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Continuous synchronous measurements of sulfur dioxide, formaldehyde, nitrogen dioxide and ozone concentration by open path analyzer DOAS-4R at Obninsk in summer 2002.

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1. Introduction

Purity of the atmospheric air is one of the major parameters of ecological condition of the environment. Ecology deterioration in large cities is recently observed, and first of all, it is bound up with the sharp increase of vehicle traffic. Trans-boundary transport of gas pollutions from the territories of CIS and Western Europe plays not a minor role in the atmospheric pollution of rural areas of European Russia [1]. In this connection, development of instruments for ecological monitoring of the atmospheric gas pollution is of great importance. Standard practice of trace gases detection is based on sampling with subsequent laboratory analysis, and that does not meet modern requirements from the point of view of efforts, efficiency and opportunity of automatic continuous measurements. As an alternative in many cases, the method of differential optical absorption spectroscopy (DOAS) [11] can be used, which has been successfully developed for the last two decades, from pilot measurements to creation of commercial instruments. Now on the agenda is development of officially authorized measurement techniques and implementation in practice the instruments of ecological monitoring of the atmospheric gas pollution.. The important steps toward that have been made by the American agency on environment protection (EPA) which has approved a DOAS system made by OPSIS as an equivalent method of measurements of three atmospheric gas pollutants: SO2, NO2, and O3. Actually, the list of the gases, measured by a DOAS gas analyzer, is much longer, and the opportunity of parallel measurement of a number of gas components is important advantage of this instrument. The first in Russia DOAS-based commercial gas analyzer has been developed by Eridan-1. The continuous parallel measurements of four atmospheric gas pollutants: SO2, NO2, CH2O and O3 have been done in Obninsk in the period from July, 15 until September, 30, 2002 . Measurement results and analysis are given in the present article. As it has been already mentioned, three gases from this set are referred by

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EPA as crucial, which means that they are measured everywhere, and the quality of atmospheric air is estimated by them. As to formaldehyde, it is, as well as ozone, the one of the basic components of the photochemical smog and reveals its toxic characteristics even at rather low concentration.

2. UV Open Path Gas Analyzer DOAS-4R

The instrument operates in spectral area of 200-460 nm. The principle of operation of the instrument consist in the following. Light radiation from an arc xenon lamp is collimated by a telescope and is directed along the atmospheric path. On the opposite end of the path an angular reflector (retroreflector) is placed which reflects a part of radiation back to the telescope. The part of radiation, that passed the path in the opposite direction, gets in an aperture of the receiving channel of the telescope and is focused at an entrance window of an optical guide. Through the optical guide the radiation gets on an entrance slit of a spectrograph, inside which it is decomposed into a spectrum. Depending on the selected set of gases the appropriate spectral range is chosen, 60 nm long. For registration of the spectrum in this range a photo diode line is used, the signal from which is digitized by an analog-digital converter and comes to a computer for further processing.

During processing the spectrum of radiation, passed the path, is compared to a spectrum of the source therefore the changes caused by absorption of radiation by the atmospheric gas components are discovered. Application of the differential method enables to exclude those parts of the spectrum that vary slowly against the wavelength, because of, for instance, influence of molecular and aerosol backscattering of radiation along the atmospheric path. As each gas has its individual spectrum of absorption, the analysis of changes of the spectrum allows to identify absorbing gases and to determine their concentration. The instrument is completely automated and after adjustment works in an independent mode without intervention of the operator. The additional information on the instrument and the measurement technique contains in [10].

3. Experimental environment

Measurements were conducted in Obninsk, a town located about 100 km southwest from Moscow. The atmospheric path was near the meteorological mast (MM) of STC "Typhoon".

The instrument was set up in a one-store laboratorial premise with a window.. The retroreflector was set up on the first balcony of MM at height of 25m above the ground. The length of the light path (there and back) was 450 m. There was an opportunity to use continuous measurements of meteorological parameters being conducted on the MM for interpretation of the measurements.

Incidental measurements have begun from the end of May. Continuous measurements for all four gases had been performed from the middle of July up to the end of September. It is known, that in the period since July up to the middle of September, 2002, very dry and hot weather has been observed, that has resulted in a plenty of forest fires . Forest fires are sources of aerosol and gas pollution of the atmosphere, so the measurement results for the given period are also interesting from the point of view of studying the possible influence of extensive forest fires on concentration of polluting gases.

4. Measurement results

290-350 nm spectral range has been chosen for measurements, that allowed to make parallel measurements of four gases in the atmosphere - SO2, CH2O, NO2 and O3. Periodicity of measurements was 5 minutes at the time of signal accumulation of about 2-3 minutes. All data set from the middle of July up to the end of September has made about 20000 measurements.

In parallel with calculation of gases concentration the error estimate of concentration was carried out by taking in account the current values of the residues during adjustment by the least squares method. Average concentration measurement errors for all period of measurements have made 0,1; 0,5; 1,0 and 1,8 ppb for SO2, CH2O, NO2 and O3.

Average values of gas concentration for the various measurement periods are submitted in tab. 1 according to which the average concentrations of SO2 and NO2 were much lower than the daily average maximum permissible concentration (MPC), while the averages of CH2O and O3 for all time of measurements were 1.7 and 1.9 times as much as the appropriate daily average MPC.

During observation there was no any day with excess of SO2 and NO2 daily averaged MPC. For O3 the daily average MPC was exceeded for 90% of all days of observation, and for CH2O - for 60% of days. It says about a high enough level of atmospheric air pollution by CH2O and O3 for that period of time.

In tab. 2 for each gas the three of the maximal values from all registered concentration is shown. The measurement data were averaged on a 20 minute interval appropriate to the averaging time of determination of MPCs. The latter values, as is known, make 17, 26, 42 and 75 ppb for SO2, CH2O, NO2 and O3 accordingly. From comparison of MPC with data of tab. 2 it follows that the maximal registered values were close to single MPC for NO2 and O3 and were significantly lower than those for SO2 and CH2O. Maximal concentrations of NO2 were observed at night, and O3 - at the end of day. Increased concentration of CH2O in the beginning of September were measured when smog situation was being observed at this time in the central areas of Russia. So, for instance, on September, 5 in Obninsk, according to MM observers, visibility range in the morning was only 0.5 km.

Probability distributions of concentration for each of gases (fig. 1) were constructed from the observation data . It turned out, that in the most part of the concentration range the logarithm of distribution functions is well enough approximated by a parabolic or a linear (for SO2) dependence, that is, in this case, the drop-down part of distribution is described by the normal or exponential distribution. As may be seen from fig. 1, at maximal concentrations the really observed number of cases is overestimated in comparison with the approximating distribution (except for O3), that points to existence of the separate mechanism responsible for formation of the maximal concentration. However, less than 1% of all measurements can be related to this area of data.

Factors of mutual correlation of concentration of the gases are given in tab. 3. We can note the high enough level of SO2 and CH2O correlation and anticorrelations of NO2 and O3. Correlation of SO2 and CH2O concentrations points to their common source. Anticorrelation of NO2 and O3 concentration of is concerned with interconversions of these gases as a result of the following photochemical reactions in the atmosphere:

$$(R_1)\ NO + O_3 \rightarrow NO_2 + O_3\,; \qquad (R_2)\ NO_2 + hv \rightarrow NO + O; \qquad (R_3)\ O + O_2 + M \rightarrow O_3 + M.$$

5. **Comparison with the data of other measurements**

Approximately at the same time, CAO employees measured O3 ground concentration in a suburb of Moscow [4]. According to their data, O3 peak concentrations were observed on July 8, 13, 20, 27 and 31. The increased ozone concentration were also observed at those dates in Obninsk, although the maximal concentration were registered in the beginning of July. Values of peak concentration for the specified days in Obninsk were 1,5-1,9 times less than in the Moscow suburb. The best conformity was obtained on monthly averaged concentrations that were calculated the same way as [4], in order to compare, i.e. averaged values for 11 and 14 hours were taken. Concentrations in mkg / m3 for suburb of Moscow and Obninsk have made 95 and 80 for July, 72 and 73 for August, and 50 and 42 for September. It folows that the difference. obtained by the averaged values, does not surpass 20% , that can be partly connected to distinctions in a measurement technique (time of averaging, height above a ground surface etc.) and with measurement errors . It follows from results of comparison, that monthly averaged concentrations of ground ozone are formed as a result of factors of regional scale. At the same time the affinity of a large megacity that Moscow is, renders essential influence on a value of peak ozone concentrations in its nearest vicinities. We note, that the similar picture was mentioned in [7] at comparison of ozone concentration measurements in Budapest and Sarvash (160 km from Budapest).

6. Time dependence of daily average concentrations

On fig. 2 the time dependence of average daily concentrations (ADC) of measured gases is submitted: for NO2 and O3 by months (second half of July - fig. *2a*, August - fig. *2b*, September - fig. *2c*), and for SO2 and CH2O for all period of observation (fig. *2d*). The trend of curves shows significant variations of gas concentration day by day, and fluctuations of NO2 and O3 concentration frequently occur in an antiphase, and SO2 and CH2O concentration in part correlate among themselves. Below we attempt to reveal the factors essentially influencing variations of daily average values of concentration of the examined gases.

Meteorological data obtained by MM SPO Typhoon were used for time dependence analysis of NO2 and O3. Automated measurements of: wind speed and direction (at 8, 121 and 301 m levels), temperature (at 2, 121 and 265m levels), and atmospheric pressure (at 2 m) are carried out at the MM . Besides, atmospheric precipitations are recorded as well as estimation of visibility range. Unfortunately, temperature recording during the gas measurements was only at 2 m level, and only in September at two levels - 2 and 121 m. And so, data on inversions presence were available only for one month of measurements for the bottom 120-meter layer of the atmosphere.

First let's consider comparison of the ADCs with the wind speed and a direction . For analysis all ADC values were divided into three groups by concentration value, so that in every group (low, average and high) contained about 1/3 from all measurements. At that splitting, in the group of high concentrations there were ADC values exceeding 0.67, 3.5 and 10.0 ppb for SO2, CH2O and NO2. The direction of a wind was subdivided into 8 points, and speed - into 3 gradation (weak, moderate and strong). The gradation of the wind speed was relative enough as it concerns only to a set of wind speeds observed and was done only for the purpose of analysis of possible correlations between the concentrations and the wind speed.

The preliminary analysis has shown that really there are correlations between the gas concentrations and the wind speed and direction and the most distinct is the correlation with wind characteristics at the height of 121 m . Therefore, we will consider comparisons to wind parameters at this height. In tab. 4 relative frequencies of increased gas concentrations for various wind directions, and in tab. 5 - the same frequencies for various gradation of wind speed are shown. Relative frequency here is meant as the relation of number of observations with the increased concentration to the common number of observations for the given point or a range of wind speeds . Significantly increased concentration values (at a significance level of 0.66 and higher) are shown in bold.

From tab. 4 follows, that for all gases the increased frequency of registration of high concentrations is observed for the east direction of the wind, and, on the contrary, the lowered frequency for the western wind. The increased frequency of registration of high concentrations of all gases for east wind, probably, is connected to advection of gas pollutions from the area of forest fires in the east the Moscow region. According to tab. 4, for each gas there are distinct points at which high concentrations of the given gas are frequently observed. So, for SO2, the N and NW directions are distinguished by high concentrations, and for CH2O the SE direction is added. For NO2 high concentration are observed for SE and adjoining to it E and S. The maximal frequencies of observations of high concentration for O3 are marked for SW when air is rather less polluted with other gases. From tab. 5 follows, that for NO2 the maximal frequency relates to a case of a weak wind, and for SO2, CH2O, on the contrary, the frequencies grow with increase of wind speed .

Increase of frequencies at weak wind for NO2 shows that the source responsible for variations of NO2concentrations, is local and ground-based. It agrees well with the known fact, that one of the basic sources of NO2 emissions in the atmosphere is motor transport [9]. The arrangement of the measurement path is that the most of city streets are south and southeast from it, and the east direction is a shortest to a large Kiev highway. And it is just that direction of wind at which the increased NO2 concentrations are often observed.

Nox emissions by vehicles influence O3 contents indirectly. As is known, in immediate proximity from motor roads the NO and NO2 concentration ratio is in the range from 5 up to 10 [8]. At the further mixing with the purer atmospheric air NO reacts with O3 with formation of NO2. From here it is clear, why the maximal frequency of registration of high concentrations of NO2 for SE matches to the lowered frequency of high concentrations of O3 (see tab. 4).One might assume, that without the influence of vehicle emissions in the immediate area of Obninsk, observation frequencies of high concentration O3 for E, SE, S and SW would be approximately identical and met to the certain average regional level.

Besides the wind speed, pollution concentrations are influenced by the atmospheric temperature stratification and precipitations. It is known that the increase of gases concentration from ground sources is more probable at stable stratification especially at presence of inversions in the boundary layer of the atmosphere. During precipitation the vertical exchange in the atmosphere decreases, that can also result in increase of pollution concentration during a rain [2]. On the other hand, during precipitation fall the gas and aerosol pollutions of the atmosphere are washing away . Influence of temperature inversions and precipitations on a trend of daily NO2 concentration is illustrated by fig. 2. Days with appreciable precipitations (more than 1 mm of the precipitated water) are marked on fig. *2a* - *2c* by black squares on curves of NO2 time dependence. Besides, on fig. *2c* by daggers (also on the curve of NO2 time dependence) the days of September are marked when night and morning inversions in the layer from 8m up to 121m were observed, and from this figure one can see, that all local peaks of NO2 concentrations were observed under conditions of temperature inversions . At the same time fig. *2a* - *2c* show, that significant precipitations always resulted in decreasing of NO2 ACD either on the day of precipitations , or the next day.

The September, 17, when the highest NO2 ADC for September was observed, is a special case. This day both inversions and precipitations were observed. The analysis has shown, that this case of sharp increase of NO2 level is connected to advection from any local source or from areas of forest fires under conditions of low vertical mixing in the boundary layer of the atmosphere. Thus , rather intensive precipitations has not resulted in decrease of NO2 concentration.

Increase of observation rate of high concentrations for SO2, CH2O with increase of wind speed points to the fact that the source of these gases is high-altitude. In this case, when the turbulent diffusion factor increases with the wind speed, the surface concentration of these gases also increases. The vertical distribution of SO2 concentration in Moscow [6] can be an additional argument for the conclusion about SO2 accumulation and transport at some altitude.

Since the wind direction dependence for CH2O is weak in rather wide range of directions from NE to S, one can conclude that pollution of the atmosphere by CH2O has local character. For SO2, E and NE are some more distinguished Possibly it is influenced by the Moscow region where a plenty of electric power stations [5] are located or by the forest fires.

In order to verify the influence of forest fires on observable gas concentrations, the comparison of daily concentration trends for SO2 and CH2O with the dynamics of forest fires in Moscow region (fig. *2d*), which is the nearest to Obninsk region, where a big number of forest fires was observed, was made. The data on forest fires has been taken from messages of the press-service of the Ministry of natural resources of Russian Federation. As can be seen from fig. *2d*, indeed, two waves of increase of forest fires at the end of July and at the beginning of September were accompanied by the raise of SO2 and CH2O concentrations .

7. A daily trend of concentration of measured gases

The average daily trend of NO2 and O3 concentrations is given on fig. *3a*, SO2 and CH2O concentrations - on fig. *3b*. NO2 and O3 data have been averaged over months, and SO2 and CH2O - over all period of observation. From fig. *3a* and *3b* one can see that only NO2 and O3 gases have a distinct daily trend. At that, the daily changes of concentration of these gases substantially occur in reversed phase that is bound to the mentioned above photochemical reactions. Day time trend of O3 is formed as a result of overlapping of time profiles of NOx (NO + NO2) sources (including a secondary maximum of sources in the evening), speed of NO2 photo dissociation, determined by UV illumination from direct and scattered sunlight, and dynamics of the vertical exchange processes [7]. As can be seen from fig. 3, reduction of light day from July to September results in reduction of absolute values of O3 concentration and to reduction of duration of a day time maximum. Rise of O3 concentration in the early morning when light illumination in UV is still negligible, can be connected to development of vertical mixing and ozone pumping from higher layers of the atmosphere. Falling of O3 concentration after 6pm and parallel growth of NO2 concentration are connected to gradual de-energizing of the mechanism of photochemical generation of O3. At night time concentration continues to fall as a result of the ozone expenditures in oxidizing chemical reactions in the polluted atmosphere, and also due to ozone drain to the underlayer. In some periods of time, for example, from August, 29 till September, 5, in addition to day time maxima of ozone, night maxima were observed as well, that is connected, apparently, with advection of this gas from more polluted areas.

The received data on daily trends of NO2 and O3 meet as a whole to existing conceptions and published data on dynamics of these values [7, 12]. Prominent feature of O3 structure is preservation of high O3 concentrations till 7pm during summer months (July, August). Such structures were observed in many areas, free from anthropogenous sources of gas pollution [7, 12]. At the same time there are some differences in comparison to the daily profiles for the summer season in Moscow [3]. So, for Moscow, NO2 daily trend is considerably smooth, and drop of O3 concentration begins after 4pm, not after 6 pm as our measurements show.

Daily dynamics for SO2 and CH2O (fig. *4b*) is much less distinguished. The morning maximum, similar to the same maximum for NO2, is only observed. Apparently, the same mechanism is responsible for formation of this maximum, which is concerned with reduction of concentration near the surface owing to the drain to the underlayer at night, night accumulation of these gases under the inversion layer and development of vertical exchange at the mentioned morning hours that results in increase of concentration of these gases. It is possible, that the certain influence is exerted by morning switching-on of vehicle sources for NO2 and CH2O. Further, with destruction of inversion, there is a pumping of purer air from overlying layers, and concentration decreases.

8. Conclusion

The results of synchronous continuous measurements of concentration of four atmospheric polluting gases: SO2, NO2, CH2O and O3 by the method of differential optical absorption spectroscopy in Obninsk are presented in this article . The period of measurements spans two and half months, from July, 15 till September, 30, 2002. In total for that time about 20 thousand of independent measurements with averaging of 5 minutes have been performed. The place of observation represents the nonindustrial city located in 100 km from Moscow. Meteorological conditions from July, 15 till September, 15 was characterized as a steady anticyclone with hot, dry weather. During measurements a plenty of forest fires in many areas was observed.

On average, for the period of measurements the level of pollution of the atmosphere in comparison with existing MPCs is characterized as rather high for CH2O and O3, moderate for NO2 and low for SO2. Rather significant variations of daily average concentration for all gases are observed. Time variations of SO2 and CH2O concentration correlate among themselves, and for NO2 and O3, on the contrary, occur in antiphase. For NO2 the increased concentration, as a rule, was observed during days with temperature inversions. Precipitations resulted in decrease of NO2 concentration either on the same or next day. It was noticed, that average daily concentration of SO2 and CH2O rose during increase of quantity of forest fires in the Moscow area.

For an average daily trend the presence of deep day time minimum of NO2 and maximum of O3is typical, and in summer months the latter survived 7pm. For SO2 and CH2O the feebly distinguished daily trend with a maximum in area of 10am was obtained, that approximately conforms to the time of the beginning of inversionsdestruction. The analysis of a dependence of occurrence of the increased concentration of gases from the direction and force of the wind results in a conclusion that the source, that is responsible for variations of NO2concentration , is local and ground-based (most likely - vehicles). At the same time the increased concentration of SO2 and CH2O are concerned with pollution transport at some altitude from regional or more distant sources.

The carried out prolonged continuous measurements have shown, that DOAS-4R gas analyzer can be used successfully for gas pollutions monitoring .

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Table 1

Average gas concentrations (ppb) for the various periods of measurements

Period	SO_2	CH_2O	NO_2	O_3
July (2nd half)	0,49	3.2	9,0	34
August	0,64	3.4	7.9	29
September	0,63	3.3	9.3	18
All period	0,60	3.3	8.7	26

Table 2

Extreme values of concentration (20 minutes averaging)

Gas	Concentration, ppb	Date	Time, hr
SO_2	6,6	29.07	06
	6,9	14.08	16
	8,0	17.08	09
CH_2O	14	30.07	10
	15	05.09	09
	20	08.09	17
NO_2	48	23.07	22
	53	17.08	00
	45	18.09	00
O_3	71	29.07	18
	76	30.07	17
	73	16.08	18

Table 3

Factors of correlation of gas concentrations measured by DOAS-4R in Obninsk, July, 15 - September, 30, 2003.

	SO_2	CH_2O	NO_2	O_3
SO_2	1	0.532	0.120	0.129
CH_2O	0.532	1	0.206	0.110
NO_2	0.120	0.206	1	-0.413
O_3	0.129	0.110	-0.413	1

Table 4

Relative observation frequencies of the increased gas concentration against wind direction at 121 m

Rhumb	SO_2	CH_2O	NO_2	O_3
N	-	-	-	-
NE	**0.40**	**0.40**	0.30	0.11
E	**0.54**	**0.46**	0.38	**0.50**
SE	0.33	**0.40**	**0.60**	0.21
S	0.36	0.36	**0.45**	**0.44**
SW	0.24	0.29	0.24	**0.58**
W	0.20	0.20	0.13	0.13
NW	-	-	-	-

Notice: N and NW lines are blank because of absence of stable wind for those directions that time.

Таблица 5

Относительные частоты наблюдения повышенных концентраций газов в зависимости от скорости ветра на уровне 121 м

Wind speed, m/s	SO_2	CH_2O	NO_2	O_3
< 4	0.14	0.19	**0.57**	0.35
4 - 6	**0.40**	**0.40**	0.30	0.23
> 6	**0.54**	**0.46**	0.38	**0.46**

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