Investigation of carbon monoxide variability over Russia on the basis of TROICA experiment data

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The paper presents some results of preliminary analysis of the spatial distribution and temporal variability of the CO concentration over continental Russia obtained from measurement data of TROICA experiments along the Trans-Siberian Railway from Moscow to Khabarovsk. It is shown that positive anomalies of the CO concentration in spring are mainly caused by the anthropogenic activity, while in summer they are connected with the biomass burning. The revealed features of the intra-annual variability of the CO concentration are in a good agreement with the observations at the background sites. The main feature of the spatial distribution of carbon monoxide over the continent is an increase of the concentration toward the east in summer and toward the west in spring.

Introduction

Carbon monoxide (CO) is quite a reactive gas and plays an important role in the atmospheric chemistry. Sources of CO are both the anthropogenic activity and biomass burning. The importance of this compound is determined, first, by the role CO plays in the spatial distribution and concentrations of atmospheric oxidants, such as ozone (O_3), hydroperoxy radical (HO_2), and hydroxyl radical (OH). In the troposphere, the reaction of CO with hydroxyl radical provides for 90–95% of the CO sink[6] and up to 75% of the OH sink.[7] It is currently discussed that CO causes recycling of OH and a decrease of the OH residence time in the troposphere, not changing the OH concentration.[5] Since CO is the main partner in reactions with OH and its concentration in the atmosphere is an important index of the state of the climatic system, CO is an object of long-term monitoring.

The measurements of CO at the global network of NOAA stations have shown that CO emissions in highly developed industrial regions and developing countries lead to the change of the global background of carbon monoxide in the troposphere. Meanwhile, the regions of anthropogenic emissions in the mid-latitudes themselves are subjected to the effect of biomass burning in the tropics and boreal forests. On the global scale, the CO concentration decreased by 0.5 ppb a year for the period from 1991 to 2001,[8] while the model estimates predict the increase of the mean global concentration of CO up to 190 ppb by 2100.[12]

It is worth noting the problem of the temporal drift of the CO content in gas standards.[7,8] For this reason, the long-term variations of the CO concentration at a level of 0.5 ppb a year, discussed in Ref. 8, may have a significant uncertainty. This paper discusses large variations of CO, and the reliability of data at this level causes no doubts.

The long CO lifetime in the atmosphere (~2 months) leads to the situation that the effect of some emission sources, for example, forest fires, can determine the air quality over a vast region.[11,13] Until now the significant controversy is observed in the estimated contributions of both natural and anthropogenic CO sources to its global balance. For example, the estimated emission of carbon monoxide due to forest fires in the latitude zone higher than 30°N varies from 50 to 121 Tg CO/yr in different papers.[4] A huge uncertainty exists also in the estimated contribution of forest fires on vast Siberian territories. Thus, the problem of the global and regional balance of CO in the Earth's atmosphere is still to be addressed.

To improve the understanding of the contributions from anthropogenic and natural processes to the carbon monoxide balance over Russia, the Institute of Atmospheric Physics RAS (Russia) in cooperation with the Max Planck Institute for Chemistry (Germany) has organized a series of expeditions using specially equipped ecological laboratory railroad car (TROICA experiments). Preliminary analysis of features in the spatial distribution and seasonal variability of the carbon monoxide concentration obtained from the data of five TROICA experiments is presented in this paper.

1. Measurements

TROICA (Trans-Siberian Observations Into the Chemistry of the Atmosphere) experiments have been conducted since 1995 in order to study the features in the behavior of chemically active and greenhouse gases in the lower atmosphere over continental regions,

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where there are almost no atmospheric monitoring stations and where natural and anthropogenic sources of such gases are concentrated. The experiments are conducted using specially equipped laboratory railroad car, moving as a part of a passenger train along the Trans-Siberian Railway. The detailed description of the objectives and tasks of the experiments, participants, and the instrumentation used can be found in Refs. 2, 9, and 14. For the on-line measurements of the CO concentration in these experiments, a TE48S gas analyzer manufactured by Thermo Environmental Instruments Inc. (USA) was employed. Certified calibration mixtures were used, the zero level was controlled with the use of a SOFNOCAT catalyst (Molecular Products; UK), which efficiently destroys CO. This excludes the appearance of artifacts in the measured CO signals.

The influence of various processes on the variability of the gas composition of the atmospheric surface layer was studied during some expeditions,[1,3] and the effect of the train itself on the measured gas composition was investigated in Ref. 10.

For the period since 1995 through 2004, eight Russian–German TROICA experiments have been conducted. The routes and the periods of the experiments are summarized below in the Table. In this paper, we use the measurements obtained in TROICA experiments 2, 3, 5, 7, and 8.

Routes and periods of TROICA experiments

Experiment	Period	Route
TROICA-1	Nov 17–24, 1995	N. Novgorod–Khabarovsk
	Nov 26–Dec 2, 1995	Khabarovsk–Moscow
TROICA-2	Jul 26–Aug 2, 1996	N. Novgorod–Vladivostok
	Aug 6–13, 1996	Vladivostok–Moscow
TROICA-3	Apr 1–7, 1997	N. Novgorod–Khabarovsk
	Apr 8–14, 1997	Khabarovsk–Moscow
TROICA-4	Feb 17–26, 1998	N. Novgorod–Khabarovsk
	Mar 1–7, 1998	Khabarovsk–N. Novgorod
TROICA-5	Jun 26–Jul 2, 1999	N. Novgorod–Khabarovsk
	Jul 3–7, 1999	Khabarovsk–Novosibirsk
	Jul 11–13, 1999	Novosibirsk–Moscow
TROICA-6	Apr 6–9, 2000	Murmansk–Kislovodsk
	May 23–27, 2000	Kislovodsk–Murmansk
	Jun 23–25, 2000	Murmansk–Moscow
TROICA-7	Jun 27–Jul 3, 2001	Moscow–Khabarovsk
	Jul 4–10, 2001	Khabarovsk–Moscow
TROICA-8	Mar 19–25, 2004	Moscow–Khabarovsk
	Mar 26–Apr 1, 2004	Khabarovsk–Moscow

To study the influence of geophysical conditions and the level of anthropogenic load on the spatial distribution and temporal variations of CO, the whole route of the expedition was divided into four zones with different geographic and meteorological conditions and the level of anthropogenic load:

1) Moscow – Ekaterinburg (East European Plain). It is a region with the high density of anthropogenic pollution sources and subjected to the effect of the transborder transport of pollutants.

2) Ekaterinburg – Novosibirsk (West Siberian Plain). It is a vast plain mostly with forests and wetlands. The role of anthropogenic sources in the pollutant balance is much lower.

3) Novosibirsk – Irkutsk (southern part of the Central Siberian Plateau). It is a large industrial region. In the cold season, it is under the dominant effect of the vast Siberian High, and therefore some pollutants are accumulated in the surface atmospheric layer, because of the practically permanent temperature inversion.

4) Irkutsk – Khabarovsk (Trans-Baikal region, mountains and foothills). Here the railroad passes mostly in mountain valleys, whose pollution level is determined by the presence and intensity of anthropogenic sources, in particular, forest fires and air inflows from China and Japan.

2. Results

2.1. Distribution of the CO concentration in different regions

Figure 1 shows the distribution of the CO concentration observed in the different expeditions. Since the measurements in the different expeditions were conducted at different time, but mostly in the spring–summer period, the effect of the forest and peat fires during summer months (experiments 2, 5, and 7) and powerful anthropogenic sources in spring (experiments 3 and 8) is most pronounced in the CO distribution. It should be noted that the strongest effect of forest fires has been observed in the Trans-Baikal region (zone 4), while peat fires are most pronounced in Moscow region, and powerful anthropogenic sources are present in all zones mostly being associated with big cities and industrial zones. A feature of anthropogenic sources is their unchanged location during all the experiments, while the forest and peat fires are observed at different places of the same region and depend, to a high degree, on weather conditions. Comparing, for example, the summers of 1999 (TROICA-5) and 2001 (TROICA-7), we can see that the former was drier and warmer and was accompanied by the larger number of forest fires as compared to the latter.

In the region of a forest fire, the maximum measured concentrations achieved 3500 ppb in all the experiments. In the most cases, the peak concentrations coincide spatially with urban (populated) regions, and therefore it is quite difficult to separate the contributions of the natural burning and the anthropogenic activity in such regions. The maximum concentrations measured in big cities in the absence of natural burning are also close to 3000 ppb.

The largest number of local peaks of the anthropogenic CO concentration is observed in the Western and Eastern Siberia (zones 2 and 3). The highest concentrations for all the observation periods took place in the region of peat fires near Moscow in summer of 1999 (up to 7 400 ppb), which demonstrates the particular role of low-temperature burning (peat fires), whose efficiency in production of CO is much higher than that of the high-temperature burning.

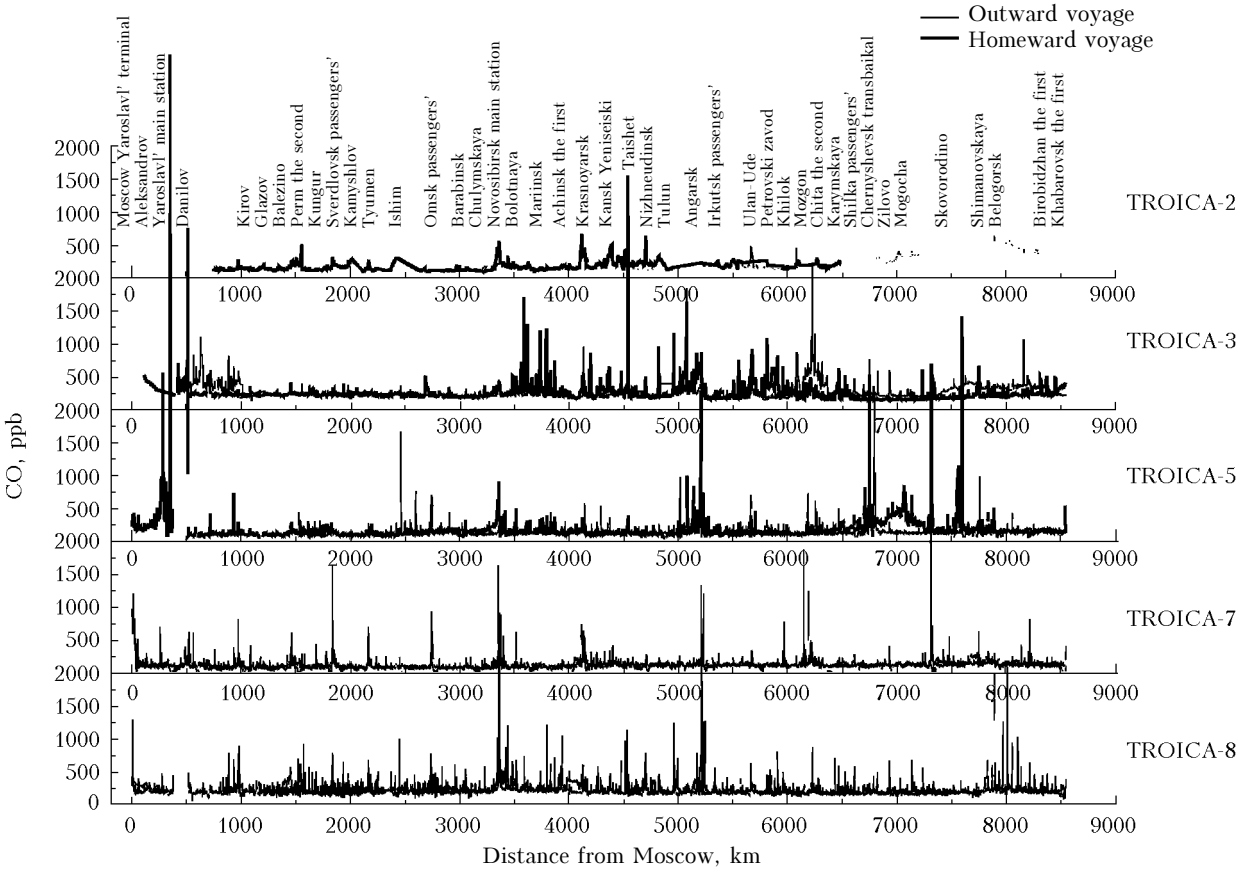

Fig. 1. Spatial distribution of carbon monoxide concentration in TROICA experiments along the Trans-Siberian Railway. The experiment number is indicated on the right.

A distinct feature of "natural episodes" is their extent. In particular, in the regions subject to the effect of forest fires, the extent of the zones of enhanced CO concentration can achieve 1 000 km, while the increased concentration associated with the human activity extends from 5 (in the case of weak sources) to 100 km (plumes of big cities with the wind directed along the railroad). The spatial structure of the CO distribution can be most easily interpreted in the spring, when the uniform background distribution is overlapped by narrow spatial peaks of anthropogenic origin. Such a structure of the CO field is confirmed by the high (up to 0.9) correlation coefficients of CO with nitrogen oxides for some zones, for example, in TROICA-8 experiment.

2.2. Distribution of CO concentration levels (percentals)

To study the variability features of the CO concentration in each geographic zone, the distribution of occurrence of different concentrations (percentals) was drawn for each zone (Fig. 2).

As can be seen from Fig. 2, almost no low CO concentrations were observed in the TROICA-3 and TROICA-8 experiments. The number of cases with the measured concentrations below 150 ppb is respectively 0.5 and 5% for the European part of Russia, 0 and 4% for Western Siberia, less than 0.5% for Eastern Siberia in both of the experiments, and less than 4% for the Far East. At the same time, for the summer TROICA-7 experiment, the number of cases with low values amounts to 80–90, 90–95, 75–80, and about 70% for the corresponding zones.

In the European part of Russia, the number of cases with high concentrations (higher than 500 ppb) does not exceed 4% for all the experiments, except for the outward voyage of TROICA-3 (about 7%). The large number of cases with high concentration values in this experiment may be connected with the use of a diesel generator for 480 km of the trip; these data are not excluded from the further consideration.

In Western Siberia, the number of high CO concentration values does not exceed 3% for all the experiments. In Eastern Siberia, the number of high values does not exceed 4% for all the experiments, except for the homeward voyage of TROICA-3 (about 11%). In the Eastern Siberia, the CO concentration increases along with the concentration of nitrogen oxides for almost 650 km. The cause for this growth is still unclear.

A systematic bias toward increased values was observed in the same TROICA-3 experiment in the Far East. The cause of this bias is also unclear yet. Since in the homeward voyage of the TROICA-3 experiment the laboratory railroad car was at the trail end of the train, the increased CO values may be connected with the coal heating of the train in this part of the route.

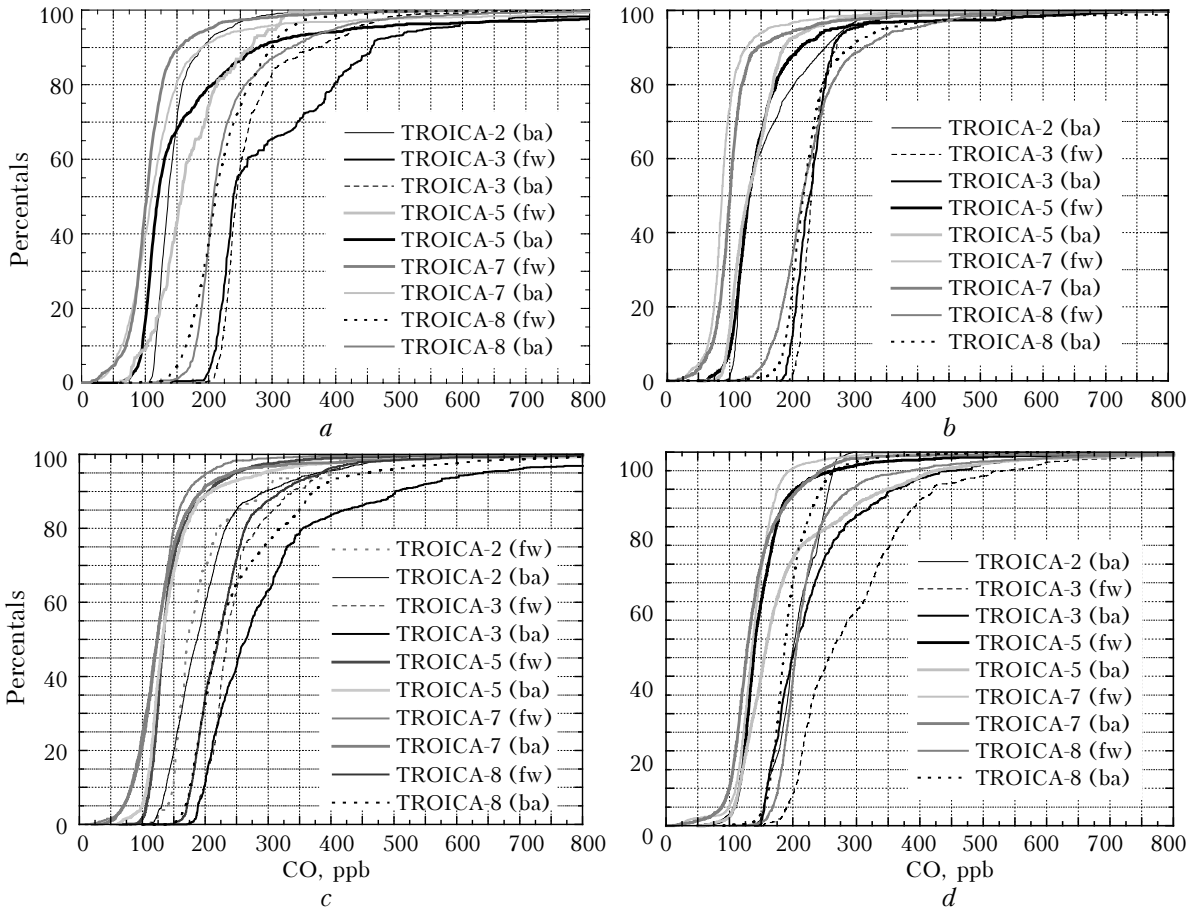

Fig. 2. Distribution of the CO concentration levels for different zones: European territory of Russia and Ural (*a*); Western Siberia (*b*); Eastern Siberia (*c*); Trans-Baikal region and Far East (*c*); outward voyage to the east (fw) and homeward voyage to the west (ba).

It is interesting to note that though TROICA-5 and TROICA-7 were conducted in the same season (with a two-year difference), the values in the former are biased systematically toward higher values in Western Siberia and, to a smaller degree, in other regions. This is likely connected with the interannual features determined by a number of factors, which call for further analysis.

2.3. Annual variations of CO concentration

As a representative (characteristic) concentration for each zone and each experiment, we took the concentrations corresponding to the maximum of the distribution function under the corresponding conditions. Figure 3 depicts the characteristic CO concentrations, which allow estimating both the annual variations for the warm season and the spatial gradients of the concentration between the zones.

In the TROICA experiments, the minimum characteristic CO concentrations have been observed in summer expeditions (June–July). Their values vary from 90–120 to 120–140 ppb in different zones for different experiments. This scatter is explained by the difference in the observation conditions and short time of the observations. The highest concentrations in this period are observed in the Far East, which is connected with a significant influence of forest fires in

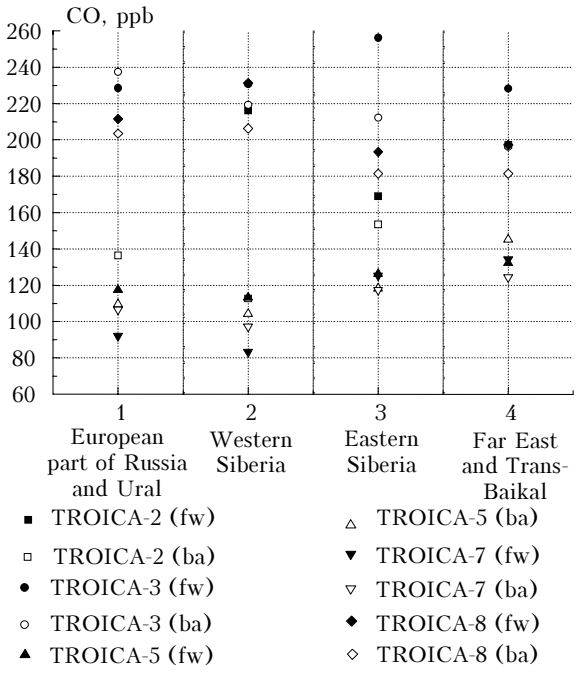

Fig. 3. Distribution of characteristic CO concentrations in different experiments in the selected spatial zones.

this region. However, despite the fact that TROICA-5 and TROICA-7 were conducted in virtually the same season with a two-year interval, somewhat different characteristic concentrations have been obtained in these expeditions. The widest scatter between the values takes place in Western Siberia (about 30 ppb), which is likely connected with different weather conditions in years 1999 and 2001.

The maximum characteristic concentrations are observed in early spring (TROICA-3). Their value amounts to 250–260 ppb for different zones.

Thus, the general tendency in variation of the CO concentration during warm season with higher spring values and decreased summer values is similar to that observed at the most international background stations.[7] The comparison with the data of, for example, the Spitsbergen station indicates that the absolute values of the concentrations exceed the seasonal extremes of remote regions by more than 20 ppb. It should be noted that the performed analysis of the annual variability should be considered as qualitative. The time-limited data set does not allow us to draw a rigorous conclusion about the seasonal behavior, since the measurements were conducted only in spring and summer and in different years. In this case, the seasonal variability may overlap with the long-term variability of the concentration.

2.4. Spatial gradients of the CO concentration

Figure 3 clearly demonstrates the spatial gradients of the CO concentration in different seasons. In the summer months (June–July), the maximum concentrations are observed in the Far East, while the minimum values take place in Western Siberia. This spatial structure can be connected, on the one hand, with the presence of powerful natural sources of CO in summer in the Far East (forest fires) and in the European part of Russia (peat fires) and, on the other hand, with peculiarities of local circulation in some regions.

In April, the maximum CO concentration is observed over Eastern Siberia. In this region, the characteristic concentration is minimum as compared to other zones in March. At this month, the maximum characteristic concentration is observed over Western Siberia. The maximum values of the CO concentration in the cold period over Siberia are likely connected with the high density of anthropogenic sources in this region (the strongest effect of the heating season).

Generally, it can be concluded that the characteristic CO concentration increases eastward during summer months and westward in spring.

Conclusions

The investigations carried out have allowed us to estimate qualitatively for the first time the contributions of the anthropogenic and natural factors to the variability of the CO concentration observed. It is shown that in the spring period the positive anomalies of the CO concentration are mostly attributed to the anthropogenic activity, while in the summer period they are connected with biomass burning. The revealed features of seasonal variations (in the spring–summer period) are well within the global pattern of the CO variability.

The presented preliminary analysis of a large array of unique measurements conducted during the TROICA experiments forms the basis for further investigation into the features of the CO concentration variations over the continent, the determination of the mechanisms of short-period variability, the estimation of the effect of individual factors, such as forest fires, urban conditions, temperature inversions, and others. These issues will receive sufficient attention in our following publications.

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