Dynamics of sulfur dioxide surface concentration in Moscow

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The variability of sulfur dioxide surface concentration in Moscow has been investigated. Two sources of data have been used: long-term measurements at stations of Hydro-Meteorological Service and Ministry of Health since 1957 and automatic every-minute measurements at the Ecological station of the Institute of Atmospheric Physics and the Geography Faculty of the Moscow State University for 2004–2007. During last half of century, the sulfur dioxide concentration in Moscow has been sharply reduced and became closer to its background estimations. The highest values are recorded in winter, the lowest ones – in summer and fall. The daily variation of SO_2 in spring and summer is characterized by a morning maximum, probably connected with frequent raised inversions at this time. In fall, this maximum covers the daytime as well. A spread in monthly average values in winter is significantly larger in comparison with other seasons. A sharp asymmetry in mid-season conditions has been revealed (SO_2 concentration is much higher in spring than in fall). A probable explanation of this effect is a large amount of precipitation in fall. Cases of anomalously high SO_2 ground level concentrations, exceeding the maximum concentration limit, have been observed in Moscow very seldom, i.e., when using black oil in city heating during hard frosts in winter and, as a rule, in presence of low raised inversion at small heights (by the sodar data).

Introduction

Study of regularities of trace gases variability in the ground layer is necessary for more thorough understanding of the atmospheric composition in general as well as proper planning of environmental protection. Sulfur dioxide or sulphurous anhydride SO_2 is one of the main air pollutants, along with nitrogen oxides, carbon monoxide, and ozone, though its amount has essentially decreased during last decades. SO_2 concentrations have correspondingly decreased among other pollutants, as well as its human health hazard level at present levels.

As is known, not less than 80% of SO_2 emission in industrial areas is related to human activity (see, e.g., Ref. 14). Combustion of coal most contributes to the emission (about 70%) while the black oil – in a less degree. A high SO_2 concentration in air adversely affects human and animal respiratory organs. Among other living organisms, lichens are mostly attackable. It is known, that large cities with high SO_2 concentrations can be called "lichen deserts," poor in their species.[3,5]

Simultaneous presence of high SO_2 levels and smoke particles in air is the most dangerous for human health, resulting in sharp strengthening (synergism) of their complex effect on an organism, multiply exceeding the individual toxicity of each matter.[3] In the beginning and middle of the last century, overaccumulation of SO_2 and smoke particles in the ground layer resulted in several catastrophes in different countries, i.e., in Maas value (Belgium) in 1930, in Donor (USA) in 1948, and in London (Great Britain) in 1952. During these tragic incidents, SO_2 concentrations were extremely high: 5.7 mg/m^3 in Donor and 3.8 mg/m^3 in London.[1] As a result, tens of people perished, and even thousands of people – in London.[3]

Thus, sulfur dioxide is one of dangerous pollutants, and its variability with time requires a thorough study.

1. SO_2 concentration variability in Moscow during the last half of century

In the second half of the 20th century, a significant decrease of SO_2 ground level concentration occurred due to a change of fuel type and sharp decrease of fractions of coal and black oil, containing a lot of sulfur, in the fuel general composition. We have analyzed the data on SO_2 ground level concentration, measured at two stationary measurement stations in Moscow, i.e., at the Moscow State University (southwestern part of the city) and on the Baltschug hotel in the city center. At MSU, routing measurements of this pollutant began by the Ministry of Health in 1957 and continued till 1981. Later on, in 1966, the Hydro-Meteorological Service of USSR (now the Moscow Center on Hydrometeorology and Environmental Monitoring with Regional Functions, MSHEM-R) organized a net of air pollution monitoring stations, including the Baltschug one, operating till now. Beginning from 1967, the measurements at this station became routine (several

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tens measurements per month, and after 1973 – 80–100 measurements per month at the average) while at MSU station – 50–60 measurements per month at the average in 1970th. During all the period of monitoring net existence, SO_2 concentration has been measured using the photocalorimetric technique with standard gas analyzers; this provides for homogeneity of data sequence and comparability of values for different years.

As is seen from Fig. 1, the available sequence of data can be divided into three parts: high concentrations without a pronounced variation tendency in the beginning of the measurements, their sharp decrease in the middle of the sequence, and stabilization at a much lower level in last years.

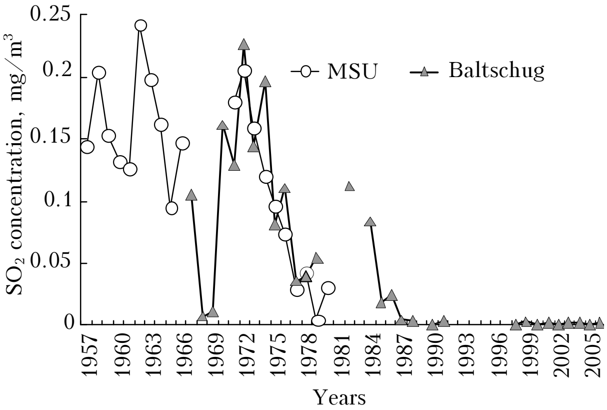


Fig. 1. Dynamics of annual average SO_2 ground level concentration in Moscow.

Till the beginning of 1980th, comparatively high annual average SO_2 concentrations have been recorded both at the Baltschug and MSU stations, usually higher than 0.05 mg/m^3, i.e., values corresponding to the present maximum concentration limit per day. On an average for a year, SO_2 concentration amounted to 0.15–0.20 mg/m^3 in Moscow in 1950th and 1960th.

A local maximum is noticeable in 1972, evidently due to catastrophic forest and peat fires in Moscow Region during the unusually hot and torrid summer. The annual average value (0.23 mg/m^3) at the Baltschug station in 1972 turned out to be the highest on 40 years of observations. At MSU, where the observations began earlier, the annual average SO_2 concentration in 1962 (0.24 mg/m^3) was higher than those in 1972 (0.21 mg/m^3). It is seen from MSU data (Fig. 2) that the high annual average value in 1972 was connected just with anomalously high SO_2 ground level concentrations in summer months, which were as much as in winter, in contrast to usual decrease in the warm season, noted in other years.

According to both stations, a persistent decrease of annual average values from year to year began to show after 1972, especially rapid in Moscow in 1970th. In this period, last houses with wood and coal heating within the city were redeveloped; small black-oil heating plants were closed; and Moscow thermal stations began to use gas as a fuel. As a result, the annual average SO_2 concentration did not exceed 0.05 mg/m^3 after 1984 and 0.01 mg/m^3 after 1987. Later on, the value decreased in one order of magnitude in the center of the city.

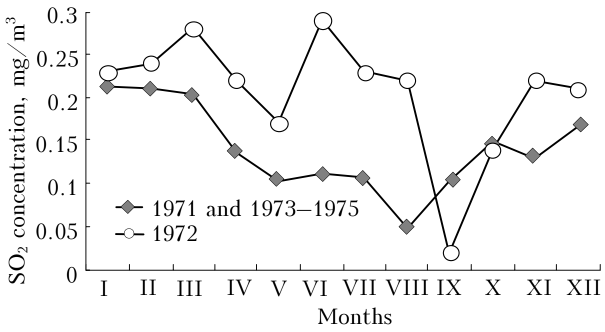


Fig. 2. Annual variations of SO_2 ground level concentrations in Moscow (MSU) in the beginning of 1970th.

According to Baltschug data, during last decades beginning from 1998, the annual average SO_2 concentration varied from 0.0005 to 0.0030 mg/m^3 and was about 0.001 mg/m^3 at the average. Thus, according to the Russian Hydro-Meteorological Service data, the SO_2 ground level concentration during the last half of century decreased in Moscow by about two orders of magnitude, i.e., more than 100-fold.

Such trend, i.e., sharp decrease of the SO_2 ground level concentration in large cities, was noted in last decades in many countries. Thus, in London and New York, a rapid decrease of the concentration began in the middle of 1960th,[3] and a persistent decrease in Paris and cities of Federal Republic of Germany at the same time.[1] The concentration decreased by 25–40% in France from 1965 to 1975. In USSR, the SO_2 also decreased by 24% on an average from 1968 to 1975.[1] The sharp decrease in London resulted from the effect of the Clean Air Act of 1956, passed after the catastrophe of 1952.

However, some decrease of SO_2 ground level concentration (not so rapid) is observed not only at urban monitoring stations, but at background ones as well. Such trend for forest reserves in the European Russia was first noted in Ref. 13 and confirmed by the data of last 15 years.[10] In these years, the annual average values became significantly less then 0.001 mg/m^3 [Ref. 10], while they were 0.003–0.006 mg/m^3 20 years ago.[13] Earlier, in 1970th and 1980th, SO_2 concentration was measured in these forest reserves just casually. Nevertheless, fragmentary data of such measurements, at their large spread, also showed background values equal to several μg/m^3 on an average.[14] Thus, unidirectional changes with different rates resulted in a decrease in differences between SO_2 concentrations in urban and rural areas. At present, the level of SO_2 air pollution in the centre of Moscow exceeds the background values just a little.

Relative stabilization of SO_2 concentration in Moscow at the new level is indirectly confirmed by generalized estimations in Russia.[9] According to the data for 1999–2003, both SO_2 emissions and its ground level concentrations remained virtually invariable from year to year. It is notable that SO_2 is the only main atmospheric pollutant, the ground level concentrations of which, even maximum values, are much less that its maximum concentration limit, both in Moscow (according to measurements data of 16 monitoring stations[11]) and in Russia (according to data of measurements in 248 cities[10]).

Thus, present SO_2 levels in urban air are virtually nonhazardous for human health. Nevertheless, the pollutant is routinely monitored, as it was the reason of the most known cases of catastrophic air pollution in the past.

2. Peculiarities of annual and daily behavior of SO_2 in Moscow

The MSHEM-R network monitoring data, averaged over long periods, allow the general trend of long-term variations to be followed. However, the detailed study of the daily behavior of a pollutant concentration is impossible from these data, since single measurements are carried out only 2–4 times per day. Last years, an alternative network of air quality monitoring stations (of the state unitary enterprise "Mosecomonitoring") has appeared and is rapidly developing in Moscow. But the network equipment is not standardized and reliability of its calibration is not high enough.

Beginning from February, 2002, the joint ecological station of the Obukhov Institute of Atmospheric Physics of RAS and the Geography Department of the Lomonosov Moscow State University operates on the territory of MSU Meteorological Observatory in the southwestern part of Moscow. Here, the ground level concentrations of main atmospheric contaminants (O_3, NO, NO_2, CO, SO_2, airborne particulates, etc.) are continuously measured every minute [Refs. 4 and others]. All measurement devices are regularly calibrated by international standards and standard mixes. SO_2 measurements have been carried out here beginning from January, 2004 by the fluorescence technique with a commercial gas analyzer APSA-360, used at the stations of BMO Global Atmospheric Service. The gas analyzer sensitivity is $\pm$ 0.5 ppb. Preliminary data on daily and annual SO_2 variability are given in Ref. 4 by the results of the first measurement year. In this work, the results of continuous SO_2 measurements are generalized for four years.

According to the data from the background stations of European Russia, annual variability of SO_2 ground level concentration is characterized by cold-season maxima and warm-season minima[13]; this is evidently caused by increased emission of SO_2 at fuel heating of houses on the one hand and stable stratification of lower troposphere, predominated in winter and providing for pollutant accumulation in the surface air on the other hand.[8] Qualitatively close behavior during a year with winter maxima was earlier noted in many Siberian cities (Omsk, Irkutsk, and so on[1]), in Krakov (Poland).[16]

The annual SO_2 variability in Moscow is shown in Fig. 3 according to the measurement results of the joint monitoring station.

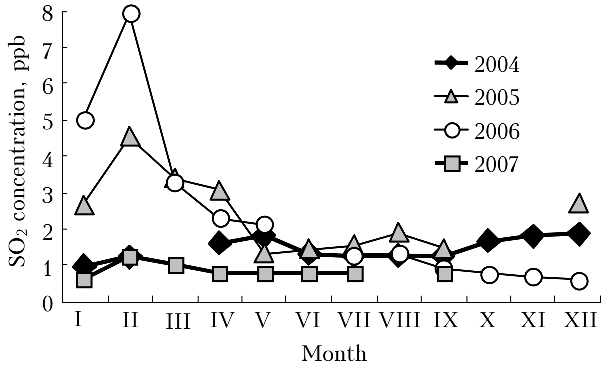


Fig. 3. Annual variability of SO_2 ground level concentration in Moscow (MSU).

As is seen, the above-mentioned general regularity (winter maxima) is confirmed for Moscow by our data for last years, as well as the measurement data in 1970th (see Fig. 2), but the annual behavior itself is more complicated. First, the concentration minimum is not limited to the summer months, but spans fall as well. Second, average values of some winter months are characterized by a very wide spread, e.g., from 0.6 ppb (1.7 $\mu g/m^3$) in December, 2006 to 8.0 ppb (23.8 $\mu g/m^3$) in February, 2006, i.e., differ in one order of magnitude. Maximum values were recorded in January and especially in February, 2006 in hard frosts. According to the data of the joint monitoring station, sum annual SO_2 concentration in Moscow was 1.5 ppb (0.004 mg/m^3) in 2006 and 2.4 ppb (0.007 mg/m^3) in 2005 and 2006.

Note that the obtained values essentially (in several times) exceed the average estimates for the same years by Baltschug measurement data. This can be because of both inhomogeneous distribution of SO_2 sources inside the city and time-discrete measurements (four times per day) at the Baltschug station.

The daily variations of SO_2 ground level concentration are shown in Fig. 4 for different seasons. Here average values are shown as well as confidence intervals with 5% confidence level for every 10 min during a day, calculated by the 2004–2006 measurement data. Daily variations are evidently qualitatively similar for spring and summer; the main peculiarity is the clearly pronounced morning maximum – statistically significant with accounting for the confidence intervals. After 07:00, SO_2 ground level concentration rapidly rises with maxima at about 10:00 and again decreases till 19:00. At other time, in the evening and night, SO_2 ground level concentration is steadily low and invariable.

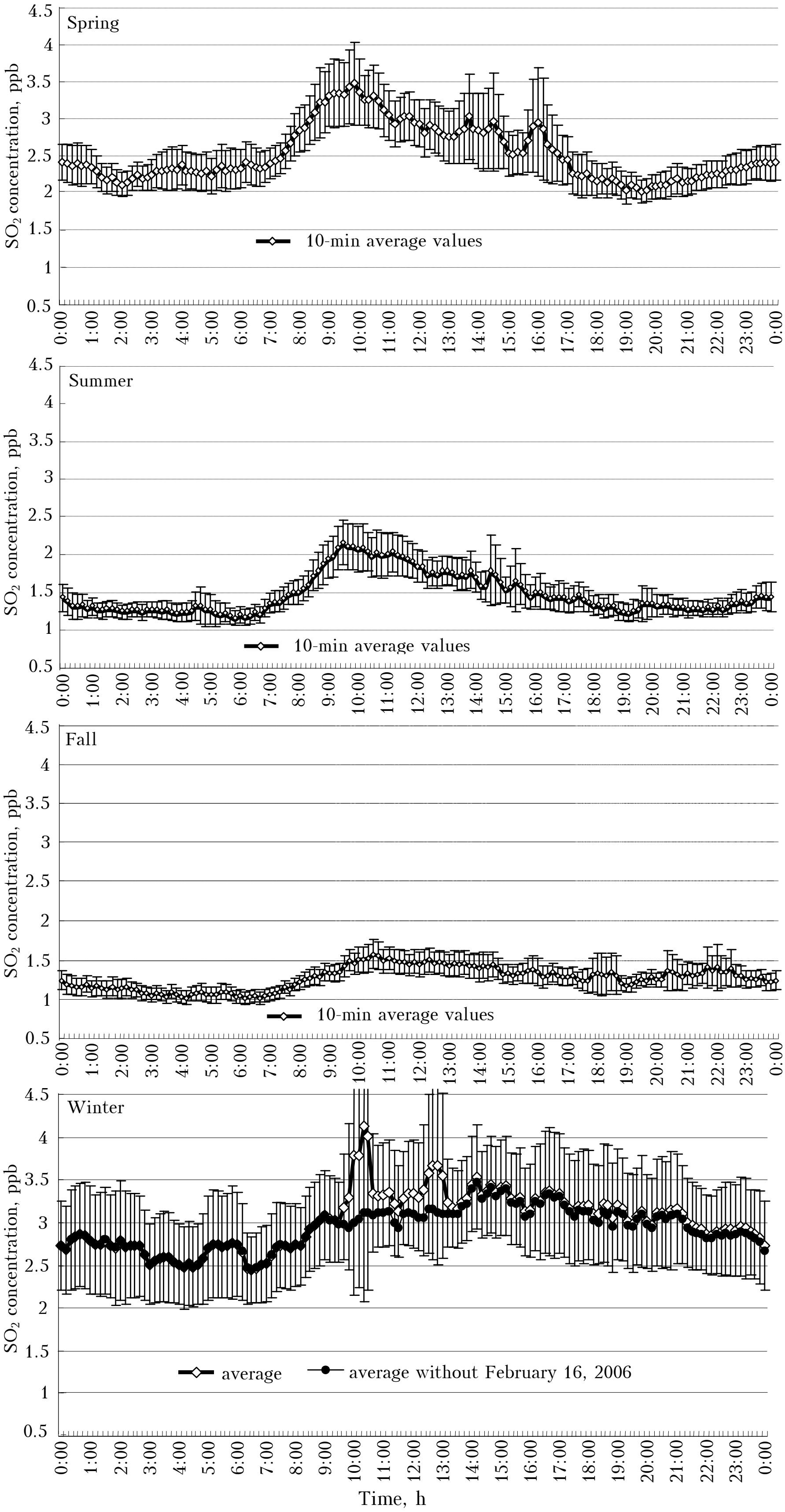


Fig. 4. Daily variations of SO_2 ground level concentration in Moscow (MSU) in different seasons according to the measurement data of 2004–2006, ppb (*a*).

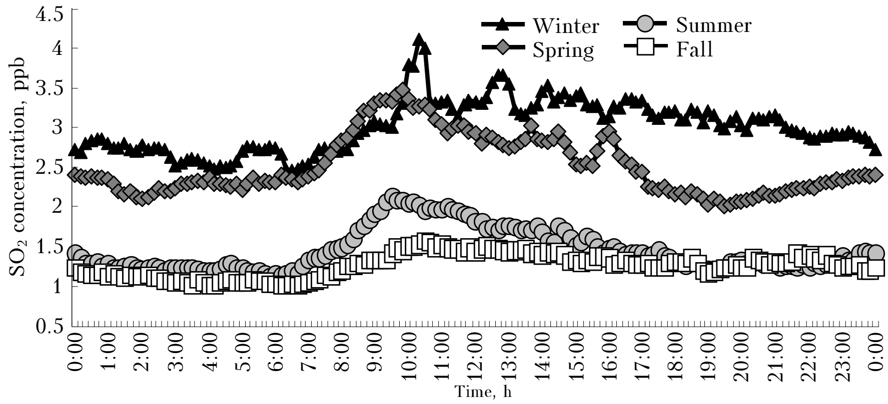


Fig. 4. (Continued) Summary plot of average values (*b*).

According to the data of joint monitoring station, none of other contaminants shows such daily behavior.[4] This is seemingly because urban sources of SO_2 are mainly lofty in contrast to those of other gases. Due to this, SO_2 is accumulated in the ground layer in the morning, when the ground radiative inversion comes off the ground and mechanically exists during several hours in the form of already raised inversion at heights up to 300–400 m.

According to long-term acoustic sensing data in Moscow, the raised inversion is observed in the morning in 40% of cases in spring and in about half of the cases in summer.[8] The thermal convection, developing in the layer under the inversion, makes for intensive vertical mixing of SO_2 emissions and rise of its ground level concentration.

After the inversion break-up, SO_2 is intensively scatters into the upper layers, and its ground level concentration in day hours rapidly decreases. During the night time, SO_2 emitted by thermal heating plants propagates either in the upper part of ground inversion, within which turbulent exchange is weak, or above its top so that the ground level concentration of the gas is virtually invariable.

Morning rise of SO_2 ground level concentration is observed in fall and winter as well, while thermal convection is noticeable at this time much more seldom, and the morning maximum turns out to be long and includes the day hours al well. An extremely wide spread of values is characteristic for winter months; hence, differences in winter daily variability are statistically insignificant. Another feature of the winter season is quite irregular daily variations with 10-min step due to predominance of some days when SO_2 emission significantly exceeds the usual level. Note, that daily variation recalculation for winter (Fig. 4, black circles) excluding the only February 16, 2006 has shown a noticeable shift of average estimates in the morning and midday. Weather conditions of the days with very high SO_2 ground level concentrations will be considered below.

Note, that daily variations of SO_2 concentration in 1970th[1] were different in cities of USSR (e.g., Dnepropetrovsk) and characterized by morning and evening maxima. It is probable that significant emission reduction in the following years has resulted in qualitative change of daily variations.

Figure 4 also shows a summary plot of average SO_2 concentrations, measured at MSU, for more obvious comparison of the conditions in different seasons. The highest SO_2 concentration is observed in Moscow in winter as well as at background stations in forest reserves.[13] Along with this, an asymmetry of mid-season conditions is evident: SO_2 concentrations in Moscow in spring is nearly the same as in winter, while in fall even less than in summer. It is necessary to note that mean air temperature in Moscow was +5.8°C in spring and +4.8°C in fall for a period 1961–2000; hence, in general spring is 1°C warmer than fall,[15] though the heating season in Moscow usually begins in the beginning of October and ends in the end of April, taking similar time in spring and fall.

To understand the nature of difference between mid-seasons, consider the data on precipitation amount in Moscow for the above 40-year period. It was 42 mm in spring on an average and 60 mm in fall.[15] As is known, solution and washout by precipitations is the principal runoff of SO_2 from the lower troposphere. It is probable that a large amount of precipitation in fall results in the difference between mid-season conditions.

3. Reasons of extremely high SO_2 accumulation in Moscow environment

As is known, the main part of pollutant emission in the majority of large cities falls at motor transport. This part in Moscow in 1970th was about 70% of total emission.[2] At present, in conditions of setback in production and rapid rise of the number of cars, this part in Moscow is 84% according to the Mosecomonitoring data and 92% according the data of Russian Hydrometeorological Service.[11] But the contribution of lofty sources in the total air pollution can became significant, e.g., when city heating system works more intensive.

The maximum daily-average concentration limit of SO_2 is 0.05 mg/m^3, and one-time maximum is

0.5 mg/m^3 [Ref. 2]. There were only six days for the whole 4-year observation period in Moscow (MSU), when daily-average SO_2 ground level concentration exceeded the maximum concentration limit (17.0 ppb in volume units with accounting for winter-average air temperature), i.e., on January 19, 20, and 21, February 7, 8, and 16, 2006. As for individual 10-min average measurements, they exceeded the maximum concentration limit four times successively only on February 16, 2006. That day, SO_2 concentration at MSU reached 216, 202, 274, and 240 ppb (0.66, 0.62, 0.84, and 0.73 mg/m^3 in mass units) at 10.00, 10.10, 10.20, and 10.30, respectively, – record high values for the 3-year observation period.

Thus, the highest measured 10-min average SO_2 concentration 115-fold exceeded the annual average one. Several tens of years ago, the highest concentrations in different cities just 5–10-fold exceeded the average ones.[1] An evident reason of the change of this relation is a sharp decrease of usual levels of SO_2 concentrations.

Figure 5 shows the variations of daily-average SO_2 ground level concentration and air temperature for the first two months of 2006. As is evident, a sharp increase of the concentrations up to 20–25 ppb and more occurred just on the above dates against very small usual values, which were about 1 ppb and lower.

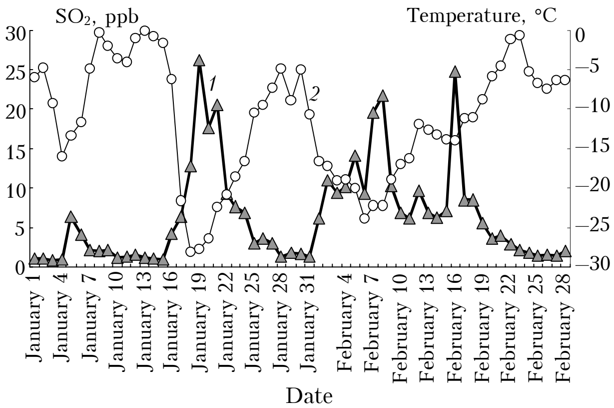


Fig. 5. Daily-average variations of SO_2 ground level concentrations (*1*) and air temperature (*2*) in Moscow (MSU) in winter, 2006.

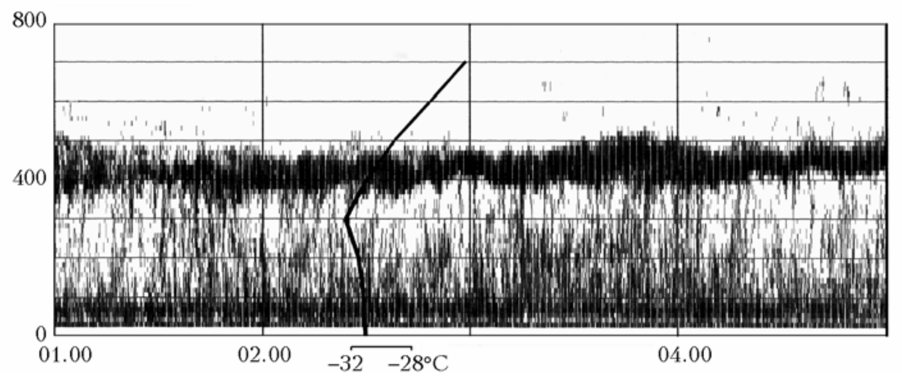
Such sharp increase was observed in two case of three just after sharp decrease of air temperature. Thus, on January 18, daily average air temperature at MSU station was –28.0°C and the morning minimum was –30.1°C. Note, that the air temperature in Moscow for the last twenty years was lower only once, in 2003.

Figure 6 presents the microring chart of near the ground analysis for three hours for this day. As is evident, the axis of high pressure passed near Moscow, which was near the edge of area of intensive gradient flows between the anticyclone, centered above the coast of the Kara Sea, and the cyclone above the Kazakhstan. As is seen, the stable area in the Arctic front system reached the Black Sea coast, so that the arctic air predominated all over the European Russia. Just at this time, in conditions of hard frosts, back-up fuel (black oil with high sulfur concentrations) began to be used at heating plants in Moscow along with the conventional gas.

An additional factor, determining an increased SO_2accumulation in the surface layer, was the temperature stratification. As is known, the altitude-timebase of echo signal of an acoustic locator (sodar record) is the source of the detailed data on temperature stratification, including its type up to the sign of temperature vertical gradient and the boundaries of characteristic turbulent structures, related to the trapping inversion layers [Refs. 6, 7, etc.]. Continuous acoustic atmosphere sensing is carried out at the Meteorological Observatory of MSU with two sodars: "ECHO-1" made in East Germany and "MODOS" made by METEK (Germany). An altitude range of the "ECHO-1" sodar is 800 m, vertical resolution is 12.5 m.[8] Data of this sodar is used for detailed study of temperature stratification. As is seen from Fig. 6, in the beginning of the first episode of extremely high SO_2 concentration on January 18, 2006, a raised inversion structure in the form of intensive echo-signal layer was observed on the sodar record of MSU station all through the day.

A strong ground inversion was expectable to be observed at so frosty weather. However, below this layer, connected with the inversion base, random echo-signal structures are evident on the record, characteristic for the weakly stable stratification. Indeed, according to the radio sensing data at the nearest aerological station Dolgoprudnyi, 25-km distant from MSU (the temperature profile superimposed onto the sodar record), the inversion at this time was raised with a lower boundary of about 300 m. The temperature was almost invariable with height in the ground layer. It is probable that cold advection from the Western Siberia, continuing at this hours, determined the absence of the surface inversion in the center of European Russia. Another reason of the raised inversion formation in Moscow could be a surface temperature raise due to intensive heating of the city. A raised inversion of such type can be called "urban"; its qualitative mechanism is described in Ref. 12.

This inversion continuously existed over Moscow within the bottom 800-m layer from the morning of January 17 to the noon of January 21, i.e., during all the first episode of extremely high SO_2 concentration. A very low raised inversion with the bottom boundary not higher then 200 m was observed in the morning on February 7, 8 and 16, 2006. Just at 06:00 in February 7, at the presence of trapping inversion layer, the SO_2 ground level concentration sharply increased up to 70 ppb. During these days, the SO_2 ground level concentration increased (also up to 70 ppb) in the period from 16:00 to 19:00 only once, where the inversion was absent, according to sodar data.



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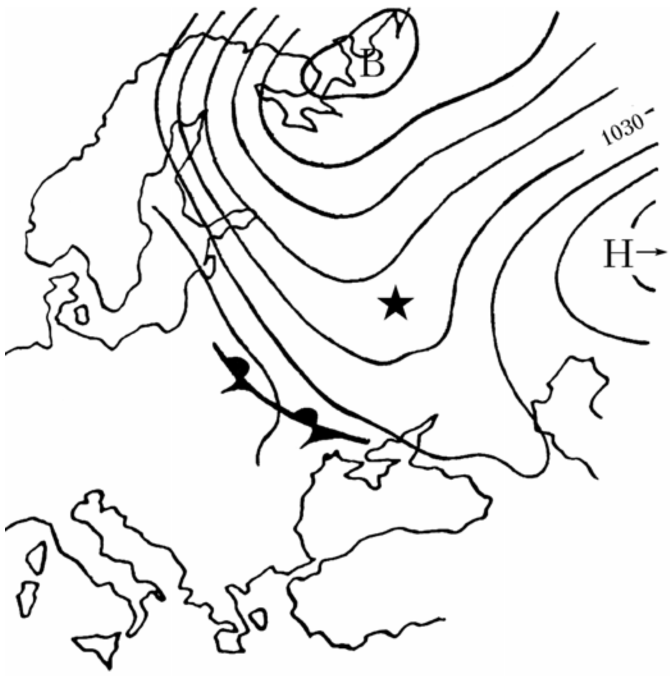

b

Fig. 6. The turbulent structure of raised inversion in the sodar record on January 18, 2006 at MSU station in hard frost (*a*) and the microring chart of near the ground analysis for three hours of this day (*b*). Moscow is singed by the star. The temperature profile corresponding to the radiosonde data at 02:30 is superimposed onto the sodar record. Isobars are marked with the 5 hPa step.

As for the wind velocity V at heights, measured at MSU with the "MODOS" sodar, its explicit connection with the conditions of SO_2 accumulation was not found. The wind was very weak in the lower 100-m layer on February 16 ($V < 3$ m/s), while its velocity in this layer was close to usual winter values (5–7 m/s and more) on January 19–21. Probably, the wind direction from the nearest emission sources is defining for the SO_2 ground level concentration dynamics rather than the wind velocity.

Finally, a sharp increase of SO_2 ground level concentration above usual values is probable in winter when using a backup fuel for city heating in hard frosts; it is usually accompanied by unfavorable weather conditions, i.e., trapping raised inversion.

Conclusion

1. SO_2 ground level concentration significantly decreased in Moscow for the last half of century; the decrease was especially rapid in 1970th due to excluding solid and liquid fuel from the use at the city heating system. As a result, the difference between urban and background values of SO_2 concentration decreased as well.

2. In annual variations of SO_2 ground level concentration in Moscow, maxima are recorded in winter in hard frosts and minima – in summer and fall. Significant differences in average SO_2 ground level concentrations in mid-seasons (higher in spring than in fall) can well be due to a large amount of precipitations in Moscow in fall months.

3. Daily variations of SO_2 ground level concentration in Moscow is characterized by a statistically valuable morning maximum hypothetically connected with increased accumulation of SO_2, emitted by lofty sources (chimneys of industrial enterprises and thermal heating plants), under the raised inversion.

4. Some decrease of average SO_2 levels results in the 100-fold and higher increase of the ratio of one-time maximum and average values in Moscow. During last several years, one-time SO_2 concentration exceeded the maximum concentration limit only once, and daily average concentration – only six times. It happened in 2006 in the conditions of hard frosts and more intensive work of city heating system with the use of backup fuel (black oil). A raised inversion at small heights (according to sodar data) also made for SO_2 accumulation.

5. More intensive heating of the city in hard frosts can be an independent reason of "urban" raised inversion formation.

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