

Russian Studies of Atmospheric Ozone and Its Precursors in 2019–2022

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Abstract—We present the most significant results of Russian scientists in the field of atmospheric ozone research for 2019–2022 and examine observations of tropospheric ozone, its distribution and variability on the territory of the Russian Federation, its relation with atmospheric parameters, modeling of formation processes, and its impact on public health. The state of stratospheric ozone over Russia, modeling of processes in the ozonosphere, and methods and instruments being developed are also analyzed. The review is a part of Russia's national report on meteorology and atmospheric sciences, which was prepared for the International Association of Meteorology and Atmospheric Sciences (IAMAS). It has been reviewed and approved at the 28th General Assembly of the International Union of Geodesy and Geophysics (IUGG).

Keywords: atmosphere, ozone, ozone layer, atmospheric composition, trace gases, air quality, ozone chemistry, transfer processes

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1. TROPOSPHERIC OZONE AND ITS PRECURSORS

1.1. *Observations*

The Russian network for monitoring ground-level ozone concentrations (GOCs) and its predecessors partially changed over the past four years relative to the previous period (Elansky, 2020).

According to the distribution of responsibilities between departments, basic information on the ozone content in the ground layer of air must be provided by Roshydromet, which monitors its composition in more than 240 cities of Russia. However, there is no ozone data in its reviews published annually (Review, 2021; Review, 2022), although the network was modernized in recent years.

In the two largest metropolises of Russia, St. Petersburg and Moscow, there are systems for monitoring ground-level ozone and other pollutants that are comparable to foreign analogues. In Moscow, the environmental monitoring network of the State Environmental Budget Institution (SEBI Mosekomonitoring), a specially authorized organization for state environmental monitoring, has been operating since 2002 (<https://mosecom.mos.ru/>). Ground-level ozone concentrations are regularly measured at 17 automatic air pollution control stations (APCSs) hourly and around the clock. The average values for a 20-min time interval are recorded in the database. At the network of Mosekomonitoring stations in Moscow, measurements are carried out with three types of gas analyzers operating based on ultraviolet photometry,

Casella Monitor ME 9810B, Environment S.A. O3 42M, and HORIBA Ltd APXA-370 model APOA-370, and one OPSIS AB AR500 device based on differential optical absorption spectroscopy. The devices are included in the State Register of Measuring Instruments and verified by the State Metrological Service. Analytical materials on the state of the environment in the city of Moscow (<https://www.mos.ru/eco/documents/doklady/view/>) are published in the annual report and are partially included in quarterly reviews (Ivanova et al., 2019a, 2019b, 2019c, 2019d, 2020a, 2020b, 2020c, 2020d, 2021a, 2021b, 2021c, 2021d, 2022a, 2022b, 2022c, 2022d).

In the rest of the territory of the Russian Federation, ozone observations are carried out on an initiative basis, mainly by scientific or university organizations. The established informal consortium of such stations began to publish reviews of ozone concentrations in the troposphere over the territory of Russia (Andreev et al., 2020, 2021, 2022).

According to the information published in the reviews, measurements continued at the Kislovodsk High Mountain Scientific Station (KHSS); in the Karadag State Nature Reserve; on a 300-m tower in Obninsk (Kaluga oblast, NPO Typhoon); at three stations in St. Petersburg (ORTEK-N located in the area of the Alexander Nevsky Lavra, ORTEK-P on Vasilyevsky Island, and ORTEK-PR based in Leningrad oblast); at the Gromovo station in the Priozersky district; at a monitoring station for ground-level ozone, its predecessors, and basic meteorological parameters at the Peoples' Friendship University of Russia with the participation of the Prokhorov Institute of General Physics, Russian Academy of Sciences (RAS); within the Third Transport Ring at 3 ul. Ordzhonikidze; at the Vyatskie Polyany station located in the south of Kirov oblast; at the TOR station and Fonovaya observatory in Tomsk oblast; and in Ulan-Ude. Then, the stations of Apatity, Murmansk oblast, and Boyarskii, Buryatia, were added to these points; in 2021, measurements were restored at the Listvyanka station, Irkutsk oblast, and Tarusa, Kaluga oblast, and the OPTEK-Karelia station was opened. The stations are equipped with network instruments recommended by the Global Atmosphere Watch (GAW WMO). All instruments were regularly calibrated.

Along with stationary measurements, expeditionary studies of ozone and components of ozone cycles were carried out on the territory of Lake Baikal and the surrounding area (Zayakhanov et al., 2019; Hodger et al., 2019; Tcydypov et al., 2020; Zhamsueva et al., 2021, 2022; Obolkin et al., 2022), as well as in the Arctic region (Pankratova et al., 2020).

The vertical distribution in the troposphere was measured using a Tu-134 Optik laboratory aircraft. The current composition of the equipment is presented in (Belan et al., 2022). During the entire period under review, monthly flights were carried out over the

southern regions of Western Siberia. In September 2020, a unique experiment was conducted to measure the composition of air, including ozone, over all seas of the Russian sector of the Arctic. Another experiment was carried out in September 2022. It consisted of measuring the air composition in the meridional direction. The route began near 56° N latitude and ended over the waters of the Kara Sea, where support for surface measurements was carried out by the *Akademik Mstislav Keldysh* research vessel.

The vertical distribution of ozone in the upper troposphere—lower stratosphere was measured in Tomsk using a differential absorption laser locator (lidar). The lidar operates at wavelengths of 299–341 and 308–353 nm and makes it possible to measure the vertical distribution of ozone in the 5–45 km column (Matvienko et al., 2019).

Currently, regular measurements of nitrogen dioxide content from satellites are carried out using the TROPOMI, OMI, and GOME-2 instruments. The horizontal spatial resolution they achieve with global coverage is tens of kilometers, which is sufficient for studying stratospheric NO₂. In 2016–2017, a team from the Institute of Atmospheric Physics, Russian Academy of Sciences (IAP RAS), performed the first experiments on the highly detailed sounding of tropospheric NO₂. In this case, measurements from the GSA spectrometer, which is installed on spacecraft of the Resurs-P series, were used. Based on the survey, the world's first algorithm for determining the integral NO₂ content in the troposphere with a spatial resolution of ~2.4 km on a 120 m grid was developed with measurement error of 10¹⁵ molecule/cm² typical for satellite methods. To validate large-scale structures detected in the reconstructed NO₂ distribution fields, comparisons were made with data from the TROPOMI and OMI equipment (Postylyakov et al., 2019a, 2019b, 2020a, 2020b) and chemical transport models (Davydova et al., 2021; Zakhарова et al., 2021), which confirmed the reliability of the results.

1.2. Distribution and Variability

Data collected in reviews (Andreev et al., 2020, 2021, 2022) indicate a significant scatter in the values of the ozone concentration in the ground air layer in different geographical regions of Russia. As an example, we consider a figure that shows the annual average and maximal ozone concentrations in 2021.

As can be seen in Fig. 1a, the average annual values of GOC differ from each other by a factor of 2.5. The highest values are recorded at a high-mountain station in Kislovodsk, in Crimea, and on the shore of Lake Baikal; the smallest values are recorded at the city station in Obninsk.

The maximal concentrations (Fig. 1b) are observed in large cities, where there are additional emissions of

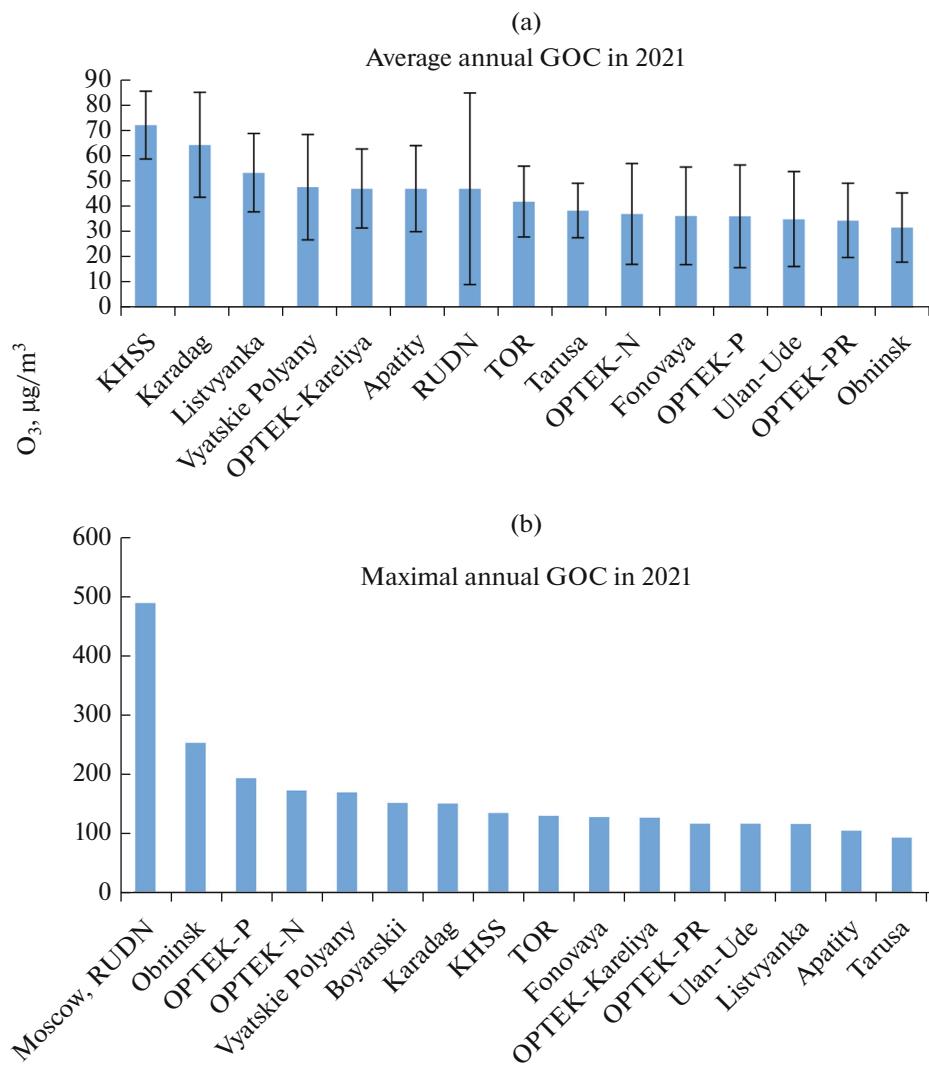


Fig. 1. (a) Average annual and (b) maximal ozone concentrations in 2021 in Russia.

ozone precursor gases. In this case, the order of distribution of stations changes.

It also follows from the figure that there is no longitudinal or latitudinal dependence for the annual average values. Perhaps this reflects the effect of local sources of ozone precursors and anthropogenic factors, or perhaps long-term interannual variability of ozone concentration, when the average annual concentration can change up to four times (Antokhin et al., 2010). A separate study is required to answer this question.

The article (Andreev et al., 2022) carried out a detailed analysis of the reasons for high average annual concentrations at KHSS. For this purpose, a trajectory analysis of the air masses arriving at KHSS was made. The method for calculating 7-day reverse trajectories is described in the review (Andreev et al., 2021). Because of omissions in the 2021 measurements due to technical reasons, fewer trajectories were simulated than in 2020: ~17 000. Unlike urban condi-

tions, where a drop in the ozone concentration to very low values is a sign of severe pollution with nitrogen oxides, at KHSS located in a clean area and above the boundary layer of the atmosphere, abnormally low values of the ozone concentration are associated not so much with long-range transport, but with dry deposition on the Earth's surface. This process is most active in a sedentary air mass when the contact of the analyzed air with a surface covered with vegetation is the longest. The effect of the transfer of pollution from lower levels from the city of Kislovodsk (the altitude is 750–850 m above sea level) on days with favorable conditions for the development of mountain–valley circulation, as was shown in (Senik et al., 2005), leads, on the contrary, to an increase in the daily ozone maximum, but a very slight one. Fogs help reduce ozone concentrations. In this regard, reverse trajectories for days characterized by high humidity (more than 80%) at the end point of the

trajectory at KHSS were excluded from analysis. The results indicate that extremely high anomalies of ground-level ozone at KHSS were associated with air transport from southern directions, while extremely low values were associated with air transport from northwestern directions.

The features of ozone production in the Karadag region were analyzed in a series of studies (Shalygina et al., 2019; Lapchenko et al., 2022; Fedorova et al., 2022; Borisov et al., 2022). It was established that highest GOCs are observed in dry, hot weather and are of advective nature. Trajectory analysis showed that the movement of air masses occurs over the Black Sea from Ukraine, Turkey, Romania, and Bulgaria in spring and over land and mainly from Ukraine and the southern regions of Russia in the summer. The regime of GOC is also significantly affected by breeze circulation and slope winds at night.

The features of ozone dynamics in seven cities of the Baikal region (southeast of Siberia) are analyzed (Obolkin et al., 2022). It was revealed that significant differences in the spatiotemporal variability of average daily ozone concentrations depend on various anthropogenic loads. In large cities with heavy industry located in the Angara River valley, ozone concentrations were minimal and changed little throughout the year: less than $5 \mu\text{g}/\text{m}^3$ in Angarsk and $20\text{--}30 \mu\text{g}/\text{m}^3$ in Irkutsk. In populated areas of a less polluted region, the Selenga River valley, ozone concentrations were significantly higher, and the annual variability of ozone is typical for Eastern Siberia: maximum in spring ($60\text{--}70 \mu\text{g}/\text{m}^3$) and minimum in autumn and winter (from 10 to $30 \mu\text{g}/\text{m}^3$). Maximal ozone concentrations were observed in rural conditions (Listvyanka station, western coast of southern Baikal), and up to $80\text{--}100 \mu\text{g}/\text{m}^3$ during the spring maximum.

Based on the results of observations at the Zvenigorod Scientific Station (ZSS) at the IAP RAS and the Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences (IAO SB RAS) (Tomsk), estimates of the temporal variability of the integral content of formaldehyde H_2CO in the lower troposphere were obtained (Bruchkovsky et al., 2019). The existence of a statistically significant positive trend in the integral content of formaldehyde depending on temperature at $T > 5^\circ\text{C}$ at both points was shown. The observed positive trend is apparently associated with an increase in biogenic emissions of isoprene and other nonmethane VOCs with increasing temperatures, as well as areas of forest and peat fires. In the air masses arriving at the ZSS from Moscow, there is a stable excess of the formaldehyde IC on average by $0.4 \pm 0.1 \times 10^{16} \text{ molecule}/\text{cm}^2$ at positive temperatures and by $0.8 \pm 0.2 \times 10^{16} \text{ molecule}/\text{cm}^2$ at negative temperatures. Despite the significant distance from Moscow, the values observed at the ZSS are generally 10% higher than those observed in Tomsk.

1.3. Role of Atmospheric Processes and Phenomena in Ozone Changes

In (Antokhin et al., 2020), the relation between changes in the concentration of CH_4 , CO , CO_2 , NO , NO_2 , O_3 , SO_2 , the count concentration of aerosols with a particle diameter of more than $0.4 \mu\text{m}$ and air temperature, atmospheric pressure, direction and speed wind, total solar radiation and ultraviolet radiation in the range of 295–320 nm, relative humidity, and water vapor pressure was studied. For the study, data of air composition monitoring (for 1993–2018) carried out at the TOR station located in the Tomsk Akademgorodok area were used. Based on average monthly data, it was established that ozone has a significant positive or negative correlation with almost all analyzed meteorological quantities, with the exception of wind direction. High values of negative correlation between carbon dioxide concentration and solar and UV-B radiation, air temperature, and water vapor pressure were recorded. Besides its positive relation with atmospheric pressure, nitrogen dioxide has two significant negative relations with air temperature and wind speed. Atmospheric aerosol, as well as gaseous impurities in the air, has a stable positive relation with air pressure and negative relations with solar radiation, UV-B radiation, air temperature, and water vapor pressure. No significant relations were found between meteorological variables and components such as SO_2 , CO , and NO .

The effect of water aerosol on the ozone content in the atmospheric air was studied in (Kotelnikov et al., 2019). In field experiments, a sharp decrease in the ozone content in the surface atmosphere was observed during a short-term rainstorm in a metropolis. The process of ozone decomposition in the presence of water was also studied under laboratory conditions in a reaction chamber. It was shown that the decomposition of ozone in the air is accelerated at high relative humidity values, as well as in the presence of aqueous aerosol. The rate of ozone destruction depends on the aerosol size: the smaller the particles, the higher the rate of decomposition. This may indicate a significant role of heterogeneous binding processes on the aerosol surface. This stable relation was not found in (Arshinova et al., 2019). The study showed that precipitation can cause both an increase and a decrease in the ground-level ozone concentration, regardless of its type, intensity, and measurement area. The greatest changes are associated with frontal precipitation and reflect a “jump” in concentrations when air masses change. In intramass precipitation, the sign of changes in ozone content depends on the period of day in which it fell. If precipitation is observed during a wave of growth in the diurnal variation of O_3 , then, in most cases, this leads to an increase in the ozone content. If precipitation falls on a wave of decreasing diurnal variation, a drop in the ozone content is recorded.

The role of absolute humidity in ozone formation was studied in (Belan et al., 2019). The analysis

revealed a neutral dependence at positive temperatures and an unexpectedly large and alternating variability at negative temperatures. Absolute humidity has a negative effect on the formation of ozone in the ground layer of air, causing a decrease in its concentration at temperatures from 0 to -30°C . At very low temperatures (below -30°C), the effect changes to positive, with a significant increase in the contribution of absolute humidity.

The role of solar radiation in the photochemical generation of ground-level ozone is studied in (Khuriganova et al., 2022). According to the presented data, it begins in the morning when the radiation intensity reaches more than 200 W/m^2 and continues to the same values in the evening, so the ozone maximum usually lags behind the daytime maximum solar radiation by several hours.

The contribution of CO and 15 volatile organic compounds (VOCs) to the formation of ozone in the ground air layer in the summer of 2011–2013 in Moscow was analyzed in (Berezina et al., 2020, 2022). The highest concentration of O_3 (up to $210 \mu\text{g/m}^3$) was observed during daytime periods under anticyclonic meteorological conditions, with weak mixing of the atmospheric boundary layer and high temperatures. On the contrary, the content of NO_x , CO, and benzene decreased from 8:00 a.m. to 5:00–6:00 p.m. local time. The high positive correlation of daytime O_3 with secondary VOCs confirmed the important role of photochemical O_3 production in Moscow. The main source of anthropogenic VOCs in Moscow was local emissions from vehicles. However, only $\sim 5\%$ of the observed isoprene was attributed to anthropogenic sources, indicating a significant contribution of biogenic sources to overall ozone precursor levels. The contribution of various anthropogenic and biogenic VOCs to measured ozone values was estimated. The ozone-forming potential (OP) of total VOCs averaged $31\text{--}67 \mu\text{g/m}^3$ and exceeded $100 \mu\text{g/m}^3$ in 10% of high-ozone events, reaching $136 \mu\text{g/m}^3$. Gases such as acet-aldehyde, 1,3-butadiene, and isoprene have the highest ozone production potential in Moscow when compared to other measured VOCs.

The conditions for ozone formation near a 300-m tower in Zotino are considered in (Moiseenko et al., 2021). High levels of O_3 and NO_x are observed here in air coming from industrial areas of Western Siberia and the Ural Mountains, while background air comes from remote areas of northern Eurasia within $55^{\circ}\text{--}70^{\circ}\text{ N}$. Ozone in continental air has a distinct maximum in April, like in the midlatitudes of the Northern Hemisphere. During hot weather conditions in spring and early summer, regional anthropogenic and wildfire emissions are an important source of ozone in the continental boundary layer over southern and central Siberia. During the remainder of the year, central northern Eurasia is a hemispheric sink for tropospheric ozone.

Based on large-scale measurements of ozone and its cycle components, (Thorp et al., 2021) assesses the impact of the two dominant sectors of anthropogenic emissions (transport and energy) and vegetation fires on ground-level concentrations of NO_x and O_3 over Siberia and the Russian Arctic. The results suggest that regional ozone is more sensitive to anthropogenic emissions, especially from the transport sector, and the contribution of fire emissions occurs in June and is largely limited to latitudes south of 60° N . The impact of fires on dry deposition ozone within the region is small compared to anthropogenic emissions and insignificant north of 60° N . These results suggest that ground-level ozone in the region is controlled by the interaction between seasonality in atmospheric transport models, dry deposition on vegetation, and the dominance of emissions from the transport and energy sectors.

The long-term variability of the total content (TC) of carbon monoxide, as one of the precursors of ozone and meteorological parameters, is studied in (Rakitin et al., 2021). Characteristics of the accumulation of carbon monoxide in the atmospheric boundary layer in the Moscow metropolis on calm days are also obtained. A decrease in the average annual values of TC CO in 2000–2018 in Moscow ($-2.56 \pm 0.52\%/\text{year}$) and in the ZSS ($-1.15 \pm 0.37\%/\text{year}$) was established. However, the rate of decrease at both points in different seasons and periods is different. After 2007–2008, the rate of decrease in TC CO decreased at both locations. During the period of 2008–2018, at ZSS, an increase in the total CO content was recorded in the summer and autumn months at a rate of $\sim 0.7\%/\text{year}$. An increase in wind speed in the atmospheric boundary layer of Moscow is observed in different periods of 2000–2018 at a rate of $0.4\text{--}1.6\%/\text{year}$. In this case, no statistically significant changes were found in Kaluga oblast. The frequency of calm days in Moscow in the period 2006–2017 decreased ($-7.06 \pm 3.96\%/\text{year}$) with a decrease in the anthropogenic part of the CO content in the same period ($-6.72 \pm 3.48\%/\text{year}$). The results indicate the effect of climatic (meteorological) factors, including ozone, on air quality in Moscow.

Dry ozone deposition in the Baikal region was studied in (Zayakhanov et al., 2019). Based on the eddy covariance and gradient methods, including the aerodynamic gradient method, the modified Bowen method, and the modified gradient method, and based on experimental data, quantitative estimates of fluxes and dry deposition of ozone on the underlying surface were obtained for various environments (meadows and forests). The average dry ozone deposition rate was 0.37 cm/s at night (0–3 h) and 0.91 cm/s during the day (12–18 h). The ozone flux was $0.24 \mu\text{g m}^{-2} \text{ s}^{-1}$ at night and $0.72 \mu\text{g m}^{-2} \text{ s}^{-1}$ during the day. Quantitative estimates show a higher absorption capacity of forests compared to soil vegetation.

The weekly cycle and the influence of weekend days on the concentrations of O_3 , NO , NO_2 , CO , CH_4 , SO_2 , NMHC, and PM_{10} were studied in the Moscow metropolis using field measurements from January 1, 2005, to December 31, 2014, at 49 stations of the Moscow monitoring network environment (Elansky et al., 2019). The O_3 diurnal cycle is typical for large cities. On weekdays, its predawn minimal concentration is observed at 7:30 a.m., and its maximum is observed at 3:00–4:00 p.m. There is no predawn minimum on weekends, because reduced NO_x emissions on roads at this time reduce ozone depletion. Daily variations in CO , NO_x , NMHC, and PM_{10} concentrations depend mainly on vehicle emissions and the vertical stratification of the atmospheric boundary layer. One characteristic feature of Moscow is the coincidence of rush hours and the inversion of surface temperatures during the cold season, which leads to the accumulation of pollutants in the ground layer of the atmosphere. Ground-level concentrations of pollutants (except for ozone and methane) were found to decrease on weekends. Weekday (Tuesday–Friday)–Sunday differences in daytime concentrations (8:00 a.m. to 10:00 p.m.) of NO , NO_2 , CO , SO_2 , NMHC, and PM_{10} relative to weekday concentrations averaged over all stations for 2005–2014 years were 23.9 ± 5.8 , 16.7 ± 2.8 , 13.6 ± 3.3 , 7.6 ± 6.5 , 6.3 ± 2.2 , and $14.5 \pm 5.1\%$, respectively. The ozone concentration increased on Sunday by $16.5 \pm 4.8\%$. Methane concentrations on weekends were the same as on weekdays. The effect of weekends on all pollutant concentrations was weakened within the green zone around Moscow. In different sectors of Moscow, the impact of pollutants, with the exception of SO_2 , on weekends was approximately the same. The vertical structure of the output effects of NO , NO_2 , and CO was analyzed based on data obtained from measurements at a 500-m high television tower. These weekend effects decreased nonlinearly with altitude. Estimates obtained for the main criteria for the activity of photochemical processes that determine the formation of the weekly cycle and the effect of ozone on weekends (NMHC/ NO_x ratio, the fraction of radical losses due to chemical exposure of the NO_x and O_x concentration) show that a chemical composition with a limited content of VOCs is characteristic of Moscow.

1.4. Anomalies and Extreme Events

Undoubtedly, the extreme event during the reviewed period was the COVID-19 coronavirus pandemic. In (Skorokhod et al., 2022), changes in the composition of the atmosphere were studied during various periods of 2020 in Moscow associated with measures to prevent the pandemic and a corresponding reduction in pollutant emissions. Ground-level concentrations of nitrogen dioxide NO_2 , carbon monoxide CO , ozone O_3 , aerosol fraction PM_{10} , and meteorological param-

eters in various periods of 2020 were compared with similar data for the previous 5 years. An analysis of ground-based measurements, as well as high-resolution satellite data on the distribution of CO and NO_2 , indicates that the content of the main pollutants and its spatial distribution in the Moscow region were significantly affected by both restrictive measures and abnormal meteorological conditions in 2020.

In (Stepanov et al., 2022), the results of monitoring ground-level ozone in the Moscow atmosphere in 2020 and 2021 under the strict restrictions related to the COVID-19 pandemic can be seen. These two years differed significantly in meteorological conditions and the level of anthropogenic load on the environment. In 2020, a relatively low level of ground-level O_3 concentrations for a metropolis was observed in Moscow. The annual average was $28 \mu\text{g}/\text{m}^3$, and the maximum for the year was $185 \mu\text{g}/\text{m}^3$. This is due to a combination of relatively cool summer weather with low levels of pollutants in the air. In the summer of 2021, intense heat waves were observed under conditions of a blocking anticyclone, with daytime temperatures rising to 35°C . Combined with higher ambient air pollution, this resulted in unusually high O_3 concentrations. The average annual value was $48 \mu\text{g}/\text{m}^3$, and the maximal annual value was $482 \mu\text{g}/\text{m}^3$.

At the same time, abnormally low concentrations of ozone in the surface atmosphere were recorded in central Russia in the spring of 2020 (Kotelnikov et al., 2021). The usual increase in the ozone content in spring that is caused by a seasonal increase in temperature and light was replaced by a monotonous decrease. The monthly averaged maximal daily values of the observed values in April 2020 were three times lower than the values recorded at the same time in 2019. Both a decrease in regional background ozone concentrations in the surface atmosphere and a decrease in the intensity of its photochemical formation were observed. The authors consider the most likely reason for the observed phenomenon to be a decrease in emissions of combustion products into the atmosphere in China, Europe, and Russia due to the introduction of special regimes in connection with the COVID-19 pandemic.

1.5. Modeling the Processes of Formation and Transformation of PKOS

In (Shtabkin et al., 2019, 2020a, b), the sensitivity of the O_3 field to the values of total emissions of ozone precursors was calculated employing the global transport-chemical model GEOS-Chem with databases on anthropogenic (EDGAR) and biogenic (MEGAN, GFED) emissions for 2007–2012 using a reduction approach.

Detailed quantitative estimates of the effect of individual factors determining seasonal variations in ground-level ozone content in Central Siberia were

obtained. A quantitative estimate of anthropogenic and biogenic signals in measured O_3 concentrations was carried out using the GEOSChem global chemical transport model with allowance for all the main sources and sinks of this compound. The effect of climatically significant regional sources of emissions of nitrogen oxides ($NO_x \equiv NO + NO_2$), CO, and biogenic volatile organic compounds (VOCs) on the photochemical generation of ground-level ozone (O_3) in the regions of Europe and Siberia was studied. The value of photochemical ozone production in the summer months was found to correlate well with the age of the air mass that is established in relation to the total reactive nitrogen at an average contribution of regional sources of ~ 10 –15 ppb. The quantitative estimates of the production efficiency are in good agreement with the conclusions of the photochemical theory of tropospheric ozone for conditions of slightly polluted air.

The relative importance of isoprene and monoterpenes in the formation of ground-level ozone in Russian cities along the Trans-Siberian Railway is estimated in (Berezina et al., 2019; Safronov et al., 2019). For this purpose, the potential of its formation (OFP) in the daytime was calculated. Calculated OFPs for isoprene and monoterpenes along the Trans-Siberian Railway average 15 ± 13 and 18 ± 25 ppb ozone, respectively. In most cities along the Trans-Siberian Railway, where high concentrations of NO_x (10–20 ppb) were observed along with high daytime temperatures ($>25^\circ C$), monoterpenes made the main contribution to the formation of tropospheric ozone. Only in the Far Eastern cities, where the largest deciduous vegetation of the Trans-Siberian Railway grows, isoprene played a major role in the formation of tropospheric ozone.

Based on measurements of the concentrations of ozone and nitrogen oxides at a ZOTTO (Zotino Tall Tower Observatory) high-rise mast in Central Siberia, the rates of production (P) and destruction (L) of ozone, as well as the content of peroxide radicals (OX), were estimated using the photostationary approximation (Moiseenko et al., 2019, 2022). The maximal daily variations of the considered quantities occur in the period from 11:00 a.m. to 3:00 p.m. local time and reach ~ 6 billion $^{-1}/h$ (P), 1.4 billion $^{-1}/h$ (L), and 115 trillion $^{-1}$ ([OX]). In the range of measured NO_x concentrations from 0.2 to 0.8 ppb, there is a linear dependence of P on $[NO_x]$ that corresponds to NO_x -limiting ozone production with a proportionality coefficient of $P(O_3)/[NO_x] \sim 13$ (ppb $^{-1}/h$)/ppb $^{-1}$. The high content of peroxide radicals, along with the $P \gg L$ condition, indicates the processes of intense oxidation of biogenic volatile organic compounds and photochemical production of ozone. The estimates reveal the significant role of regional NO_x emissions in the balance of ground-level ozone and the need to take this factor into account when predicting environmental risks in regions of Siberia that are traditionally classified as environmentally friendly.

The agreement between the results of chemical transport modeling of NO_2 using the SILAM and COSMO-ART models in the Moscow region and measurements using the DOAS method is examined in (Borovski et al., 2019, 2020; Postylyakov et al., 2020; Ponomarev et al., 2020). Based on comparisons of modeling with observed surface concentrations and IC determined by the DOAS method, adjustments to the spatial distribution and power of sources in Moscow are proposed in order to improve model estimates of air quality there in (Ponomarev et al., 2020).

The emission sources of ozone precursors are clarified in (Ponomarev et al., 2019; Elansky et al., 2020; Ponomarev et al., 2021; Lokoshchenko et al., 2021; Zakharova et al., 2022; Elansky et al., 2022). To optimize the spatial distribution of sources and the magnitude of emissions in the Moscow metropolis, the fields of ozone and other impurities for the summer and winter months were calculated using the SILAM and COSMO-ART chemical transport models, both calculated and taken from the database of inventory of TNO emissions. A comparison of observational data obtained in the Moscow Environmental Monitoring Network (MEM) with the results of numerical modeling based on the use of the SILAM chemical transport model showed that errors in determining the concentrations of ozone and other substances in the urban atmosphere have a more complex structure than those assumed when using conventional data assimilation algorithms.

The Federal State Budgetary Institution Hydrometeorological Center of Russia is carrying out work to create and improve technology for forecasting pollutant concentrations, including ozone, based on chemical transport models (CTMs) (Kuznetsova et al., 2022; Nakhaev et al., 2021). At the initial stage, a calculation technology was implemented using the open access CHIMERE chemical model with assimilation of data from the WRF-ARW model. At the next stage, the calculations using CHIMERE CTM were provided with data from the COSMO-Ru07 numerical atmospheric model, which made it possible to ensure the stability and efficiency of the calculation. Owing to computational modernization and the development of a numerical model of the atmosphere, calculations of pollutant concentration fields are being carried out today for part of the Central European region of Russia (36.6° – 44.2° E and 55.1° – 56.5° N) in an experimental mode using the CHIMERE-COSMO-Ru2.2 CTM. Also, on a grid with a horizontal step of 2 km, COSMO-Ru2.2-ART (COntsortium for Small-scale MOdelling) calculations are performed for the Moscow region. A specific feature of COSMO-Ru2.2-ART (unlike CHIMERE CTM) is the joint calculation of meteorological quantities and chemical transformations at each time step, which makes it possible to take into account the reverse influence of aerosols and gases on radiation processes and the meteorological regime of the atmosphere. The most important ele-

ment of the functioning automated air quality forecasting technology using two CTMs, CHIMERE-COSMO-Ru2.2 and COSMO-Ru2.2-ART, is the verification of models based on pollution observation data. Verification showed an overestimation of the concentrations by CTM CHIMERE and an underestimation by COSMO-ART, and both CTMs predominantly underestimate pollution in transport-type areas. The correlation coefficient (R) between the model and measured average concentrations of NO_2 and CO was 0.6–0.7, according to calculations of the O_3 concentration of CHM CHIMERE, $R = 0.7–0.8$, and according COSMO-Ru2ART calculations, $R = 0.4–0.5$. Seasonal variability of model deviations with a change in sign for each model and each pollutant was revealed. The largest model deviations were observed under abnormal weather conditions: during heat waves in summer and during the advection of dusty air in spring. Recommendations for drawing up an operational consolidated forecast using the integration of calculations of two CTMs are formulated with allowance for the established model errors of each CTM.

1.6. Ozone and Health

An increase in the ozone content in surface air that is caused by changes in the global climate and increased air pollution can lead to increased morbidity and mortality in the population. The relation between abnormally high GOC in Moscow with morbidity and mortality in various age groups of the population in the summer of 2010 and with the incidence of cardiovascular diseases and mortality in a semiurbanized area in the south of Kirov oblast was studied in (Kotelnikov et al., 2019). It was shown that a statistically significant relation is observed in groups of men and women aged 31–60 years and older, while this relation is absent in the corresponding age groups of 15–30 years. In the south of Kirov oblast, when the average daily maximal permissible ozone concentration (MPC_{ad}) was exceeded for several days, the frequency of emergency calls related to cardiovascular diseases significantly increased. This confirms the validity of establishing the domestic MPC_{ad} standard for ozone equal to $30 \mu\text{g}/\text{m}^3$.

Ivashkin et al. (2020) also suggested that, during the COVID-19 period, when ozone enters the body with inhaled air, it can have a detrimental effect on the main systems of the body: cardiovascular, nervous, respiratory, and immune. In particular, as a strong oxidizing agent, it causes the formation of free radicals in the respiratory tract, which provoke lipid peroxidation, which suppresses the immune system.

Further studies (Stepanov et al., 2022) showed that, in the summer of 2021, there was a rare combination of the spread of another wave of SARS-CoV-2 infection (delta strain) and meteorological conditions conducive to the formation of abnormally high ground-level ozone concentrations in Moscow. Other

than the high frequency of infections at this time, the highest mortality rate due to this virus during the pandemic was also recorded in Moscow. The correlation coefficients between the incidence of infection and mortality with the concentration of ground-level ozone were ~ 0.59 ($p < 0.01$) and ~ 0.60 ($p < 0.01$), respectively. The observed correlation may be due to the combined pathological effect on the respiratory and circulatory system of high concentrations of ozone and the SARS-CoV-2 virus, which can lead to both easier transmission of infection and a more severe course of the disease and increased mortality.

The same scientific group (Stepanov et al., 2019) draws attention to the fact that ground-level ozone concentrations observed in Russia significantly exceed the thresholds for negative impacts on vegetation.

2. STRATOSPHERIC OZONE

2.1. Observations

The State Monitoring System was created in Russia to monitor the total ozone content (TOC). The Main Geophysical Observatory (MGO) continues to support the operation of the ground-based ozonometric network of Roshydromet. Observations at 28 stations have been carried out since 1973. Long-term data series make it possible to analyze spatial and temporal variability and identify the relation of anomalies in the TOC field with the general circulation of the lower stratosphere and upper troposphere. The results of estimating long-term changes in the thickness of the protective ozone layer, the main trends and tendencies, and the current state are presented in the annual “Reviews of the State and Pollution of the Environment in the Russian Federation” (Solomatnikova et al., 2020, 2021, 2022a, b). A separate analysis is carried out for stations in the Arctic region. Measurements of erythema UV radiation continue at 12 stations. Calibration of measuring equipment plays a significant role in ensuring ground-based measurements. The binding of instruments to the global scale is carried out through regular calibrations against the standard of the ozonometric network of Roshydromet (Dobson spectrophotometer no. 108).

Work continues to re-equip the Roshydromet ozonometric network. During the trial operation of UVOS spectrometers designed for complex measurements of the spectral composition of the total UVR and total ozone content, the software, calibration methods, and TOC calculations were improved. For several instruments, series of parallel observations with M-124 ozonometers were accumulated, demonstrating satisfactory consistency and homogeneity of the series. In 2022, Zenith spectrometers for TOC measurements were manufactured, intended for operation in regions with severe climatic conditions. Their testing begins in 2023.

In 2022, MGO and AARI teams began joint work on organizing a network of regular automatic observations of UV radiation with high time resolution at polar stations (Arctic and Antarctic) and AARI research vessels. The array of TOE data received from the Russian Antarctic stations Mirnyi, Novolazarevskaya, and Vostok and from the scientific expedition vessels of AARI is annually replenished. Until the beginning of the 2000s, at Antarctic stations, there was a steady downward trend in the total ozone content in the Antarctic spring. Currently, there is a tendency for the ozone content to return to the values characteristic of the period preceding the manifestation of the ozone hole effect (Sibir et al., 2020).

Observations of the integrated optical density (IOD) of the atmosphere that began in the 1970s are ongoing. The results of the data analysis are presented in the annual “Reviews of the State and Pollution of the Environment in the Russian Federation” (Rusina et al., 2022a, 2022b). The nature of the interannual variability of the IOD makes it possible to trace the consequences of powerful volcanic eruptions, periods of atmospheric self-purification, a reduction in industrial activity in postperestroika years, and a decrease in optical turbidity of the atmosphere. Since the beginning of the 2000s, a relatively calm state of the atmosphere is observed; no statistically significant trends in the optical density of the atmosphere were recorded.

Observations of the aerosol optical depth of the atmosphere in Antarctica also continue. The values obtained from the results of direct spectral solar photometric measurements and the integral optical thickness determined from standard actinometric observations of direct solar radiation are indicators of the optical state of the atmosphere. A comparison of the data with estimates for other natural regions and conditions indicates that, during periods without the influence of volcanic eruptions, the levels of aerosol turbidity of the atmosphere in Antarctica over the past decades were minimal around the world and can be considered global background characteristics (Radionov et al., 2020).

Taking into account significant climate changes on the planet as a whole, databases and archives of data on the main climate-forming characteristics of the atmosphere that are collected over long periods of time in various regions of the globe and, in particular, in the polar regions, acquire a special role. Total solar radiation is one of the most important parameters affecting the energy balance of the Earth–atmosphere system. The database of hourly and daily sums of total radiation at Russian stations in Antarctica is described in (Sibir et al., 2021). It is designed to study the radiation regime of Antarctica from the beginning of actinometric observations to the present. It passed the state registration procedure and was registered under no. 2020621401. Based on the information it contains, estimates of the variability characteristics of daily, monthly, and annual sums of total radiation at Bell-

ingshausen, Vostok, Mirnyi, Novolazarevskaya, and Progress stations were obtained for the entire observation period in 2019. Results of their analysis indicate the absence of significant changes in the flow of total solar radiation onto the Antarctic surface over more than 60 years of actinometric observations.

In previous years, on the initiative of the WMO Ozone Commission, observations of the total ozone content were carried out at KHSS, Obninsk, and Tomsk stations equipped with Brewer spectrophotometers. Data collected from these stations was regularly transmitted to the World Ozone and Ultraviolet Solar Radiation Data Center WOUDC. Spectrophotometers were regularly calibrated using a mobile standard Brewer spectrophotometer no. 17 (Dorokhov et al., 2015). Due to political reasons, the next calibration did not take place. Therefore, the reliability of the data currently obtained is questionable.

Other than the state and international networks, the study of TOC and components of the ozone cycles was carried out in Russia in educational and scientific organizations of St. Petersburg State University, IAP RAS, IAO SB RAS, etc.

Thus, at St. Petersburg State University, at the Department of Atmospheric Physics and in the Laboratory for Research of the Ozone Layer and Upper Atmosphere, ozone measurements are carried out using satellite and ground-based equipment to study spatiotemporal variability. Information processing methods are being improved. An original algorithm for solving the inverse problem to obtain the total ozone content from spectra measured by the IKFS-2 Fourier spectrometer on the Russian Meteor-M no. 2 satellite was proposed in (Polyakov et al., 2019; Timofeev et al., 2021; Polyakov et al., 2020). The algorithm is based on the use of the artificial neural network method, the method of principal components, and TOC measurements by the OMI instrument on the Aura satellite. The error in determining TOC is $\sim 3\%$; the method makes it possible to analyze the global distribution of TOC, including in the absence of solar radiation, for example, during the polar nights. The authors applied the DOAS differential spectroscopy technique when interpreting the measurement results of the ground-based ultraviolet ozone spectrometer UFOS to determine TOC (Ionov et al., 2021). Comparisons of the calculated TOC values with data from independent measurements showed their systematic discrepancy, which can be eliminated with the more careful adaptation of the DOAS algorithm to the conditions of the problem and the characteristics of the UVOS device. An improved technique for processing ground-based spectral measurements from a Bruker 125HR Fourier transform spectrometer to obtain information about TOC and other stratospheric gases is present and the use of ground-based measurements to interpret processes occurring in the ozonosphere and demonstrated in (Virolainen et al., 2021).

The IAP RAS carried out daily measurements of the NO_2 content in the vertical atmospheric column, which is closely related to TOC and which is necessary to study changes in the state of the ozone layer at KHSS, ZSS, and in Tomsk.

At the Siberian lidar station of the Zuev Institute of Atmospheric Optics, SB RAS, in Tomsk (56.5° N , 85.0° E), vertical sounding was used to continue the study of ozone dynamics in the tropopause region and monitor global changes in the ozonosphere (Dolgii et al., 2019). Probing is carried out by differential absorption using pairs at wavelength of 299/341 and 308/353 nm with allowance for temperature and aerosol corrections. The lidar system covers an altitude range of ~ 5 –45 km. The most optimal sets of absorption cross sections were tested and selected to restore the vertical distribution of ozone in the upper troposphere–stratosphere layers (Dolgii et al., 2022), and a temperature correction technique was developed that increases the accuracy of data acquisition (Dolgii et al., 2020).

Measurements of the vertical distribution of ozone continued with a microwave spectroradiometer over Nizhny Novgorod (Ryskin et al., 2012; Kulikov, 2022), which covered the altitude range of 25–60 km.

The results of ground-based TOC measurements using different equipment are regularly compared, which makes it possible to estimate the homogeneity of data series and the reliability of the information. The results of ground-based TOC measurements with a Dobson spectrophotometer, an M-124 filter ozonometer, and a Bruker 125HR Fourier spectrometer located near St. Petersburg at a distance of ~ 50 km from each other are compared in (Nerobelov et al., 2022). A comparison of the results of average daily values showed that the spread of data between different ensembles of TOC measurements does not exceed the measurement errors of the methods. Temporal changes in monthly average TOC from three sets of ground-based measurements in the St. Petersburg area showed no obvious gradual interannual increase or decrease in gas content over the period 2009–2020.

Information about spatiotemporal changes in TOC that is obtained using various observation methods and models may differ significantly due to measurement and modeling errors, differences in ozone search algorithms, etc. Therefore, data obtained by various methods must be checked regularly. Comparisons of TOC data series obtained by ground-based instruments (Bruker IFS 125 HR, Dobson, and M-124), satellite (OMI, TROPOMI, and IKFS-2) instruments, and models (ERA5 and EAC4 reanalysis; EMAC and INM RAS–RSHU models) near St. Petersburg (Russia) in the period from 2009 to 2020 demonstrate good agreement (correlation coefficients are 0.95–0.99). All data sets reproduce a pronounced seasonal variation in TOC with a maximum in spring and a minimum in autumn. In 2004–2021 there was a significant positive

trend in TOC near St. Petersburg ($\sim 0.4 \pm 0.1$ units per year) for all massifs (Nerobelov et al., 2022).

TOC data are periodically compared at IAO, SB RAS and IMCES SB RAS with other instruments. TOC measurements using M-124 instruments, as well as the Aura OMI satellite sensor, were compared in (Bazhenov et al., 2022; Bazhenov et al., 2022). The comparison showed that they correlate well with each other in terms of pronounced variations that occur in time behaviors, but the amplitudes of these emissions differ. In general, it can be noted that the IAO SB RAS instrument overestimates the values of the other two instruments, while the lowest are the Aura OMI TOC values.

Lidar and satellite data from MLS/Aura and IASI/MetOp on ozone in the stratosphere are compared in (Dolgii et al., 2020b, c). The average relative difference between LiDAR and MLS/Aura measurements is shown to be negative in the altitude range of 16–38 km and reaches -49.81% at 38 km. The average relative difference between LiDAR and IASI/MetOp measurements is positive in the altitude ranges of 6–18 km, where it reaches 43.68% at 16.80 km, and negative above, where it reaches 43.86% at 20 km.

Measurements of ozone content profiles in the atmosphere of St. Petersburg using the Bruker 125HR ground-based FS and a satellite microwave instrument (MLS) for a period of 2018–2020 are compared and the vertical course of the mismatch between two types of ozone profile measurements is studied in (Dolgii et al., 2020a). The comparison showed satisfactory results.

One of the main problems of ground-based measurements is to ensure the validation of satellite equipment. Satellite remote sensing methods make a significant contribution to the analysis of the spatial distribution and temporal evolution of the ozone content and its anomalies. The method developed at the St. Petersburg State University makes it possible to determine TOC based on the results of measurements by the IKFS-2 instrument (infrared Fourier transform spectrometer) located on board the Meteor-M N2 satellite (Polyakov et al., 2021). A comparison of the results of satellite measurements with ground-based observations in 2019–2020 demonstrated the consistency of the global IKFS-2 TOC distribution fields with measurements by OMI equipment, ECMWF ERA5 reanalysis data, and the results of ground-based measurements.

The capabilities of GOME-2 products are estimated in (Chan et al., 2023; Trifonova-Yakovleva et al., 2017). The averaged values of ground-based measurements and satellite estimates were established to be in good agreement with each other for an averaging period of 30 days. It is also shown that satellite estimates are suitable for describing regional pollution and plausibly reflect both the annual variation and spatial changes in concentration, but there are limitations on the use of these estimates to describe instantaneous concentrations, as well as urban pollution itself.

2.2. Study of Stratospheric Ozone Dynamics

A large series of papers presents the results of long-term measurements of the temporal variability of the total content of O_3 and NO_2 at the KHSS and ZSS (IAP RAS) (Gruzdev et al., 2021, 2022a, b; Gruzdev et al., 2021a, 2021, 2022a, 2022b, 2022c; Savinykh et al., 2021a, 2021b). The long-term variability of measurement data were analyzed performed using the multiple linear regression method. Annual and seasonally dependent estimates of the linear trends of O_3 and NO_2 were obtained. A common feature of the long-term trends in O_3 TC at KHSS and NO_2 TC at ZSS and KHSS are significant trends in the winter–spring season. They are negative at both stations, and at KHSS they are stronger than those at ZSS. The TOC trend is positive in 1989–2002 (1.6% per decade) and negative in 2003–2020 (−1.2% per decade). The characteristics of ozone variability indicate the special nature of the interannual and long-term evolution of TOC over the North Caucasus. In particular, the TOC trends in the North Caucasus region are opposite to the trends of the zonal average TOC values. Dependent estimates of linear trends and interannual variations in all ozone that are associated with the effects of the 11-year solar cycle, the quasi-biennial oscillation (QBO) in the equatorial stratosphere, the North Atlantic Oscillation (NAO), and the El Nino–Southern Oscillation (ENSO) were obtained. Changes in total ozone during the 11-year solar cycle in the Caucasus are especially significant in summer and are ~4%. QBO-related interannual fluctuations in total ozone with an amplitude of ~6% occur during the cold season. General ozone fluctuations caused by NAO are pronounced in the winter–spring period. The effects of ENSO on total ozone are prominent in the summer and lag by approximately a year behind regional sea surface temperature changes, such that total ozone decreases after El Nino events and increases after La Nino events. The obtained characteristics of total ozone variability indicate a special nature of long-term and long-term changes in total ozone in the North Caucasus.

In a series of studies by the IAO SB RAS, the distribution of aerosol and ozone was studied by the lidar method using satellite information for interpretation (Bazhenov, 2021; Bazhenov et al., 2019, 2020, 2021; Bazhenov et al., 2021a, 2021b, 2022; Nevzorov et al., 2021a, b; Nevzorov et al., 2021, 2022). Lidar measurements at the Siberian lidar station showed the presence of stratospheric aerosol layers and a TOC deficit over the city in the winter of 2017–2018. Aura OMI/MLS data indicated that total ozone and stratospheric NO_2 over northern Eurasia, as well as stratospheric temperatures, were well below normal during December 2017–January 2018. An analysis of back trajectories and integral (by profile) TOC revealed that the dynamic disturbance of the Arctic stratosphere in December 2017 led to the displacement of cold air masses with an excessive content of aggressive chlorine

(due to NO_2 deficiency) beyond the Arctic Circle and their intrusion into the stratosphere of Tomsk.

The effect of increased humidity in the Arctic stratosphere on the level of ozone destruction was studied in (Bazhenov, 2019). An analysis of Aura MLS data showed that the temperature in the Arctic stratosphere was much lower than normal throughout the period January–March 2011 in the altitude range of 20–35 km. This led to a significant spread of polar stratospheric clouds (PSCs), which formed most intensively at altitudes and during periods of minimal temperatures (maximal temperature drop below the PSC formation threshold). The main ozone losses were observed in March. This was facilitated by the photochemical release of chlorine that avoided deactivation due to nitrogen deficit caused by denitrification during frequent dehydration events, as was evidenced by fluctuations in the height of the maximal deviation of humidity from the long-term norm. Increased humidity in the stratosphere increased the threshold temperature for the formation of PSCs observed until the end of March; as a result, the activation threshold for chlorine was increased and thus its deactivation was delayed. This further increased the level of total ozone losses in March 2011.

The results of ground-based microwave measurements of the evolution of the vertical distribution of ozone in the middle atmosphere over Nizhny Novgorod (56°20' N, 44° E) in the winter of 2017–2018 are present in (Belikovich et al., 2021). They were compared with satellite sounding data obtained using the MLS instrument on the Aura satellite and with ERA5 reanalysis data. In particular, the degree of dependence of the ozone distribution in the stratosphere on the position of the polar vortex boundary at different altitudes relative to the observation point was established. It was recorded that, in January 2018, the vortex approached Nizhny Novgorod and then, until its destruction (February 12), its border oscillated over the city, so that various altitude levels alternately appeared inside or outside the vortex. Such dynamics of the vortex most noticeably affected the evolution of the stratospheric ozone maximum, the position of which tracked the change in the vortex boundary and changed quasi-periodically in the altitude range of 30–35 km. Ground-based microwave sounding results average lower relative ozone abundance than MLS data, with a maximal systematic difference of ~0.8 ppm at an altitude of 38–39 km. However, the analysis of ground-based measurements made it possible to register a clearer response of ozone to changes in the structure of the vortex over Nizhny Novgorod than the analysis of satellite data and reanalysis data.

Employees at the Institute of Applied Physics, RAS, were the first to experimentally record in the Earth's atmosphere a nonlinear photochemical response to daily variations in solar illumination at the second subharmonic of this effect (Kulikov et al.,

2021). As a result of a theoretical study on 2-day photochemical oscillations of the components of the families of odd oxygen O_x (O , $O(^1D)$, O_3) and hydrogen HO_x (H , OH , HO_2) at mesopause altitudes (80–90 km), indicators of the presence of this phenomenon in rocket and satellite sounding were determined using models of varying complexity data. The most pronounced feature of these oscillations is the significant (several orders of magnitude) difference between two successive H concentration values at the end of the night. It was established that the necessary conditions for the manifestation of these oscillations in the H profile before sunrise are certain restrictions on the lifetimes of the HO_x - and O -family at the corresponding moments of local time. The processing of data from the SABER/TIMED satellite campaign made it possible to obtain the first experimental evidence of the existence of 2-day photochemical oscillations at mesopause altitudes.

There is still an ozone deficiency in the atmosphere over the polar regions (Kiselev, 2020). This makes the study of “ozone holes” relevant, and a number of studies are devoted to them.

In studies (Vargin et al., 2020; Frolkis et al., 2021) carried out for Antarctica, it was shown that the hypothesis about the possible existence of a relation between the quasi-biennial oscillation and the state of the Antarctic ozone hole is most likely unfounded. The variability of the parameters of the Antarctic ozone anomaly was studied based on satellite monitoring of the ozone layer TOMS/OMI, MERRA-2 reanalysis and balloon sounding of the vertical distribution of ozone and temperature at the South Pole. Dynamic processes in the Antarctic stratosphere that determine the conditions for the severe destruction of the ozone layer, which over the past 8 years, despite a decrease in the concentrations of ozone-depleting substances, was observed in Antarctica in 2011 and 2015, are analyzed.

The ozone anomaly in the Arctic was analyzed in (Nikiforova et al., 2019), and its characteristic features were established.

Joint ozone research in the Arctic region continues with colleagues from European institutes. An analysis of ground-based observations at 38 European stations made it possible to estimate the response of the ozone layer over Europe to extreme ozone depletion in the Arctic in 2020 (Petkov et al., 2023). The influence extended to the mid-latitudes of Europe, but with a decrease in amplitude and a time delay of up to 20 days. The development of the situation was similar to what was observed after significant ozone depletion in the Arctic in 2011.

In winter–spring 2019–2020, the most significant ozone anomaly in the Arctic in the entire history of observations was observed (Bazhenov, 2021; Tsvetkov et al., 2021). It was caused by an unusually strong and prolonged polar vortex, which resulted in unprece-

dented chemical destruction of ozone. An analysis of Aura OMI/MLS data showed that total ozone decreased steadily to 230 DU on March 18 at Alert site, 222 DU on March 18 at Eureka, 229 DU on March 20 at Thule, and 226 DU on March 18 in Resolute. The minimal temperature was 9–10% below normal from December to April in the stratosphere over Tomsk and the Arctic. Ozone concentrations decreased to 4 and 6% of the long-term average at an altitude of 20 km on March 27 at Eureka and at an altitude of 19 km on April 16 at Ny-Ålesund, respectively. This phenomenon fits into the context of climate change leading to a cooling of the stratosphere.

In (Sitnov et al., 2021), the appearance of the ozone hole is associated with the blocking process. The TOC anomaly was mainly due to a decrease in ozone in the lower stratosphere, reaching 50% near the 70-hPa level. Given the key contribution of atmospheric dynamic processes to the formation of the ozone “minihole,” the possibility of the contribution of ozone destruction in heterogeneous reactions on the surface of polar stratospheric clouds due to a strong decrease in temperature in the stratosphere above the blocking region was noted.

Interesting phenomena observed in the middle atmosphere include stratospheric warming. One of these is described in (Vargin et al., 2019). It was recorded over Canada at the end of December 2017 and at the beginning of January 2018. The main sudden stratospheric warming in February 2018 was accompanied by a change in the direction of the zonal wind, the separation of the stratospheric polar vortex, the spread of stratosphere circulation anomalies to the lower troposphere, cooling in the mesosphere, changes in the height of the stratopause, and a decrease in the temperature of the lower stratosphere in the tropics.

2.3. Modeling Processes in the Ozonosphere

Research carried out in the Laboratory of Chemistry and Atmospheric Dynamics of the Central Aerological Observatory on the creation and use of global numerical models of the atmosphere is reviewed in (Krivolutsky et al., 2021). Several studies are relevant to the topic of this review.

In (Ivanova, 2021), a polar ozone model was built in the Arctic and Antarctic for the winter–spring period to study the variability and relation of the polar ozone content based on data on polar temperature at levels of 30, 70, and 100 hPa and on the average zonal wind in the latitude band 45–75° at levels of 10 and 70 hPa. The model was tested using measurement data in 1979–2020, and errors in the calculation of polar ozone were estimated.

The dynamic processes and changes in the ozone layer in the Arctic stratosphere in the winter of 2019–2020 are analyzed in (Smyshlyayev et al., 2021; Lukyanov et al., 2021). The analysis was performed using numerical experiments with a chemical transport

model (CTM) and reanalysis data. The dynamic conditions of winter–spring 2019–2020 described a decrease in ozone to 100 DU in the Eastern Hemisphere and over 150 DU in the Western Hemisphere. In this case, photochemical ozone destruction in both the western and eastern hemispheres at its maximum was ~50 DU, with peaks in April in the Eastern Hemisphere and in March–April in the Western Hemisphere. The heterogeneous activation of halogen gases on the surface of polar stratospheric clouds, on the one hand, led to a sharp increase in the destruction of ozone in the catalytic cycles of chlorine and bromine. On the other hand, it decreased its destruction in the nitrogen catalytic cycles. An analysis of wave activity using 3D Plumb streams showed that increased propagation of rising wave activity in mid-March over the Gulf of Alaska was observed during the development of a minor sudden stratospheric warming event, which led to a shift of the stratospheric polar vortex to northern Canada and a decrease in the volume of polar stratospheric clouds. Due to low planetary wave activity, the polar vortex in 2019–2020 remained stable until the end of April, creating the conditions for record ozone depletion in the Arctic.

The research of (Vargin et al., 2020; Krivolotsky et al., 2020; Tsvetkova et al., 2020) is devoted to issues of testing and improving models. Using data from five 50-year calculations with the fifth version of the Institute of Numerical Mathematics (INM) RAS climate model for modern conditions, the interannual variability of the characteristics of the stratospheric polar vortex in the Arctic and the dates of the spring restructuring of the stratosphere circulation are analyzed in comparison with reanalysis data. Early rearrangements are accompanied by stronger wave activity compared to later ones. Winter seasons with the maximal volume of air in the polar stratosphere and conditions sufficient for the formation of polar stratospheric clouds are, on average, characterized by early spring changes. Numerical seasonal temperature forecasts were carried out using two interactively operating numerical global models: the photochemical model of the CHARM Central Aerological Observatory (0–90 km) and the seasonal forecast model of the GMC/INM RAS PLAV (0–30 km).

The forecast results were compared with the reanalysis data. It was established that the new combined model FOROZ (Forecast with Ozone) showed stability when implementing numerical scenarios. Seasonal forecast temperature fields of the PLAV model and the combined FOROZ model with reanalysis data are close in the lower troposphere and differ in the stratosphere. The coupled FOROZ model improves temperature forecasts in the upper troposphere and stratosphere.

To study changes in the Arctic polar stratospheric vortex in the near future, modeling using version 5 of the INM RAS climate model for the period 2015–

2100 under two scenarios, SSP2-4.5 and SSP5-8.5, of growth in greenhouse gas concentrations was performed in (Vargin et al., 2022). An increase in the propagation of wave activity and stationary planetary wave no. 1 in the middle and upper stratosphere, an acceleration of the meridional circulation, an increase in the winter mean polar stratospheric volume (V_{psc}), and an increase in the interannual variability of the Arctic stratosphere after the mid-21st century (especially under the SSP5-8.5 scenario) were revealed. March monthly V_{psc} values in some winters can be approximately twice as large as those observed in the Arctic stratosphere in the spring of 2011 and 2020, which in turn can lead to large ozone depletion. A comprehensive analysis shows that “warm” winters with the lowest average V_{psc} values are characterized by an increased propagation of wave activity from the troposphere to the stratosphere in December, but weaker propagation in January–February compared to winters with the highest V_{psc} values.

The behavior of the ozone layer in the past and future is actively modeled at the St. Petersburg State University. The basis for the research is both the previously developed chemistry and climate models of the SOCOL (Muthers et al., 2014) and HAMMONIA (Schmidt et al., 2006) families, as well as the new SOCOL4 Earth system model (Sukhodolov et al., 2021), which includes interactive ocean, dynamic vegetation, atmospheric chemistry, and microphysics of sulfate aerosol. To further improve the models, the possible impact of iodine-containing impurities on the ozone layer was studied (Karagodin-Doyennel et al., 2021). Ozone depletion by naturally occurring iodine-containing contaminants was shown to have some effect on the climatology of the ozone layer, more noticeable in the troposphere. At the same time, the doubling of current emissions of iodine-containing impurities that are expected in the future has little effect on the ozone layer in the lower stratosphere and reduces the total ozone content in the atmospheric column by 1.5–2.5%. The results demonstrate a relatively low sensitivity of atmospheric ozone to iodine chemistry for future periods, but uncertainty remains high due to a lack of observational data for iodine compounds. Thus, to calculate the evolution of the ozone layer from 1980 to 2100, the basic version of the SOCOL4 model was used (Sukhodolov et al., 2021) with no allowance for iodine-containing impurities. Changes in the ozone layer during the historical period were calculated using observed parameters for all impact factors, including concentrations of greenhouse and ozone-depleting impurities, emissions of gases from sources, solar radiation, and volcanic eruptions. The calculated trends were compared with the results of the analysis of ozone changes obtained from the BASIC and MSRv2 multisensor composite data and the MERRA-2 and ERA-5 reanalysis data. Trend analyses were performed separately for the depletion

period (1985–1997) and ozone recovery period (1998–2018). During the 1998–2018 period, SOCOLv4 shows statistically significant positive trends in mesosphere, upper, and middle stratosphere ozone and a sustained increase in tropospheric ozone. The SOCOLv4 results (Karagodin-Doyennel, 2022a) also indicate some negative trends in the lower tropical and midlatitude stratosphere, which are not consistent with the BASIC data in terms of magnitude and statistical significance. Despite the somewhat lower magnitude and scale of the model results, it was concluded that modern CCMs such as SOCOLv4 are generally capable of reproducing observed changes in ozone concentrations. This finding substantiates the use of these models to predict the future evolution of the ozone layer.

Changes in the ozone layer in the future were estimated using the SOCOLv4 model with scenarios of changes in the concentration of greenhouse and ozone-depleting impurities, gas emissions from sources, solar radiation, and volcanic eruptions (Karagodin-Doyennel, 2022b). Simulations were performed based on two potential IPCC scenarios: SSP2-4.5 and SSP5-8.5. In both scenarios, the model shows a future decline in tropospheric ozone starting in the 2030s in SSP2-4.5 and after the 2060s in SSP5-8.5 and associated with decreasing concentrations of ozone precursors such as NO_x and CO. The results also indicate a very likely increase in ozone in the mesosphere, upper and middle stratosphere, and lower stratosphere at high latitudes. Under SSP5-8.5, the increase in stratospheric ozone is higher due to greater cooling (>1 K per decade) caused by greenhouse gases, which slows the cycles of catalytic ozone destruction. In contrast, ozone concentrations decrease in the tropical lower stratosphere but increase over the middle and high latitudes of both hemispheres due to increased meridional transport, which is stronger for the SSP5-8.5 scenario. The evidence of ozone decline in SOCOLv4 suggests that the evolution of stratospheric ozone throughout the 21st century will be largely determined both by declines in halogen concentrations and by future greenhouse gas emissions. Therefore, although the problem of anthropogenic halogen emissions was now brought under control, future changes in ozone on a global and regional scale are still unclear and largely depend on the development of future human activities.

The resulting generally optimistic estimates of how the ozone layer will change in the future contrast sharply with the situation if measures to protect the ozone layer were not taken. New estimates using the SOCOLv4 model (Egorova et al., 2022), which includes an interactive ocean and dynamic vegetation, confirmed the dramatic ozone depletion in this case that was previously calculated with less complex models. In this study, it was also shown that the introduction of restrictions on the production of ozone-depleting impurities made it possible to prevent additional warming of the global climate by more than 2 K.

Much attention was devoted to the impact of space weather-related factors on the ozone layer. The use of the HAMMONIA chemical-climate model (Schmidt et al., 2006) made it possible to estimate the impact of solar flares in September 2017 on the chemical composition of the atmosphere (Pikulina et al., 2022). It was shown that solar flares at the beginning of September 2017 led to a significant increase in the concentrations of active nitrogen and hydrogen oxides in the equatorial and southern high latitudes. However, this increase did not affect the change in the ozone content in the tropical stratosphere, since the process of ozone destruction by nitrogen oxides (NO_x) is not effective in the upper mesosphere and there are no downdrafts of air that could transport additional NO_x into the stratosphere. Hydrogen oxides (HO_x) do not have a significant effect on ozone during the considered seasons. However, some small ozone depletion correlated with increased HO_x is modeled in the Southern Hemisphere. In the paper, it was concluded that electromagnetic radiation has a weak effect on the Earth's atmosphere during solar flares. As is shown in (Mironova et al., 2022) and (Grankin et al., 2023), energetic electrons precipitating from the magnetosphere can have a much greater impact on ozone.

The simulation of the consequences of an extreme event over Moscow in December 2009 using the HAMMONIA model showed the almost complete destruction of the ozone layer in the mesosphere and lower thermosphere of the Northern Hemisphere. Precipitation of energetic electrons over the city of Apatity and calculated changes in the concentrations of ozone, electrons, and nitrogen and hydrogen oxides that were caused by these events are considered in (Grankin et al., 2023). For the events of November 9, 1998, and September 1, 2000, the calculated drop in ozone concentration was 14 and 30% at an altitude of 75 km. The results indicate a potentially significant effect of energetic electrons on atmospheric chemistry.

The condition of chemical equilibrium of nighttime ozone is widely used to retrieve the spatiotemporal distributions of nighttime O, H, and some other characteristics in the altitude range of 80–100 km from satellite data. In (Kulikov et al., 2019), a boundary, below which the equilibrium of nighttime ozone is significantly disrupted, was found using a previously created analytical criterion. The annual (for 2004) SABER/TIMED database of simultaneous nighttime measurements of profiles of temperature, pressure, ozone concentration, and volumetric rate of OH^* emission near $2 \mu\text{m}$ as a result of transitions (9–7) and (8–6) in the range altitudes 75–100 km, was processed. It was found, firstly, that the position of the equilibrium boundary of nighttime ozone varies in the range of 77–86 km depending on the season and latitude, which generally confirms the conclusions of theoretical studies (Belikovich et al., 2018; Kulikov et al., 2018). This boundary was found to be a sensitive indicator of the evolution of the

middle atmosphere. In particular, the results of processing SABER data in 2003–2005 showed that the anomalous latitudinal dependences of the position of the ozone equilibrium boundary above 60° N in January–March 2004 are associated with the very unusual dynamics of the stratospheric polar vortex during the Arctic winter of 2003–2004, which was a “remarkable winter in the 50-year record of meteorological analyses” and was accompanied by the phenomenon of elevated (up to 80 km) stratopause (Manney et al., 2006). Secondly, the spatiotemporal distributions of nighttime O and H concentrations were retrieved according to SABER data for 2004. The application of the ozone equilibrium condition below its equilibrium limit was found to lead to a significant (up to 5–8 times) underestimation of the O concentration in an altitude range of 80–86 km, but has virtually no effect on the quality of the H retrieval. In a recent study (Kulikov et al., 2023a), this criterion was improved, as a result of which the position of the equilibrium boundary of nighttime ozone found using the criterion almost perfectly corresponds to the results of chemical transport modeling. Moreover, the study (Kulikov et al., 2023a) presented the a general theory of photochemical/chemical equilibrium of minor atmospheric constituents and strictly mathematically derives a set of conditions that ensure that the concentration of a particular constituent is close to its instantaneous equilibrium value.

In (Kulikov et al., 2020a), a new source of O(¹D) in the mesopause region due to the OH(v ≥ 5) + O(³P) → OH(0 ≤ v' ≤ v – 5) + O(¹D) process was first used to retrieve the spatiotemporal distribution of nighttime O(¹D) according to SABER/TIMED data for 2003–2005. Using the condition of nighttime chemical equilibrium of ozone, it is shown that, during the year, depending on the month, the monthly distributions of O(¹D) have from 2 to 4 maxima with values up to 340 cm^{–3}, which are localized in altitude (~92–96 km) and latitude (at ~20°–40° S, N and ~60–80° S, N). Annually averaged distributions in 2003–2005 have one weak maximum at ~93 km and ~65° S with values of 150–160 cm^{–3} and three pronounced maxima (with values up to 230 cm^{–3}) at ~95 km and ~35° S, at ~94 km and ~40° N, and at ~93 km and ~65–75° N, respectively. In general, the Northern Hemisphere has slightly more O(¹D) than the Southern Hemisphere. The results provide a unique database for the subsequent estimate of the effect of nighttime O(¹D) on the chemical composition of the mesopause region.

In (Kulikov et al., 2020b), the mechanism of generation of reaction–diffusion waves in the mesopause region (80–90 km) was analytically studied for the first time. These waves are nonlinear phase fronts of oscillations O, O₃, H, OH, and HO₂ with concentrations a period of two days that move in the zonal direction (due east) with a constant velocity. They appear when the photochemistry of the mesosphere subhar-

monically (with a period of 2 days) responds to (external periodic) with allowance for horizontal turbulent diffusion. The photochemical system in the mesopause region is a nonlinear oscillator, which is described by a system of two differential nonautonomous equations with power-law nonlinearity, which was derived in earlier studies of the authors. It was established that reaction–diffusion waves are caused by a specific “wind” type transport that arises in the equations for the amplitudes of 2-day photochemical oscillations of O and H concentrations due to the zonal heterogeneity of the external forcing. The resulting expression for the velocity of wave propagation completely confirmed the previously obtained numerical results that the velocity value is proportional to the diffusion coefficient and the phase gradient of the external forcing. The direction of wave propagation is determined by specific phase relations and depends only on the internal parameters of the system. The research is of fundamental importance, for example, from the point of view of predicting the occurrence of similar phenomena in atmospheric photochemistry in other regions due to both diurnal variations of solar radiation and the presence of many other periodic forcing. From a practical point of view, this result makes it possible to determine the main indicators of reaction–diffusion waves necessary for their subsequent experimental detection under real mesopause conditions and quantitative estimate of the value of the coefficient of horizontal turbulent diffusion that is one of the most important, but not measured, transport parameters at altitudes in a given region of the atmosphere.

The quality of retrieving daytime distributions of O, H, OH, HO₂, and the rate of chemical heating at altitudes of 77–100 km using the long-term (2003–2015) SABER/TIMED database with the photochemical condition daytime ozone equilibrium is analyzed in (Kulikov et al., 2022a). It was found that the generally accepted rejection of the O₃ + H → O₂ + OH reaction in this condition leads to an underestimation (up to 35–40%) of the O concentration and the rate of chemical heating and a significant overestimation (up to ~50–85%) of the HO₂ and OH concentrations. In the subsequent study (Kulikov et al., 2022b), an improved model of excited OH with constants corresponding to published data was used to retrieve the daytime distributions of O, H, OH, and HO₂ from the same SABER/TIMED data. Changes in the parameters of the retrieval procedure were found to lead to a noticeable (up to 80%) increase in the O concentration below 85–86 km; a significant (up to 170%) increase in the H, OH, and HO₂ concentrations below 90 km; and their noticeable (up to 40%) decrease near 100 km.

The use of upgraded equipment created at the IAP RAS with the high spectral resolution (~12 kHz) made it possible to determine the resonant frequency of this ozone emission line with previously unattainable accu-

racy equal to $110\ 835.909 \pm 0.016$ MHz. It was shown that the Doppler frequency shift by the horizontal wind, as well as variations in tropospheric absorption, do not affect the result. The value is 130 kHz lower than the laboratory-measured value and differs from the results of calculations using modern spectroscopic models, while is close to the results of the first semiempirical calculations carried out more than 40 years ago.

3. METHODS AND INSTRUMENTS

The methods used for ozone research have already been covered in the text to varying degrees above. What remained largely unaffected were the methods developed for data processing.

Based on the NOAAHYSPLIT_4 trajectory model and NCEP/NCAR reanalysis, a method for calculating ultralarge sets (millions of trajectories) of forward and backward trajectories was developed at the IAP RAS (Shukurov et al., 2019). Fields of potential sources of aerosol and gas particles are identified using arrays and trajectory methods. The distributions of potential source areas of ammonium nitrate, ammonium sulfate, and silicate, which contribute to ground-level aerosol, as well as tropospheric formaldehyde and stratospheric nitrogen dioxide at the ZSS, stratospheric ozone at the KHSS, and aerosol column content at AERONET stations in Tomsk and Ussuriysk were analyzed. The method is also used to identify hard-to-reach regions associated with anomalies in winter surface air temperature in Moscow and precipitation anomalies in the basin of Lake Baikal.

In (Gruzdev, 2019a, 2019b), a method for taking into account the serial correlation (autocorrelation) of data in a multiple linear regression problem was proposed. The method is effective in analyzing long-term trends and temporary variations in atmospheric pollutants. It makes it possible to take into account the autocorrelation of data on large scales. The residual series is represented as an autoregressive process, the k order of which can be much greater than unity, and the autocorrelation function of the process is calculated by solving the system of Yule–Walker equations. Using the autocorrelation function, an autocorrelation matrix, which is included in the formulas for estimating regression coefficients and their standard errors, is constructed. The effectiveness of the method is demonstrated based on multiple regression analysis of data from 26 years of measurements of total NO_2 content at the ZSS IAP. Estimates of regression coefficients and their errors depend on autoregression order k . First, the error increases as k increases. Then, it reaches a maximum and, after that, begins to decrease. In the case of NO_2 , the error at the maximum more than doubles its initial value. The decrease in error after reaching the maximal stops if k reaches a value, at which the autoregressive process makes it possible to describe important features of the autocorrelation function of

the residual series. Estimates of seasonally dependent trends and the effects of natural factors on NO_2 , such as the 11-year solar cycle, quasi-biennial cyclicity, and North Atlantic Oscillation, were obtained.

In (Stepanov, 2022), a new approach to processing long series of ozone monitoring data in the surface atmosphere, which is called Data Parallel Processing in Block Streams, is described. The proposed methodology is based on dividing a sequential series of initial data into blocks filled with the results of monitoring ground-level ozone during one day. Next, a chain is formed from such blocks, the length of which is determined by the total length of the observation process. Along this chain of blocks, parallel processing of the initial data that is aimed at smoothing out rapid fluctuations is carried out. The smoothed data are then used to determine the daily ozone production due to photochemical reactions, its minimal nighttime levels, and the magnitude of the nighttime maxima. The capabilities of the proposed approach are demonstrated by analyzing ground-level ozone monitoring data in Moscow in 2020.

The IAP RAS continues developing and improving the ground-based method of multiangle differential spectroscopy (MADS) for determining the content of NO_2 , H_2CO , and other chemically active gases in the atmospheric boundary layer. In 2016, the IAP RAS group took part in international comparisons of instruments and techniques for measuring NO_2 and other gases using the DOAS method: CINDI-2. The CINDI-2 comparisons featured 36 spectral instruments from 26 different scientific groups. In (Kreher et al., 2020; Wang et al., 2020), the comparison results of methods for the recovery of chemically active substances that affect ozone chemistry such as NO_2 , O_4 , O_3 , H_2CO , and HNO_2 are present. Based on the comparison results, recommendations on measurement modes and measurement processing parameters of the DOAS method were formulated.

A new lidar was developed at the IAO SB RAS for measuring tropospheric ozone and aerosol (Nevzorov et al., 2022). The lidar system is based on a QX 500 laser (SOLAR LS, Belarus) and a Cassegrain telescope with a receiving mirror diameter of 0.35 m and a focal length of 0.7 m. It operates at wavelengths of 299/341 nm and must cover the altitude range from ~ 0.1 to 12 km. There, the ability to monitor UV solar radiation at the Fonovaya observatory was significantly expanded (Belan et al., 2022) and a new UV radiation detector was developed (Tentyukov et al., 2021).

A singlet oxygen gas analyzer was created at AO OPTEK (St. Petersburg, Russia) (Iasenko et al., 2019). The principle of the device is based on the chemiluminescent reaction of 9,10-dephylanthracene. The new gas analyzer is designed to solve a wide range of fundamental and applied problems related to processes and phenomena at the boundary between biogenic and abiogenic nature. Its capabilities were

demonstrated by examples of monitoring the concentrations of pollutants in atmospheric air by in vivo and in vitro experiments on recording singlet oxygen on the surface of snow and near plants infected with a pathogenic fungus, as well as by testing photocatalytic materials developed for use in medicine and protection architectural and sculptural monuments from biodeterioration.

CONCLUSIONS

In 2019–2022, atmospheric ozone research on the territory of Russia continued both within the framework of state monitoring systems and by initiative groups in university and scientific organizations. The network of stations measuring ground-level ozone concentrations significantly expanded. The publication of reviews on GOCs in the Russian Federation began.

Data processing methods were improved and new instruments were developed. A large amount of research was carried out on the spatiotemporal variability of the ozone concentration and the factors determining it.

The components of the ozone cycles, as well as trends in ozone changes until 2100, were estimated using numerical modeling.

The publication of a monograph on the history of ozone research that covers the period from the discovery of oxygen to the present should be also noted (Larin, 2022).

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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