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OPTICAL MODELS  
AND DATABASES

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## Surface Ozone Concentration in Russia in the Second Half of 2020

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**Abstract**—We present information on ozone concentration in the surface air layer in the second half of 2020. Data were obtained at 13 stations located in different regions of Russia. We estimated the excess over hygienic standards of the Russian Federation, both in the second half of the year and throughout 2020. It is shown that the daily average maximum permissible concentration of ozone is regularly exceeded at all stations. There are cases of exceeding the one-time maximum permissible concentration.

**Keywords:** atmosphere, air, concentration, ozone, maximum permissible concentration, surface layer

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### INTRODUCTION

This paper continues a cycle of publications, aimed at informing the scientific community about ozone content in the surface air layer on the territory of Russia (addressing the second half of 2020). This information is important because ozone in the troposphere is extremely hazardous both for biological and environmental structures. At the same time, the governmental-level monitoring of ozone concentration is not organized. The population does not have such information and, hence, cannot adequately respond to ozone concentrations exceeding maximum permissible concentration (MPC). Medical practitioners know nothing about the specific ozone effect on individuals and have no methods for neutralizing this effect.

In the period of time considered in this review, we can single out two specific features. The first is associated with the coronavirus pandemic, fighting which has weakened the economic activities and, hence, anthro-

pogenic emissions, with ensuing air cleansing in cities. The second feature is that 2020 had been the warmest on Earth throughout the observation period [1]. This is despite the development of an El Niño event, which has a cooling effect on the planet. However, the pandemic is considered by the scientific community to not eliminate, but just to postpone, the implementation of measures to mitigate the consequences of global warming on the environment [2–4].

As numerous studies showed, the lockdown, which weakened the economic activities of population, did reduce the air pollution level in a number of cities. Based on work [5], the PM<sub>2.5</sub>, PM<sub>10</sub>, NO<sub>2</sub>, and CO concentrations decreased by 41, 52, 51, and 28%, respectively, in Delhi, Mumbai, Chennai, Calcutta, and Bangalore in March–April 2020. In central Europe, the NO, NO<sub>2</sub>, and CO concentrations and the total number of particles with diameters <100 nm decreased by 68, 46, 27, and 28% in 2020 relative to the

(2017–2019) average reference [6]. Based on data of work [7], the level of the main pollutants in the atmosphere decreased by 30–50% in Moscow in the period of restrictive measures.

At the same time, the ozone content increased despite reduced precursor gas concentrations. Ozone increase by 69.7% was noted in Shenyang (China) [8], by 42% in Great Britain [9], and by 14 to 27% in European cities [10]. This effect is quite justified considering the distortion of the balance in the NO–O<sub>2</sub>–NO<sub>2</sub> triad [11, 12].

Authors of work [13] hypothesized that ozone can influence the spread of coronavirus itself. Their regression analysis showed that the SARS-CoV-2 spread decreased as ozone concentration grew from 48 to 94 µg/m<sup>3</sup> at the 0.04 significance level. Unfortunately, no other similar studies were found.

Of course, the level of ozone content in the atmosphere during 2020 was influenced not only by lockdown announced due to the coronavirus. There were also atmospheric processes in the course of which ozone could have been generated or destructed. This was addressed in work [14], which showed that, upon the lockdown announcement, the air pollution level decreased and the ozone generation rate increased, but not in every city.

Ozone concentration in the surface air layer may vary several-fold in the long-term behavior; therefore, the existing ozone trends should be accounted for in assessing lockdown consequences. The consortium of organizations arranged to prepare reviews does not yet have a long time series of surface ozone concentrations. Therefore, no independent task was formulated in this review to elucidate the lockdown consequences. Possibly, we will return to this issue in subsequent publications after the necessary number of measurements is accumulated.

## DESCRIPTION OF STATIONS AND INSTRUMENTS USED

The total list of stations and their instrumentation, as well as a description of the operational mode and calibrations, were given in [15]. Here, we will describe the Apatity and Boyarsky stations, which remained beyond the scope of the previous review.

Ozone measurements in Apatity, Murmansk oblast, are carried out on the territory of Akademgorodok, most of which is a park zone. Coordinates of the site are 67°34'14" N, 33°23'51" E, altitude 180 m above sea level. A UV ozonometer Dasibi 1008-AH is used as the measuring instrument. The measurements are carried out at one-minute time resolution. Air is collected at an altitude of 15 m above the Earth's surface. Data on the surface ozone concentration (SOC) in the region are complemented by series of measurements in the background regions, which are currently not regular. An electrochemical ozonometer is used for

this. The description of the instrument and its metrological properties were presented in [16].

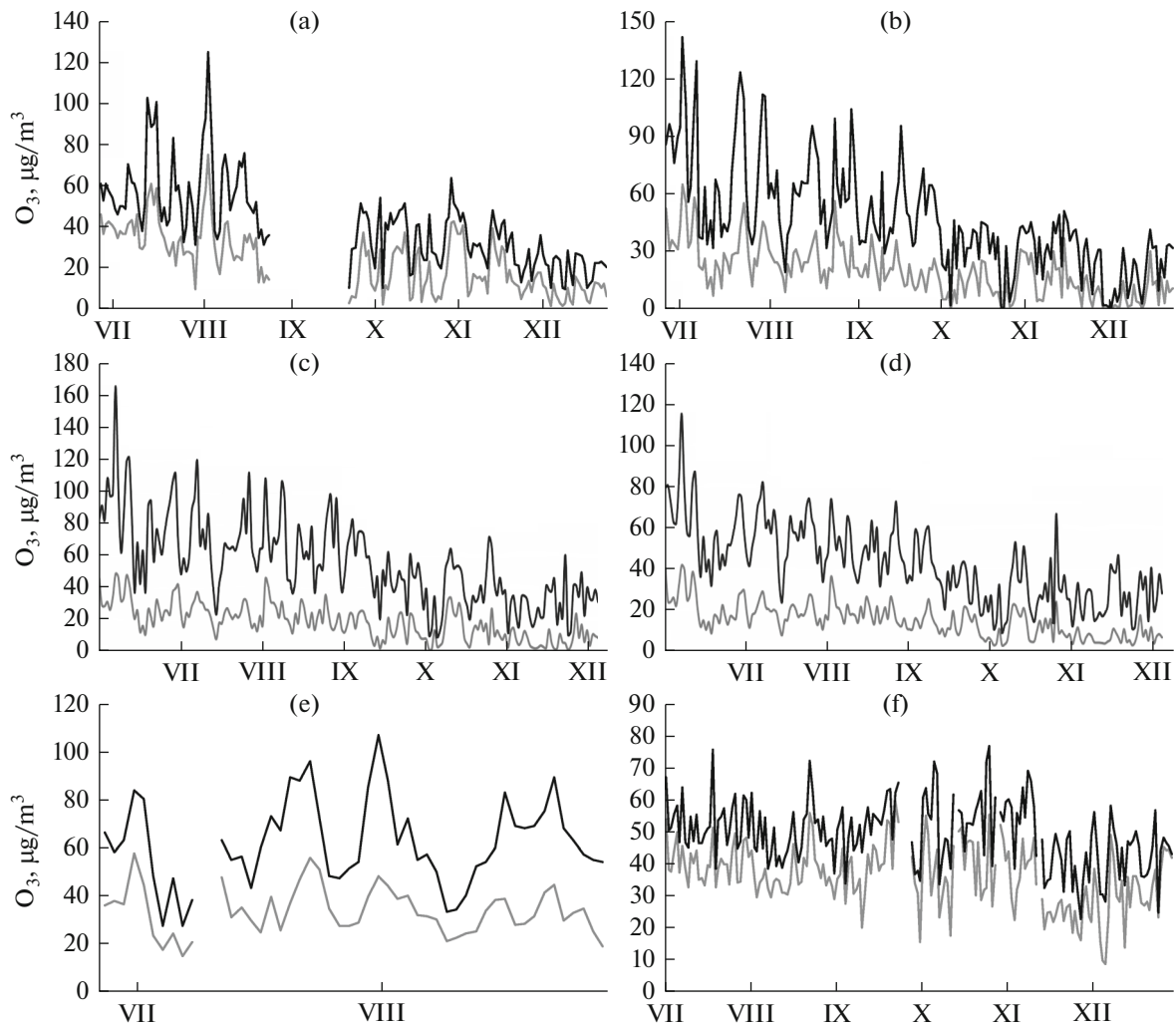
The Boyarsky monitoring station is located in the Republic of Buryatia, on the southeastern coast of the Lake Baikal. Its coordinates are 51°51'10" N, 106°02'28" E, and its altitude is 516 m above sea level. The region is characterized by large temperature contrasts between the lake and adjoining territory, which are enhanced due to closed position of Baikal, surrounded by mountain ridges in all directions. The temperature gradient between the lake hollow and adjoining dry depressions, reaching 20°C and larger, is one of the main factors of formation and development of intrahollow circulation and its propagation into the lake basin, often favoring accumulation of atmospheric pollutants. Boyarsk village can be considered to experience a weak anthropogenic effect. Certain effects can be exerted by small industrial centers: Babushkin 22 km away, Kamensk settlement 50 km away, and Selenginsk settlement 60 km away. A mixed forest (birch, pine, and cedar) lies in the immediate vicinity. There is a 30-m mast at the station. To determine the concentration of surface ozone, air is collected at altitudes of 2 and 20 m above the Earth's surface via Teflon pipes. Measurements are carried out using a chemiluminescent gas analyzers 3.02 P-A. The instrument is calibrated and zeroed automatically, using built-in ozone sources at the commands of the gas analyzers processors. Additionally, measurement error was episodically controlled by testing the gas analyzer with the use of a Mod. 8500 Monitor Labs calibrator. At the same altitudes, meteorological observations are also carried out with AMK-03 and EXMETEO acoustic meteorological complexes.

The coronavirus pandemic adversely impacted not only human health, but also many industrial processes and, in particular, the observations of the state of the environment, sometimes to a very significant degree [17]. Pandemic-associated restrictions had also an effect on ozone measurements in Russia. A few stations, mentioned in the previous review, had been closed, and some could only be operated in periods when restrictions were relaxed.

## MEASUREMENT RESULTS

We begin our analysis with urban stations, located on densely populated territories (Fig. 1). All urban stations show a classical annual behavior of ozone, with concentration decreasing from summer toward winter.

In Moscow, there is a regional network of ecological monitoring at the State Nature Conservation Organization, Mosecomonitoring, which is specially authorized to carry out state ecological monitoring [18]. In this review, we present the data averaged over measurements at urban and roadside stations [19]. In the analysis, there are no data from suburban sites, or from the Losiny Ostrov nature reserve site.



**Fig. 1.** Daily average (gray line) and daily maximal (black line) ozone concentrations in the surface air layer at stations: (a) OPTEC-P; (b) RUDN; (c) urban stations of Moscow; (d) roadside stations of Moscow; (e) Obninsk; and (f) Apatity.

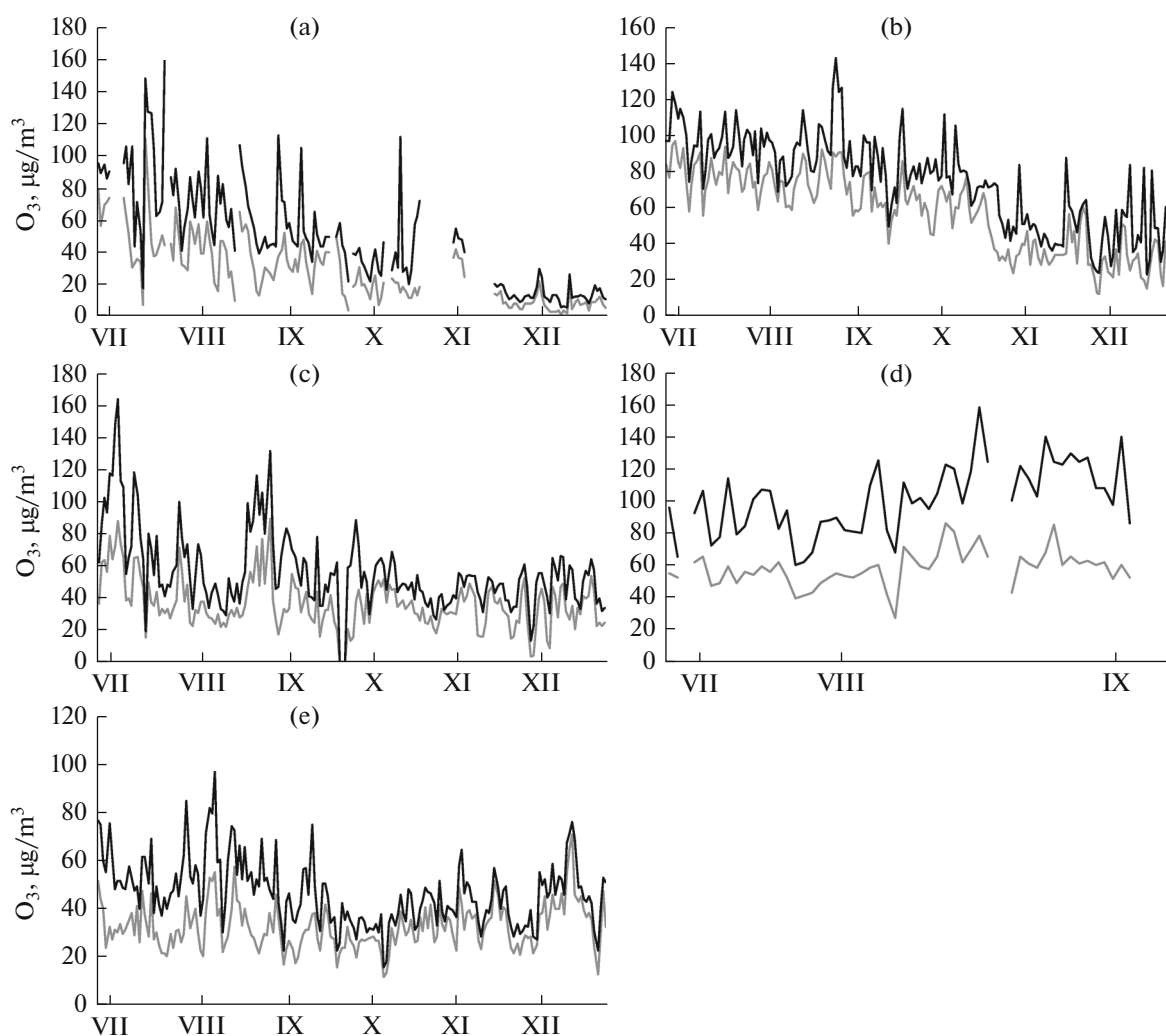
Figures 1c and 1d show the area-averaged data from seven urban and five roadside stations. In the second half-year, there was a natural decrease in ozone content in the atmosphere and in the surface air; the seasonal ozone decrease ended with the formation of the annual SOC minimum in December. The monthly average SOC from July toward December decreased by the factors of 3–4: from 30 to 8  $\mu\text{g}/\text{m}^3$  in residential regions, and from 23 to 7  $\mu\text{g}/\text{m}^3$  on roadside territory. It is noteworthy that the monthly average SOC in August and September had been 5–10  $\mu\text{g}/\text{m}^3$  smaller than annual average concentrations.

Owing to weather anomalies (predominant cloudy weather with frequent rainfalls), which prevented active photochemical ozone generation, the summer maximum of surface ozone, occurring most often in July–August, was barely formed. As was indicated in [15], the main annual (April) SOC maximum has also been very weak, primarily because of the anomalously cold and

rainy weather during spring in Moscow and, to a lesser degree, because of the sharp decrease in the emissions of pollutants to the atmosphere in the period of restrictive measures.

At Mosecomonitoring stations, the only ozone episode of the year was recorded on July 7. Ozone abruptly increased in the afternoon hours after the daily temperature increased to  $+30^\circ\text{C}$ . SOC attained 167  $\mu\text{g}/\text{m}^3$  at a single urban station (Maryinsky Park automatic air pollution monitoring station).

Characteristic features of SOC time behavior, recorded at RUDN monitoring station (Fig. 1b), located within the Third Ring Road in Moscow, nearly coincide with data obtained at Mosecomonitoring stations (Figs. 1c, 1d). There are only minor differences in the spans of the peaks in the amplitudes of the daily maximal SOC values, which can be explained by the specific positions of the stations and local features.



**Fig. 2.** Daily average (gray line) and daily maximal (black line) ozone concentrations in the surface air layer at stations: (a) OPTEC-PR; (b) SBEM Karadag; (c) Vyatskiye Polyany; (d) Boyarsky; and (e) Fonovaya.

In small cities, Obninsk and Apatity, the ozone concentrations were markedly lower (Figs. 1e, 1f) than in megalopolises, i.e., in Moscow and St. Petersburg (Figs. 1a–1c). In the period of time considered here, SOC values in Apatity were very far from the maximum permissible one-time concentrations ( $MPC_{m.o} = 160 \mu\text{g}/\text{m}^3$ ). The largest SOC values were recorded on October 26 and were only  $81 \mu\text{g}/\text{m}^3$ . The average maximal SOC values of  $53 \mu\text{g}/\text{m}^3$  were in July, when temperatures are the highest and the period with solar insolation is the longest (the polar day in the region lasts from May 29 to July 14); and they were  $43 \mu\text{g}/\text{m}^3$  in December, i.e., in the period with minimal illumination and polar night (from December 15 to 27). These values are lower than long-term average concentrations, respectively, by 5 and  $15 \mu\text{g}/\text{m}^3$ . However, long-term measurements indicate that maximal SOC values in these periods, which strongly differ by meteorological characteristics and by the level of UV radi-

ation, usually turn out to be almost the same. In particular, long-term average maximal SOC values in Apatity are  $58 \mu\text{g}/\text{m}^3$  from July 1 to 14 (polar day) and  $56 \mu\text{g}/\text{m}^3$  from December 12 to 27 (polar night).

Five stations refer to background ones: OPTEC-PR, station of background ecological monitoring (SBEM) Karadag, Vyatskiye Polyany, Boyarsky, and the Fonovaya Observatory. Measurements at these stations are presented in Fig. 2.

From the figure, it can be seen that time behavior of ozone concentration has its own specific features. For instance, Vyatskiye Polyany and Fonovaya (Figs. 2c and 2e) record the minimal concentration in October and not in December, as would be logical. It is still difficult to understand how natural this fact is. Possibly, these are anomalies in just a single year.

Spring and summer maxima in May and August 2020 ( $142$  and  $143 \mu\text{g}/\text{m}^3$ ) are noted in the seasonal

behavior of SOC at SBEM Karadag. Minimal monthly average values were observed in November and December 2020 (37 and 31  $\mu\text{g}/\text{m}^3$ ). The maximal hourly average SOC value was recorded on August 31 at 18:00 LT; it was 143  $\mu\text{g}/\text{m}^3$  at an air temperature of 28.3°C and relative humidity of 44%. Minimal hourly average SOC value in the second half of 2020 was noted on December 19; it was 7  $\mu\text{g}/\text{m}^3$  at an air temperature of 4.0°C and relative humidity of 84%. During this day there was small-droplet rainfall with 2.1 mm of precipitation. The analysis showed that in the summer period the SOC value was maximal under southeasterly and southerly winds. With respect to the position of SBEM Karadag, this was transport from the seaward.

The behavior of ozone concentrations at SBEM Karadag is mainly determined, especially in warm season, by meteorological parameters and, primarily, by temperature. An intense photochemical ozone generation is observed in the cases of a favorable combination of meteorological conditions and the relationship between  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) concentrations and volatile organic compounds (VOCs). Such conditions occur at Karadag for high solar irradiance in the hot time of the year. VOC concentrations, sufficient for ozone generation, seem to occur due to natural sources (enhanced emissions from plants at high temperature) and/or long-range transport [20].

Based on measurements at six (both urban and background) stations, i.e., Vyatskiye Polyany, Apatity, OPTEC-P, OPTEC-PR, Karadag, and Tropospheric Ozone Research (TOR) station, there were short-term, but strong, increases in the concentrations of surface ozone on August 9–10, 15, and 21–22, 2020. Probably, this was due to episodic decreases of the total ozone content (ozone anomaly) in the Northern Hemisphere during that period [21], which led to increased UV radiation. Thus, SOC increased during secondary photochemical reactions with the participation of ozone precursors—pollutants of atmospheric air—for increased intensity of UV radiation.

In contrast to urban stations (see Fig. 1), background stations (Fig. 2) show stronger and more variable time dynamics of ozone concentration in the second half of 2020. This seems to be due to high concentrations of VOCs, released by plants in forest massifs surrounding the stations [22, 23].

We turn to the remaining suburban station, i.e., the TOR station in Tomsk. Theoretically, owing to its position, this station should show an intermediate pattern between urban and background conditions. Measurements at the TOR station are presented in Fig. 3.

Since the TOR station and Fonovaya Observatory are separated by small (60 km) distance, the time dynamics of ozone concentration at both stations are similar in character (Figs. 2e and 3). However, there are also some differences: a higher daily average and maximal concentrations at the suburban station. Evi-

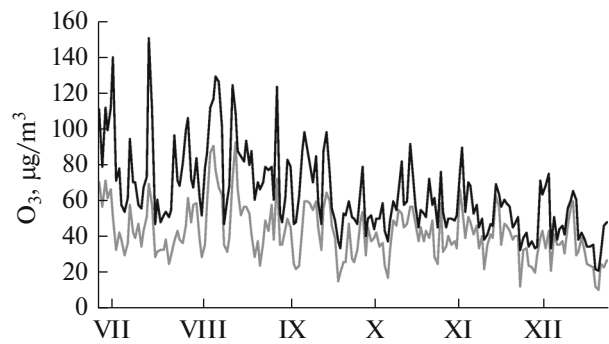


Fig. 3. Daily average (gray line) and daily maximal (black line) ozone concentrations in surface air layer at TOR station.

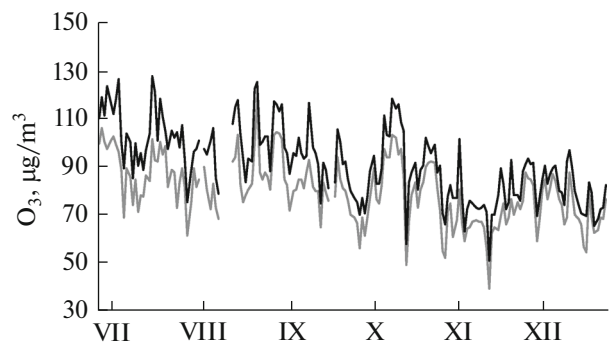
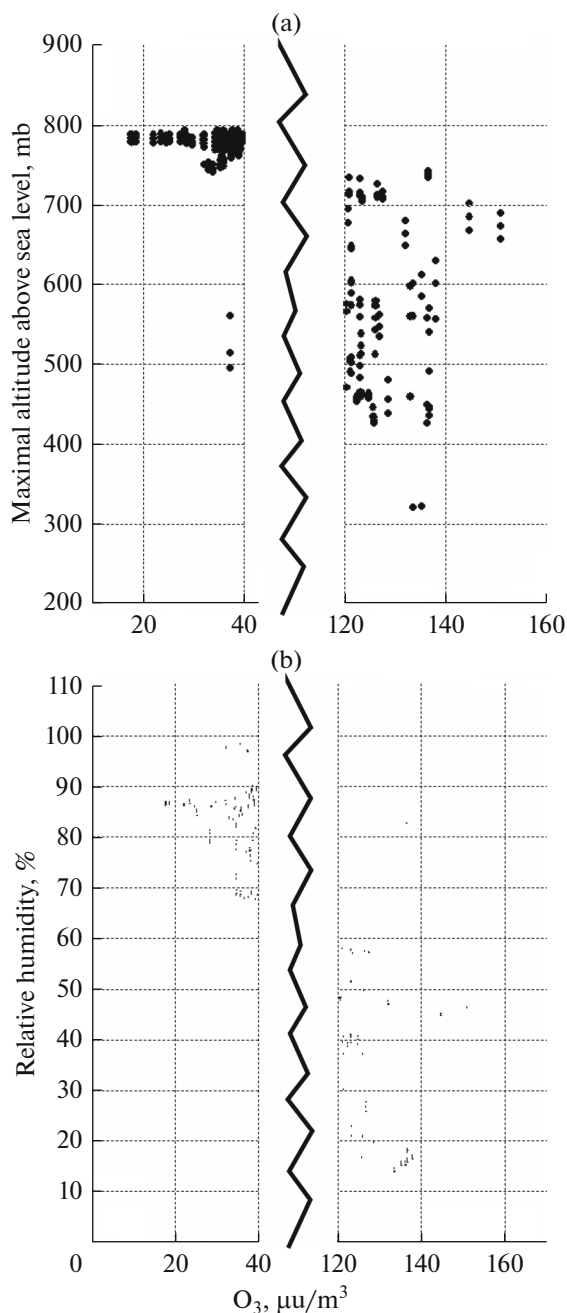


Fig. 4. Daily average (gray line) and daily maximal (black line) ozone concentrations in surface air layer at Kislovodsk station.

dently, the TOR station records higher concentrations because it is episodically in the plume of emissions from Tomsk, where there is an additional amount of ozone precursors.

The Kislovodsk high-mountain scientific station (KHMSS) occupies a special position (Fig. 4). Among all high-mountain stations, KHMSS stands out with a good topography and moderate climate, ensuring it is in free air most of the time.

In general traits, variations in surface ozone content at KHMSS in 2020 echoed those revealed in the previous observations: the seasonal behavior showed two local maxima (in spring and summer) and a minimum (in fall and winter) [24]. The annual absolute ozone maximum during 2020 was in March: from March 8 to 11 the hourly average values repeatedly exceeded 120  $\mu\text{g}/\text{m}^3$  (see Fig. 4 [15]) and attained yearly maxima of 150  $\mu\text{g}/\text{m}^3$ . This was due to air transport from overlying layers, which was accompanied by an increase in the ozone concentration in the surface air layer, a decrease in air humidity, and wind strengthening. In addition to orographic effects, the long-range transport from southern direction cannot also be ruled out, will be considered below. In the period of the secondary sum-



**Fig. 5.** KHMSS station: (a) maximal altitude of trajectory of an elementary air mass; and (b) relative air humidity for extreme surface ozone concentrations in 2020.

mer maximum, the level of  $120 \mu\text{g}/\text{m}^3$  was exceeded on July 4, 8, and 20 and August 27.

The KHMSS-observed daily variations in the ozone content were much smaller than those from mainland stations: the amplitude of the daily variations even during summer does not exceed  $10 \mu\text{g}/\text{m}^3$ , with the minima in midday and with increased values at night (the surface atmosphere gains ozone due to transport from the direction of mountains, from the

upper layers of the free troposphere, and, in particular, owing to the action of the mountain–valley circulation). In summer, a diurnal maximum was observed sometimes (possibly due to VOC and hay movers on days of hay making on meadows).

The trajectory analysis of air masses that arrived at KHMSS was carried out in order to consider the contribution of long-range transport to the observed extreme values of surface ozone. The trajectories were calculated using trajectory and dispersion model NOAA HYSPLIT\_4 (HYbrid Single-Particle Lagrangian Integrated Trajectory) [25, 26] and global reanalysis archive of meteorological data NCEP/NCAR Reanalysis [27, 28]. Trajectories ended in the surface air layer 100 m thick above KHMSS. A total of  $\sim 24000$  back trajectories were modeled for all times of measurements of surface ozone in 2020 at KHMSS.

The back trajectory analysis shows that high hourly average concentrations ( $>120 \mu\text{g}/\text{m}^3$ ) are associated with the arrival of ozone-rich air of the free troposphere from altitudes up to 400 mb (Fig. 5a). At the same time, the average trajectory altitude was 600 mb. These cases are characterized by low air humidity, up to 15%.

Low hourly average ozone concentrations ( $<40 \mu\text{g}/\text{m}^3$ ) at KHMSS were recorded under high relative humidity ( $>70\%$ , Fig. 5b) and were concurrent with its local cause, i.e., fogs (low, surface clouds). The trajectory analysis also showed that air in that case came from the valley: the maximal altitude of the corresponding trajectories in 2020 was 750–800 mb (Fig. 5a), and the average altitude of the trajectories was 800–1000 mb. Low values of surface ozone under the conditions of high humidity in dense fog (usually more than 85%) do not characterize the regional ozone field because a cloud is a local “regulator” of ozone concentration.

All the calculated trajectory array was processed to select two sets of trajectories, corresponding to extreme negative and extreme positive ozone anomalies in, respectively, the first and last deciles of the distribution function of  $\text{O}_3$  anomalies, calculated with respect to the second-order polynomial fit. Using the method in [29], for extreme  $\text{O}_3$  anomalies of both signs, we retrieved the fields of transport probability of elementary air masses (air particles) from spatial cells of  $1^\circ \times 1^\circ$  in size toward KHMSS. Figure 6 shows annual average probability of transport of elementary air masses for extremely high and extremely low ozone anomalies at KHMSS.

As can be seen from Fig. 6, regions of the most probable transport of elementary air masses for extreme anomalies of both signs (1) show preferential directions and (2) intersect only in a small region near the station, probably indicating a relationship between extreme ozone concentrations at KHMSS and the horizontal advection of air. Otherwise, such as in the presence of a strong local ozone source or sink, the transport probability spacial distribution would be uniform for extremes of anomalies of both signs. Based

on Fig. 6, the extremely low ozone concentrations in 2020 can be statistically related to the transport from Krasnodar krai; while the extremely high ozone concentrations can be related to the transport from the regions of Transcaucasia and Turkey across the Main Caucasian Range.

COMPLIANCE WITH HYGIENIC STANDARDS

Russian Federation authorities established the following hygienic standards for ozone concentration in surface air layer [30, 31]: 0.03 mg/m<sup>3</sup>, or 30 µg/m<sup>3</sup> for the daily average maximum permissible concentration (MPC<sub>d.a</sub>); 0.16 mg/m<sup>3</sup>, or 160 µg/m<sup>3</sup> for the maximum one-time permissible concentration (MPC<sub>m.o</sub>); and 0.1 mg/m<sup>3</sup>, or 100 µg/m<sup>3</sup> for maximum permissible concentration of harmful substance in the air of a work zone (MPC<sub>w.z</sub>).

Relying on these standards, we compiled Table 1, which summarizes the cases where the abovementioned MPCs were exceeded.

Data in Table 1 indicate that, according to the national standard, an increase in the background ozone concentration in the surface air layer remained at all these sites in the second half of 2020. Although the excess was observed much less frequently than in the first half-year [15]. The ozone content decreased most strongly at urban stations in Moscow. The excess of 2MPC has also been rare, except at the high-mountain station KHMSS, under the effect of the free troposphere; 50% of days with a concentration of 2MPC<sub>d.a</sub> are noted in Karadag. Cases with excess of 3MPC<sub>d.a</sub> are

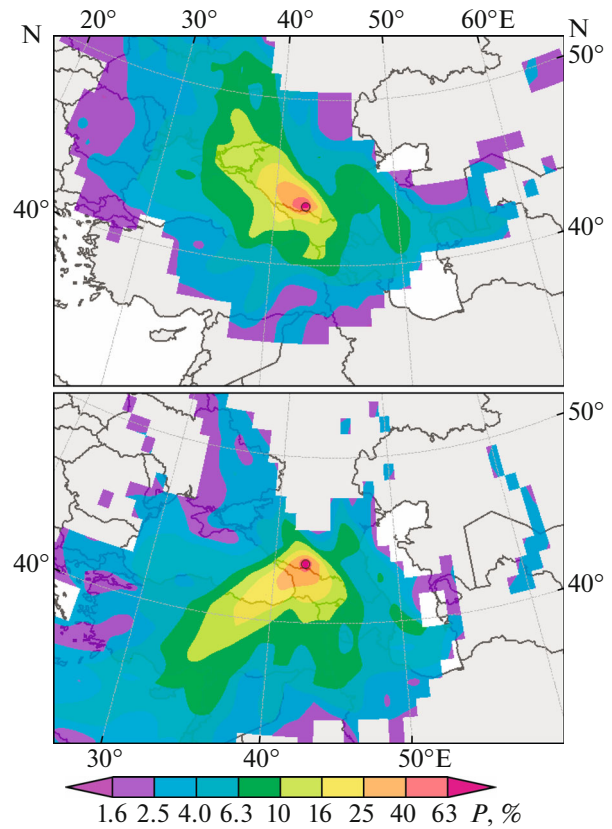


Fig. 6. Probability (P) of passage of elementary air masses, associated with 10% of the lowest (top panel) and 10% of the highest (bottom panel) anomalies of surface ozone concentration at KHMSS in 2020, over different territories.

Table 1. Excess over maximum permissible ozone concentrations in the surface air layer on the territory of Russia in the second half of 2020 (days/%)

Station	MPC <sub>d.a</sub> (30 µg/m <sup>3</sup> )			MPC <sub>w.z</sub> (100 µg/m <sup>3</sup> )	MPC <sub>m.o</sub> (160 µg/m <sup>3</sup> )
	1MPC	2MPC	3MPC		
OPTEC-PR	67/44	10/6.5	1/0.7	12	0
OPTEC-P	49/31	2/1.3	0/0	3	0
SBEM Karadag	162/88	92/50	9/4.8	27	0
Obninsk	30/60	0/0	0/0	1	0
RUDN	32/17	1/0.5	0/0	26	
Moscow urban	30/16	0/0	0/0	0/0	1
Moscow roadside	8/4	0/0	0/0	0/0	0
KHMSS	178/100	168/94	35/20	49	0
Vyatskiye Polyany	118/65	15/8	0/0	13	1
TOR station	150/82	18/10	2/1.1	15	0
Fonovaya	100/54	2/1.1	0/0	0	0
Boyarsky	54/100	20/37	0/0	27	0
Apatity	133/75	0/0	0/0	0	0

**Table 2.** Excess over maximum permissible ozone concentrations in the surface air layer on the territory of Russia per year (days/%)

Station	MPC <sub>d.a</sub>			MPC <sub>w.z</sub>	MPC <sub>m.o</sub>
	1MPC	2MPC	3MPC		
OPTEC-PR	201/70	116/40	26/9.1	25	2
OPTEC-P	72/21	4/1.2	0/0	3	0
SBEM Karadag	341/93	212/58	26/7.1	56	0
Obninsk	168/77	15/7	0/0	1	0
RUDN	142/42	10/2.9	0/0	42	1
KHMSS	347/100	168/96	70/20	59	0
Vyatskiye <i>Polyany</i>	118/82	82/23	0/0	27	1
TOR station	331/90	59/16	18/4.9	60	1
Fonovaya	281/77	50/14	0/0	0	0

recorded in Tomsk region, St. Petersburg, Karadag, and KHMSS.

Surprisingly, Table 1 shows the quite high frequency of exceeding the MPC in the working zone, in the second half of 2020. Cases with  $\text{MPC}_{w.z} > 100 \mu\text{g}/\text{m}^3$  were not recorded at only four out of 13 sites.

In contrast to the first half-year, the maximal one-time MPC in that period of time was exceeded just once at the two sites.

In regard to the observed [32] and forecasted [33] increases in ozone concentration in the surface air layer, serious efforts are required to reduce the emissions of ozone precursor gases, more so considering that positive consequences of reducing their amount do exist in certain regions [34]. It should also be remembered that ozone effects on human health are cumulative when MPCs are simultaneously exceeded for other compounds, and also that it is enhanced during heat waves [35, 36].

At nine sites, ozone measurements were carried out throughout the year (Table 2).

Data in Table 2 indicate that MPC<sub>d.a</sub> can be exceeded in all regions where monitoring was performed. If KHMSS is disregarded as a special station, the frequency of occurrence of daily average concentrations of  $30 \mu\text{g}/\text{m}^3$  and larger is within 21–90%. Concentrations of  $60 \mu\text{g}/\text{m}^3$  and larger are also observed in all regions, and the frequency of their occurrence varies from 1.2 to 58%. Also, MPC<sub>w.z</sub> is exceeded in almost all regions. MPC<sub>m.o</sub> is exceeded in five regions.

## CONCLUSIONS

Our review shows the ozone concentration in the surface air layer to exceed the national hygienic stan-

dards in most sites on the territory of Russia in the second half of 2020. This requires a more comprehensive analysis of ozone-forming substances and a development of measures to reduce their supply to the atmosphere.

It is also obvious that the data presented in the review are mosaic: there are no data for many large regions of the country. This indicates that the ozone monitoring sites should be increased in number.

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## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.



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