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Variations of Organic and Inorganic Atmospheric Boundary Layer Gaseous Species by Observations in Moscow and Zvenigorod

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Abstract: Anthropogenic pollution of the atmosphere with organic and inorganic gaseous species has been studied using constant high-quality monitoring of the atmosphere composition both in megacity of Moscow and in its countryside. The article considers continuous measurements of the main climatically and chemically active atmospheric gaseous species concentrations, including volatile organic compounds. The main attention is paid to the comparative analysis, mainly between the megacity and its suburban area, by average species concentrations and some quality features of their seasonal and diurnal variations. The obtained results confirmed the previously studied features of the daily variations of inorganic gaseous species in Moscow and showed such features for organic compounds in the countryside.

Keywords: minor gaseous species of the atmospheric boundary layer, volatile organic compounds, seasonal and daily variations of concentrations.

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1. Introduction

Currently, in the course of human production activities, a significant amount of various chemical compounds is emitted into the atmosphere. New compounds appear in the atmosphere that were previously either absent on Earth at all, or were present in insignificant quantities. This leads to changes in the composition of the Earth's atmosphere and its radiative and dynamic properties. As a result of these processes, the climate of the Earth is changing [*GAW WMO*, 2012].

Numerous adverse consequences of the impact of atmospheric pollution on the human environment require a thorough study of the processes leading to global shifts in the concentrations balance of atmospheric species. One of the main research methods for this is the constant monitoring of the main air pollutants concentrations.

At the national level in the Russian Federation, such monitoring is carried out by Roshydromet. In addition, monitoring of the atmospheric air composition is carried out in Moscow by BEPI "Mosecomonitoring", and in St. Petersburg – by SBU "Mineral". Also, the monitoring of atmospheric air composition parameters is carried out by observation stations, created on the initiative of some academic and branch scientific institutions. Among them, the Institute of Experimental Meteorology RPA "Typhoon" (Obninsk), the Institute of Atmospheric Optics of the Siberian Branch of the Russian Academy of Sciences (Tomsk), and some others should be mentioned. Similar stations for observing the composition of the atmosphere also operate at the A. M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences (hereinafter – IAP RAS).

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2. Equipment and observation technique

Observations in Moscow were carried out on the territory of the IAP RAS at Pyzhevsky per., 3, (Central administrative okrug, Yakimanka district), in the courtyard of the building. In the vicinity of the observation site there are streets with fairly heavy traffic, residential buildings and offices of institutions. In the countryside, the observations were carried out on the territory of the Zvenigorod Scientific Station (hereinafter – ZSS) of the IAP RAS (Moscow region, Odintsovsky city okrug, village Novoshikhovo). This observation site is placed more than 1 km away from highways and rural residential areas. There are no industrial enterprises and other sources of air pollution in the vicinity.

Measurements of the concentrations of minor gaseous species in the atmospheric surface layer were carried out using automated integrated hardware and software systems developed and manufactured at the IAP RAS (hereinafter – complexes) [*Berezina et al.*, 2020, 2022]. The complexes are built on the basis of a set of measuring instruments manufactured by leading foreign and domestic manufacturing companies.

Table 1 shows the main parameters of the instruments used for observations in Moscow, and Table 2 shows the instruments used for observations at the ZSS. As can be seen from the tables, the instruments used make it possible to determine impurity concentrations in a very wide range, from values significantly exceeding the maximum permissible concentrations to values typical of an unpolluted atmosphere.

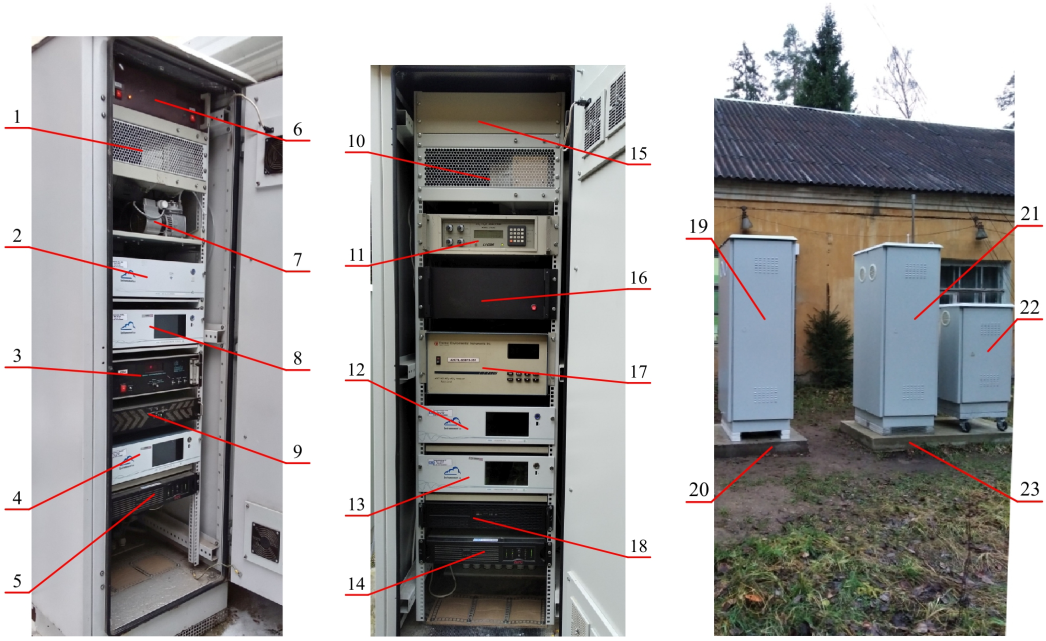
Table 1. Equipment used for observations in Moscow.

No.	Instrument type	Manufacturer	Measured parameter	Measurement range	Accuracy	Response time
1	1008AH	Dasibi Inc. (USA)	O_3 concentration	1–1000 ppb	±1 ppb	60 s
2	TE48S	Thermo Inc. (UAS)	CO concentration	0.05–10 ppm	±1%	60 s
3	AC32e	ENVEA Inc. (France)	NO, NO_2 and NH_3 concentrations	0.2–1000 ppb	±1%	40 s
4	AF22e	ENVEA Inc. (France)	SO_2 concentration	0.4–1000 ppb	±1%	60 s
5	G2132-i	Picarro Inc. (USA)	CH4 concentration	1.8–12 ppm	±5 ppb	30 s
			CO_2 concentration	200–2000 ppm	±1 ppm	
			H_2O concentration	0–2.4%	±0.01%	
			$\sigma^{13}C$	—	±0.8‰	
6	HC51M	ENVEA Inc. (France)	CH4 and NMHC concentrations	0.05–10 ppm	±1%	60 s
7	MTP-5	LLC RPO ATTEX (Russia)	Vertical temperature profile in 0–600 meters layer	−30–+30 °C	±1.0 °C	5 min
8	ACAT-3M	RPA "Typhoon" (Russia)	Atmospherics pressure	800–1080 hPa	±0.5 hPa	0.08 s
			Air temperature	−40–+50 °C	±0.5 °C	
			Air relative humidity	10–100%	±5%	
			Wind direction	0–360 deg.	±5 deg.	
			Wind speed	0–40 m/s	±0.2 m/s	
9	HMP-233	Vaisala Oyj (Finland)	Air temperature	−40–+50 °C	±0.1 °C	15 s

The complex for observations at the ZSS included a unique (according to some information, the only one at Russia territory) device for measuring the concentrations of a number of volatile organic compounds (VOCs) in the surface air, the Compact PTR-MS proton mass spectrometer manufactured by Ionicon Inc. (Austria). The device is based on the so-called method of proton mass spectrometry. This method was first developed in 1995 at the Institute of Ion Physics of the University of Innsbruck (Austria) [*de Gouw and Warneke*, 2006]. In recent years, instruments of this type have become widely used for observing VOCs concentrations in the atmosphere [*Belousov et al.*, 2018; *Berezina et al.*, 2020, 2022; *Jordan et al.*, 2009; *Taipale et al.*, 2008].

A feature of the complexes is location of all their components not in laboratory rooms, but in the so-called all-weather racks installed outdoors at the observation sites. Such a technical solution ensures fire safety of continuous and round-the-clock operation of the devices of the complexes, and also eliminates interference with the work of personnel from significant noise generated by operating devices. To accommodate the equipment of the complexes, rack of the ShKK-42U and ShKK-24U models manufactured by the Telecom Group company (Russia, Belgorod) were used.

Figure 1 shows an internal view of racks with open doors in Moscow and at the ZSS, as well as a general view of the placement of racks at the observation site at the ZSS.



(a) **(b)** **(c)**

Figure 1. Internal views of all-weather racks in Moscow (a) and at the ZSS (b) and a general view of the location of all-weather racks at the ZSS territory (c).
1, 10 – ventilation grille; 2 – converter for measurement of ammonia ENVEA CNH3; 3 - ozone gas analyzer Dasibi 1008-AH; 4 – SO_2 gas analyzer ENVEA AF22e; 5, 14 – uninterruptible power supply; 6 - power supply unit of the meteorological complex; 7 - compressor unit for ENVEA AC32e instrument; 8 – NOx gas analyzer ENVEA AC32e; 9, 18 – registering computer; 11 – CO_2 gas analyzer Li-Cor LI6262; 12 – ozone gas analyzer ENVEA O342e; 13 – CO gas analyzer ENVEA CO12e; 15 – plug of the power supply socket; 16 – compressor unit for Thermo TE-42CTL instrument; 17 – NOx gas analyzer Thermo TE-42CTL; 19, 21 – all-weather racks ShKK-42U; 20, 23 – ferroconcrete pedestal; 22 – all-weather rack ShKK-24U.

The PTR-MS instrument was periodically calibrated using permeation tubes. The calibration procedure was in detail described in [*Berezina et al.*, 2022]. Functioning checking and calibration of other instruments is carried out out at least quarterly, using calibration gas mixtures manufactured by the company "Linde Gas Rus" (Russia, Balashikha), with accuracy of about 4%. Zero shift checking and correction of most instruments was carried out automatically, using built-in scrubbers, at least daily or even more often.

A specialized part of the software of the complexes is used for primary processing of observational data in order to remove data classified as unreliable. First of all, automated software processing is performed, and then all data is viewed by a specialist. As a result, data series of concentrations of all measured gas and aerosol species and meteorological parameters are formed, with averaging over intervals of 1 minute, 20 minutes, 3 hours (corresponding to the standard period of meteorological observations) and 1 day.

Table 2. Equipment used for observations at ZSS.

No.	Instrumen type	Manufacturer	Measured parameter	Measurement range	Accuracy	Response time
1	O342e	ENVEA Inc. (France)	O_3 concentration	0.2–10,000 ppb	±1 ppb	20 s
2	CO12e	ENVEA Inc. (France)	CO concentration	1–300 ppm	±1%	35 s
3	TE42C-TL	Thermo Inc. (USA)	NO and NO_2 concentrations	0.05–200 ppb	±1%	60 s
4	LI6262	LI-COR Inc. (USA)	CO_2 concentration	1–3000 ppm	±1 ppm	1 s
5	HC51M	ENVEA Inc. (France)	CH_4 and NMHC concentrations	0.05–10 ppm	±1%	60 s
6	Compact PTR-MS	Ionicon Inc. (Austria)	Acetylene, methanol, acetonitrile, acetaldehyde, ethanol, 1,3-butadiene, butenes, acetone, acetic acid, isoprene, methyl vinyl ketone, peroxyacetyl nitrate, benzene, monoterpenes, toluene, phenol, styrene xylenes, propylbenzene and trichloroacetic acid concentrations.	0.5–1000 ppb	±0.5 ppb	0.5 s
7	Vantage Pro 2	Davis Inc. (USA)	Atmospherics pressure	880–1080 hPa	±0.1 hPa	2.5 s
			Air temperature	−40–+65 °C	±0.5 °C	10 s
			Air relative humidity	1–100%	±3 %	2.5 s
			Wind direction	0–360 deg.	±7 deg.	2.5 s
			Wind speed	1–67 m/s m/s	±1 m/s	2.5 s
			Precipitation amount	0–9999 mm	±0.25 mm	10 s
8	WXT536	Vaisala Oyj (Finland)	Atmospherics pressure	6001100 hPa	±0.5 hPa	15 s
			Air temperature	−52–+60 °C	±0.3 °C	
			Air relative humidity	0–100%	±3%	
			Wind direction	0–360 deg.	±3 deg.	
			Wind speed	1–60 m/s	±3 %	
			Precipitation amount	0–200 mm/h	±0.01 mm	

3. Analysis of results

One of the significant parameters characterizing the patterns of variations of gaseous boundary concentrations in the atmospheric surface layer is their monthly averaged concentrations. Figure 2 shows diagrams of monthly averaged concentrations obtained from observational data in Moscow and at the ZSS during 2022 and part of 2023.

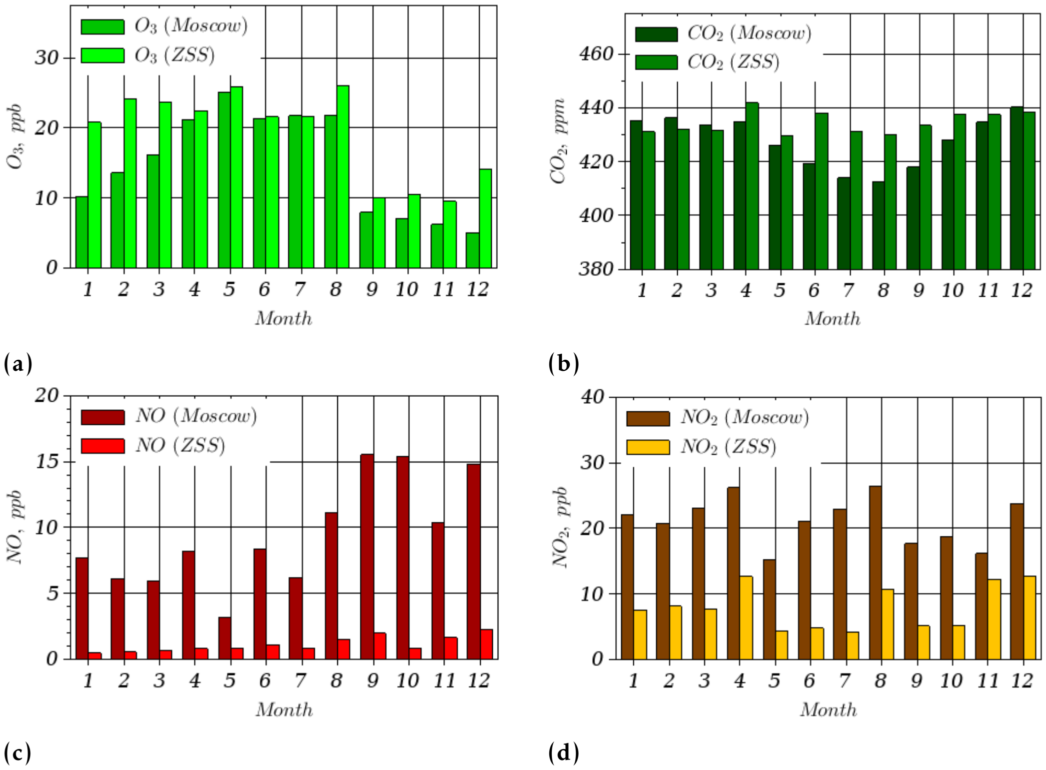


Figure 2. Monthly averaged concentrations of gaseous species in Moscow and at the ZSS.

The performed analysis confirms the previously studied [*Elansky et al.*, 2007, 2015] features of the seasonal course of the ozone concentration with a pronounced maximum in the spring. In winter, solar illumination is low, and ozone depletion on the underlying surface in the presence of snow cover is also small. With the onset of spring, the illumination increases, and ozone generation increases, but the ozone sink does not increase, since the snow cover has already disappeared, and green vegetation has not yet appeared. This leads to an increase in average ozone concentrations in the spring period. In summer, when there is green vegetation, the ozone sink increases and the average ozone concentration decreases.

A similar character of seasonal variations in ozone concentration is also observed for the countryside. The decrease in the ozone concentration in the winter period is less pronounced, which may be due to the overall lower atmospheric pollution in the suburban area with species that react with ozone, which will be discussed below.

The seasonal course of the concentration of nitrogen dioxide and monoxide, in general, does not show pronounced variations during the year. As is known [*Elansky et al.*, 2015], the main source of air pollution in cities is motor transport, the intensity of which in winter is now decreasing slightly [*Elansky et al.*, 2018]. Attention is drawn to significantly (more than an order of magnitude) lower values of nitrogen oxide concentrations in the countryside than in the metropolis of Moscow, which is explained by significantly lower emissions of these species.

The seasonal course of carbon dioxide is characterized by a slight decrease in average monthly concentrations in summer, which is usually associated with plant respiration processes, as well as with a decrease in the intensity of urban heating systems [*Elansky et al.*, 2015]. In the countryside, the anthropogenic contribution to the growth of CO_2 concentration is significantly less than in the metropolis, which, apparently, leads to smaller seasonal variations in CO_2 concentration.

The seasonal variations in VOCs concentrations in the countryside are of significant interest. According to available information, at the moment there are no publications of the results of observations by the PTR-MS instrument in Russia outside megacities in the scientific periodical press. Figure 3 shows graphs of monthly averaged concentrations of some VOCs. Seasonal variations of the same VOCs in the metropolis were previously studied using the same instrument and published in [*Belikov et al.*, 2019]. In particular, it was found that the concentrations of acetone and acetic acid increase in summer, which can be explained by an increase in the volatility of these substances with an increase in air temperature. As can be seen from the above diagrams, in the suburban area, these substances show a similar pattern of seasonal variations.

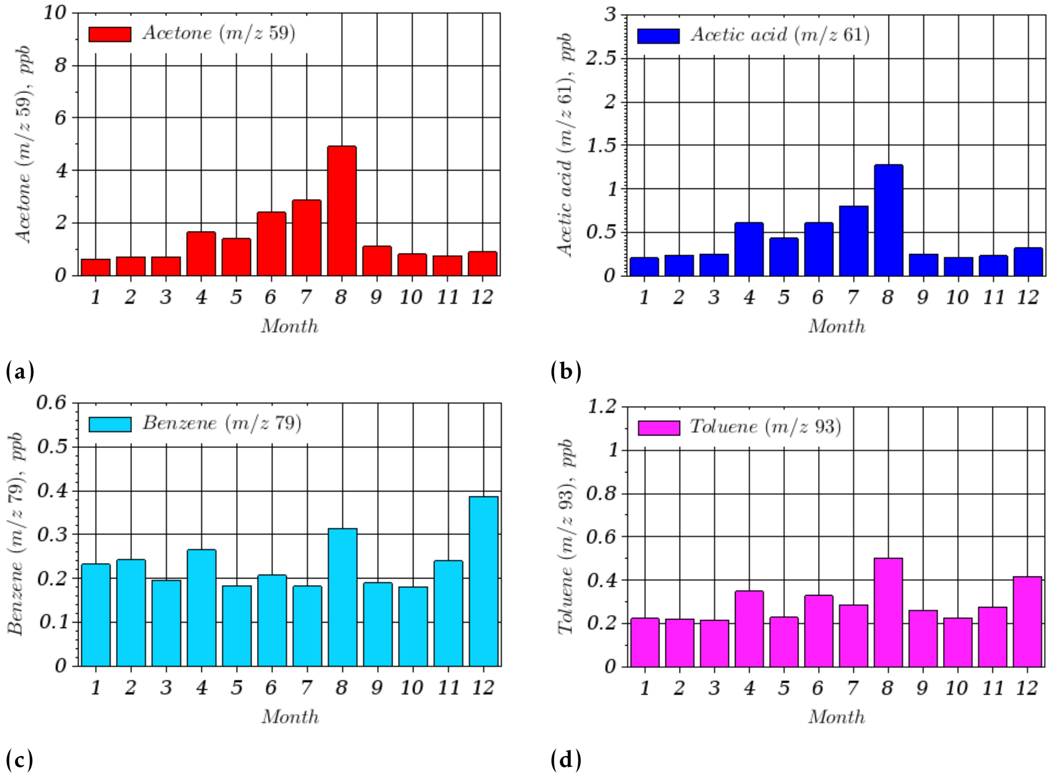


Figure 3. Monthly averaged concentrations of VOCs at the ZSS.

The significance of the detected seasonal variations can only be determined after accumulation of sufficient (several years or even more) observation statistics. In the above diagrams, a significant peak of impurity concentrations in August 2022 attracts attention. Figure 4 shows a diagram of the monthly averaged air temperature in 2022 and for 2019–2021. As can be seen from the diagram, in August 2022 there was a clear excess of the average monthly temperature over the average over the past 3 years by more than 5 °C. Apparently, this anomaly was the reason for the significant increase in impurity concentrations.

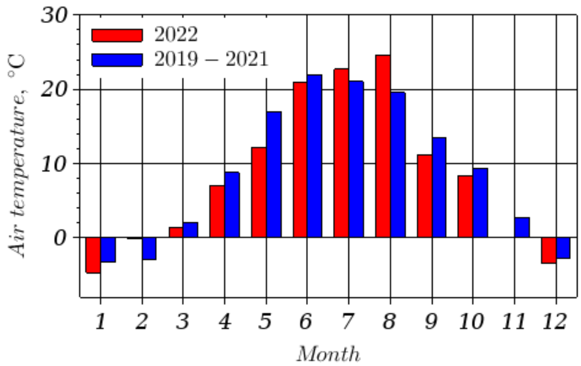
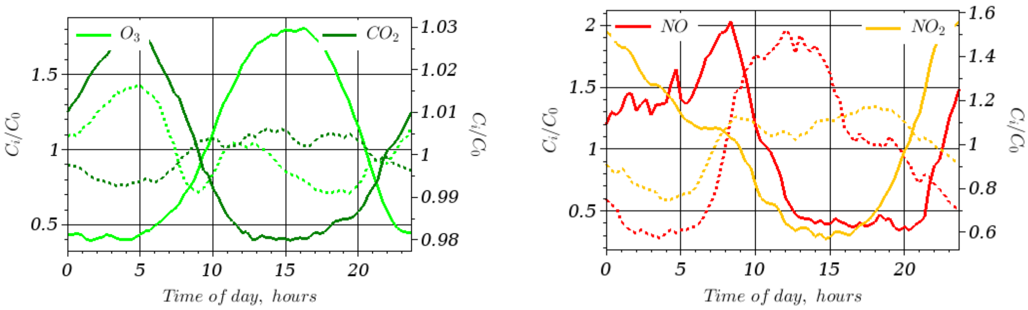


Figure 4. Monthly averaged air temperatures in 2022 year and for 2019–2021 years.

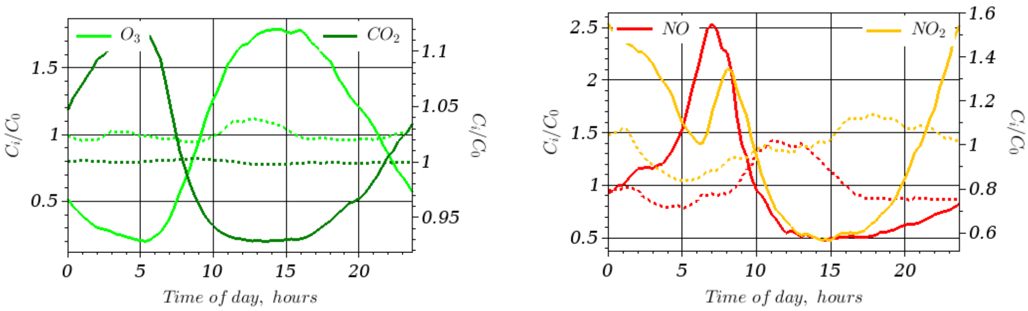
Another significant parameter that characterizes the patterns of variations in the concentrations of gaseous boundary in the atmospheric surface layer is their diurnal variations in different seasons of the year.

Figures 5 and 6 show diagrams of diurnal variations (relative to Moscow local time UTC +3) obtained from observations in Moscow and at the ZSS in winter (December to February) and summer (June to August) periods of the year. In order to exclude the effect of daily variations in the concentration of these species, we analyzed the ratio of a single concentration Ci (for 20 min) to the daily averaged concentration Cc for a given day.



(a) **(b)**

Figure 5. Diurnal variations of species in Moscow in summer (solid lines) and winter (dotted line) periods.



(a) **(b)**

Figure 6. Diurnal variations of species at ZSS in summer (solid lines) and winter (dotted lines) periods.

For diurnal variations, confidence intervals were also calculated for the probability of 0.95, which turned out to be equal to 0.05–0.10 of the ratio of Ci to Cc. Confidence intervals are not shown in the graphs given to preserve the clarity of the display.

The analysis performed also confirms the features of diurnal variations in surface concentrations of nitrogen monoxide and nitrogen dioxide previously studied [*Elansky et al.*, 2007, 2015]. In summer, these variations are characterized by the presence of two pronounced maxima in the morning and evening, and periods separating them with lower values in the middle of the day and in the early morning. During the cold period, in the daytime, the temperature inversion, as a rule, persists, and does not collapse, as in the warm period, which leads to the formation of an extended period of high impurity values throughout the day. Diurnal variations in ozone concentration in winter are characterized by daytime and nighttime maxima and morning and evening minima, which are explained by an increase in car traffic in the metropolis, leading to an increase in nitrogen oxide emissions and a decrease in ozone concentration. During the warm period, the diurnal variation of ozone is characterized by a pronounced maximum in the daytime, when the photochemical generation of this gas in the atmosphere is most intense [*Elansky et al.*, 2007, 2015, 2022].

In the countryside (Figure 6), the nature of the daily variations of the considered species is preserved, but much less pronounced, which can be explained by less anthropogenic pollution of the atmosphere.

The nitrogen monoxide concentrations peaks at Figure 5 between 0:00 and 5:00 o'clock could be explained by complex pollutant emission sources at the densely built area surrounding the measuring site [*Berezina et al.*, 2022]. Measurements at the ZSS (Figure 6), where there are no such emission sources, don't show such peaks, as well as measurements at the site in Moscow, but located far from local emission sources [*Elansky et al.*, 2007].

The patterns of diurnal variations in VOCs in the countryside area are of great interest. Figure 7 shows the diurnal variations obtained from the PTR-MS observations on the ZSS.

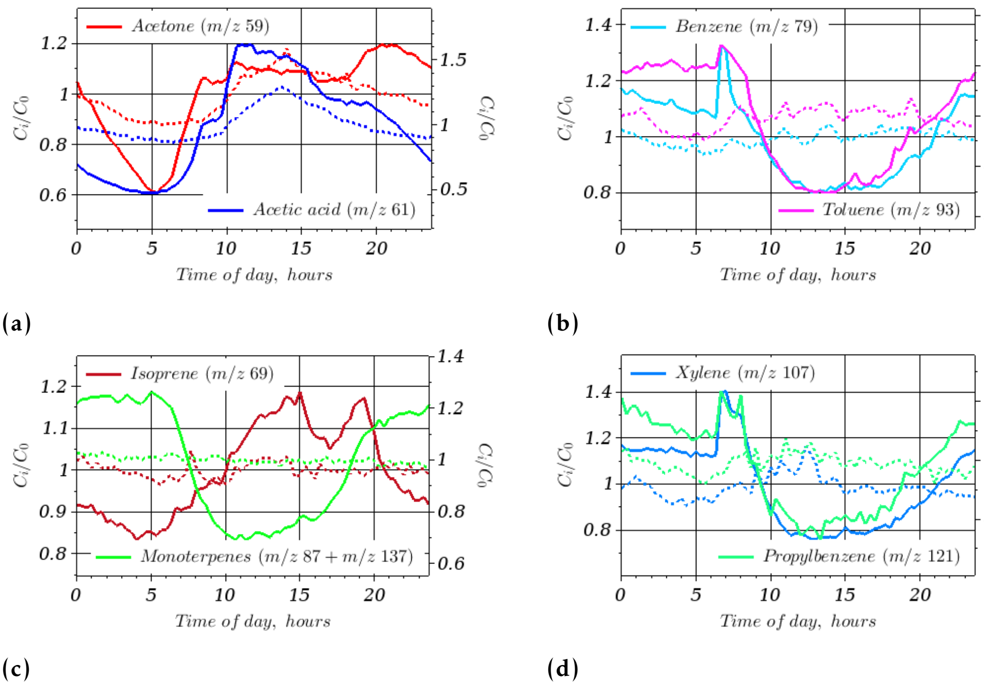


Figure 7. Diurnal variations in VOCs at ZSS in summer (solid lines) and winter (dashed lines).

The diurnal variations of such VOCs as acetone and acetic acid are completely similar to those for observations in a metropolis [*Belikov et al.*, 2019; *Berezina et al.*, 2020, 2022; *Jordan et al.*, 2009]. The concentrations of these VOCs, both in the metropolis and in the countryside, have a pronounced maximum in the daytime, and a minimum - at night. Variations in the concentrations of anthropogenic VOCs, in particular, benzene and toluene, on the contrary, are characterized by their increase at night due to accumulation under the inversion layer. Similar results were previously obtained for the same VOCs for observations in a metropolis [*Belikov et al.*, 2019]. The diurnal variation of isoprene concentration is similar to that of acetone and acetic acid, while the diurnal variation of monoterpenes concentration is similar to that of benzene and toluene, i.e. characterized by their accumulation under the inversion layer.

The results of data analysis are generally in good agreement with previous observations [*Belikov et al.*, 2019; *Berezina et al.*, 2020, 2022; *Elansky et al.*, 2007, 2015; *Gubanova et al.*, 2018; *Jordan et al.*, 2009], which indicates the representativeness of the data obtained.

4. Conclusions

The performed analysis of the data shows the following characteristic features of variations in surface concentrations of gaseous species, as well as volatile organic compounds in both the metropolis and countryside:

- significantly lower concentrations of nitrogen oxides in the countryside than in the metropolis, which is explained by a significantly smaller number of sources of their emissions (mainly vehicles) in the suburban area;
- low concentrations of almost all measured VOCs in the surface air, much lower than their maximum allowable concentrations;
- pronounced diurnal variations in anthropogenic VOCs: benzene and toluene, with their accumulation in the boundary layer during the nighttime temperature inversion;
- an increase in the concentrations of almost all VOCs, especially acetone and acetic acid vapors, with an increase in air temperature during the transition from spring to summer seasons.

With the accumulation of data series of continuous observations of gaseous species concentrations in the atmospheric boundary layer in Moscow and at the ZSS, their analysis will be continued in the future. The data obtained will also be used to estimate emissions of atmospheric pollutants, in particular, according to the methods described in [*Berezina et al.*, 2022; *Elansky et al.*, 2018, 2022].

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