

# Statistical analysis of maximum and daily mean concentrations of carbonic monoxide in the air basin of Moscow

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Variations of maximum and daily mean concentrations of carbonic oxide in Moscow have been analyzed. Diurnal variability of maximum single concentrations has been studied. The method for maximum concentration retrieval has been worked out.

## Introduction

The environmental situation in the surface layer of the urban atmosphere is defined by the statistics excesses of certain level and, particularly, daily mean and single “maximum permissible” concentrations of atmospheric pollutants (MPC<sub>dm</sub> and MPC<sub>s</sub>), including carbon monoxide CO [Refs. 1 and 2]; however, regularities of their variability are still poorly studied.

In this work, the maximum single ( $N^s$ ) and daily mean ( $N^d$ ) CO concentrations, measured in Moscow in 2002–2006 at the net of automated air quality control stations are under analysis.<sup>3–5</sup> The maximum single CO concentrations have been daily measured and compared with the daily mean concentrations.

## Measurement instrumentation

At present, more than 30 automated control stations of air quality are operating in Moscow<sup>5</sup>; a majority of them measure the CO concentration. For CO monitoring, K-100 (“Optek”, St. Petersburg) and ML-9830 (“Monitor Labs,” France) gas analyzers are used.<sup>3</sup> ML-9830 gas analyzers have a single measurement error of  $\pm 0.25$  mg/m<sup>3</sup> at an averaging time of 20 s. A random error of CO concentration measurement noticeably decreases due to following averaging over 20-minute periods. The averaged measurement results are

automatically stored in the database of the State Unitary Enterprise “Mosecomonitoring.”<sup>4,5</sup>

## Variations of daily mean CO concentrations

The daily mean CO concentrations  $N^d$  were calculated from the single concentrations, measured in 2002–2006;  $N^d$  variations were statistically analyzed. Table 1 presents annual mean  $\bar{N}^d$  for some stations and the corresponding standard deviations<sup>6</sup>:

$$\sigma^d = \sqrt{(k-1)^{-1} \sum_i (n_i^d)^2},$$

where  $n_i^d = N_i^d - \bar{N}^d$  is the deviations of the daily mean concentrations  $N_i^d$  from the mean values  $\bar{N}^d$ ,  $i$  is the current day number ( $i = 1, 2, \dots, k$ ),  $k$  is the number of days of measurements.

In addition, the coefficients of variations  $\gamma^d = \sigma^d / \bar{N}^d$ , parameters of asymmetry

$$A^d = (k^d)^{-1} (\sigma^d)^{-3} \sum_i (n_i^d)^3$$

and excess

$$E^d = -3 + (k^d)^{-1} (\sigma^d)^{-4} \sum_i (n_i^d)^4$$

( $k^d$  is the number of days) are also given in Table 1 [Ref. 6].

**Table 1. Statistical characteristics of daily mean CO concentration variations in Moscow**

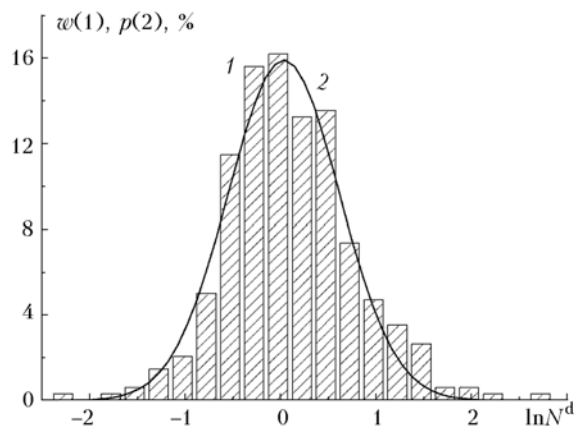
Year	Station	$\bar{N}^d$	$\sigma^d$	$\gamma^d$	$A^d$	$E^d$
		mg/m <sup>3</sup>				
2003	MRTI	2.47	1.24	0.50	0.92	0.94
2003	Lyublino	1.40	0.75	0.54	2.09	6.88
2003	Biryulevo	1.05	0.54	0.52	2.42	10.70
2004	Lyublino	1.35	0.71	0.53	1.90	5.74
2004	Vernadskogo ave.	0.68	0.43	0.63	2.93	11.10
2006	Vernadskogo ave.	0.64	0.41	0.64	2.20	6.95
2006	Chayanova str.	0.82	0.44	0.54	1.98	6.90

The coefficients of variations  $\gamma^d$  are noticeably less than the corresponding coefficients  $\gamma$  for single concentrations.<sup>3</sup> In 2003,  $\gamma$  exceeded  $\gamma^d$  by 40% at the MRTI station and by 60% at Biryulevo. Asymmetry and excess of empirical distribution functions (EDF) of daily mean concentrations are usually significantly less than the corresponding values of EDF for single concentrations.<sup>3</sup>

The above relations are stipulated by data averaging when going from single to daily mean concentrations. The given examples are characteristic for the entire observation period, including 2002, when smoke was observed in the urban atmosphere.<sup>7,8</sup> An evident asymmetry and large excess of  $N^d$  distributions show that the corresponding EDFs are to be approximated not to Gaussian but to lognormal distributions.<sup>6</sup> The  $N^d$  EDF is exemplified in Fig. 1, built by the measurement data of Shabolovka station in 2003, which is approximated to the function

$$p(\ln N^d) \cong 1.7 \exp[-1.45(\ln N^d - 0.03)^2]$$

with a reasonable accuracy.



**Fig. 1.** EDF  $w$  of daily mean CO concentrations (1), built by the measurement data of Shabolovka station in 2003 and the approximating lognormal distribution  $p$  (2).

The maximum permissible daily mean CO concentration equals to  $3 \text{ mg/m}^3$ . Probabilities of excess for  $\text{MPC}_{\text{dm}}$ ,  $2 \text{ MPC}_{\text{dm}}$  ( $6 \text{ mg/m}^3$ ), and

$3 \text{ MPC}_{\text{dm}}$  ( $9 \text{ mg/m}^3$ ) were calculated. Some calculation results of the above probabilities are given in Table 2.

**Table 2.** Excess probabilities (%) of CO  $\text{MPC}_{\text{dm}}$  ( $3 \text{ mg/m}^3$ ) and its multiple levels according to the measurements data in Moscow in 2004

Station	$\text{MPC}_{\text{dm}}$	$2 \text{ MPC}_{\text{dm}}$	$3 \text{ MPC}_{\text{dm}}$
MRTI	21.0	—	—
Veshnyaki	7.6	0.3	—
Lyublino	3.5	—	—
Kazakova str.	3.1	0.9	0.3
Tolbukhina str.	2.0	—	—
Vernadskogo ave.	0.3	—	—

The highest CO  $\text{MPC}_{\text{dm}}$  excess probability (21%) was attained at the MRTI station (Lenigradskii ave.) in 2004. The comparatively large probability (7.6%) was observed also at the Veshnyaki station. The probability did not exceed 3–4% at the majority of stations; it was about 0.3% (1 day) in Vernadskogo ave. In 2004, the  $2 \text{ MPC}_{\text{dm}}$  level was once exceeded at the Veshnyaki station and thrice in Kazakova str., while  $3 \text{ MPC}_{\text{dm}}$  level — only once in Kazakova str.

### Variations of maximum single CO concentrations

The highest single (20-min averaged) concentrations were determined for each day.<sup>9</sup> Statistical characteristics of maximum single concentration variations are given in Table 3 for some cases. As expected, mean (for 1-year period) values of the above concentration noticeably exceed the corresponding daily mean concentrations for full series of single concentrations as well.<sup>3</sup>

The coefficients of variations  $\gamma^s$  usually exceed the corresponding values of  $\gamma^d$  and are less than the corresponding  $\gamma$ .<sup>3</sup> This regularity is characteristic for variations of asymmetry and excess parameters to a lesser degree.<sup>3</sup>

Similarly to the case of statistical ensembles of single concentrations, EDF of maximum single CO concentrations are satisfactorily approximated by the lognormal distributions (Fig. 2).

**Table 3.** Statistical characteristics of maximum CO concentration variations in Moscow

Year	Station	$\bar{N}^s$	$\sigma^s$	$\gamma^s$	$A^s$	$E^s$
		$\text{mg/m}^3$				
2003	MRTI	4.84	2.35	0.49	0.87	0.96
2003	Lyublino	7.04	5.69	0.81	2.19	9.90
2003	Biryulevo	2.44	1.67	0.69	3.56	23.50
2004	Lyublino	4.81	3.71	0.77	2.16	6.78
2004	Vernadskogo ave.	1.86	1.54	0.83	2.43	7.73
2006	Vernadskogo ave.	1.62	1.35	0.84	2.30	6.29
2006	Chayanova str.	1.73	1.11	0.64	3.19	18.50

EDF of  $\ln N^s$ , shown in Fig. 1 and built by the MRTI measurement data in 2003, is approximated to the function

$$p(\ln N^s) = 16 \exp\{-2.4(\ln N^s - 1.5)^2\}$$

with a reasonable accuracy.

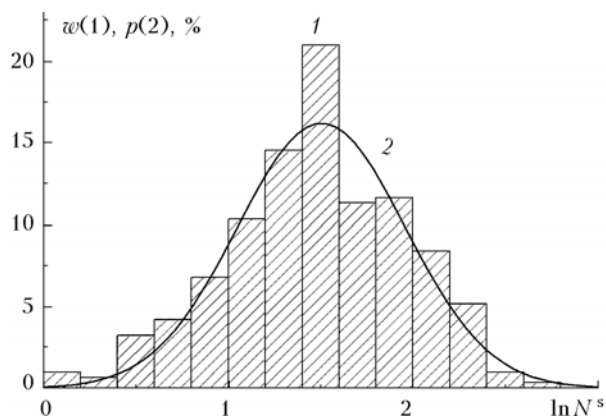


Fig. 2. The EDF  $w$  of maximum single CO concentrations (1), measured at the MRTI station in 2003 and the approximating lognormal distribution  $p$  (2).

Estimating the excess probabilities of CO  $MPC_s = 5 \text{ mg/m}^3$ , it is reasonable to consider all cases of  $MPC_s$  excess instead of limiting to the only maximum excess for each day.<sup>3</sup>

Examples of calculation results of the excess probability for CO  $MPC_s$  and multiple (up to fivefold)  $MPC_s$  levels are given in Table 4.

### Diurnal distribution of maximum single concentrations

The data on diurnal distribution of probabilities of occurrence of maximum single concentrations and their typical levels are of great practical interest. Examples of diurnal distributions of maximum single concentration for a year are given in Fig. 3.

Consider the diurnal distribution of single maximum CO concentrations at the Lyublino station (Fig. 3a), where multiple excess of  $MPC_s$  was mostly observed. The morning maximum (approximately, from 7:00 to 8:00 a.m.) is noticeable, when maximum excess probabilities of CO  $MPC_s$  and its multiple levels are observed, as well as a maximum mean value of the maximum

concentrations. The second strongly smoothed maximum is observed in evening and night hours. Besides, the day and night maxima are clearly pronounced at the Lyublino station (see Fig. 3a).

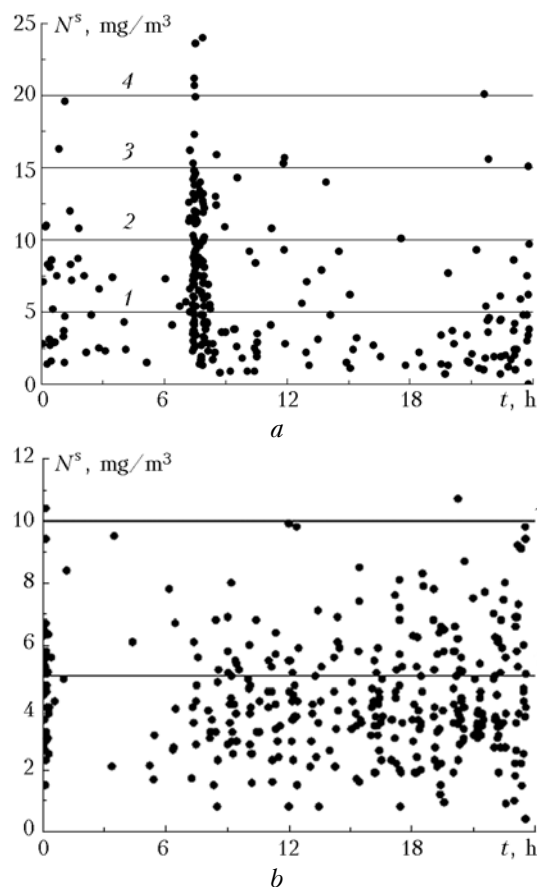


Fig. 3. Diurnal distribution of maximum single CO concentrations at the Lyublino station in 2003 (1, 2, 3, 4 are the concentrations divisible by  $MPC_s$ ) (a) and in Leningradskii ave. in 2002 ( $MPC_s$  (1) and  $2MPC_s$  (2)) (b).

The diurnal distribution of maximum CO concentrations at the MRTI station (Leningradskii ave.) noticeably differs from those at other stations; here, only a night maximum is pronounced (approximately, from 1:00 to 5:00). The maximum in night hours (23:00–1:00) is weakly pronounced. The distribution is close to uniform at other time. Diurnal distribution of maximum single concentrations can be judged from daily mean variations of pollutant concentrations.<sup>3</sup>

Table 4. Excess probabilities (%) of CO  $MPC_s$  ( $5 \text{ mg/m}^3$ ) and its multiple levels according to the measurement data in Moscow in 2004

Station	$MPC_s$	2 $MPC_s$	3 $MPC_s$	4 $MPC_s$	5 $MPC_s$
MRTI	6.10	0.04	—	—	—
Veshnyaki	4.50	0.57	0.08	0.01	—
Lyublino	3.10	0.43	0.07	0.02	0.01
Kazakova str.	1.40	0.30	0.06	—	—
Tolbukhina str.	1.40	0.08	—	—	—
Vernadskogo ave.	0.37	0.01	—	—	—
Losinyi island	0.10	—	—	—	—

## Correlation between daily mean and maximum single concentrations

The prediction of urban air pollution is of great importance now.<sup>2,10–12</sup> Hence, it is important to estimate the possibility of prediction of maximum single concentrations. When retrieving  $N^s$ , it is reasonable to use the daily mean concentrations  $N^d$  as input parameters.<sup>10</sup>

Figure 4 shows the correlation diagram, built by the CO concentration measurement data of the MRTI station in 2002 and illustrating the random connection between the maximum single and daily mean concentrations.

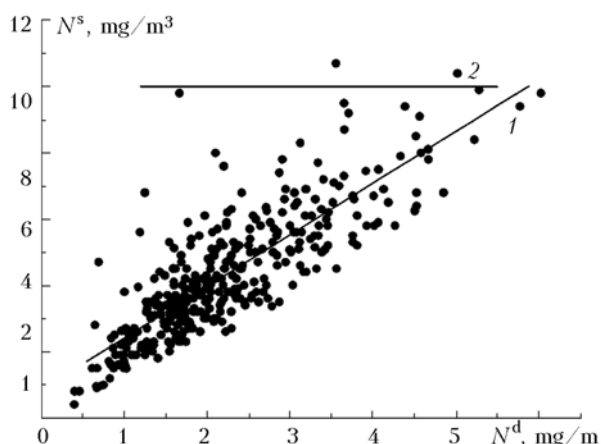


Fig. 4. The correlation diagram of maximum single and daily mean CO concentrations, measured at the MRTI station in 2002; regression straight line (1) and 2 MPC<sub>s</sub> (2).

The maximum single CO concentration can be retrieved from the known daily mean value with the help of linear regression relationship (1 in Fig. 4)

$$N^s = 0.85 + 12.5 N^d, \quad (1)$$

which is true within the  $N^d$  variation range from 0.5 to 6.0 mg/m<sup>3</sup>. The error of  $N^s$  retrieving with Eq. (1) does not exceed  $\pm 3$  mg/m<sup>3</sup> with a probability of 97%. The  $N^s$  upper boundary for the MRTI station can be obtained for all  $N^d$  from the condition  $N^s < 10$  mg/m<sup>3</sup> (2 in Fig. 4), fulfilling with a probability of 99%. Poorly predictable large CO MPC<sub>s</sub> excesses are observed sometimes at the Veshnyaki, Lyublino, Kazakova str., and Shabolovka stations (see Table 1). For other stations, the probability of large errors of  $N^s$  retrieving is less than those for the MRTI station.

## Conclusion

Main results of this work are the following.

1. According to environmental monitoring data in Moscow, statistical characteristics of daily mean variations of CO concentrations have been calculated. It has been shown, that all other

statistical characteristics for arrays of daily mean concentrations usually noticeably differ from the corresponding characteristics for maximum single concentrations.

2. Main statistical characteristics have been calculated for variations of maximum single CO concentrations. Statistics of variations of single, maximum single, and daily mean concentration have been compared.

3. Diurnal distributions of maximum single CO concentrations for two stations with different types of variability have been analyzed. As exemplified by the Lyublino station, there are morning and evening-night maxima in the diurnal distribution of probabilities of occurrence of the maximum single concentration. An anomalous distribution of the above probability was noted for the MRTI station.

4. The regression technique has been suggested for estimating the range of variations of maximum single CO concentrations at known daily mean values.

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