RESULTS OF CLIMATIC–ECOLOGICAL MONITORING AT THE TOR STATION.
II. GASEOUS COMPOSITION OF NEAR–GROUND AIR

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Gaseous composition and diurnal and annual variations of ozone, carbon oxide and dioxide, and methane in the Tomsk region have been analyzed from the data obtained at the TOR station in 1993. The peculiarities of temporal behavior of concentration of the above–indicated gases have been revealed and discussed. Spatiotemporal scales of their variability have been estimated.

The data on spatiotemporal variability of gaseous composition of air are of interest for estimating the global change of the environment and climate for two reasons. First, the variations of concentration of many gases determine the value of absorption of the solar radiation in the Earth's atmosphere and its radiation budget, intensifying or lessen the total greenhouse effect. Second, a part of gases is the product of anthropogenic activity. So the data on their concentration are indicative of the quality of the environment in one place or another. For the above–listed reasons, routine monitoring of gaseous composition of air became an integral part of the Project of Climatic–Ecological Monitoring of Siberia (CEMS)[1] and was performed at the TOR station of the Institute of Atmospheric Optics.[2]

Recall that the TOR station operated in round–the–clock regime with a data sampling interval of 1 hour. Gaseous composition was determined by means of instruments whose parameters were described in Ref. 2. Concentration of ozone (O_3) and carbon oxide (CO) and dioxide (CO_2) was measured using these instruments. Measurements of methane (CH_4) concentration began on August of 1993. To determine the methane content in air, the KPM–4 gas chromatograph with a flame–ionization detector and a column 2 m long filled with silipore–200 was used. The column temperature was 40°C, the gas–carrier was He, with a rate of flow of 30 ml/min. To calibrate the chromatograph the gas mixture of H–alkanes with He (500 ppm CH_4) was used. An air sample with a volume of 2 ml entered the chromatograph without preliminary concentrating.

This paper of the entitled series is devoted to an analysis of the data on the dynamics of variations of gaseous composition of air in the Tomsk region obtained during 1993 as part of CEMS and TOR Projects.

First we consider the annual behavior of the gaseous components shown in Fig. 1.

Figure 1 *a* demonstrates that the ozone concentration in the Tomsk region sharply increased from January to March (24–64 $\mu g/m^3$). From March to May, its concentration in near–ground air insignificantly decreased down to the first minimum of 54 $\mu g/m^3$ in May, and then increased again up to the second July maximum of 67 $\mu g/m^3$. This is the absolute maximum of the year. From July to September, the concentration decreased down to the second minimum of 24 $\mu g/m^3$. In November, the concentration decreased to its minimum value of 16 $\mu g/m^3$. In December, the ozone concentration slowly increased.

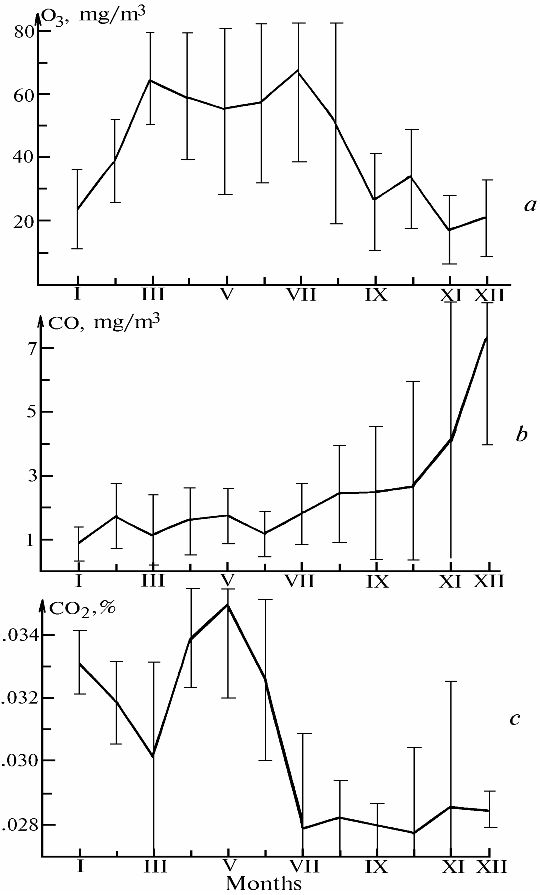

FIG. 1. Seasonal behavior of ozone (a), carbon oxide (b), and carbon dioxide (c) concentration in the Tomsk region in 1993. Vertical bars show the standard deviations.

The ozone variations recorded at the TOR station and averaged over the period from 1989 to 1992 were presented in Ref. 3. The comparison of the plots presented in Ref. 3 with the data obtained in 1993 shows that they are essentially different. The principal single maximum in long–term behavior occured in March, and the minimum was observed in October–November.

Such difference in ozone concentration variation in 1993 and its long–term average behavior can be explained by the peculiarities of air circulation in spring and summer of the

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year under consideration. As was noted in Ref. 3, the ozone concentration increase in the Tomsk region was caused by intensification of the vital activity of plants and by formation of the photochemical smog of natural origin.[4] A heat wave reached the Tomsk region in March of 1993 and made the vital activity of coniferous plants more intensive. They release up to 35 mg/hour·kg of terpenes that provide the basis for photochemical formation of ozone.[5] The prolonged cold period that had come then and lasted till the middle of June, hindered the growth of deciduous trees (they were coming into leaf only at the end of June). This caused the occurence of the second maximum in July (Fig. 1 *a*). It should be noted that such a late maximum of ozone concentration was not recorded from 1989 to 1993. Its occurence may be due to release of isoprene by deciduous trees, with the rate of release of dry residue of leaves varying from 0.3 to 56 mg/hour·kg. As is known, isoprene is one of the elements of photochemical mechanism of ozone formation. Hence, two factors affected the annual behavior of ozone concentration in Tomsk in 1993: the geophysical factor, namely, location of the region in the zone of boreal forests, and the circulation factor.

Annual behavior of the carbon oxide concentration shown in Fig. 1 *b* indicates nearly monotonic increase of its concentration from January to October and sharp increase in November and December. The data obtained in 1994 indicate that CO concentration decreased in January almost 3 times in comparison with December of 1993. The CO concentration values obtained in Tomsk were intermediate between those under background and urban conditions.[7–9] It seems likely that this is due to the location of Tomsk.[2]

The similar annual behavior of CO concentration was reported only in Ref. 10. The only difference is that the concentration maximum occured in October rather than in December; however, the authors of Ref. 10 did not explain this fact.

Carbon dioxide in Tomsk also revealed some peculiarities in its annual behavior in 1993 (Fig. 1 *c*). Its mean concentration varied from 0.0345 to 0.0278%, which is indicative of relatively clear air of the measurement site. The correlation of the shape of the plot in Fig. 1 *c* is greatest with the data generalized in Ref. 11 for the station Barrow Cape. Differences are the intensity of the March minimum and slower recovery of CO_2 concentration in fall. The pronounced decrease of concentration in March can be caused by the fact that we had incomplete data set for this month, as was pointed out in Ref. 12. Prolonged duration of the summer minimum till the beginning of winter in comparison with usually observed annual behavior[13] is possibly connected with the following reasons.

In Lumis[14] opinion, the ecosystem respiration is carbon released in a process of vital activity of plants and microorganisms in soil. Early coming of the fall cold in the Tomsk region leads to the sharp decrease of the intensity of vital activity of plants, and the snow falling in October exhausts the source connected with the activity of microorganisms in soil.

By comparison of three plots shown in Fig. 1, another possible reason of slow increase of CO_2 in fall and winter can be considered. It is that the known cycle of oxidization of CO into CO_2 that is usually realized by the chain[8]

$$\begin{array}{l} CO + OH \rightarrow H + CO_2 \\ H + O_2 + M \rightarrow HO_2 + M \\ HO_2 + O_3 \rightarrow OH + 2\,O_2 \\ \hline CO + O_3 \rightarrow CO_2 + O_2 \text{ (pure cycle)} \end{array}$$

was realized incompletely in 1993.

The data in Fig. 1 show that CO and O_3 concentration is enough for generating CO_2 when other sources are absent. Evidently, disruption in the cycle can be due to the fact that the key component, OH, was not recovered.

According to the data of Ref. 15 for effective oxidization of CO into CO_2 it is necessary that nitrogen oxides were included into this cycle. Then the reaction chain is the following:

$$\begin{array}{l} CO + OH \rightarrow CO_2 + H \\ H + O_2 + M \rightarrow HO_2 + M \\ HO_2 + NO \rightarrow OH + NO_2 \\ NO_2 + h\nu \rightarrow NO + O \ (\lambda < 410 \text{ nm}) \\ O + O_2 + M \rightarrow O_3 + M \\ \hline CO + 2\,O_2 \rightarrow CO_2 + O_3 \text{ (pure cycle)} \end{array} .$$

In this case two gases, CO_2 and O_3, should be generated. This is confirmed by the data shown in Fig. 1. The lack of measurements of NO and NO_2 in our experiment remains the preceding as a hypothesis.

Let us discuss another aspect of the dynamics of variations of gaseous composition. Ecological monitoring is one of the problems of CEMS. The All–Union State Standard on O_3 and CO sets their maximum permissible concentration (MPC) in air of populated areas, namely, the maximum instantaneous and average daily one. Since the TOR station is situated in the populated area, in Tomsk Akademgorodok, let us consider the dynamics of variations of the above–indicated gases from ecological standpoint.

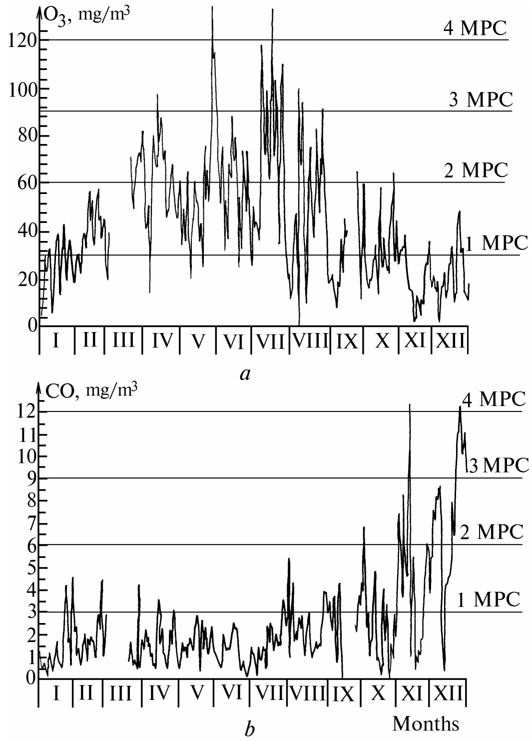

FIG. 2. Average daily concentration of ozone (a) and carbon oxide (b) in Tomsk in 1993. Horizontal lines denote the MPC levels.

The average daily values of O_3 and CO concentration are shown in Fig. 2 for every day of 1993. Ozone concentration exceeds the MPC almost continuously from February to August, and periodically in the rest of months.

Some days the ozone concentration in Tomsk reached 4 MPC. For CO, the pattern is somewhat different. The concentration in excess of MPC was occasionally observed from January to October. In November and December, one could observe long periods during which the concentration exceeded the level of 1–2 MPC, and some days – of 3–4 MPC.

The data of Fig. 2 obtained in the region where industrial enterprises are absent[2] are indicative of the fact that in order to improve the air quality it is necessary to organize and to carry out a number of measures for salvaging our environment.

The interest in investigation of methane is caused by a number of circumstances. It follows from the data of Ref. 16 that 1 kg (1.395 m^3) of CH_4 has 70 times stronger deleterious effect on the atmosphere than 1 kg (0.505 m^3) of CO_2 due to more intensive absorption of the IR radiation. Methane oxidation in the atmosphere leads to generation of formaldehyde, more toxic substance, according to the scheme[17]

$$
\begin{aligned}
&CH_4 + OH \rightarrow CH_3 + H_2O\\
&CH_3 + O_2 + M \rightarrow CH_3O_2 + M\\
&CH_3O_2 + NO \rightarrow CH_3O + NO_2\\
&CH_3O + O_2 \rightarrow CH_2O + HO_2\ .
\end{aligned}
$$

In daylight this cycle transforms and ozone is generated together with formaldehyde[18]:

$$
\begin{aligned}
&CH_4 + OH \rightarrow CH_3 + H_2O\\
&CH_3 + O_2 + M \rightarrow CH_3O_2 + M\\
&CH_3O_2 + NO \rightarrow CH_3O + NO_2\\
&NO_2 + h\nu \rightarrow NO + O \quad (\lambda < 410\ \text{nm})\\
&CH_3O + O_2 \rightarrow CH_2O + HO_2\\
&HO_2 + NO \rightarrow OH + NO_2\\
&NO_2 + h\nu \rightarrow NO + O \quad (\lambda < 410\ \text{nm})\\
&CH_2O + h\nu \rightarrow H_2 + CO\\
&2\,(O + O_2 + M) \rightarrow 2\,(O_3 + M)\ .
\end{aligned}
$$

Thus, methane is one of the key components in a number of problems of atmospheric optics and chemistry. Since boreal forests, marches, lakes, and rivers that are abundant in the Tomsk region are the main sources of atmospheric methane,[19] methane must be included in a set of elements being monitored as part of the CEMS without question.

As is seen from Fig. 3, methane concentration in the Tomsk region varies from 0.7 to 2.25 mg/m^3. The minimum of its concentration was observed in October–December, and the maximum was in summer (August of 1993 and June of 1994).

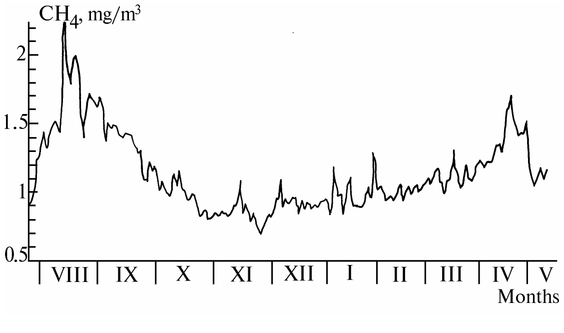

FIG. 3. Seasonal behavior of the methane concentration in the Tomsk region in 1993–1994.

The values obtained are in good agreement with absolute values recorded in the other regions,[7,20–22] but differ by their dynamics. It was pointed out in Ref. 22 that the minimum of CH_4 was observed in summer (August), and the maximum was observed from November to April. Similar behavior was also recorded in Ref. 23. Possible reason of such disagreement is forest fires that are often in summer in the Tomsk region and release a lot of methane into the atmosphere. In cold season the snow cover screens its principal sources.[19]

The data of calculating the correlation coefficient between air temperature and methane concentration over all series shown in Fig. 3 support the last assumption. The value of correlation coefficient between them was 0.77 ± 0.02.

The aforementioned cycle of ozone generation through methane oxidization described in Ref. 18 is confirmed by the correlation coefficient $R(O_3, CH_4)$ calculated from the data obtained in 1993. It was equal to 0.59 ± 0.07, and its significant value was equal to 0.28 at a confidence level of 0.9995 (see Ref. 25).

The dynamics of CO, CO_2, and O_3 concentration variations is manifested through diurnal variations of gases seen from Fig. 4. First of all, it manifests through increasing daily amplitude during the period of seasonal maxima.

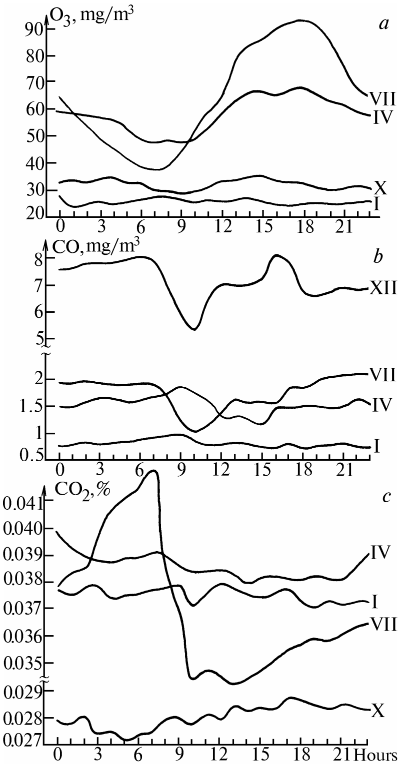

FIG. 4. Diurnal variations of ozone (a), carbon oxide (b), and carbon dioxide (c) concentration in Tomsk in 1993. The Roman numbers adjacent to each curve indicate months.

It is seen from Fig. 4*a* that almost neutral behavior is characteristic of ozone in January, and the amplitude of its variations increases in April and reaches its maximum in July. Diurnal variations in October become again several μg/m^3. Evidently, this is caused by photochemical processes in the atmosphere, where the ozone generation occurs in the daytime, and its sink – at night. The data presented here are in good agreement with classical schemes. They do not differ from the data obtained in the other regions.[4,26]

The diurnal variations of carbon oxide concentration shown in Fig. 4 *b* also tends to increase the amplitude during seasonal maximum periods. However, the patterns of diurnal variations of its concentration depend on the season. At the beginning of a year (from January to April) the maximum of its concentration is observed in the morning (from 7 till 9 a.m.). At the end of a year the well–pronounced minimum is observed.

It is difficult now to explain such diurnal variations because the major part of available data was obtained under urban conditions, where the behavior of CO mainly reflects the motor transport exhausts,[9,10,27–29] that give two diurnal maxima of carbon oxide concentration: in the morning and in the evening. The traffic was not heavy in the observation site,[2] and according to the aforementioned cycles, CO should take an active part in photochemical processes. So the result obtained needs further experimental examination.

In contrast with CO and O_3, diurnal variations of CO_2 do not tend to increase their amplitude during seasonal maximum periods. As is seen from Fig. 4 *b*, the amplitude of diurnal variations of CO_2 is maximum in July, when the minimum is observed in annual behavior (see Fig. 1). During the rest of periods the variation of CO_2 concentration is practically neutral. In July, diurnal variations have standard behavior reflecting the daily rhythm of vegetation activity, namely, respiration and release of CO_2 at night and photosynthesis and absorption of CO_2 in the daytime.[14] It has even reverse behavior in October. Possibly, such a peculiarity of diurnal variation of amplitude of carbon dioxide concentration is connected with vegetation age and its composition. According to the data of Ref. 30, day flux of CO_2 is on the average 10–20% larger than the net assimilation of CO_2 by vegetation. During the most intensive vegetation growth it is less or equal to the net assimilation. When growth stops, its excess can be about 50%. Recall that the period of the most intensive growth of vegetation in 1993 was in July.[12] According to Ref. 31, all kinds of plants can be divided into three types. The first type makes CO_2 fixation at night. The produced organic acids are subject to decarboxylation in the daytime with release of CO_2. The loss of assimilated carbon by photorespiration for the second type of C_3–plants reaches 50% of their pure productivity. And the visible release of CO_2 in the daytime is practically absent for the third group of C_4–plants. Possibly, the maximum growth is alternately observed for one or another type of vegetation during a year.

When measuring the atmospheric parameters in a specific site, the question arises: For what region can the results obtained be extended? The approach developed in Ref. 32 and based on the Drozdov–Shepelevskii method[33] makes it possible to determine the region size with the known structural or correlation function of the corresponding parameter. True, the problem then arises of determining the correlation length, or more exactly, the informative level of the correlation function. There are some approaches to a solution of this problem[34]: the values up to 0.5 are taken as the informative level. In our opinion, since the normalized correlation function is a series of correlation coefficients, one can apply the standard procedure of estimating the confidence level of the correlation coefficient taking into account time delay or spatial shift with which the calculation is made.

The temporal autocorrelation functions of three gases are shown in Fig. 5 for January and July of 1993. The correlation times on a 0.9995 confidence level[25] are shown by horizontal lines for the greatest time delay.

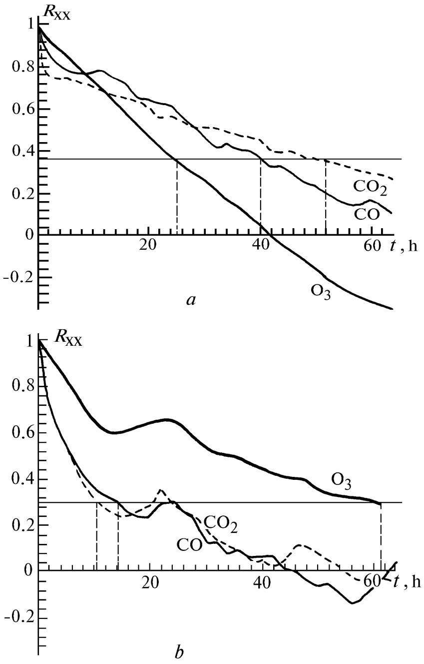

FIG. 5. Temporal autocorrelation functions of gases in Tomsk in January of 1993 (a) and July of 1993 (b).

As is seen from Fig. 5 *a*, the correlation times in January were 22.5, 40, and 52 hours for O_3, CO, and CO_2, respectively. In July their value changed and became 62 hours for O_3, 10.5 hours for CO_2, and 14 hours for CO. This evidently reflects the nature of atmospheric processes in different seasons.

To pass to the spatial scales, let us consider the data on the average wind velocity[12] that was 3.6 m/s in January and 2.4 m/s in July, of 1993. Let us do a transition by the known relationship that connects spatial and temporal correlation functions[35]:

$$R(L + \Delta L) = R\,[\overline{V}\,(t + \Delta t)]\ .$$

The calculated data are given in Table I. As is seen from the table, the scales of data representativity undergo the least change for ozone. Its correlation radius is 292 km in winter and 536 km in summer. Carbon dioxide undergoes the greatest transformation, and its scale decreases from 674 km in winter to 91 km in summer. The same tendency is observed for CO, only it decreases by a factor of four.

To explain these facts in detail, the information is insufficient. So one should consider the data presented in the table as an estimate. Possibly, such differences are caused by cooperative effect of some factors, i.e., the circulation, daily, photochemical, and geographical ones.

TABLE I. Spatial scales (km) of variation of gaseous components in the Tomsk region in 1993.

Month	O_3	CO	CO_2
January	292	518	674
July	536	121	91

In conclusion, it should be noted that we have succeeded in explanation of not all peculiarities of the variations of gaseous composition during 1993. The results presented here reflect only the first stage of monitoring that is being continued now and further it will provide the means for tackling many formulated problems.

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