Abstract—The location of Moscow on a plain within higher latitudes when compared to other megacities creates conditions for the chemical transformation of pollutants in the urban atmosphere and their transport and accumulation. Observational data on surface concentrations of NO, NO\(_2\), CO, CH\(_4\), O\(_3\), nonmethane hydrocarbons (NMHCs), and aerosols (PM\(_{10}\)), which were obtained at the Moscow Ecological Monitoring (MEM) network from 2005 to 2020, have been processed and analyzed. Both temporal and spatial parameters characterizing the dynamics of atmospheric pollution of Moscow’s air basin have been calculated. It is noted that the content of most pollutants in the urban air has decreased due to the renewal of the vehicle fleet; the introduction of restrictions on the entry of freight transport in the city; and the modernization of industrial enterprises, treatment facilities, and the gas transmission system. Significant negative trends have been obtained for NMHCs, CO, NO\(_x\), and PM\(_{10}\) (4.3, 4.0, 2.6, and 1.7% y\(^{-1}\), respectively). An insignificant negative trend has been obtained for O\(_3\) and no negative trend has been found for CH\(_4\). Total emissions from urban sources of substances determining the air quality have been calculated. Their values also manifest negative trends. The content of ozone almost did not change within such a long period, which suggests a weak sensitivity of the oxidizing properties of the Moscow atmosphere and the rate of ozone generation to variations in the atmospheric content of nitrogen radicals and their high sensitivity to volatile organic compounds.

Keywords: megacity atmosphere, atmospheric composition, air quality, emissions, pollutants, surface concentrations, diurnal and seasonal variations, weekly cycle

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1. INTRODUCTION

The growth of both the urban population and urban areas in the world, infrastructure changes, and applications of new materials and technologies affect the atmospheric composition and the state of the climate system. At the same time, the inverse effect of climate changes on the air quality in cities becomes more pronounced. Choosing the path of sustainable development for any country requires a sequential modernization of the air-composition monitoring system, as well as a detailed study of the physicochemical transformation of pollutants in the urban atmosphere and the formation of extreme situations [1-5]. The international complex atmospheric investigations carried out in Mexico and Paris showed that, based on scientific results, one can develop effective measures to reduce anthropogenic effects on urban environment and improve the air quality [6-8]. These measures should provide not only a general decrease in anthropogenic emissions, but also changes in their composition, and, thus, affect the oxidizing properties of urban air and accelerate the removal of toxic compounds from the atmosphere. Results obtained from monitoring the atmospheric state and its numerical chemical transport simulation (whose efficiency depends on the accuracy of given pollutant emissions determining, first and foremost, the state of the photochemical system in a given city) form the basis for making decisions in each specific case. Data of both global and regional emission inventories, including the European one, for approximately 40 types of sources are currently used in simulations [9]. Because of the variety of sources and conditions under which they operate and the need to use numerous assumptions, calculation results obtained by different groups of experts differ significantly from one another [4, 10, 11; Megapoli (http://megapoli.info/); TNO (https://topas.tno.nl/emissions/);
EDGAR (https://edgar.jrc.ec.europa.eu/); CAMS-REG-AP (https://atmosphere.copernicus.eu/); ACCMIP (https://www.giss.nasa.gov/projects/accmip/)]. This circumstance makes one pay special attention to direct measurements of urban emissions. The emission estimates for the Moscow megacity, for example, according to data on pollutant concentrations measured at the network of Moscow stations in 2005–2014 [12, 13], show that the inventory data are inaccurate for most chemical compounds; moreover, for some components, discrepancies may amount to 400% and more.

Moscow, with a population of about 13 million residents, ranks 15th among the largest megacities in the world in regards to population and is among the leaders in population density. In the past three decades, the city has rapidly increased in area and occupied the immediate vicinities outside its official border, passing mainly along the Moscow Ring Road (MRR). The shape of the historically formed urban development is almost circular, and the absence of large industrial centers in its immediate vicinity makes it possible to consider Moscow an isolated city, which distinguishes it from other megacities. The location of Moscow on a plain within high latitudes is also an important distinguishing characteristic. The urban infrastructure and the state of industry have significantly changed over the past 30 years. The number of cars has increased from 2 to 6 million over the same period. Industrial production has increased by 10%; however, some large enterprises making the main contribution to atmospheric pollution have stopped operating [14; https://www.fedstat.ru/]. Moscow has become a financial and administrative center, with the composition of anthropogenic emissions that are characteristic of such cities [15]. At present, the air quality in Moscow depends, to a greater extent, on motor transport, urban infrastructure, and both meteorological and climatic variations [13, 16, 17].

Long-term observational data obtained at the stations of the Moscow Ecological Monitoring (MEM) network [https://mosecom.—mos.ru/] form the basis for studying processes that determine atmospheric composition in Moscow. The network of automatic stations continuously operating, which was organized in 2002, initially included 11 stations and, in the 2010s, the number of stations increased to 56. These stations are more or less uniformly distributed over the territory of Moscow. Ten stations are located outside the
SO2, and PM10 showed that, according to the Gurjar [12] for the atmospheric content of CO, NO, NO2, CH4, and O3 atmospheric surface concentrations; the total content of nonmethane hydrocarbons (NMHCs); and the mass of aerosol particles of size 10 μm (PM10), which were obtained at the MEM network from January 1, 2005, to December 31, 2020, are used to determine the features of time variations in the air quality in the megacity of Moscow. By the beginning of this period, the number of MEM stations had increased to a few tens, the stations were provided with up-to-date expensive observation instruments, and the standard methods of measurements and instrument calibration were worked out. Table 1 shows the relative number of stations at which the indicated pollutants were continuously measured from 2005 to 2020.

Pollution data series obtained at the MEM stations have a large number of outliers in their statistical distributions. This, may be, first, associated not only with physical phenomena in the atmospheric surface layer (ASL), such as frequent inversions and stable ASL stratifications in urban built-up areas, but also with random emissions due to the location of a car with a running engine or other random pollution source near one of the stations.

In addition to outliers in the data series, negative values are often observed immediately after the calibration of measuring instruments, as well as zero values if pollutant concentrations are below the sensitivity threshold of the measuring instruments. All values that are less than or equal to zero were removed from the total sample using simple frames. Special filters were used to eliminate outliers in data series that have a large number of fluctuations with different periods.

While working with observational data, we built up probability density functions for each pollutant; in this case, the data sample consisted of an array of measurement data for each year for all stations. The two-parameter distributions, such as the normal, lognormal, Pearson, Chi, and Laplace distributions, were used as potential approximating functions. The most probable parameters describing the distribution functions of data series were found using the maximum

### Table 1. Average (over the 2005—2020 period) relative number of stations at which the pollutants were continuously measured (total number of stations is 56)

| Pollutant       | CH4 | CO | NO | NO2 | NMHCs | O3 | PM10 |
|-----------------|-----|----|----|-----|-------|----|------|
| Relative number of stations, % | 45  | 90 | 80 | 80  | 45    | 30 | 55   |

megacity to monitor the average regional background of atmospheric pollution (Fig. 1). The measurements at heights of 10, 130, 248, and 348 m are performed at the Ostankino TV tower, located 7 km north of the city center. In regards to the number of stations, the principle of their distribution, and the methods and frequency of measurements, the MEM network meets the requirements that are imposed by the World Meteorological Organization upon air quality monitoring systems in cities. In accordance with the legislative acts adopted in recent years in the area of the environmental policy of Russia (the RF Presidential Decree of February 8, 2021; the Federal Law of July 2, 2021; and others), the Moscow atmospheric monitoring system continues to evolve.

The common (with other megacities) basic pollution sources (motor transport, both industrial and public facilities, and housing sector) bring Moscow’s air quality closer to megacities in the United States, Japan, and Europe [12]. The analysis performed in [12] for the atmospheric content of CO, NO, NO2, CH4, and O3, showed that, according to the Gurjar classification [3], by 2010, in terms of air quality, Moscow had gone from being one of the 6 most polluted megacities (all in all, the 19 largest megacities in the world with a population of over 12 million were considered) to one of the 6 cleanest. However, one should take into account that there is some arbitrariness in choosing a territory for which the quality of air and pollutant emissions is determined. In different publications, estimates are given for isolated cities, cities with industrial surroundings, urban agglomerations, and entire provinces, which makes it difficult or impossible to compare air quality and anthropogenic emission data.

Regular observations of the content of gas pollutants and aerosols at the MEM network in recent years have allowed one to refine, correct, and supplement earlier obtained data [18–21] on spatiotemporal variations in the composition of the atmospheric surface layer over Moscow. Using the method based on calculations of the distribution functions of concentrations of different pollutants makes it possible to increase the efficiency of data filtering and minimize information loss. The database, significantly extended, is also used to estimate integral emissions of the key gas pollutants and aerosols into the atmosphere over the Moscow megacity, and their annual variability is considered. Since Moscow may be considered an isolated city, in this work, both air quality and emission estimates are given (as earlier in [13, 18]) for the territory with a mean radius of 25 km, which includes new residential areas annexed to Moscow (Fig. 1). Earlier such studies were conducted based on data obtained at 48 stations of the MEM network and, in this work, data obtained at 56 stations are used.

#### 2. DATA PROCESSING AND FILTERING

The 20-min average values of the CO, NO, NO2, CH4, and O3 atmospheric surface concentrations; the total content of nonmethane hydrocarbons (NMHCs); and the mass of aerosol particles of size 10 μm (PM10), which were obtained at the MEM network from January 1, 2005, to December 31, 2020, are used to determine the features of time variations in the air quality in the megacity of Moscow. While working with observational data, we built up probability density functions for each pollutant; in this case, the data sample consisted of an array of measurement data for each year for all stations. The two-parameter distributions, such as the normal, lognormal, Pearson, Chi, and Laplace distributions, were used as potential approximating functions. The most probable parameters describing the distribution functions of data series were found using the maximum
likelihood estimation (MLE) method. Figure 2 gives an example of the results.

The distribution functions of most pollutants are not symmetric, and the lognormal approximation is more suitable for their description when compared to the often-used normal approximation. A sufficiently high temporal variability of pollutant concentrations and their rapid increase, especially under anomalous weather conditions, lead to the fact that the right-hand tail of the distribution significantly contributes to their estimated average. It was important to take into account this fact in validating the quality of data and choosing the method of their filtering. The exception is the methane measurement data; their distribution function proved symmetric and well approximated using the Laplace distribution. This result is quite natural, because CH₄ is a sufficiently passive pollutant that has the longest lifetime among all the pollutants under consideration in this work; its concentration varies rather slowly and within a comparatively narrow range.

The observational data series of all pollutants (except CH₄) for each station have no explicit normal distribution (Fig. 2). Therefore, each data series was stored in two-dimensional matrix $A$ with dimension...

![Fig. 2. Probability density functions (PDF) for observational NO₂ and CH₄ data obtained at the MEM stations from January 1 to December 31, 2012.](image)

| Order number | Measurements within a month |
|--------------|----------------------------|
| 1            | 26  26  25  23  21  ...    | 14  17          |
| 2            | 15  14  13  13  13  ...    | NaN  NaN        |
| 3            | 26  27  27  30  32  ...    | 54  56          |
| 4            | 60  60  61  62  60  ...    | NaN  NaN        |
| 5            | 31  34  NaN  33  40  ...    | 57  55          |
| ...          | ...  ...  ...  ...  ...  ...| ...            |
| 190          | 32  27  25  30  36  ...    | 28  27          |
| 191          | 25  24  22  22  21  ...    | NaN  NaN        |
| 192          | 14  12  12  13  13  ...    | 20  18          |
Here, 192 is the number of matrix lines, which is equal to the number of months over a calculated period of 16 years, 72 is the number of 20-min measurements per day, and 31 is the maximum number of days in a month (Table 2). Within every line and every column of matrix \( A \), the sample approached the normal distribution, and the standard statistical operators could be applied to this sample. In matrix \( A \), there were values of unavailable numbers (NANs) obtained after the elimination of both zero and negative values and other omissions associated with the absence of data, for example, when some station did not operate.

Then, the cycle started through the lines of matrix \( A \) and the linear trend was removed from each line; thereafter, the standard deviation (STD) was calculated. In the sample, the coordinates of cells in which concentration values went beyond four STD were stored. According to the stored coordinates, the concentration values in the cells of matrix \( A \) were replaced by NANs; i.e., they were eliminated. When the cycle through the lines of matrix \( A \) was completed, the cycle through its columns started and the same operations were performed. The alternation of the cycles through the columns and lines of matrix \( A \) was iterated until the number of NANs became constant, i.e., until all outliers were removed.

After filtering, matrix \( A \) was decomposed back into a filtered series. As an example, Fig. 3 shows the NO\(_2\) measurement data obtained at the Mar’ino station before and after filtering.

3. SPATIAL DISTRIBUTION

The MEM network data were used in plotting the dependence of average concentrations on the distance to the city center (Fig. 4). On average, the obtained distribution of the pollutants over the megacity shows a significant decrease in CO and a slight decrease in NO\(_x\) in the direction from the center to its outskirts. No significant spatial gradients are observed for other pollutants. The distribution of pollutant concentrations over the megacity territory is nonuniform and associated with the location of pollutant sources. The characteristic features of the distribution have not changed compared to those that were described in detail in [18], which was performed using observational data carried out before 2014 at a smaller number of stations. Therefore, we present here the main conclusions. The South-Eastern Administrative Okrug (SEAO), in which the Moscow Petroleum Refinery (MPR), urban aeration fields, four large heating stations, and other polluted objects are located, is most polluted. Pollutants, together with prevailing westerlies and northwesterlies, also arrive in this okrug from the North-Western Administrative Okrug (NWAO), South-Western Administrative Okrug (SWAO), and Central Administrative Okrug (CAO). There is the highest road density and, correspondingly, the most intensive traffic in the CAO. The highest concentrations of CO are observed in the CAO, because motor transport is its main source. The concentration of PM\(_{10}\) also depends on motor transport, but the fact that there is no significant difference in its concentrations between the center of the city and its outskirts is associated with the traffic restrictions within the MRR for heavy trucks that are the main source of PM\(_{10}\).
North-Eastern Administrative Okrug (NEAO) is the cleanest one; the Losiny Ostrov National Park and Sokolniki Park cover most of it.

Maximum CH$_4$ concentrations were recorded in Moscow’s dwelling zones at a distance of 8 to 18 km from the center. It is Moscow’s old dwelling zones, gasified in the 1950s—1970s, that are the main source of methane. The concentration of O$_3$ varies significantly from one place to another because, it is significantly affected by micrometeorological conditions and dry deposition on the surface. Descending airflows around buildings, in the vicinity of which a network station is located, may significantly increase the concentration of O$_3$. High NMHC concentrations are observed at stations located in the vicinity of the Third Transport Ring with a radius of about 5 km and the MRR with a radius of 13 to 18 km, along which most heating stations, the MPR, both Kur'yanovo and Lyubertsy aeration fields, and treatment facilities are located. The effects of other industrial objects and urban infrastructure will be discussed in analyzing time variations in pollutant concentrations in the Moscow air basin.

4. DIURNAL VARIATIONS

Figure 5 shows the diurnal variations in the CO, NO, NO$_2$, O$_3$, CH$_4$, NMHC, and PM$_{10}$ concentrations averaged over all stations over the 2005—2020 period. During nighttime, from Monday to Friday, the CO, NO, NO$_2$, NMHC, and PM$_{10}$ concentrations decrease and reach their minima at 04:00 and, for NO, at 03:00 (Moscow time). The main reason for such a night pollution decrease is the airing of Moscow against the background of slight night pollutant emissions. In the concentration of O$_3$, the inflow of clean air is manifested in its increase, but after 04:00 both processes of its chemical decomposition and dry deposition onto the land surface begin to prevail, which results in the formation of its morning minimum. The morning increase in the concentration of NO begins at 04:00—05:00, which is one hour earlier than that of NO$_2$, first, due to increased anthropogenic NO$_x$ emissions that include about 90% of NO and only 10% of NO$_2$; second, due to a weak sink of NO in the reaction with O$_3$ at this time of the day, which is associated with its low concentration; and, third, due to a rapid photodissociation of NO$_2$ and N$_2$O$_5$ accumulated during night and the formation of NO at the beginning of daylight. At about 05:00, the concentrations of all other pollutants and the general level of the ASL pollution begin to rapidly increase up to 08:00—09:00, when they reach their morning maximum. The early start of such a rapid increase in the concentration of most pollutants is caused not only by the activation of urban sources, but also by their accumulation under the surface temperature inversion that usually collapses over the megacity at 06:00—07:00 in summer and 08:00—09:00 in winter [22, 23]. Such a seasonal cycle of temperature stratification is probably responsible for the formation of the bimodal structure of the morning maximum of CO (08:00 and 11:00), which is well manifested in individual seasons and weakly pronounced in its average annual values due to time shift.

A postmeridian decrease in the concentration of all pollutants, which is characteristic of their diurnal cycle, is caused by the destruction of inversion and the vertical mixing in the ASL. Highly active motor transport during evening rush hours, when the ASL stability increases, results in an increase in the pollution level after its daytime minimum at 14:00—15:00 and, for NO, after 18:00. Evening maximum pollutant concentrations occur at 22:00 (23:00 for NO). If the morning maximum of NO prevails over its evening maximum, the evening maximum of NO$_3$ is significantly higher than its morning maximum. The interaction of NO, NO$_2$, NMHC, and O$_3$ forms their state, which is close to the photochemical equilibrium and determines the features of their diurnal variations. The photochemical imbalance (manifested, in particular, in a time shift of the evening concentration maximum of NO (with respect to NO$_3$)) occurs as a result of the formation of NO in reactions of NO$_2$ with SO$_2$ [13]:

$$\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{SO}_3;$$

$$\text{H}_2\text{O} + \text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{H}_2\text{SO}_4.$$ (1)

The diurnal variability of CO—a pollutant chemically less active than nitrogen oxides—depends, to a great extent, on its accumulation in the subinversion layer, which is manifested in its rapid evening maximum. The diurnal variability of O$_3$ (Fig. 5) is characteristic of most large cities. On workdays, its minimum concentration is observed at 07:00 and 23:00, and its maximum concentration is observed at 15:00. On Sundays, the morning minimum of O$_3$ is not observed, because the traffic is not as intensive when compared to workdays, and its chemical sink in reaction with NO decreases [24].

The anthropogenic methane sources—leakages from the gas-supply system, housing sector, both sewage and treatment systems, etc.—are weakly dependent on the time of day and a day of the week. The diurnal cycle of CH$_4$ is determined by the number of daylight hours, air temperature, weather conditions, and variations in the ASL vertical stratification. The CH$_4$ diurnal cycle may be used as an indicator of the influence of inversions on the level of pollution in the megacity. The method of estimating the emissions of CH$_4$ and other substances from both natural and anthropogenic sources according to the rate of methane accumulation in the subinversion layer was proposed in [25]. Extracting the methane 24-h harmonic from all observational data series, one can obtain diurnal variations in the intensity of urban pollutant sources and the activity of photochemical processes.
From Friday evening and throughout the entire subsequent night, the CO, NO, NO₂, and NMHC concentrations exceed their values for this time of the day on other days of the week. Thus, the nightlife of the city at the end of the workweek is most active. However, from the early morning on Saturday, the concentrations of these pollutants and PM₁₀ become significantly lower than on workdays. In the Sunday diurnal cycles of CO and NMHCs, their characteristic morning maximum vanishes, and, for NO₂ and PM₁₀, this maximum becomes hardly noticeable.

5. WEEKLY CYCLE

Weekly variations in the pollutants show the dependence of their concentrations on the activity of their sources that affect the composition of the atmosphere over the Moscow megacity during a week. Day-
time concentrations averaged over an interval of 07:20—00:00 and average night concentrations within an interval 00:20—07:00 (Moscow time) were used to obtain the weekly cycle of the pollutants. In [13], the weekly variations within a period of 2005—2014 were obtained using the Fourier analysis, followed by the synthesis of oscillations with periods of no more than 8 days by the method of inverse Fourier transforms. However, before using the Fourier analysis, it was necessary to retrieve omissions in the observational data series for each pollutant at each MEM station. After the oscillation synthesis, the data omissions returned to their places and weekly cycles were calculated for each station and, on average, for the city for each season using the superimposed epoch method (SEM). The classical SEM, in which all Sundays of time series served as reference points, is used in this work. As a result, the average (over 16 years from 2005 to 2020) week of variations in average pollutant concentrations for Moscow was obtained for each pollutant individually for daytime and nighttime (Fig. 6).

The weekly cycle demonstrates the so-called “weekend effect” (SE)—a decrease in the level of urban air pollution on Saturday-Sunday. Relative variations in pollutant concentrations during an average week were calculated from the formula

$$\delta = \frac{D - WD}{WD} \times 100 \%,$$

where D is the pollutant concentration for each day of the average week and WD is the average concentration from Tuesday to Friday inclusive (on workdays). The SE is clearly manifested in weekly cycles calculated using the whole data volume (Fig. 6). On workdays from Tuesday to Friday, the pollutant concentrations vary slightly. The daytime concentrations of CO, NO, NO₂, NMHCs, and PM₁₀ maximally decrease on Sunday. On Saturday, the daytime decrease in their concentrations amounts to about 40—50% and, on Monday, the decrease amounts to 20—30% of their Sunday daytime values. The night from Sunday to Monday is characterized by the lowest night pollutant concentrations, which is explained by lowest activity of motor transport and breaks in the work of many industrial enterprises.

The situation with variations in the concentration of O₃ at the weekend is quite opposite. On Saturday, its daytime concentration is higher than on workdays and, on Sunday, its concentration reaches maximum values for a week. On Monday, the night concentrations of O₃ exceed its night concentrations for other weekdays. On Monday, in the daytime, the SE for O₃ vanishes. On the weekend, a slight decrease in the concentration of CH₄ is observed in the daytime and at night; however, this decrease is insignificant. Natural gas as a fuel is used by only a few percent of the total vehicle fleet; therefore, the temporal cyclicity of traffic slightly affects the methane weekly variations.

Leakages of CH₄ in the gas-supply system and its emissions from other sources, including natural ones, slightly depend on weekdays.

Table 3 gives the relative values of the decrease in pollutant concentrations on Sunday (SE), which are

| Pollutant | Daytime | Nighttime |
|-----------|---------|-----------|
| CH₄       | -0.1 ± 0.3 | -0.3 ± 0.4 |
| NMHCs     | -10.4 ± 3.2 | -4.1 ± 3.8 |
| PM₁₀      | -13.9 ± 4.3 | -8.2 ± 5.2 |
| CO        | -15.1 ± 3.0 | -4.3 ± 4.1 |
| NO        | -27.2 ± 2.0 | -13.7 ± 5.9 |
| NO₂       | -18.4 ± 2.4 | -10.3 ± 3.5 |
| O₃        | 13.6 ± 4.7 | 9.1 ± 6.3 |

Fig. 6. Weekly pollutant concentration variations (δ, %) averaged over the 2005—2020 measurement period and the entire megacity area for daytime (07:20—00:00) nighttime (00:20—07:00).

Table 3. Average (over the 2005—2020 period and all urban stations) pollutant concentration variations in the atmospheric surface layer on Sunday in relation to workdays (Tuesday—Friday)
averaged over the entire 2005–2020 observation period. The daytime (07:20–0:00) variations show that the concentrations of the pollutants decrease on Sunday in relation to their values averaged over Tuesday–Friday, and the nighttime variations show that, during the night from Sunday to Monday (00:20–07:00), their concentrations decrease in relation to their average values for the same time within the Tuesday–Saturday period.

The maximum SE is observed for NO. Its daytime and nighttime values amount to 27.2 and 13.7%, respectively. The minimum SE is observed for NMHCs; its daytime and nighttime values amount to 10.4 and 4.1%, respectively. The intermediate SE is observed for NO_2 (18.4 and 10.3%, respectively). As for the SEs for PM_{10} and CO, their daytime values are approximately the same (14–15%) and the nighttime values amount to 4–8%. On Sunday, the concentration of ozone, unlike the other pollutants, exceeds its values on workdays by 13.6% in the daytime and 9.1% at night. The SE nighttime values averaged over the 16-year period are significant only for NO, NO_2, PM_{10}, and O_3.

6. SEASONAL VARIATIONS

Seasonal variations in the concentrations of the pollutants in the urban air are determined by weather conditions and the activity of their anthropogenic sources. There is some relation between these factors. The operation of the centralized heating system from October to April noticeably affects the anthropogenic emissions of CO; NMHCs; NO_2; and, to a lesser extent, the other pollutants. Almost all Moscow heat power enterprises operate on natural gas. However, in winter, at very low air temperatures, liquid fuel may additionally be used, which results in a rapid increase in pollutant emissions. Within such periods, larger amounts of natural gas are burned in the residential sector, which increases the emissions of CH_4. In heat power engineering, liquid fuel is most often used in February, when the air temperature in central European Russia decreases to extremely low values. The frequent occurrence of stable stratification in the ASL is also observed in February, which additionally contributes to the accumulation of pollutants. Both NMHCs and CO, which are among the basic mazut combustion products, have clearly pronounced February maxima in their seasonal concentrations (Fig. 7). Such an increased power consumption in February is also accompanied by both PM_{10} and NO_2 emissions. Low seasonal temperatures affect not only the operation of heat and power enterprises, but also the activity of motor transport. Under such weather conditions, it takes much more time and fuel to warm up an internal-combustion engine; at low temperatures, the fuel is not completely burned out in these engines, which

![Seasonal monthly average pollutant concentration variations averaged over the megacity and the 2005–2020 measurement period.](image)
leads to additional emissions of NMHCs and CO—the products of liquid fuel combustion (Fig. 7).

The summer (June—July) minimum pollution level in Moscow is caused by low economic, business, and social activities due to the season of vacations and the departure of Muscovites outside the city, as well as the washing out of some pollutants from the ASL due to the rains common at this time of the year [23] and the maximum height of the ASL. One more seasonal maximum of the pollutants is formed in August—September due to the increased activity of motor transport after vacations and before the start of the school year. The main maximal seasonal concentrations of suspended particles PM10 are observed in April—May and in the absence of grass cover, the wind lifts soil particles and sand, dry leaves, and de-icing agent residues accumulated on roadsides during the winter into the air. The situation is exacerbated by vehicles that still use winter studded tires, which greatly increases the wear of the roadway and aerosol emissions into the atmosphere, as well as the advection of smoke aerosol from the burning of dry grass and agricultural waste. Minimum PM10 concentrations are observed in winter, when the soil is under the snow layer and the abrasion of cold road surfaces and tires is insignificant.

The seasonal cycle of O3 in the urban atmosphere is the manifestation of its global variability in the troposphere of the Northern Hemisphere, the characteristic features of which are its maximum concentrations in spring and minimum concentrations in fall [26]. The influence of the city is manifested in the activation of both ozone-formation and destruction processes in photochemical reactions with nitrogen oxides and volatile organic compounds (VOCs). In spring—summer, high UV radiation levels and high contents of VOCs of both anthropogenic and natural origins contribute to more active ozone formation processes when compared to those outside the city, and, in fall—winter, low UV radiation levels and low biogenic VOC contents contribute to ozone destruction processes. As a result, there is an increase in the summer maximum of ozone and its winter minimum when compared to Moscow’s surroundings. The photochemical system, which is characteristic of Moscow, is a higher sensitivity of the ozone formation rate to variations in VOCs than to those in nitrogen oxides [13]; as a result, there is no secondary maximum of O3 in July—August, which is characteristic of many other large cities.

The highest NO concentration is observed in the cold season, which is associated with an intensive fuel combustion and a high stability of the atmospheric boundary layer during this season. The maximum concentration of NO2 formed in the reaction of NO with O3 coincides with the spring maximum of ozone, and its concentration decrease in fall coincides with the fall minimum of ozone.

The amplitude of seasonal variations in methane (CH4) is the smallest one when compared to the other pollutants, because, due to its long lifetime, methane is well mixed in the atmosphere. In winter, when night temperature inversions are long and frequent and there is almost no convection, methane is accumulated in the ASL. The summer minimum concentration of methane is additionally enhanced due to its oxidation by hydroxyl radical OH; the higher the concentration of it, the higher the concentrations of ozone and water vapor. The seasonal cycle of methane is only slightly affected by permanent urban pollutant sources.

7. LONG-TERM VARIATIONS AND TRENDS

The annual average pollutant concentrations averaged over the entire area of the Moscow megacity are given in Fig. 8 and Table 4. Table 4 also gives the linear trend estimates and their significance calculated as a ratio of the standard deviation to the quadratic root of sample size. Since the NO/NO2 ratio in NO varies with time, the long-term variations in both NOx concentrations and emissions are given in the mass units of nitrogen [μg N m^−3].

The concentrations of all pollutants except for ozone decreased within 2005–2020; however, their concentrations were extremely high in the first 2–3 years and, by contrast, the concentration of ozone was extremely low. This may easily be explained if we go back to the time of the MEM network establishing. The distribution of continuously operating automatic stations over the territory of Moscow was considered an extension of the capabilities of the operating air pollution monitoring system (Russian Service for Hydrometeorology and Environmental Monitoring) that measured CO, SO2, NO2, and aerosol concentrations four times a day. In the 1990s, there were serious problems associated with the operation of this system, which noticeably affected the quality and amount of data [27]. The priority task of establishing the MEM automated stations was to timely reveal pollution sources that could be the cause of extreme ecological situations. Therefore, the MEM stations were located in places in which anomalously high pollution concentrations were most frequently observed, which resulted in overestimated average levels of air pollution. The number of stations increased with time, and both measuring means and methods were improved. The efficiently operating modern air-pollution monitoring system covering the entire area of Moscow and its surroundings had been established by 2007–2008. Since then, the values of trends in pollutant concentrations may be considered characteristic of the city as a whole.

Decreased CO, NOx, NMHC, and PM10 concentrations in Moscow within the observation period are, first and foremost, associated with the closing down or removal of large industrial enterprises from Moscow, the upgrading of heat power enterprises and their conversion to gas, and the improvement of the transport structure. Upon a general increase in the number of cars, a
decrease in motor transport emissions was due to the transition to new car models with high-temperature fuel combustion, the restriction of the entry of both freight and transit vehicles into the city, the use of eco-friendly types of fuel, the modernization of the road network and filling stations, and the development of the public transport network [https://mosecom.mos.ru; 18].

The rate of decrease in the atmospheric CO content depending mainly on motor transport amounts to $-4.0\% \text{y}^{-1}$ (Table 4). The rate of decrease in the content of nitrogen oxides (NO$_x$) is noticeably lower ($-2.6\% \text{y}^{-1}$), because a significant portion is associated with the combustion of natural gas at heat and power plants and in the housing sector. The highest

Table 4. Annual average surface pollutant concentrations [μg m$^{-3}$] averaged over all stations and their trends [% y$^{-1}$] calculated for the 2007–2020 period. The NO$_x$ values are given in units of mass nitrogen concentration [μg N m$^{-3}$]

| Year | CO     | NO$_x$ | CH$_4$ | PM$_{10}$ | NMHCs | O$_3$ |
|------|--------|--------|--------|-----------|--------|-------|
| 2005 | 870 ± 39 | 39.9 ± 3.2 | 1471 ± 40 | 30.0 ± 3.8 | 334 ± 20 | 16.7 ± 0.3 |
| 2006 | 792 ± 39 | 38.4 ± 2.4 | 1436 ± 37 | 28.0 ± 1.3 | 325 ± 23 | 24.8 ± 2.1 |
| 2007 | 683 ± 28 | 35.2 ± 1.6 | 1425 ± 33 | 28.8 ± 1.5 | 279 ± 37 | 30.5 ± 2.0 |
| 2008 | 626 ± 24 | 32.9 ± 2.5 | 1340 ± 14 | 27.7 ± 1.3 | 271 ± 21 | 27.6 ± 2.5 |
| 2009 | 587 ± 30 | 26.3 ± 1.7 | 1336 ± 22 | 23.5 ± 1.1 | 241 ± 26 | 28.2 ± 1.2 |
| 2010 | 745 ± 26 | 27.9 ± 1.3 | 1300 ± 31 | 34.5 ± 1.7 | 295 ± 36 | 30.4 ± 1.9 |
| 2011 | 618 ± 93 | 23.2 ± 1.8 | 1260 ± 22 | 22.2 ± 1.6 | 217 ± 30 | 38.8 ± 3.3 |
| 2012 | 534 ± 53 | 24.1 ± 1.2 | 1346 ± 13 | 20.4 ± 1.3 | 197 ± 16 | 28.8 ± 1.7 |
| 2013 | 483 ± 37 | 24.2 ± 1.3 | 1340 ± 17 | 21.0 ± 1.0 | 224 ± 20 | 31.0 ± 4.4 |
| 2014 | 489 ± 41 | 24.3 ± 1.6 | 1353 ± 16 | 27.0 ± 1.5 | 226 ± 22 | 27.9 ± 1.9 |
| 2015 | 449 ± 34 | 21.3 ± 1.9 | 1334 ± 17 | 23.5 ± 0.8 | 197 ± 14 | 29.8 ± 2.0 |
| 2016 | 421 ± 28 | 22.5 ± 2.3 | 1376 ± 24 | 20.9 ± 1.0 | 163 ± 14 | 27.6 ± 2.5 |
| 2017 | 395 ± 24 | 22.1 ± 2.8 | 1374 ± 23 | 19.3 ± 1.1 | 136 ± 6 | 26.3 ± 1.8 |
| 2018 | 408 ± 23 | 22.4 ± 2.0 | 1358 ± 19 | 21.3 ± 1.6 | 158 ± 8 | 31.7 ± 1.9 |
| 2019 | 372 ± 23 | 19.7 ± 2.6 | 1330 ± 15 | 24.7 ± 1.3 | 148 ± 9 | 29.9 ± 2.5 |
| 2020 | 355 ± 23 | 20.8 ± 2.6 | 1368 ± 17 | 23.5 ± 1.0 | 127 ± 9 | 28.2 ± 1.4 |
| Trend, % y$^{-1}$ | $-4.0 ± 0.5$ | $-2.6 ± 0.4$ | $0.1 ± 0.2$ | $-1.7 ± 0.9$ | $-4.3 ± 0.5$ | $-0.4 ± 0.7$ |
rate of decrease was observed in the concentration of nonmethane hydrocarbons (−4.3% y⁻¹), which have the same anthropogenic sources as CO and NOₓ, but biogenic sources noticeably contribute to their content [28, 29]. In recent years, the repair and modernization of engineering structures associated with wastewater treatment have been carried out. At the same time, since the city territory is being intensively built up, urban green areas have decreased; therefore, biogenic emissions of NMHCs have also decreased.

Measures episodically taken to improve the urban transport structure and optimize road traffic together with intensive road constructions have led to significant changes in PM₁₀ concentrations from year to year. However, on the whole, the aerosol pollution of the urban atmosphere is still the main factor that negatively affects the air quality in the Moscow megacity. The rate of decrease in the PM₁₀ concentration amounts to −1.7% y⁻¹. There is no significant trend in the ozone content in the urban air. The slight increase in CH₄ and the decrease in CO, PM₁₀, and NMHCs in 2020 were apparently due to decreased business and transport activities within the quarantine period associated with the coronavirus infection.

Interannual variations in the average annual pollutant concentrations are caused, to a greater extent, by variations in the weather condition. The most pronounced effect of variations in solar radiation and high air temperatures is manifested in ozone concentration variations. A blocking anticyclones of record duration, anomalously high air temperatures, and both forest and peatbog fires in Moscow’s nearest surroundings resulted in a record increase in the concentrations of most pollutants, which affected their average annual values. This situation has been described in detail in several papers (see, for example, [30, 31]).

Significant year-to-year variations are observed in the concentration of methane that has both anthropogenic and biogenic sources. In 2005–2008, extremely high CH₄ concentrations were recorded at 8 MEM stations located in Moscow’s problem zones (including the Salar’ev landfill to the southeast of Moscow) and equipped with instruments with a low sensitivity to CH₄. In 2009–2012, the number of stations measuring CH₄ concentrations increased to 14 and new instruments with a lower sensitivity threshold were installed, which diluted observational data with values that are close to background ones. In 2008, the Salar’ev landfill was closed and, in 2009, it was completely mothballed using waterproofing materials and soil. In 2010, in Moscow, the modernization of gas distribution stations got under way and the MPR was closed for reconstruction. These events concurred with drought consequences and peatbog fires in Moscow’s surroundings in 2010, which resulted in decreased methane concentrations in 2010–2011. A slight increase in CH₄ concentrations from 2012 to 2020 is the result of a rapid increase in the megacity population and the construction and gasification of new residential zones. No significant interannual CH₄ variations were observed within this period, which is associated with a large number of stations (no less than 24) measuring CH₄.

8. EMISSION ESTIMATES

The 2005–2020 observational data obtained at the MEM network make it possible to calculate the average annual anthropogenic emissions of CO, NOₓ, NMHCs, CH₄, and PM₁₀ and their variations over the 16-year period. The method (described in [12, 18]) based on the use of a box model [32] was employed for these calculations. Pollutant flux per unit area and per unit time F and total pollutant amount Q arriving in the air mass passing through the city territory over time τ are equal [18]:

$$ F = \frac{\Delta C_i H}{\tau}, \quad Q = FS, \quad (3) $$

where S is the city area, H is the mixing layer height, and ΔC_i is the average impurity concentration at the city territory minus the regional background value (urban addition).

The upper boundary of the mixing layer was determined according to vertical temperature profiles measured at Ostankino Tower. The average annual H values vary from 230 to 260 m. The time during which an air mass was located over the city was determined under the assumption that its territory is close to circular in form. Average wind velocity values within the mixing layer were determined from sodar observational data obtained at the Meteorological Observatory at Moscow State University (the observation method is described in [33]) and surface data obtained at Moscow meteorological stations. The average wind velocity over the city territory and the entire observation period within the mixing layer (0−245 m) is 4.9 m s⁻¹. The average annual wind velocity values vary within 10%. At such wind velocities, the average time during which the air mass is over the city territory is approximately 3.5 h.

Observational data obtained at three MEM stations located 35, 40, and 53 km from the city center under clean-air conditions were used as background concentration values. The distribution of anthropogenic pollutants within the mixing layer is not uniform in height. Gradient observations at Ostankino Television Tower and a 300-m meteorological tower in Obinsk (2003−2017) showed that the NOₓ, CO, and CH₄ concentrations, on average, decrease with height; moreover, about 30−40% of this decrease occurs within the lower 25-m layer. These observational data were used in recalculating surface concentrations into their average values for the mixing layer [18].

The time variability of the city area from 1950 km² in 2005 to 2300 km² in 2020 was taken into consider-
ation in calculating annual integral emissions $Q$. Figure 9 gives the estimates of the CO, NO$_x$, NMHC, CH$_4$, and PM$_{10}$ emissions from Moscow for a period of 2005–2020. The NO$_x$ emissions are given in nitrogen mass units. In this case, the emissions of NO$_x$ do not depend on the ratio between NO and NO$_2$ at the outlet from the source. However, many researchers determine NO$_x$ emissions under the assumption that, during fuel combustion, NO$_x$ is emitted into the atmosphere in the ratio of 90% NO to 10% NO$_2$. In such a case, 1 g NO$_x$ = 2.26 g N.

The character of variations in average annual urban emissions $Q$ (Fig. 9), on the whole, corresponds to pollutant concentration variations and is determined by the effects of the same factors, which is evident. Some differences are caused by the influence of meteorological processes that favor the accumulation or removal of the pollutants from the atmosphere and, thus, change their surface concentrations at the same activity of their sources. One example is the situation observed in the summer of 2010. The duration of surface inversions rapidly increased under blocking conditions, which favored the accumulation of CO and NMHCs and an increase in their surface concentrations [30]. In this case, both CO and NMHC concentrations were characteristic of this time of the year, because the traffic activity did not change. To a lesser extent, similar differences are pronounced in NO, due to their active destruction under the conditions of high air temperatures and UV radiation. Another reason for such differences may be variations in the atmospheric composition under the influence, for example, of natural fires. Thus, a slow distribution of forest and peat-bog combustion products over the megacity territory resulted in a rapid increase in aerosol concentrations at relatively slight emission variations.

Within the observation period, the largest decrease was noted for both CO and NMHC concentrations. Their main sources are associated with motor transport: for CO, direct emissions of fuel combustion products and, for NMHCs, in addition to exhaust gas emissions, the evaporation of bitumen from roadbeds and motor fuels at filling stations and during their production at the MPR and transportation. Such a rapid increase in the number of cars had significantly slowed down by 2007. The switch to new ecologically cleaner car models and fuel types compensated for the increase in both CO and NMHC emissions. However, the large-scale reconstruction of the Moscow road network began in 2012–2015. At the same time, the longest traffic congestions in the world were recorded. In connection with this, stringent measures were taken to limit the passage of trucks and motor cars through Moscow. Electric buses began operating on Moscow passenger routes in 2018. All these processes determined such a step-by-step decrease in the key pollutant concentrations.

However, the simultaneous modernization of the road network, the construction of new highways and road junctions, and earthwork operations during the construction of buildings for various purposes increased aerosol emissions, which was manifested in a slightly positive PM$_{10}$ trend after 2012. The construction boom was only slightly reflected in both NO$_x$ and CH$_4$ emissions into atmosphere. The extension and gasification of the housing facilities were compensated for by the modernization of heat and power plants and engineering communications. The quarantine introduced in 2010 slightly affected the average annual emissions of all pollutants.
CONCLUSIONS

The processed and filtered long-term observational data obtained at the MEM network and the pollutant concentration distribution functions constructed and analyzed for each station have made it possible to increase the quality of data and the reliability of their statistical analysis. The detailed structure of diurnal, weekly, and seasonal cycles and the features of distribution over the Moscow megacity have been revealed and analyzed for the pollutants determining the urban air quality: NO, NO₂, CO, CH₄, NMHCs, O₃, and PM$_{10}$. In the diurnal cycle of all pollutants except for ozone, their extremely high concentrations are noted when both morning and evening traffic activities concur in time with surface temperature inversions. The characteristic feature of the weekly cycle is a significant decrease in the concentrations of CO, NO$_x$, NMHCs, and PM$_{10}$ on Sunday and their smaller decrease on Saturday and Monday morning. Their maximum and minimum night concentrations are observed on Saturday night and Monday night, respectively. The weekly concentrations of ozone are in antiphase, and the concentration of CH$_4$ remains constant within a week. Such a close relation between the concentrations of CO, NO$_x$, NMHCs, and PM$_{10}$ and the activity of urban sources is also observed in their seasonal variations.

The characteristic feature of the state of the urban photochemical system is a high sensitivity of the oxidation power of the atmosphere to the content of VOCs (NMHCs form their chemically active portion). As a result, the generation rate of ozone and many other toxic compounds depends first on the content of VOCs of both anthropogenic and natural origins, UV radiation, and air temperature and is weakly dependent on the content of NO$_x$. Therefore, unlike many other cities, the concentration of ozone remained almost invariable for many years in Moscow, because its increase due to a decrease in the NO$_x$ content is compensated for by its decreased generation rate during the oxidation of VOCs. This property of the Moscow atmosphere is possibly responsible for there being no noticeable ozone increase in 2020, when the anthropogenic effect noticeably decreased within the quarantine period.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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