Characterizing the anthropogenic component in diurnal variability of the gas and aerosol concentrations in urban air

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Some results on temporal variations of the urban air pollution are presented. A database on the concentration of some pollutants (NO, NO_2, SO_2, CO, aerosol) and meteorological parameters measured in a monitoring regime allowed us to study the diurnal variability of their concentrations in the atmosphere of a big city. Several types of the diurnal behavior were observed for different pollutants, as well as some seasonal variation was revealed. The morning and evening peaks were revealed in the time behavior of concentrations of all the pollutants studied. The diurnal variability of the pollutant concentrations was found to depend on some meteorological parameters, first, on the wind velocity. Analysis of the shape and amplitude of diurnal variations of the pollutant concentrations on working days and weekends showed that the anthropogenic effect is most pronounced in summer. Distribution histograms of the daily mean concentrations over a week demonstrated their increase on working days and decrease in weekends for the warm season and the absence of such dependence in the cold season.

Introduction

The growth of industry and city traffic affects adversely the urban ecology. A significant amount of pollutants is emitted into the atmosphere. Although anthropogenic pollution of the urban air is the subject of numerous publications, some considerable gaps remain in solving the problems of pollutant spread and transport, as well as in numerical estimates of the real state of air in big cities.

For a long time the methods of statistical analysis are used to study the state of atmospheric air and the atmospheric dynamics. Such studies are based on the data of ecological monitoring accumulated for long periods. A significant part of papers is devoted to the search of regularities in the time variations of pollutant concentrations and causes of these variations.

Thus, Ref. 1 presents the diurnal behavior of the mass concentration and number density of aerosol particles. It was found there that the mass aerosol concentration peaked from 09:00 to 13:00 and from 19:00 to 24:00. The effect of cold front passage on the mass aerosol concentration was estimated, and the aerosol concentration was shown to increase smoothly after establishment of anticyclone. In Ref. 2, the main attention was paid to diurnal variations of aerosol-forming substances. The concentration of aerosol-forming substances was shown to peak at nighttime: 20:00–02:00. Reference 3 concentrates on specific diurnal variations of the aerosol number density. According to the results presented, the aerosol number density has a pronounced diurnal behavior. Its increase begins at 06:00 and continues for three hours; then it stabilizes at the highest level from 10:00 to 17:00 and then decreases smoothly.

Some findings on the effect of the main parameters of the atmospheric boundary layer on the near-surface concentrations of pollutants are presented in Refs. 5–10. According to these papers, the parameters characterizing the state of the atmospheric boundary layer are the type of atmospheric temperature stratification, the height of the mixing layer, and the wind velocity. In Refs. 5–7 the high correlation was found between the concentrations of some substances and the height of the mixing layer. At the same time, in Refs. 8 and 9 it was noted that the level of air pollution strongly depends on the wind velocity.

This paper is based on the results of long-term monitoring of urban air. For six years we took part in continuous observations of the concentrations of the principal pollutants in the atmospheric boundary layer using a network of automated measuring stations. The monitoring network of five stations is located in Almetevsk [53°N, 51°E]. The stations measure the concentrations of NO, NO_2, SO_2, CO, near-ground aerosol, and meteorological parameters: temperature, relative humidity, atmospheric pressure, wind speed and direction.[4]

Diurnal behavior and its seasonal dependence

The observations were first divided into two seasons: winter (November–March) and summer (May–September), and the seasonally mean concentrations of the monitored atmospheric constituents were calculated. The processed results are summarized in the Table below.

Seasonally mean concentrations of atmospheric constituents

Constituent	Concentration, mg/m^3	
	Summer	Winter
NO	0.011	0.017
NO_2	0.012	0.019
SO_2	0.010	0.013
CO	1.48	3.02
Aerosol	0.054	0.029

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Analysis of the seasonally mean pollution level showed that the winter concentrations of such gases as NO, NO_2, SO_2, and CO are, on the average, twice as high as the summer ones, while the aerosol concentration is higher in summer than in winter.

The next step was the study of the diurnal behavior of the concentrations of the admixtures under study. The statistical reliability of calculations was estimated using the confidence intervals calculated with the Student coefficient for 95% probability. Confidence intervals are shown by bars in all plots.

Figure 1 depicts typical diurnal behaviors. In general, the plots for NO, NO_2, CO, and aerosol are similar (Fig. 1*a*).

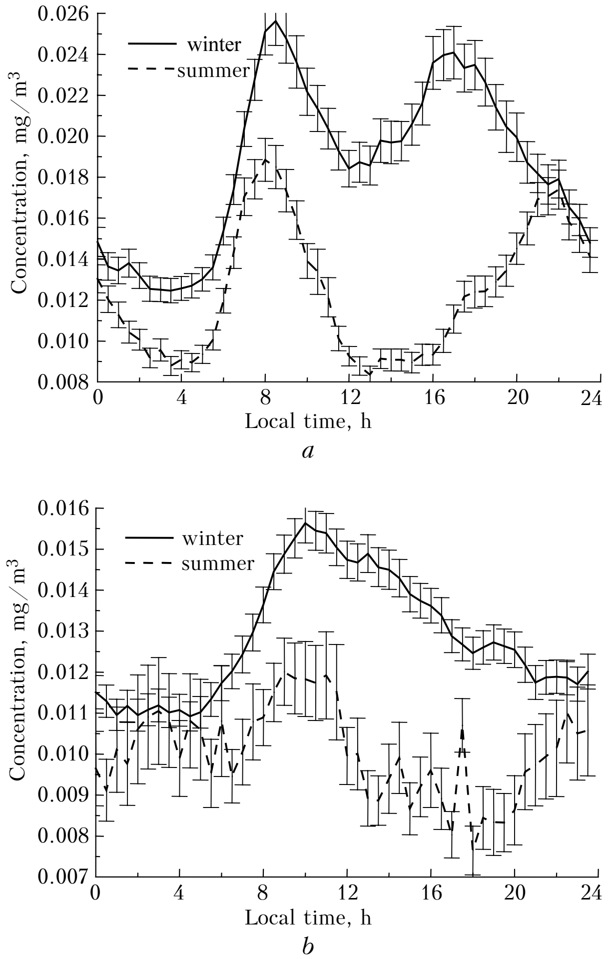

Fig. 1. Diurnal behavior of NO_2 (*a*) and SO_2 (*b*) concentrations.

In summer, the highest concentrations are observed from 07:00 to 10:00 (morning peak) and a slight increase is observed at 21:00–22:00 (evening peak). At night, as should be expected, the diurnal behavior has a deep minimum from 23:00 to 05:00 (night minimum). Besides, one more minimum is observed from 12:00 to 17:00 (day minimum). The day minimum has significant amplitude it often takes values lower than the diurnal mean and is clearly seen for these substances.

A somewhat different behavior is characteristic of SO_2 (Fig. 1*b*) – the day minimum is almost absent, and the wide morning peak falls on 08:00–12:00 period. In general, the SO_2 concentration after 11:00 decreases, and weak growths are observed only at 14:00–15:00 and 19:00–20:00.

Besides the general pattern, some peculiarities are observed for each of the pollutants. Thus, for NO_2, CO, and aerosol the height of the evening peak is close to that of the morning peak, whereas for NO the evening peak is only weakly pronounced. The pattern changes somewhat in winter. For all the pollutants, we observe a significant increase of the evening peak, which sometimes exceeds the morning one, its broadening and shift toward 15:00–19:00. The day minimum becomes less pronounced and takes the values higher than the diurnal mean.

Generally, the diurnal behavior described above agrees well with the commonly accepted idea of atmospheric processes. At night, when the pollutant income into the atmosphere is minimum, the concentrations decrease. Then, the traffic intensity increases quickly starting from 06:00, and the working day at industrial plants begins at 08:00.

After reaching some value at 08:00, the concentrations begin to decrease and stabilize after 12:00 at the minimum level for 4–6 hours in summer and 2–3 hours in winter, after that they increase again. At first glance, the day minimum can hardly be explained, because the pollutant income into the atmosphere does not decrease at that period. Certainly, at the lunch time, the traffic intensity in a city decreases somewhat, but this could only decrease the rate of the concentration increase.

Searching for causes of such a behavior, we considered the diurnal variability of meteorological (weather) parameters (Fig. 2*a*). At night, from 22:00 to 06:00, the wind speed is minimum (about 1.5 m/s), and in daytime, from 13:00 to 17:00, it is the highest – up to 3 m/s. The morning increase of the wind speed starts at 07:00 and continues until 12:00 crossing the diurnally mean level at 09:00.

To check our hypothesis, we plotted the diurnal behavior of the pollutant concentrations at different wind speed ranged into two speed intervals: higher and lower than 2 m/s. At high winds, the diurnal variations of the concentrations change insignificantly about the mean value and no new peaks arise. At daytime wind intensification, the mixing intensity increases, thus likely leading to the decrease in the air pollution level. At low winds, the morning and evening peaks keep, and the day minimum has lower amplitude, but does not disappear (Fig. 2*b*). Thus, we believe that the air pollution level strongly depends on the wind velocity, what agrees with the conclusions drawn in Refs. 8–10. There are other causes for the daytime decrease of the pollutant concentrations. Some authors associate it with the daytime increase of the air temperature in the surface layer, increase of the convective flux intensity, and destruction of the temperature inversion layer.

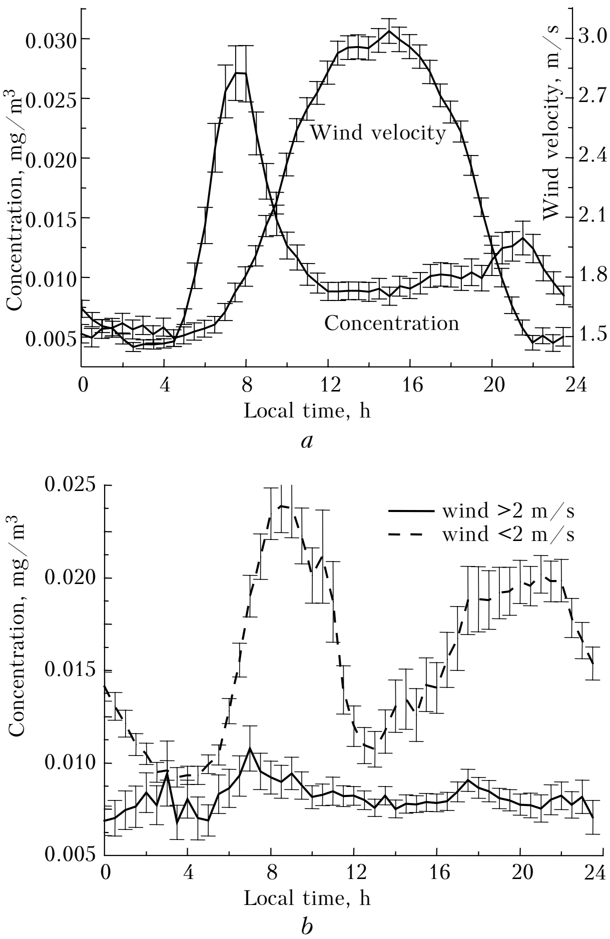

Fig. 2. Diurnal behavior of the NO concentration and the wind velocity in summer (*a*), the NO_2 concentration at different wind speed (*b*).

Thus, Ref. 10 studied the dependence of the aerosol concentration and the concentration of aerosol-forming substances in the center of Moscow on the type of air mass, the state of the atmospheric boundary layer, the emission rate of pollution sources, solar radiation intensity, temperature, and humidity. It was found that the concentrations strongly depend on the season, the type of the prevalent air mass, and wind speed. The type of temperature stratification also has a significant effect on them.

Anthropogenic component of the diurnal behavior

To study the properties of the anthropogenic component for each pollutant, we have drawn the plots of the diurnal behavior averaged over five working days and two weekend days. As an example, Fig. 3 depicts such plots for NO.

It is seen from Fig. 3 that the plots for the working day and for the weekends have similar shapes, but different amplitudes.

For NO_2 and aerosol, the evening peak occurred during 1–1.5 hours later in the weekend with its intensity at the same level as on the working days. At the same time, the intensity of the morning peak in the weekend was only 40–60% of that on working days. As a result, the evening peak in the weekends exceeds the morning one for these pollutants. As to CO, the evening peak does not shift in winter, but the ratio of its intensity to the intensity of the morning peak is even more significant. The SO_2 concentration almost halves in the weekend as compared to its value on working days.

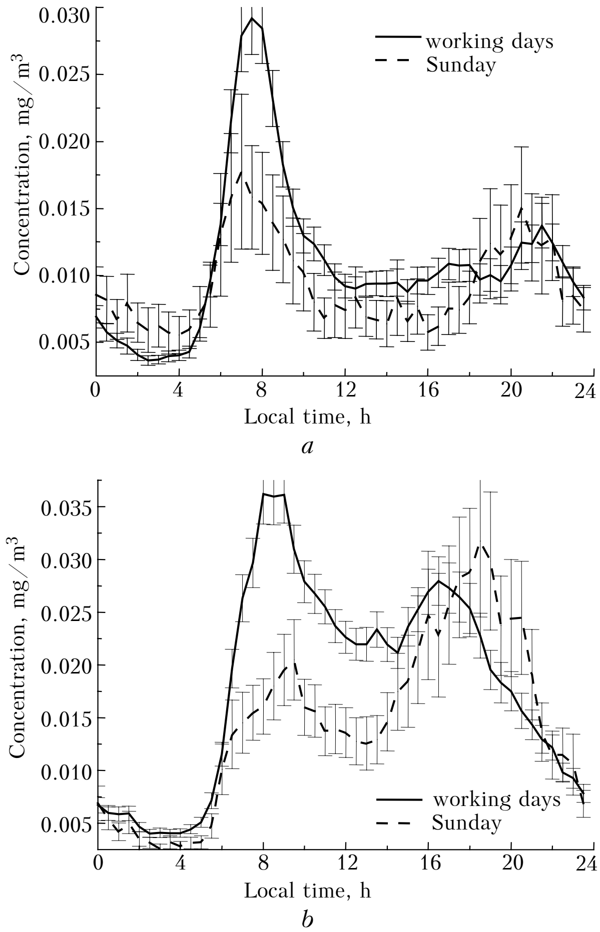

Fig. 3. Diurnal behavior of the NO concentration in summer (*a*) and winter (*b*) with the seasonal mean subtracted.

It was assumed that pollutants should accumulate in the atmosphere during the working days and spread during the weekend. Therefore, for each pollutant we plotted the seasonally mean diurnal behavior for every day of a week. This approach allows the anthropogenic effect to be estimated more correctly. It was believed that the diurnal behavior of the pollutants is least subject to the anthropogenic effect in the weekend and most subject to it on Thursday and Friday. The comparison of the plots for these days gives us the most illustrative pattern of the effect of industry and traffic on the urban air pollution.

Each pollutant has some peculiarities in its behavior. For CO in summer, we can clearly see the dependence of the morning peak on the day of a week. The morning peak of the CO concentration in the weekend reaches only 2.25 mg/m^3, while on Thursday and Friday it exceeds 3.30 mg/m^3. At the same time, the evening peak is likely weakly connected with the anthropogenic factor. The concentrations on Sunday in this period are roughly 15% lower than on working days and in the weekends they exceed the morning peak. Besides, the evening increase of the CO concentration manifests itself 0.5–1 h later in the weekend than on working days. In winter the dependence on the day of a week is almost absent, and the evening concentrations in the weekends are roughly equal to those observed on working days.

A somewhat different pattern can be seen for NO_2. On summer Sunday the NO_2 concentration remains at the level of the night minimum with the values of 0.005–0.007 mg/m^3, increasing up to 0.010–0.012 mg/m^3 only at 08:00 and 21:00–22:00. On working days the peaks take the values of about 0.040 and 0.035 mg/m^3 in the morning and evening, respectively. The shift of the peaks is not observed for NO_2. In winter the dependence on the day of a week is insignificant. The morning peak makes up to 2/3 of that on working days, and the evening one is about 5/6 of that on working days. The shift of the evening peak by 1–1.5 h in the weekend is marked.

The behavior of SO_2 is similar to that of NO_2. In summer the Sunday concentrations fluctuate about 0.0012 mg/m^3, increasing somewhat at 12:00–13:00. In winter the diurnal variations in the weekend and on working days copy each other with the only difference in the diurnally mean pollution level, which is 0.014 mg/m^3 on working days and 0.012 mg/m^3 on weekends. It can be assumed that the behavior of the SO_2 concentration is caused by the human activity to the higher degree than for other constituents considered here.

The aerosol behavior is quite different. In summer weekends, its concentration continues to decrease after 06:00, falling lower than the evening minimum, which is usually 0.020–0.025 mg/m^3, down to roughly 0.016–0.018 mg/m^3, and begins to increase only at 10:00–11:00 with marked spikes at 14:00, 17:30, 18:30, and the peak at 22:00. The height of the Sunday evening peak is almost the same as in the working days. This suggests that the summer evening peak is not of pronounced anthropogenic origin, but likely caused by variations of the weather parameters. In contrast, the morning increase of the concentration can be related to the human activity. In winter the aerosol concentration behaves similarly to other studied constituents on all days of a week. Its peculiarity is that the evening peak, as in summer, is independent of the day of a week, while the morning peak keeps to be dependent on the intensity of the human activity, and the weekend concentrations are usually 40% lower than those on working days.

Besides these factors, the differences in the shape and amplitude of the diurnal variations of the SO_2, NO_2, and, partly, NO concentrations in the cold period may be caused by the heating activity, because these substances are present in large amounts in emissions from heat and power plants and boiling houses.[10]

The distribution histograms of the diurnally mean concentrations over the days of a week demonstrate the degree of pollutant accumulation in the atmosphere during the working days and the pollutant decrease rate in the weekend (Fig. 4).

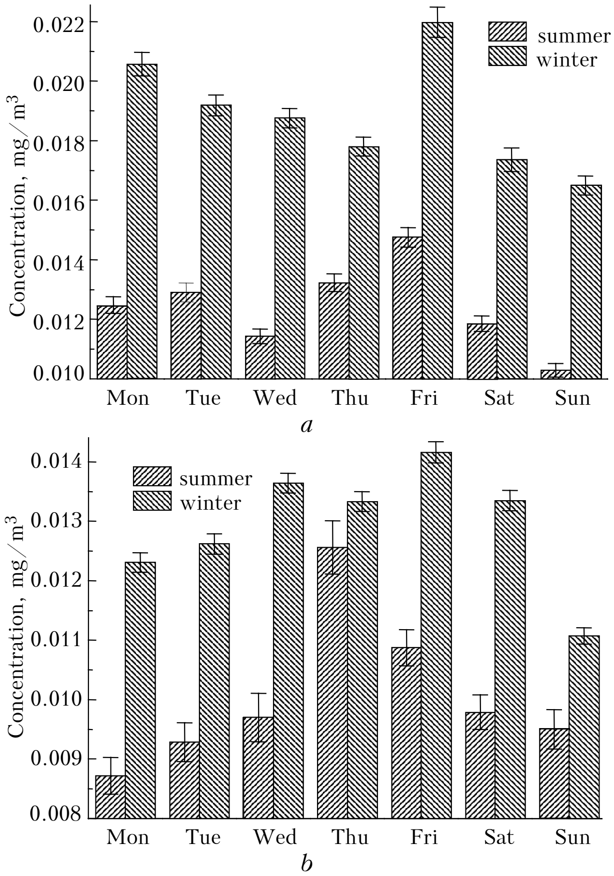

Fig. 4. Distribution histograms of seasonally mean concentrations over the days of a week: NO_2 (*a*) and SO_2 (*b*).

The summer histograms of the diurnally mean NO, NO_2, and SO_2 concentrations demonstrate rather stable increase of the concentrations on working days and their fast decrease in the weekend. The CO gas and aerosol show no pronounced dependence on the day of a week and fluctuate within a narrow range. In winter the dependence on the day of a week is observed only for SO_2. As to the behavior of other constituents, we can say that the maximum diurnally mean concentrations are most often observed on Friday, while the minimum ones are most often observed on Sunday. As for the rest constituents, no pronounced dependence of the diurnally mean concentration on the day of a week has been revealed.

Conclusion

The database of measured data on the concentrations of some atmospheric constituents and weather parameters allowed the in-depth study into various problems connected with pollution of the urban air, spread and temporal variations of pollutants in the atmosphere of a big city to be carried out. The study showed that the diurnal behavior of the pollutant concentrations in the urban air is subject to significant seasonal variations. In winter, as the seasonally mean level of chemical pollution increases, we can observe broadening of the morning and evening peaks and the shift of the evening peak to earlier time. The dependence of the diurnal variations of the pollutant concentrations on the wind velocity was found.

Consideration of the shape and amplitude of the diurnal variations on working days and the weekends showed that the anthropogenic effect is more pronounced in summer. In our opinion, the morning peak in the NO, NO_2, SO_2, and aerosol concentrations are caused by the anthropogenic effect; the maximum of the CO concentration is partly caused by the human activity. As to the SO_2, we can assert that the evening increase in the concentration may be the result of the human activity. The evening increase in the NO, NO_2, and CO concentrations likely origins from some wave processes in the atmosphere and variations of the weather conditions. The evening increase of the aerosol concentration can hardly be explained by the human activity. Probably, it is formed as a result of natural processes and variations of the weather conditions.

Acknowledgments

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