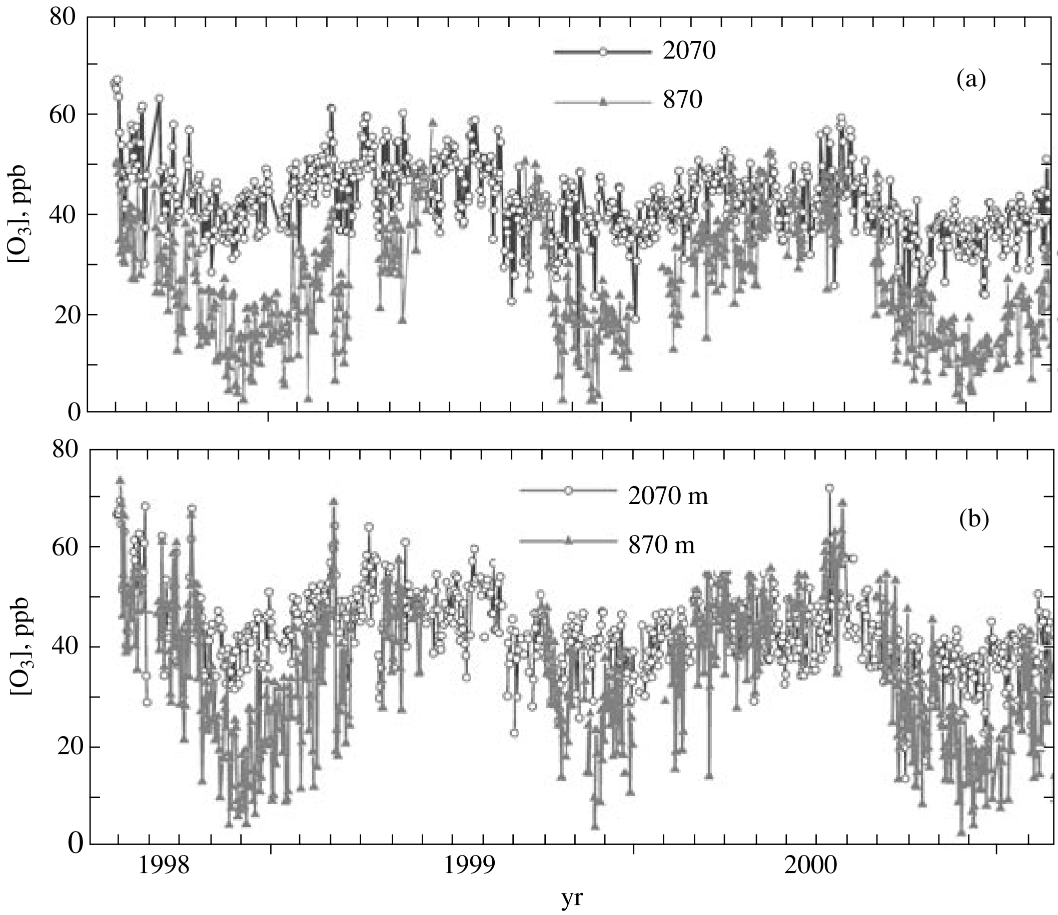

Fig. 2. Surface ozone concentration (from August 1998 to February 2001): (a) daily mean values for Kislovodsk and the KVNS and (b) mean daytime values for Kislovodsk and mean evening values for the KVNS.

(Transcontinental Observations into the Chemistry of the Atmosphere) expeditions in April–May 2000 and September–October 2001 and from episodic measurements of NO_x, CO, and aerosol, which have been performed at Kislovodsk since 1989 [6, 7].

3. CLIMATIC FEATURES

The KVNS is located 2070 m above sea level in the alpine grassland zone on the Shadzhatmaz Plateau (Fig. 1). The plateau is bounded on the south and on the north by narrow and deep ravines parallel to the Main Caucasian Ridge. Mount Elbrus (5642 m) is located 48 km to the south of the station.

Kislovodsk is located 800–900 m above sea level along the valley descending from the southeast to the northwest. The valley is bounded on the north and on the west by the Borgustan Ridge (1200 m) and by a high chain of hills forming the Berezovaya Gully, respectively. To the east, the Dzhinal Ridge (1500 m) protects Kislovodsk against easterly winds bringing cold air, fogs, and low clouds in winter and dry and warm air in summer to the neighboring regions. Observations are performed in the park area on the southern elevated edge of Kislovodsk at 870 m above sea level.

We use meteorological data of the Shadzhatmaz and Piket meteorological stations (entering into the Rosgidromet network) located in the vicinity of the KVNS (400 m away from it) and in the park area of the Kislovodsk (about 50 m above the ozone-measuring site), respectively [8].

The uphill–downhill circulation is an important local-scale topographic factor controlling the variability of the surface ozone concentration. Daily wind-direction variations characteristic of the uphill–downhill circulation were revealed at both the KVNS [5, 9, 10] and Kislovodsk [8]. Within the closed hollow of Kislovodsk, the wind regime is characterized by a clearly defined feature: the downslope wind from the southeastern (northwestern) sector prevailed in the nighttime (daytime) regardless of the direction of the main airflow in the lower troposphere.

The KVNS is located on the northern gentle slope of the Caucasian Ridge; therefore, the efficiency of uphill–downhill circulation is significantly lower here than at other high-altitude stations. At the KVNS and at

Kislovodsk, the south-southeasterly, southerly, south-southwesterly, and, much more rarely, north-northwesterly downslope winds prevailed during all seasons in the periods under consideration. The valley wind was seasonally dependent and showed a less regular behavior and a smaller speed in comparison with the downslope winds.

Kislovodsk has a continental climate, with a yearly mean air temperature of 7.9°C and monthly mean temperatures of the warmest (July) and coldest (January) months of 19.0 and –3.7°C, respectively. The yearly mean relative air humidity at Kislovodsk is 70%. The yearly mean air temperature at the KVNS is 2.5°C [8]. The amplitudes of the annual (18°C) and daily air-temperature cycles in the region of the KVNS, similarly to other high-altitude regions, are less than analogous amplitudes at the town. The mean air humidity at the KVNS for the period of the simultaneous measurements was 75%.

The ABL temperature profiles measured at Kislovodsk with an MTP-5 profiler during the TROICA expedition in April 2000 revealed the frequent occurrence of inversions even under unstable weather conditions [10]. The prevailing downslope wind brings cleaner air from upper atmospheric levels and thus stimulates radiative cooling. In April 2000, the thickness of the nighttime impeding layer was usually no more than 250 m; however, sometimes, it reached 600 m. The layer intensity was 1.0–2.5°C on the average, and its maximum value was equal to 6°C.

The mean values of the observed inversion thickness and intensity are close to the climatic characteristics of inversions typical of the regions characterized by a similar relief and located at the same height above sea level [10]. At the KVNS, surface inversions are characterized by a low frequency of occurrence; frontal inversions and inversions associated with cloud layers predominate and radiation inversions rarely happen [10].

According to the data obtained in 1989–1990 at the Kavminvody aerological station, the winter (January–February) and summer (June–September) mean heights of the PBL boundary are 1.3 and 1.8 km, respectively. In the warm season, the KVNS may be within the PBL or at its boundary; however, most of the time, it is in the free troposphere.

4. FACTORS INFLUENCING THE BEHAVIOR OF SURFACE OZONE

The level of the surface ozone concentration and its variations are influenced by the following processes:

(a) photochemical destruction and production of ozone at different atmospheric levels characterized by different radiation regimes and by different concentrations and natures of pollutants;

(b) deposition (dry and humid) on surfaces; and

(c) dynamic processes.

Out of the entire set of photochemical interactions determining the ozone content in the atmospheric surface layer, several dominating cycles and reactions can be distinguished [11, 12].

Under the conditions of low NO_x concentrations and high solar illumination levels, which are characteristic of the KVNS, cycle (1) is the determining factor:

(1.1) $O_3 + h\nu \longrightarrow O(^1D) + O_2$ ($h\nu < 315$ nm),

(1.2) $O(^1D) + H_2O \longrightarrow OH + OH$,

(1.3) $OH + O_3 \longrightarrow HO_2 + O_2$,

(1.4) $HO_2 + O_3 \longrightarrow OH + O_2$.

This cycle leads to ozone destruction during the daytime and to the formation of a noon minimum.

Cycle (2) describing photochemical ozone formation in weakly polluted urban conditions, i.e., at low concentrations of CO and volatile organic compounds (VOCs), is as follows:

(2.1) $NO_2 + h\nu \longrightarrow NO + O$ ($h\nu < 424$ nm),

(2.2) $O + O_2 + M \longrightarrow O_3 + M$,

(2.3) $O_3 + NO \longrightarrow NO_2 + O_2$.

In this cyclic process, photochemical equilibrium is reached for about 100 s [11]. Until the equilibrium in the vicinity of an NO_x source is reached, the interaction between O_3 and NO leads to losses in the ozone content.

In moist air masses moderately polluted by NO_x, hydroperoxide radicals arising from reaction (1.3) interact with NO by the reaction

(3) $HO_2 + NO \longrightarrow NO_2 + OH$,

with subsequent NO_2 photolysis and ozone formation in cycle (2).

Under the conditions of significant CO and VOC concentrations characteristic of urban air, ozone formation proceeds rather efficiently as a result of chemical reactions between NO and peroxide radicals HO_2 and RO_2 formed during the oxidation of CO and unsaturated hydrocarbons, respectively:

(4) $HO_2 + NO \longrightarrow NO_2 + OH$,

(5) $RO_2 + NO \longrightarrow HO_2 + NO_2 + CARB$,

where R is a hydrocarbon group and CARB is a carbonyl or aldehyde.

The presence of water vapor (for hydroxyl formation) and of solar radiation with a wavelength shorter than 315 nm (for NO_2 and O_3 photolysis) are necessary for cycles (1) and (2).

The above scheme gives a pictorial view of the main mechanisms of ozone destruction and production in the region under consideration. This scheme will be used below in the discussion of the results of measurements.

The most important channel for the flow of ozone is deposition on surfaces. Under the conditions of temperature inversions, downward air transport caused by turbulent mixing in the atmospheric surface layer ceases and the ozone concentration falls. Regular nighttime radiation inversions may influence the mean daily behavior of the surface ozone concentration and thus affect the daily mean SOC values.

For Kislovodsk, nighttime minima in the ozone concentration are typical. Under high-altitude conditions, the dry-deposition effect on the ozone concentration is insignificant because the surface inversions are of short duration and rarely occur.

The dynamic processes of different scales influence the SOC because they provide not only the horizontal transport (including the long-range transport [12, 13]) of air masses with different amounts of ozone and its precursors but also the vertical air exchange (including stratosphere–troposphere exchange and the exchange between the ABL and the free troposphere).

In high-altitude regions polluted only slightly, photochemical processes are of secondary importance and the effect of dynamic factors manifests itself.

The effect of mesoscale regular dynamic processes on the ozone concentrations recorded at the KVNS was discussed in [5, 14]. This effect will remain one of the basic topics for further studies because of its fundamental importance for determining the KVNS status.

In this paper, we compare the characteristics of daily, seasonal, and interannual variations in ozone observed under the urban conditions of Kislovodsk and at the KVNS.

5. GENERAL OVERVIEW OF OBSERVATIONAL DATA

The daily mean ozone concentrations at the KVNS (squares) and town (triangles) for the entire period from August 1998 to February 2001 are presented in Fig. 2a. Unlike the SOC values characteristic of high-altitude regions, the values recorded at the town are very low and sometimes are near zero. The corresponding shift between the daily mean SOC distributions is clearly pronounced in the histograms calculated for the period 1998–2000 for the KVNS and town that are presented in Figs. 3a and 3b, respectively. The maximum frequency of SOC values distributed in the wide range between 16 and 38 ppb is typical of the town, and the median value is only 0.6 ppb below the arithmetic mean equal to 27.4 ppb. About 25 and 75% of all measured values of the ozone concentration are less than 18.9 and 35 ppb, respectively. The distributions of the daily mean SOCs measured over the entire observation period at both observation sites are close to normal distributions.

To characterize variations in the ozone concentration during different days, we chose three time intervals in the daily behavior of ozone during which extreme concentrations were usually observed.

From the data obtained at the town, we chose series of morning (m) and daytime (d) ozone concentration values calculated as the means for four morning (from 4:00 to 8:00) and four daytime (from 12:00 to 16:00) hours, respectively. From the data measured at the KVNS, we chose series of nighttime (n), daytime (d), and evening (ev) SOC values calculated as the means over four hourly mean values for the following time intervals: 1:00–5:00, 10:00–14:00, and 16:00–20:00, respectively. Here, the local time is given. The choice of these time intervals for SOC averaging is associated with characteristic features of the mean daily SOC variation in high-altitude regions. Minimum SOC values are observed at noon. The nighttime SOC values characterize the state of upper tropospheric layers because of nighttime air inflows from the upper levels as a result of the uphill–downhill circulation. In the evening, the atmosphere over the KVNS can be influenced by urban pollutants brought by upslope winds. Therefore, we give special attention to the evening SOC values.

Figure 2b presents the SOC measured in the daytime at Kislovodsk and in the evening at the KVNS. The daytime and morning SOC distributions obtained for the town are presented in Figs. 3c and 3d, respectively, and the statistical characteristics of the series of data are presented in Table 1.

The range of the morning SOC variations at the town over the two-year observation period is between 2.8 and 50 ppb. The range of the maximum (daytime) SOC variations is between 4 and 73 ppb. The low daytime values were observed under the conditions of dense fog and heavy rain. For the town, the variability of the daytime values is higher than that of the morning values and the daytime values are worse described by a Gaussian distribution: a certain bimodal pattern with a deficiency of high values is observed.

It is well known that the vertical gradient of the ozone concentration in the midlatitude atmospheric layer of 1–3 km varies during the year between approximately 4 and 8 ppb/km [15]. Under the assumption that the gradient is determined by the height difference only, we should expect that the difference between the values would be 5–10 ppb. On the average, the values obtained at the town observation site are less than the values obtained at the KVNS by 16 ppb. The plot in Fig. 2 demonstrates that this difference has a well-pronounced seasonal behavior, which is associated with the evident seasonal behavior of the urban ozone concentration. In summer, the daily mean ozone concentrations in the town sometimes reach the values measured at the KVNS, which is due to both the effect of the vertical air transport and photochemical ozone production in the polluted urban air.

6. DAILY VARIATION

The daily SOC variation at Kislovodsk is well pronounced during warm seasons and less pronounced during cold seasons; this is presented in Fig. 4 for August and December 1998. These plots satisfactorily reflect the mean behavior of the SOC over the entire observation period. In the same figure, the daily SOC

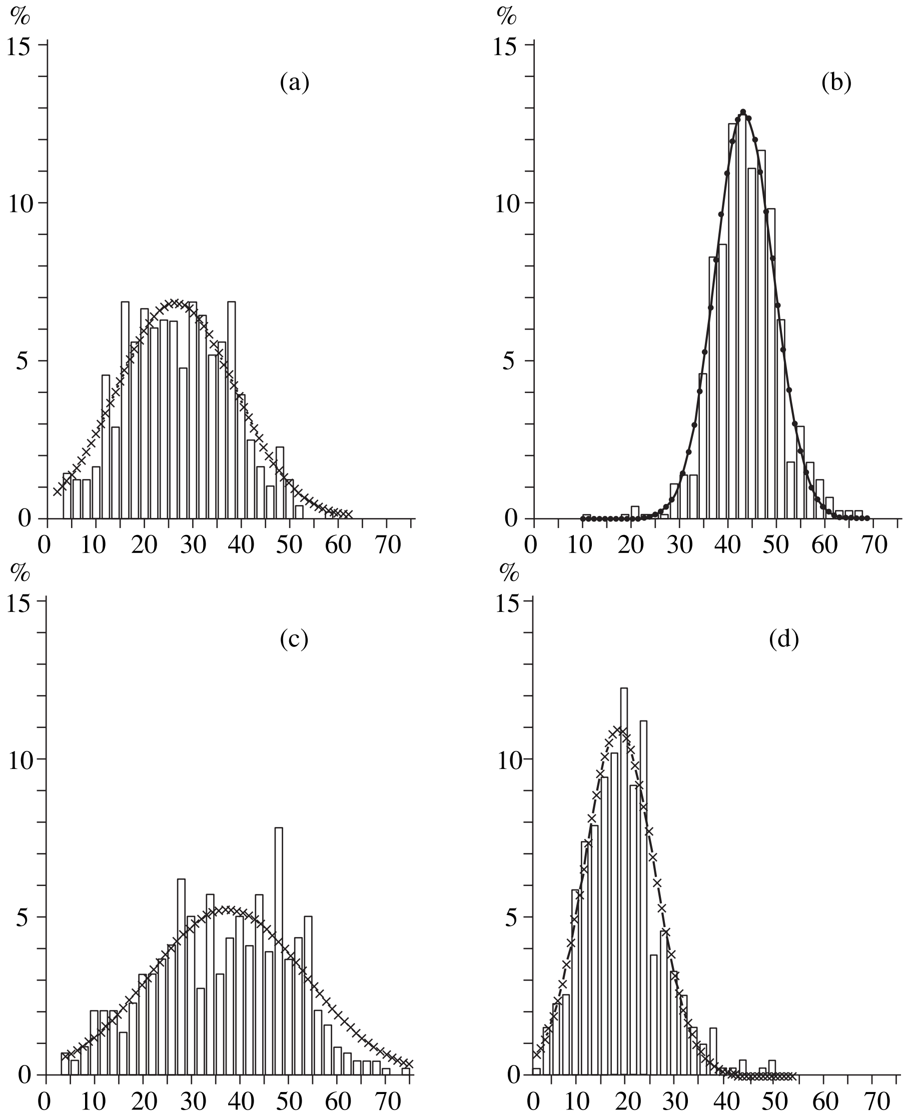

Fig. 3. Distributions of the surface ozone concentration (from August 1998 to September 2000) approximated by Gaussian curves: (a) daily mean values for Kislovodsk, (b) daily mean values for the KVNS, (c) daytime values for Kislovodsk, and (d) morning values for Kislovodsk.

variation at the KVNS averaged over the period 1990–2000 is shown. This plot was discussed in detail in [5, 14, 16, 17]; it is characterized by the following fundamental features: a noon minimum, a maximum shifted toward the night hours, and smallness of the amplitude (the amplitude is maximum in summer; its mean value is 7 ppb).

The daily SOC variations at Kislovodsk and continental lowland stations with moderate air pollution are characterized by the following common features: a rather weak morning minimum and a wide afternoon maximum, an abrupt rise to a maximum value in the morning and an abrupt fall in the evening in warm seasons, a weak or undetectable daily variation in cold seasons, and a 16.5-ppb amplitude of the yearly mean daily variation.

The NO_x concentration measurements performed earlier at Kislovodsk [18] and continued in 1999 in the TROICA experiments [19, 20] showed that the spring and fall NO_x concentrations in the Kavminvody region had local morning (at 9:00) and afternoon (between 13:00 and 18:00) maxima. These maxima are associated with the heavy motor traffic and with the surface-air pollution caused in the morning and in the afternoon by the residual nighttime temperature inversion in the mountain valley and by the termination of the slope wind and the start of surface-inversion formation, respectively.

The evening and nighttime abrupt decreases in the NO_x concentration are associated with the successive transformation of NO into NO_2, NO_3, and N_2O_5 after sunset without photodissociation and also with reduc-

Table 1. Characteristics of ozone variability at Kislovodsk (870 m above sea level) and at the KVNS (2070 m above sea level) for the observation period from August 1998 to September 2000

	Ozone concentration							
	min	10%	25%	Median mean	Mean	75%	90%	max
870 m	2.8	10.4	14.1	19.5	20.0	24.2	30.0	50.3
870 d	4.2	17.8	26.1	37.0	36.5	47.9	53.2	73.2
870 daily	3.1	13.1	18.9	26.8	27.4	35	40.9	58.3
2070 daily	10.8	36.0	39.8	43.8	44.0	47.8	51.6	67.1

Note: Averaging is performed over four-hour morning (4:00–8:00) (m) and daytime (12:00–16:00) (d) intervals and over entire days (daily).

tion of the traffic and development of the downslope wind, which transports urban pollutants to the adjacent plain.

We discuss the details of the summer daily SOC variation at Kislovodsk (Fig. 4a). The SOC gradually decreases in the nighttime and passes through a minimum in the morning. The local time of the morning minimum shifts gradually from 6:00 in summer to 9:00 in winter in accordance with the shift in the local time of sunrise. The principal mechanism of this phenomenon is as follows. In the nighttime, under the conditions of stable inversions, an ozone-poor atmospheric surface

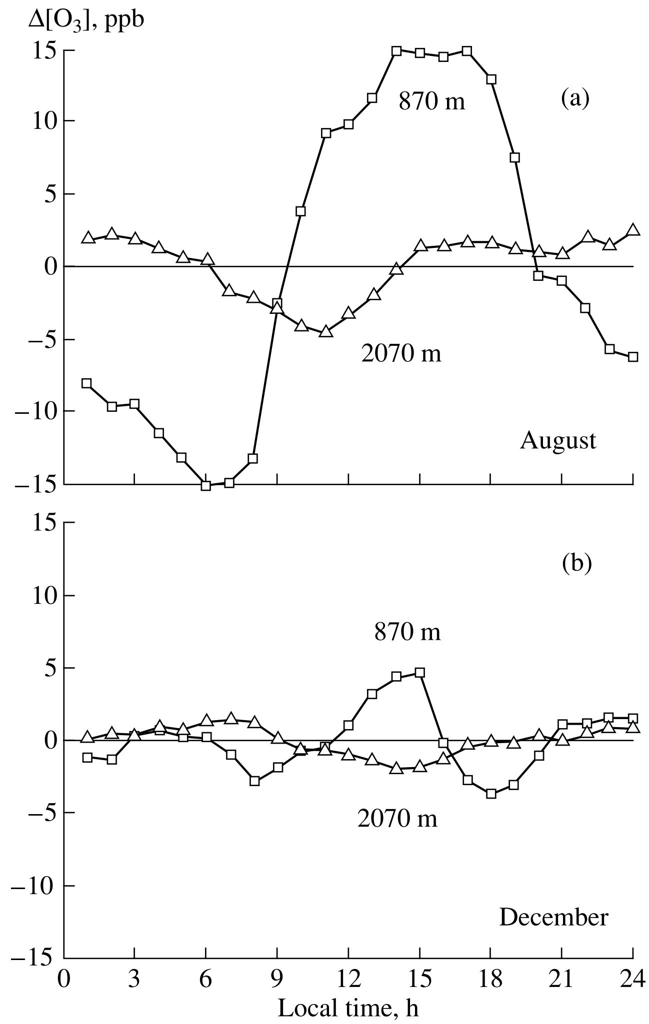

Fig. 4. Daily variations in the ozone concentration, i.e., deviations from the daily mean concentrations, for Kislovodsk (1998, squares) and for the KVNS (averaging over 1990–2000, triangles): (a) August and (b) December.

layer forms as a result of ozone sinking on the underlying surface and the lack of air exchange between the lower and upper atmospheric layers. This exchange develops after sunrise and gradual destruction of the inversion; however, at the first step, the SOC decreases by 2–3 ppb due to air exchange with the underlying air (the clinic is located on the mountain slope leading to a rather shallow valley of the Ol'khovka River, and the air samples are taken at a height of 10 m above the ground). A good repeatability of the minimum in the daily SOC variation is provided by the frequent occurrence of nighttime-inversion formation.

Radiation inversions at the KVNS rarely occur. Therefore, the nighttime air exchange between the atmosphere over the KVNS and the upper atmospheric layer enriched with ozone represents a common phenomenon. Such an exchange compensates the ozone deposition and leads to an increase in the ozone concentration to its maximum level at this time of day.

The Kislovodsk observation site is located in a high southern resort area of the town, where economic activities and motor traffic are limited. However, as the air is warmed, the atmospheric turbulent mixing and uphill–downhill circulation promote the morning upward air transport along the valley from the low business district to the high district and initiate the photochemical generation of ozone. Key chemical reactions (3)–(5) proceeding between peroxide radicals and NO_x, CO, and VOCs, whose atmospheric concentrations are high, lead to an active ozone formation and an acceleration of the SOC growth. This process is reflected in the plot of the daily SOC variation. The morning NO_x concentration is maximum at about 9:00, i.e., in the period when the rate of increase in the ozone concentration is maximum.

The increase in the ozone concentration and the daytime maximum are also influenced by another process, namely, by the daytime intensification of turbulent air mixing in the planetary boundary layer. As a result of this process and of the occurrence of a positive gradient of the tropospheric ozone concentration, the ozone-rich air from upper layers is transported to the ground surface.

The efficiency of these two mechanisms depends on the season (on the temperature and solar insolation). Therefore, the winter daily variations are rather small.

In the evening, as the UV illumination level reduces [21], photochemical ozone generation abruptly weakens and entirely ceases because the lifetime of peroxide radicals participating in ozone synthesis according to reactions (3)–(5) is a few minutes, whereas the reaction of ozone destruction with no subsequent NO_2 photolysis prevails in cycle (2). The evening decrease in the SOC is clearly pronounced.

On the days when the NO_x concentration is higher than its usual value, the SOC can fall very rapidly in the evening to a near-zero value as a result of NO oxidation by ozone with NO_2 formation. At the town observation site, such a situation occurs more rarely than once in ten monitoring days, and, at the KVNS, it does not occur at all.

As noted above, at night, when the atmospheric surface layer is isolated from the upper layers, the SOC continues to decrease as a result of dry deposition on the surface. The SOC decrease is especially rapid in the warm seasons, because the summer conditions are favorable for ozone deposition on tree crowns and grass covers.

A comparison with the data of observations performed in the TROICA expeditions [19, 22] shows that the SOC at Kislovodsk decreases not so significantly during nighttime as in the cities located on the plain lying along the Trans-Siberian Railroad. This difference is associated with the following local features of Kislovodsk: (1) total air pollution is not very severe; (2) in the evening, air polluted by nitrogen oxides flows downward to the plain; and (3) the nighttime downslope wind stimulates ozone injection from the upper atmospheric layers.

The evening and nighttime downslope wind from the mountains are a frequent occurrence in Kislovodsk. Taking into account the maximum of air pollution in the morning, we believe that the low value of the correlation coefficient (equal to 0.1) should be explained by air inflow to Kislovodsk from the atmospheric levels lying within the atmospheric boundary layer, while the KVNS is in the free troposphere.

Low (close to zero) SOC values were observed at Kislovodsk in the nights after intense daytime accumulation of pollutants in the atmospheric surface layer. In such nights, ozone dry deposition was supplemented by a more intense ozone chemical sink resulting from ozone interaction with NO. Abnormally high daytime SOC values were observed on windless sunny days when ozone generation was rather intense.

A comparison between daily variations in the ozone concentration on work days and days off showed that, in warm seasons, the surface ozone concentration on days off is decreased in the night and morning and is increased in the daytime. This phenomenon is apparently associated with the intensification of human activities on land homesteads leading to additional daytime photochemical ozone production and evening ozone consumption for NO oxidation [17].

As was noted above, the nighttime inversion is of crucial importance in the formation of a morning SOC minimum. The relation between the duration of the SOC minimum and the lifetime of the atmospheric under-inversion layer is demonstrated by the following example. The passage of a warm atmospheric front with its inherent temperature stratification, which intensified the usual surface inversion, was recorded on April 19, 2000. The intensity of this inversion reached 6°C, and its upper boundary was above 600 m. This inversion was observed until 11:00 (according to the measurements performed with the MTP-5 profiler

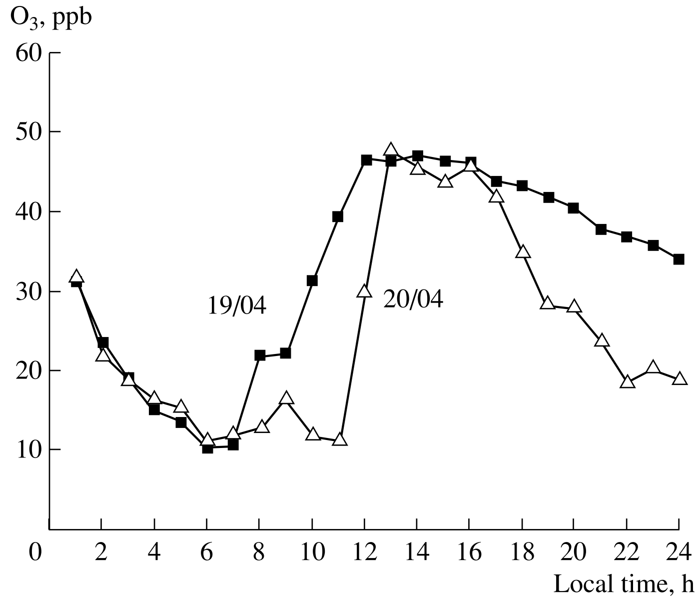

Fig. 5. Ozone concentrations before the passage of a warm atmospheric front (April 19, 2000) and in the zone of this front (April 20, 2000).

[10]). The morning minimum seen in the SOC plot given in Fig. 5 was also observed until 11:00. After the destruction of the inversion, the SOC value increased abruptly, although the SOC rise usually starts at 9:00 and continues gradually in parallel with increasing NO_x concentration rise and with the intensifying turbulent mixing.

At the KVNS, anomalies in the daily SOC variation that are associated with synoptic phenomena and large-scale atmospheric processes are defined more clearly against the background of the regular but weak diurnal variations. This statement is detailed in [9]. The days with identical anomalies in the daily SOC variations form synoptic-scale series.

For example, the biannual data set obtained at the KVNS contains 40 events (7%) of a clearly pronounced maximum observed at about 17:00 instead of the usual nighttime maximum. An analysis has shown that this unusual maximum is caused by the intensification of air exchange between the surface layer and the boundary layer under certain synoptic conditions (35% of these events) and by long-range transport from particular directions, which is also modulated by large-scale and synoptic processes. The effect of the long-range transport of ozone and its precursors on the SOC will be considered in the following paper.

7. SEASONAL VARIATION

The seasonal SOC variation averaged over the entire period of observations performed simultaneously at the town and KVNS is seen in Fig. 6. The seasonal town SOC variation with a wide summer maximum is characteristic of continental stations and is mainly of photochemical origin. The amplitude of the seasonal SOC variation at Kislovodsk is equal to 25 ppb. Maximum summer and minimum winter SOC values were observed in June–July (about 41 ppb) and November–December (16 ppb), respectively.

The seasonal SOC variation at the KVNS averaged over three years is identical to that averaged over the preceding observation period 1989–1998. These results were discussed earlier [5, 14, 17]. Two local maxima (in April–May and July–August) are typical of seasonal variations recorded at some high-altitude stations located in particularly clean regions. These maxima reflect the SOC dependences on the photochemical and dynamic processes within the PBL and, to a greater degree, the SOC dependence on the intensity of stratosphere–troposphere exchange.

Table 2 contains seasonal mean data allowing a comparison of the seasonal variations obtained by us with those described in [4]. Six observation stations are located at different heights on the southern (Italian) slope of the Central Alps; five of these stations are remote from local sources of pollutants. The Mezzoldo station (880 m) and the Passo S. Marco station (1900 m) are close in their heights above sea level to the Kislovodsk observation site and the KVNS, respectively. The SOCs at Kislovodsk are somewhat smaller than at the Mezzoldo Alpine station.

At Kislovodsk, the amplitude of the seasonal SOC variation was increased because the winter SOC values were low. In winter, photochemical processes proceed slowly and air pollution is insignificant. Therefore, the winter SOCs are more sensitive to other factors, for example, to the differences between the characteristics of the underlying surface (the ozone deposition on a

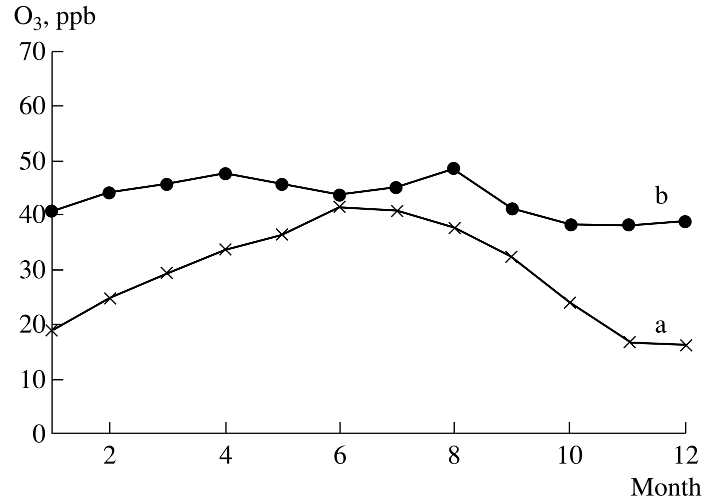

Fig. 6. Seasonal variation of the ozone concentration for the period of simultaneous measurements (1998–2001): (a) for Kislovodsk (urban conditions) and (b) for the KVNS (high-altitude conditions).

surface covered with snow is ten times slower than that on a surface free of snow; meanwhile, snowfall rarely occurs in Kislovodsk) and to differences in the conditions of air exchange with upper atmospheric layers (Kislovodsk lies along a valley sloped to the north; therefore, the uphill–downhill circulation is less effective here than along the southern slope of the Alps, where the Mezzoldo station is located).

A comparison with the Passo S. Marco Alpine station (1900 m above sea level) allowed us to state that the amplitude of the seasonal SOC variation at the KVNS is significantly smaller (by 7 ppb) than that at the Passo S. Marco station. The occurrence of small seasonal variations is a characteristic feature of background high-altitude stations, which reflect the state of the free troposphere (see also [23]). The seasonal SOC variation observed at the KVNS testifies to a weaker atmospheric pollution in comparison with the Alpine stations.

8. INTERANNUAL VARIABILITY

To overcome the nonuniformity of the data series and to obtain a notion on the character of the interannual ozone variability, we approximated all daily series (nighttime, morning, and daytime series) by a polynomial and revealed the long-wavelength components of the variations (Fig. 7). We used only the data obtained during the days when measurements were performed at two stations simultaneously. For the time scale used by us, these long-wavelength components include seasonal and interannual variations.

Table 2. Surface ozone concentration at several high-altitude stations located in the North Caucasus and in the Italian Alps

	Height above sea level	Mean $[O_3]$ ppb	
		summer	winter
Brunate	800 m	40	19
Kislovodsk	870 m	39	20
Mezzoldo	880 m	42	29
Passo S. Marco	1900 m	47	35
KVNS	2070 m	45	40

Figure 7 presents the morning and daytime town ozone concentrations processed by the procedure indicated above and, for comparison, the nighttime and evening ozone concentrations measured at the KVNS. Such a choice is due to the necessity of studying the possible mutual influence of the processes occurring at the two observation sites. Under the assumption of a significant effect of the uphill–downhill circulation, the nighttime high-altitude air can be transported to the town by the downslope wind, thereby affecting the morning SOC values. Urban air masses with increased daytime SOC values and other pollutants can be transported to the KVNS in the afternoon by airflows ascending along the slope and can form the evening SOC increase characteristic of the KVNS.

The long-wavelength components of the nighttime and evening SOCs at the KVNS are similar as a whole and in detail. At the same time, they differ strongly from the Kislovodsk daytime SOCs, which have a significantly larger seasonal amplitude and the characteristic summer rise in 2000 as compared to 1999. The tendency for a decrease in the ozone concentration observed at the KVNS during the period under consideration does not manifest itself at Kislovodsk. The variations in the high-altitude ozone concentrations are in qualitative agreement with the 12-yr SOC trend observed at the KVNS. The trend estimated on the basis of the daily mean SOCs is equal to –1.7% per year.

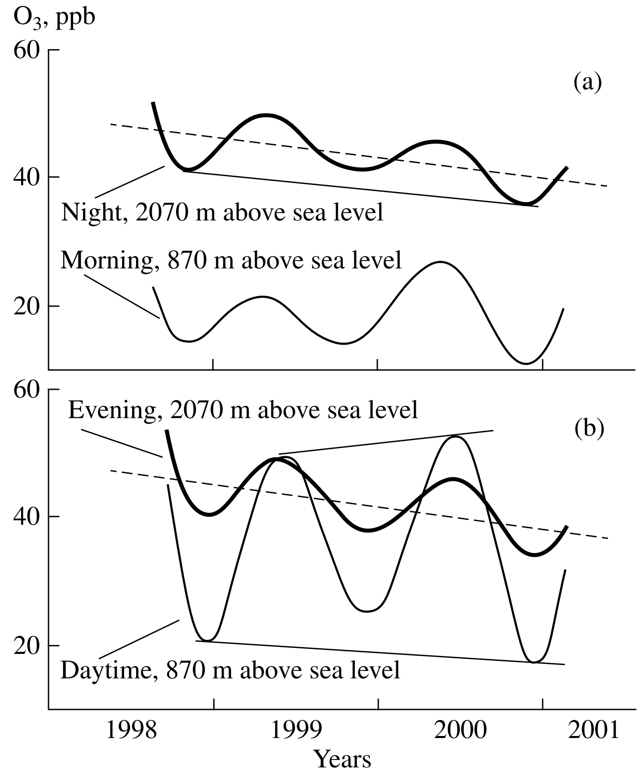

Fig. 7. Long-wavelength components of surface ozone variations: (a) nighttime values for the KVNS and morning values for Kislovodsk and (b) evening values for the KVNS and daytime values for Kislovodsk.

It is seen that the morning SOCs measured at Kislovodsk are also close to the high-altitude SOCs in behavior; however, these morning SOCs are significantly lower in the mean level than both high-altitude and daytime town SOCs. The daily morning town SOCs and nighttime KVNS SOCs after subtraction of the long-wavelength variations virtually do not correlate with each other (the R values calculated for the entire observation period and for the warm seasons are 0.14 and 0.07, respectively). This result confirms the earlier assumption that the prevailing nighttime southerly wind brings air into the town from the atmospheric levels located below the Shadzhatmaz Plateau. The downslope wind descending from the region of the KVNS, apparently, does not reach Kislovodsk. Thus, the pattern of the uphill–downhill atmospheric circulation in the region under study is beginning to emerge.

The daily SOCs observed at Kislovodsk in the summer of 2000, which are above the mean SOC level, are associated with the stable, abnormally warm, sunny weather in 2000, when the July mean temperature was almost 1.5°C higher than that in 1999. Because the warming was caused by specific features of large-scale atmospheric processes, it is evident that these processes influenced the atmospheric transport and distribution of ozone as well.

The increased SOCs were repeatedly observed, for example, in Europe, within anticyclonic baric zones characterized by high values of pressure, temperature, and insolation [2, 4, 10, 24]. In such events, an active photochemical ozone source is supplemented by a dynamic source: ordered downward flows in anticyclones transport ozone-rich air from the free troposphere to the ground surface. In July 2000, the vertical transport did not play a marked role; therefore, no significant SOC increase was observed at the KVNS. Under such conditions, another mechanism could manifest itself; namely, the intense descent of air masses could lead to the formation of a temperature inversion at a height of 1700–1800 m. Such a phenomenon was frequently observed in summer measurements performed at the Kavminvody aerological station [5]. Under the conditions of low vertical gradients of the ozone concentration, such a descent does not influence the atmospheric ozone concentration in the upper atmospheric layers; however, in Kislovodsk, located under the inversion layer (unstable or isothermal layer), the air descent can lead to the accumulation of CO and VOCs, whose oxidation in these conditions stimulates an intense ozone generation. The measurements performed in this period at Kislovodsk showing that the SOC variations in the morning are significantly smaller than those in the daytime confirm the photochemical origin of ozone. The absence of any positive changes in the summer SOC values obtained at the KVNS in 2000 testifies to the absence of a regular effect of the town on the surface ozone concentration at the KVNS.

The difference between the winter SOC values measured at 2070 and 870 m above sea level varies significantly from year to year (Fig. 2b). This conclusion follows from an analysis of the series of the daily mean values and, even more clearly, from an analysis of the series of the daytime maximum values. Figure 7 shows that this difference decreases in the cold season of 1999–2000 and that the decrease in this difference is caused by an increase in the daytime SOCs in the town. In the winter of 1999–2000, the evening SOCs at the KVNS did not change. It can also be inferred that the evening SOC at the KVNS and the daytime SOC at the town behave independently of each other in the winter season.

The causes of the interannual variations and abnormalities in the daily SOC behavior revealed in the foothills of the North Caucasus and the relation between the revealed phenomena and the large-scale synoptic processes should be studied in the future.

9. CONCLUSIONS

This work contains results of simultaneous SOC measurements performed at two observation sites located in the North Caucasus at different heights above sea level: the KVNS at 2070 m and Kislovodsk at 870 m.

On the basis of these new data, the main patterns of ozone concentration variations at the KVNS are confirmed and the characteristics and patterns of variations in the ozone concentration in the town of Kislovodsk are obtained. The SOC level and the characteristics of the daily and seasonal SOC variability confirm the status of the town of Kislovodsk as a resort town with moderately polluted air in comparison with the air of industrial cities.

The results testify that the surface ozone at the KVNS is only slightly influenced by the pollutants accumulated within the atmospheric boundary layer and contains information relating primarily to the regional and global state of the troposphere. The daytime ozone concentrations at Kislovodsk are influenced by the photochemical processes associated with the local air pollution and by the dynamic processes proceeding in the PBL. The wind that is usually fixed at the meteorological station near the KVNS as the uphill–downhill circulation most likely reflects the airflow over the Kabardinskii and Borgustanskii ridges and represents a larger-scale circulation system rather than a local one.

It is evident that synoptic processes have a substantial effect on the effectiveness of the impact of other factors on the ozone concentration at all tropospheric levels. In high-altitude regions, where photochemical processes are of secondary importance, dynamic atmospheric processes significantly influence ozone concentration variability.

ACKNOWLEDGMENTS

We are grateful to E.N. Kadygrov and A.D. Lykov (Central Aerological Observatory) for the measurements performed with the MTP-5 instrument and to the members of OAO Kavminkurortresursy for the meteorological data placed at our disposal.

This work was supported by the Russian Foundation for Basic Research, project nos. 00-05-072023 and 04-05-64587, and by the international programs INCO-COPERNICUS, project no. ICA2-CN-2000-10038, and INTAS, project no. IN-01-0016.

REFERENCES

1. F. C. Fehsenfeld, M. J. Bollinger, D. D. Parrish, *et al.*, "A Study of Ozone in the Colorado Mountains," Atmos. Chem. **1**, 87–105 (1983).
2. J. Forrer, R. Ruttimann, D. Schneiter, *et al.*, "Variability of Trace Gases at the High-Alpine Site Jungfraujoch Caused by Meteorological Transport Processes," J. Geophys. Res. D **105**, 12241–12251 (2000).
3. S. Glavas, "Surface Ozone and NO_x Concentrations at a High Altitude Mediterranean Site, Greece," Atmos. Environ. **33**, 3813–3820 (1999).
4. R. Vecchi and G. Valli, "Ozone Assessment in the Southern Part of the Alps," Atmos. Environ. **33**, 97–109 (1999).
5. N. F. Elanskii and I. A. Senik, "Measurements of the Surface Ozone Concentration at the Kislovodsk High-Altitude Scientific Station: Seasonal and Daily Variations," Izv. Akad. Nauk, Fiz. Atmos. Okeana **31**, 251–259 (1995).
6. I. B. Belikov, I. G. Granberg, E. M. Dobryshman, *et al.*, "En-Route Measurements of Atmospheric Pollution in the Region of Caucasus Mineral Waters," Izv., Atmos. Ocean. Phys. **37** (Suppl. 1), S102–S109 (2001).
7. V. M. Kopeikin and A. F. D'yachkov, "Observations of Soot Atmospheric Pollution over the Town of Kislovodsk," in *Proceedings of 2nd International Conference on the State and Control of the Air Basin and Water–Mineral Resources in Recreation and Resort Areas, Kislovodsk, 2000* (MAX Press, Moscow, 2000), pp. 87–91.
8. *Handbook on the USSR Climate* (Gidrometizdat, Leningrad, 1966), Part 2 [in Russian].
9. I. N. Kuznetsova, N. F. Elansky, and I. A. Senik, "Measurements of the Tropospheric Ozone Concentration over the Kislovodsk High-Altitude Scientific Station: Synoptic-Scale Meteorological Process As a Cause of Ozone Variations," Izv., Atmos. Ocean. Phys. **37** (Suppl. 1), S120–S130 (2001).
10. I. N. Kuznetsova, N. F. Elanskii, I. Yu. Shalygina, *et al.*, "Temperature Inversions and Their Influence on the Surface Ozone Concentration in the Environs of Kislovodsk," Meteorol. Gidrol., No. 9, 40–50 (2002).
11. J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics from Air Pollution to Climate Change* (Wiley, New York, 1998).
12. P. J. Crutzen and P. H. Zimmerman, "The Changing Photochemistry of the Troposphere," Tellus A–B **43** (4), 136–151 (1991).

13. S. Oltmans and H. Levi, “Surface Ozone Measurements from a Global Network,” Atmos. Environ. **28** (1), 9–24 (1994).

14. I. A. Senik and N. F. Elansky, “Surface Ozone Concentration Measurements at the Kislovodsk High-Altitude Scientific Station: Temporal Variations and Trends,” Izv., Atmos. Ocean. Phys. **37** (Suppl. 1), S110–S119 (2001).

15. J. P. F. Fortuin and H. Kelder, “An Ozone Climatology Based on Ozonesonde and Satellite Measurements,” J. Geophys. Res. D **103**, 31709–31734 (1998).

16. N. F. Elanskii, A. Ya. Arabov, A. S. Elokhov, *et al.*, “Observations of Trace Atmospheric Gases and UV Radiation at the Kislovodsk High-Altitude Scientific Station,” Izv. Akad. Nauk, Fiz. Atmos. Okeana **31**, 10–19 (1995).

17. I. A. Senik, “Regime of Surface Ozone under Background Conditions from the Data of the IFA Kislovodsk High-Altitude Scientific Station,” in *Proceedings of 2nd International Conference on the State and Control of the Air Basin and Water–Mineral Resources in Recreation and Resort Areas, Kislovodsk, 2000* (MAX Press, Moscow, 2000), pp. 115–122.

18. N. F. Elansky, A. Ya. Arabov, L. Weissflog, *et al.*, “Oxidizing Ability of the Atmosphere and Trichloroacetic Acid Formation in Surface Air over European Russia,” Izv., Atmos. Ocean. Phys. **37** (Suppl. 1), S58–S70 (2001).

19. A. Yu. Arabov, N. F. Elansky, D. I. Olshansky, *et al.*, “Surface Temporal and Spatial Variations of Surface Ozone As Observed at Several Sites of Russia,” in *Proceedings of Quadrennial Ozone Symposium, Sapporo, Japan, 2000* (Nasda, Sapporo, 2001).

20. N. F. Elansky, T. A. Markova, I. A. Senik, *et al.*, “Surface Ozone in Remote, Rural and Urban Regions of Russia” in *EUROTRAC-2, TOR-2 Tropospheric Ozone Research* (Annual Report 1999, 2001), pp. 65–72.

21. N. F. Elansky, V. V. Savinykh, and I. A. Senik, “Surface Ozone and UV-B Radiation Variability Observed at the High Mountain Observatory Kislovodsk,” in *Climate Variability and Climate Change Vulnerability and Adaptation*, Ed. by Ivana Nemesova (Academy of Science Press, Prague, 1996), pp. 254–259.

22. N. F. Elansky, T. A. Markova, I. B. Belikov, and E. A. Oberlander, “Transcontinental Observations of Surface Ozone Concentration in the TROICA Experiments: 1. Space and Time Variability,” Izv., Atmos. Ocean. Phys. **37** (Suppl. 1), S24–S38 (2001).

23. E. Schuepbach, T. K. Friedli, P. Zanis, *et al.*, “State Space Analysis of Changing Seasonal Ozone Cycles (1988–1997) at Jungfraujoch (3580 m above Sea Level) in Switzerland,” J. Geophys. Res. D **106**, 20413–20427 (2001).

24. P. D. Kalabokas, G. T. Amanatidis, and J. G. Bartzis, “Rural Ozone Levels at an Eastern Mediterranean Site (Attica, Greece),” Atmos. Environ. **28**, 9–24 (1994).

Translated by E. Kadyshevich