

## Carbon monoxide and aerosols contents, boundary layer parameters and estimation of the CO sources intensity in Moscow city.

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The results of measurements of the carbon monoxide total content, the soot and submicron aerosols content are given for the period 2005-2008 over Moscow. Two identical grating spectrometers of medium resolution ( $0,2\text{cm}^{-1}$ ) are used with appropriate solar tracking systems, one of which is located outside the city at Zvenigorod Scientific Station (ZSS  $56^{\circ}\text{N}$ ,  $38^{\circ}\text{E}$ , 60km West from Moscow in the rural zone) and the other one is inside a city center. This method makes possible to determine urban part of the CO content. Some simultaneous measurements of aerosols content, the CO column and CO background concentrations in Moscow, autumn 2007 are presented. The nephelometer and quartz soot sampling filters were used for aerosols measurements. Correlation coefficients between aerosols, CO background concentration and urban part of the CO content were obtained. Permanent sounding of boundary layer was carried out using acoustic locator (SODAR) LATAN-3. Applications of SODAR data (profile of wind speed and inversion height) makes possible to forecast air pollution situations in megacities area. We obtained the correlation coefficients between the urban part of the CO content with the wind speed for cold and warm seasons. Results of measurements analysis demonstrated preeminent influence of the wind in certain boundary layer (up to 500m) upon the CO extension. Systematization of CO diurnal variations for different meteorological conditions was performed. The intensity of CO sources in Moscow was estimated. Comparing our results with the results of earlier measurements period (1993-2005), we can obtain the air pollution trend from the averaged air pollution measured values. The urban part of the CO content in the surface air layer over the city did not increase in spite of more than tripled number of motor-vehicles in Moscow for period 1993-2008.

Keywords: carbon monoxide, total column, urban part of content, concentration, megacities, ABL

### 1. Introduction

Carbon monoxide plays an important role in photochemistry of regional and urban environments where, depending on the concentrations of nitrogen oxides ( $\text{NO}_x$ ) and hydrocarbons [1, 2], CO can produce ozone, which correlate with photochemical smog and haze [2, 3]. Although in most urban areas, the CO concentrations of concern are generated by combustion processes such as in automobiles, farther away from such sources the majority of CO comes from the atmospheric oxidation of methane and other hydrocarbons. An increase of CO is likely to cause a decrease of OH and  $\text{O}_3$  in the troposphere resulting in extensive chemical feedbacks. Carbon monoxide is therefore an intermediary in determining the future concentrations of many environmentally important trace gases. The global budget and trends of CO are therefore of considerable environmental importance.

At present, the pollution of the urban air by different gases, including carbon monoxide, is monitored mainly with the methods reduced to measurements of gas content

in local air samples [4]. In this approach, there are some difficulties in obtaining mean gas concentrations and their trends characterizing urban-air pollution. These difficulties are related, for example, to the need of a sufficiently large number of observation sites, to the choice of their arrangement to exclude the influence of local gas sources.

In Russia, a spectroscopic method of measurement of the total atmospheric column gas content from its absorption of solar radiation has been developed and used for several decades to monitor and validate the results of satellite carbon monoxide (CO) measurements and to study the pollution of the urban atmosphere by carbon monoxide [4–7]. The main advantage of this method is that the results averaged over a significant open path and the atmospheric column almost does not depend on local or even on individual large-scale pollution sources. Moreover, this method makes it possible to determine the characteristics of anthropogenic pollution of the urban air by carbon monoxide through a comparison of the CO contents measured at two observation sites (one located outside a city and the other one in its center).

## **2. Equipments and methods**

A sun tracking Ebert/Fastie-type grating spectrometer with 855mm focal length and a grating of 300 grooves/mm was employed for measuring absorption spectra of the atmosphere. It has a resolution of approximately  $0.2 \text{ cm}^{-1}$  at the 2152-2160  $\text{cm}^{-1}$  spectral region, signal to noise ratio better than 100 [4]. The CO total content is determined on absorption in a line R(3) of the CO fundamental band ( $2158.30 \text{ cm}^{-1}$ ). The sodar was used for measurements of wind profiles and qualitative analysis of the vertical structure of the atmospheric boundary layer (ABL). The sodar was operated with 120 cm parabolic dish antennae, 100 ms sounding pulses at 1700 Hz carrier frequency. The height coverage is 20-600 m with 20 m height resolution [8]. Nephelometer and quartz filters for soot sampling were used for aerosols measurements and surface concentration data were obtained by electrochemistry analyzer.

## **3. The main results.**

The CO contents above a city varies from day to day from values close to the background content to values that are 2.5 - 3 times larger than the background value (fig.1). These variations are determined by changes of meteorological conditions, mainly by a wind velocity. In winter, the results of measurements are noticeably affected by temperature stratification, i.e. the presence of ground and raised temperature inversions during measurements.

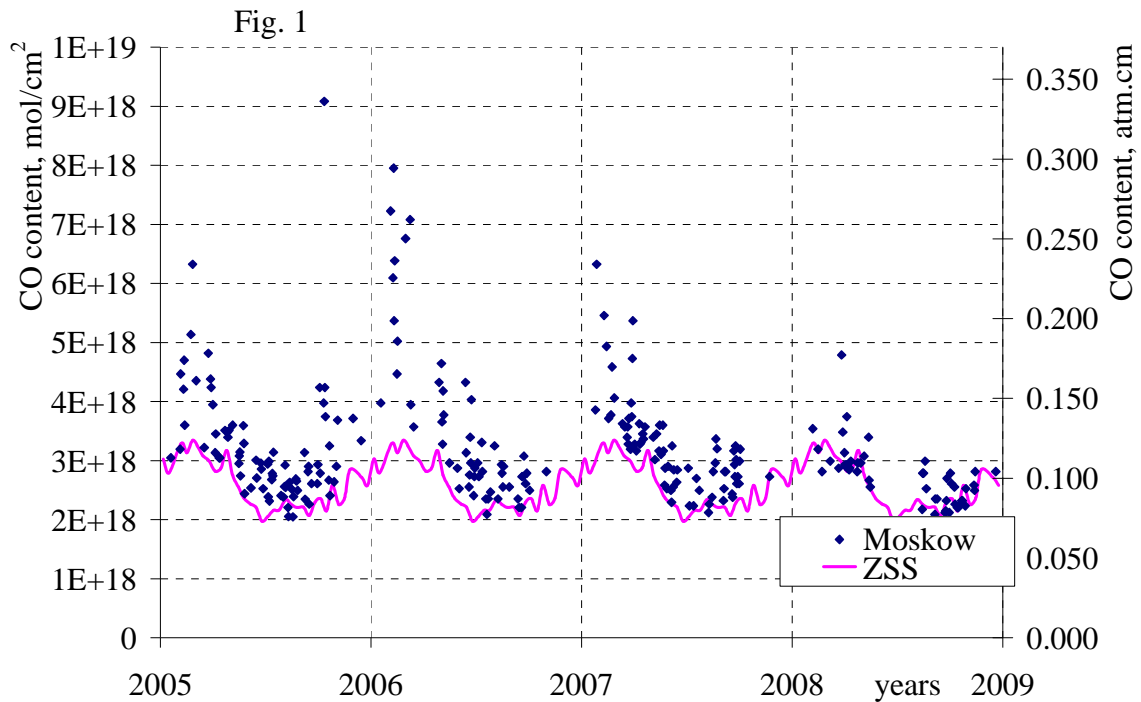


Fig.1. CO total column over Moscow and Zvenigorod

The highest contents of CO are observed during prolonged anticyclone situations, which cause the accumulation of CO of urban origin in the boundary layer. The U values that are two or more times larger than the background values are infrequent, i.e. the number of days with such high content is about 3%. Diurnal variations with a pronounced maxima (the total CO content changed within the limits of more than 80% of the minimum values during the day), are observed in almost 20% of all cases. In 30% of the cases, the maximum of CO content is insignificantly pronounced (the total content varies within the limits of 30–80%). The diurnal variations with slightly pronounced (less than 30%) variations of the total CO content during a day are observed in 50% of cases [7].

Analyzing the results we obtained for the 1993-2007 the recurrence frequencies distribution of the urban part of the CO total content  $\Delta U$  (Fig. 2a). The recurrence frequencies of  $\Delta U = (0.15 - 0.20)$  atm.cm and  $\Delta U > 0.20$  atm.cm do not exceed 2 and 0.5%, respectively. The cold seasons are characterized by a decrease in the number of days with low values of  $\Delta U$  ( $< 0.05$  atm.cm) as compared to the warm seasons and by an increase in the number of days with higher values of  $\Delta U$ . As analysis show this result is due, in particular, regards the increase of temperature inversions number and lifetime.

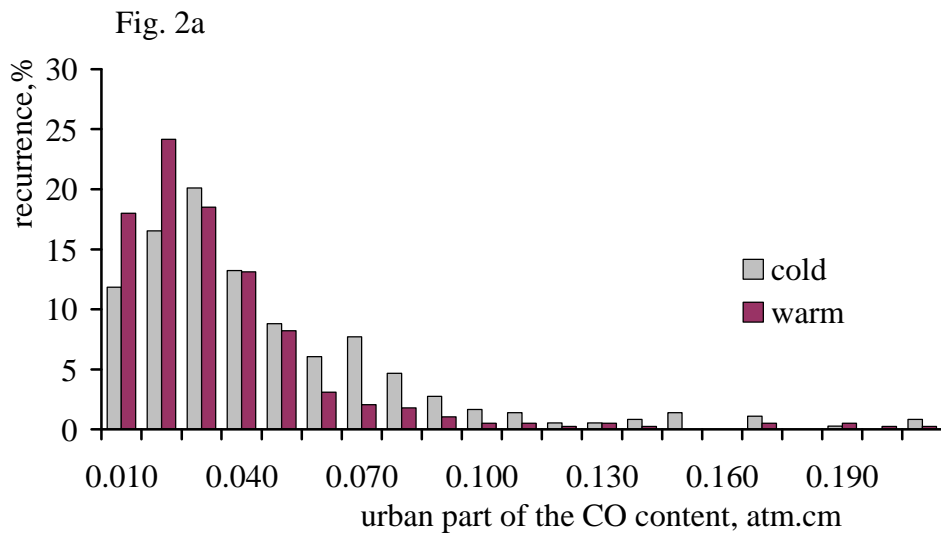


Fig.2a. The recurrence frequencies of  $\Delta U$  (an urban part of the CO content) for cold (11 oct. – 20 apr.) and warm (21 apr.- 10 oct.), Moscow, 1993-2007

The comparison of Moscow recurrence frequencies of  $\Delta U$  with another megapolis Beijing we gave fig. 2a. For Beijing extreme values of the CO content urban part are observed at about 20% cases.

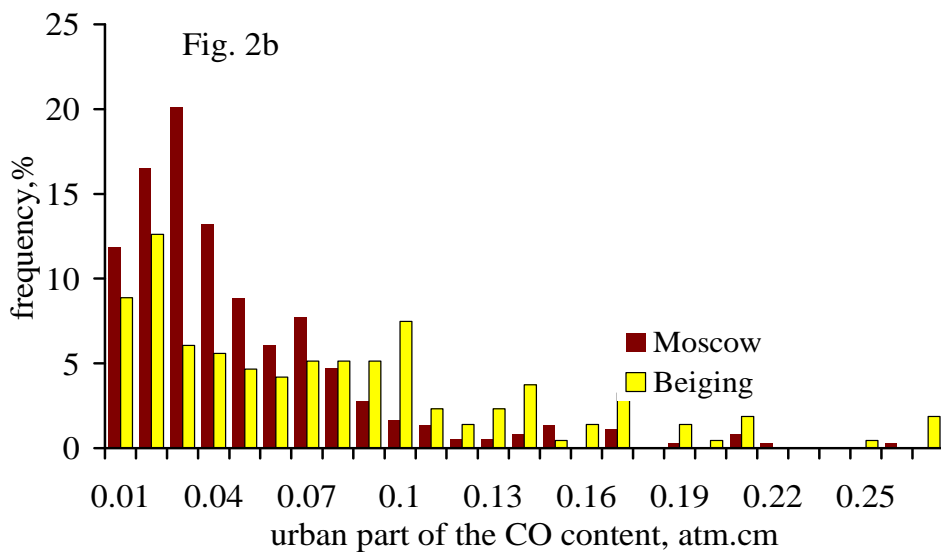


Fig.2b. Comparison of the recurrence frequencies of  $\Delta U$  CO for Moscow, 1993-2007 and Beijing, 1992-2007.

Fig. 3 presents the yearly means of  $\Delta U$ . urban part of the CO content, for the period from 1993 to 2007. An urban part means has not increased in spite of more than tripled number of motor-vehicles in Moscow during the same period. This tendency is confirmed by the measurements of the carbon monoxide surface concentrations in Moscow [10].

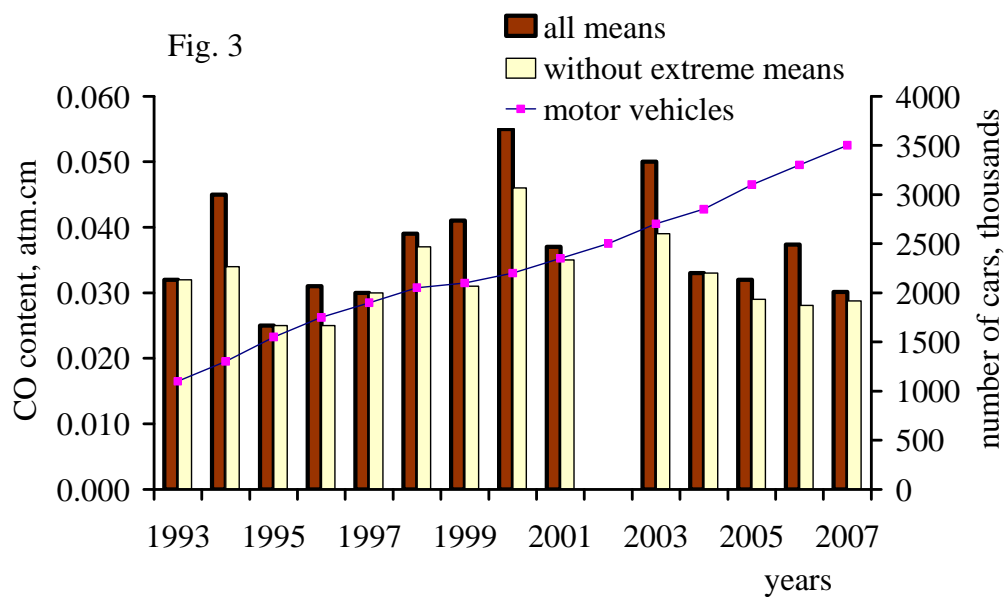


Fig. 3. Yearly means and the number of motor vehicles in Moscow, 1993-2007

As example of different characters of the CO content diurnal variations the Fig.4 is given. The different values of CO content are mainly caused by distinction of the wind velocities during measurements. Traditionally the sodars are used for measurements of wind profiles and qualitative analysis of vertical structure of the atmospheric boundary layer (ABL) [11]. Simple, flexible and open-for-improvements sodar system LATAN-3 was developed. The system has proven its ability to operate in a noisy urban environment. Using facsimile (intensity of echo signal in coordinate height-time) we can determine the character of the temperature stratification and the existence of inversions [8, 11].

Fig.4a,4b shows the diurnal variations of CO content urban part and CO surface concentration for two days 11.10.2005 and 13.10.2005. Sodar facsimiles and wind profiles are shown in this Fig. too. October 11, 2005 the wind velocity in the layer up to 300m was close to zero over the entire observation time. On that day, near-zero wind velocities (according to aerological sounding data) were observed up to the altitude of 1.7–2 km. October 13 the average wind velocity varied within the day from 1 up to 7 m/s, and changed (from 0 to 5-10 m/s) greatly with height. The presence of the raised inversions was typical for both days, but their influence was below the influence of wind.

Those meteorological conditions determine a maximum of CO content for the last 4 years observations at October 11, 2005.

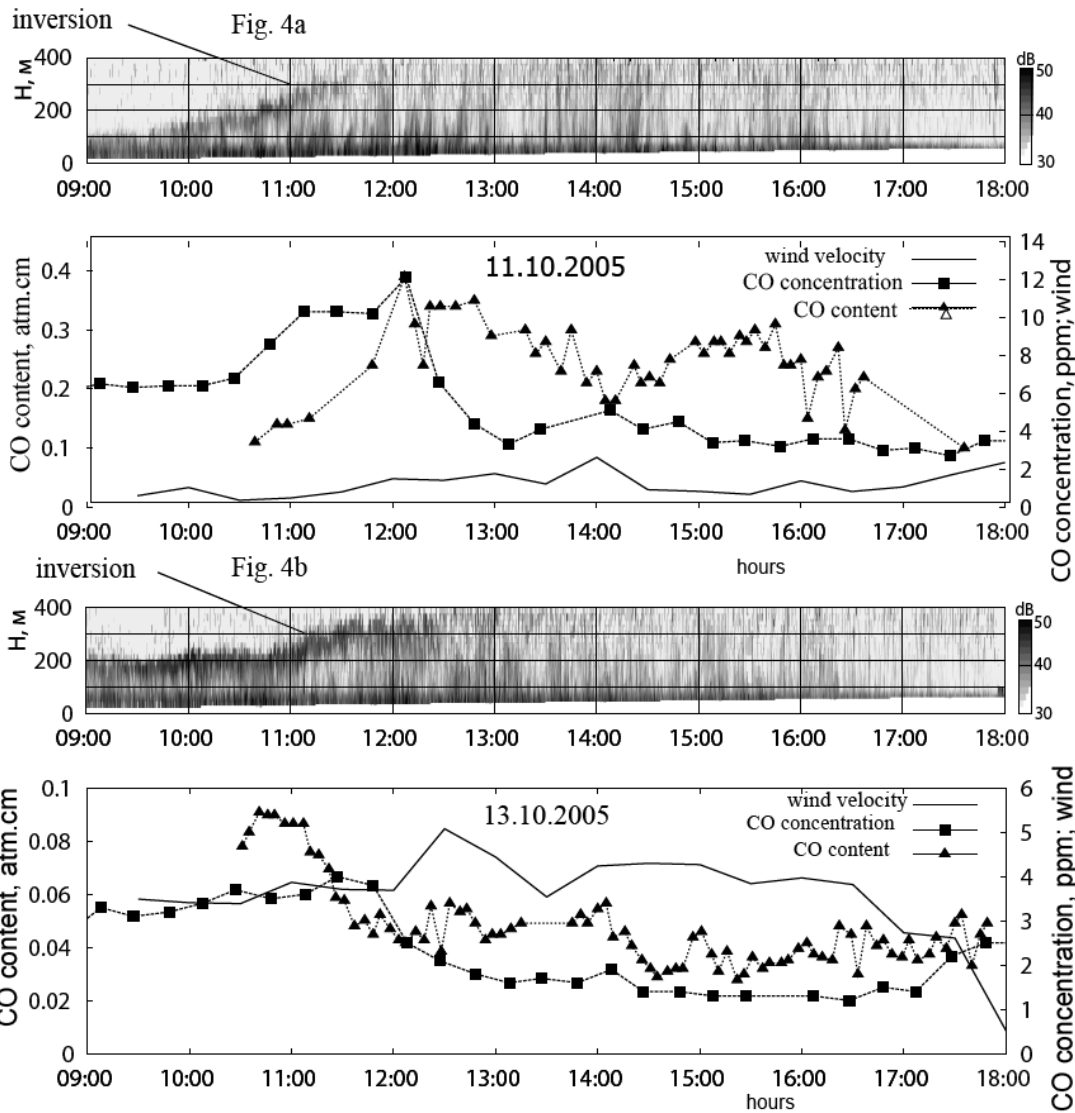


Fig.4a, 4b. Facsimile records of echo signal, the urban part of the CO content, CO concentration, and the wind velocity averaged over a layer of 300m. Diurnal variations for 11.10.2005 and 13.10.2005.

To analyze all recent results (2005-2007) the correlation coefficients of urban part CO content with average wind speed (in layers equal to 300m) were obtained (Fig.5a, 5b).

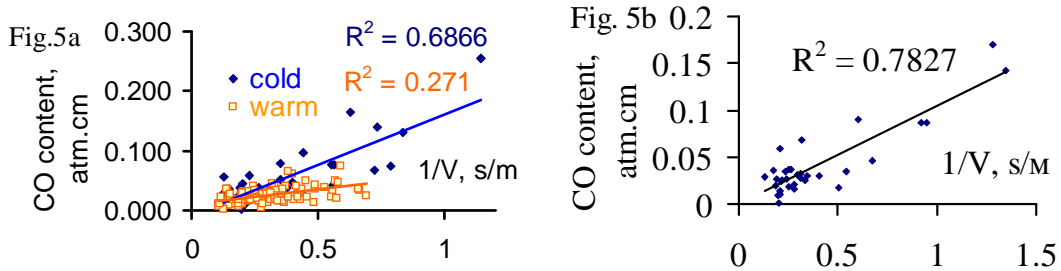
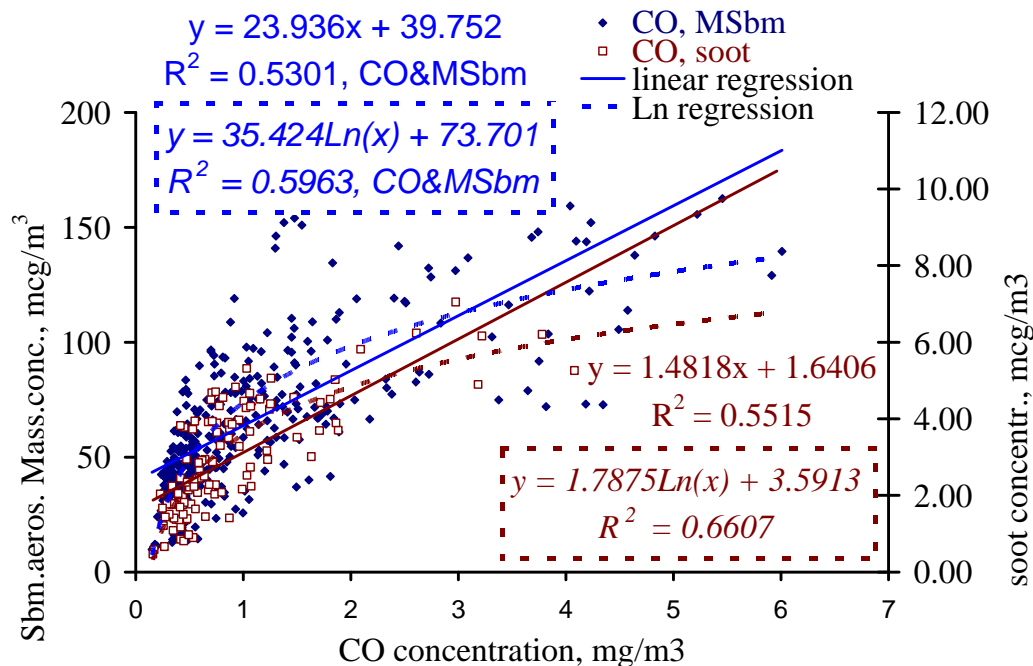


Fig. 5a, 5b. Correlation CO urban part content and wind speed, 60-300m layer, cold and warm seasons, “below inversion” layer, Moscow, 2005-2007

CO sources intensity for Moscow  $Q = 125 \pm 42 \text{ g/km}^2\text{c}$  was estimated by use of dependence  $\Delta U(1/V)$ .

Positive correlation (for linear regression correlation coefficient  $R^2 = 0.53-0.65$ ) between CO surface concentration, soot and submicron aerosols was obtained for Moscow, autumn 2007, Fig. 6. Correlation between CO urban part of content and CO surface concentration is poor that may be explained by CO concentration increasing with height in some cases.



#### 4. Conclusions

1. Analysis of the results of simultaneous measurements of the total CO content in the atmosphere over Moscow and over rural area (ZSS) from 1993 to 2008 showed that the CO content in the surface air layer over the city did not increase over this period, because, on the one hand, in Moscow, the number of cars (one of the significant sources of carbon monoxide) has increased, and, on the other hand, the quality of motor engines has improved. In addition, the portion of industrial emissions has significantly reduced in the city.
2. The extreme values of the CO content in the atmosphere over Moscow can be 2.5–3 times greater than its background values. The extreme values are usually observed in winter during prolonged anticyclone situations in the presence of surface and raised temperature inversions and a gentle wind in the surface air layer. The number of days with such CO content is 3% of the total number of measurement days.
3. In most of the cases, especially during the warm seasons, slight excess of the CO content over its background values are typical for Moscow atmosphere. For those days, as a rule, the CO content varies slightly during a day and the wind speed is a relatively

high. The maximum correlation coefficient was found for the dependence of the urban portion of the CO content on the mean wind velocity at the 60–300m atmospheric layer for cold season and at “below inversion” layer.

4. Comparison of the recurrence frequencies CO urban part of content showed the  $\Delta U$  extreme values are not exceed 3% for Moscow and 20% for Beijing.

5. Positive correlations was obtained between urban part of content and surface concentration of carbon monoxide and submicron and soot aerosols in urban atmosphere.

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