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VERTICAL STRUCTURE OF AIR POLLUTION LAYER IN POLAR INDUSTRIAL AREA

M.I. Beloglazov, L.A. Pershakov, V.C. Roldugin, S.A. Rumyantsev and V.A. Shishaev

Polar Geophysical Institute, Apatity, Murmansk region, Russia
roldugin@pgi.kolasc.net.ru

ABSTRACT

The possibility of the using of surface ozone measurements for monitoring of atmospheric pollution is estimated. It is shown that the reactions of its species for ozone is quick for nitrogen oxide, and slow for carbon oxide in winter and spring conditions. The results of surface ozone measurements at levels 1.7 and 17 meters in the polar atmosphere are presented. It is found out the three types of surface ozone reaction for atmospheric pollution episodes. Directional analysis shows the connection of disturbance types with the industrial and transport objects. It is supposed that these types are bound up with the altitude of atmospheric pollution source.

Key Words: atmospheric pollution, surface ozone, nitrogen oxide, wind direction

1. INTRODUCTION

The man-induced air pollution is always present in the modern industrial areas. Admixtures, while spreading away from sources, pollute the air around the industrial areas, changing its properties and resulting in negative effects on people's health, usually being toxic substances. The dynamics of polluting areas complex and depends much on the atmosphere condition, in the first place, on the velocities field of the atmospheric wind. Theoretical dynamics of air pollutions is studied on the basis of mathematical modeling of meteorological and chemical processes, taking place in the area of pollution (Bajin et al., 1991). When the description of a pollution near the source is used in a practical purpose, both models are used: the diffusion one for imponderable admixture (Fedosov, 1998), and the hydrodynamical model for admixtures heavier than atmospheric air (Shagapov and Galiaskarova, 2002). The theory does not answer many questions in specific meteorological conditions, in particular, the one concerning the atmospheric distribution of pollutions under a very weak wind, when admixtures are not carried away but are accumulated near, thus forming the observed structures of smog. For interpretation of the observations the altitude of the source of pollution is an important value, which tells upon its structure. For an experimental study of admixtures dynamics the chemical properties of substances, which make part of their composition, can be used. Besides, to find nitrogen oxides and carbon oxide the atmospheric ozone can be used, the quantity of which varies much under their influence. Thus, ozone observations on a regular basis can be applied for the atmosphere pollution monitoring. This approach is used in this

paper, which contains the results of experimental study of pollutions distribution at two altitudes under weak wind conditions.

2. IMPACT OF ATMOSPHERIC POLLUTION ON OZONE

Variations of the surface ozone concentration (SOC) take place both at the chemical impact of the surrounding air and due to the transport of air masses with inhomogeneous chemical composition. The arising of SOC variations is possible as well during a long existence of ground inversion, when the SOC will be reduced because of deceased inflow of ozone from above.

The gas phase of air pollution is consisted of almost by half of nitrogen oxides NO_X and carbon oxide CO. These substances actively interact with surface ozone both directly (for $NO_X = NO + NO_2$):

$$NO + O_3 \rightarrow NO_2 + O_2, \quad k_1 = 2 \cdot 10^{-12} \exp(-1400/T) \text{ cm}^3 \text{ sec}^{-1}, \qquad (1)$$

$$NO_2 + h\nu \rightarrow NO + O, \quad k_2 = 0 \div 10^{-2} \text{ sec}^{-1}, \qquad (2)$$

and forming in the case of CO an important precursor of ozone – hydroperoxide HO_2 in reactions (Crutzen and Zimmerman, 1991):

$$CO + OH + O_2 \rightarrow CO_2 + HO_2, \quad k_3 = 2.4 \cdot 10^{-13} \text{ cm}^3 \text{ sec}^{-1}, \qquad (3)$$

$$HO_2 + NO \rightarrow NO_2 + OH, \quad k_4 = 3.7 \cdot 10^{-12} \exp(240/T) \text{ cm}^3 \text{ sec}^{-1}, \qquad (4)$$

$$NO_2 + h\nu \rightarrow NO + O.$$

Here T is air temperature, the reaction with participation of quantum hν designates photodissociation. The atomic oxygen, formed in the reaction (2), is quickly transformed into ozone. The range of values k_2 represents approximately the region of change of photodissociation rate in the high-latitude atmosphere (Beine et al., 1999). The characteristic time of photodissociation ranges from the value of 100 sec up to very large values depending on the ultraviolet radiation (UVR) intensity.

The characteristic time of nitrogen dioxide formation in reaction (1) will make $\tau_1(NO_2) = [NO_2]/k_1[NO][O_3] \approx 10^2$ s with $[NO_2] = [NO] = 10$ ppb, $[O_3] = 20$ ppb. With higher SOC the reaction time $\tau_1(NO_2)$ will still be less. Concentrations of ozone and nitrogen dioxide by means of reaction (1) will be changing quickly along with the nitrogen oxide concentration change in condition of weak photodissociation, when k_2 is little. The characteristics time of HO_2 formation in reaction (3) $\tau(HO_2) = [HO_2]/k_3[CO][OH] \approx 40$ s with $[OH] = 5 \cdot 10^5$ см$^{-3}$, $[HO_2] = 10^7$ см$^{-3}$, $[CO] = 150$ ppb; the characteristic time of nitrogen dioxide formation in reaction (4) will make $\tau_4(NO_2) = [NO_2]/k_4[NO][HO_2] \approx 10^4$ s. One can see, that the concentration of nitrogen dioxide will be changing much slower in reactions (3,4), compared to the reaction (1). The key moment here is the concentration of hydroxil OH which ensures the oxidation of CO. Formation of HO_2 from CO is weak at night when OH concentration is too little. But at daytime hydroperoxide HO_2 will be generated at considerable greater quantities and will weaken ozone decrease at reaction (1), interacting with NO. Thus carbon oxide CO will exert little influence on ozone decrease under NO increase at night, but this influence will become stronger at day and ozone decrease at reaction (1) will be smaller. These conclusions are correct under the conditions of weak photodissociation.

The influencing of reactions (1) – (4) on SOC is investigated quantitatively with application of the chemical model at work (Rumyantsev and Roldugin, 2003).

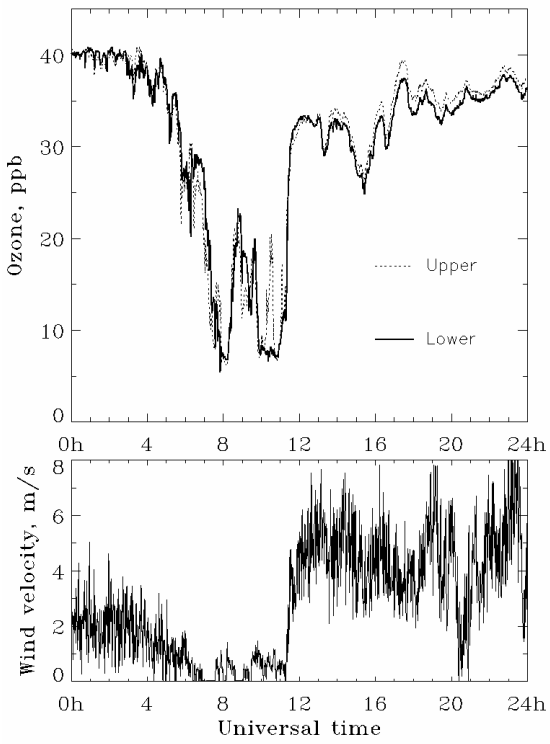

Figure 1. Surface ozone concentrations at two levels (top) and wind velocity (bottom) on 19 December 2003.

3. OBSERVATIONS AND RESULTS

The observations of SOC on two altitudes were curried out in December 2003 – April 2004 on the atmospheric station of Polar Geophysic Institute located in 1.5 km from the outskirts of Apatity town on the Kola Peninsula. Polluted air arrives to the station from the town and industrial area, which are situated on the east and north – east, and from the motorway, passed by not far (near 0.5 km) on the west, north and north – east. Long-range transport of air pollution from the industrial area of towns Monchegorsk and Olenegorsk, which are situated more than 45 km in the north – west, is possible also. There no industrial facilities or transport southwards of the station. The observational period corresponds to very weak and weak (in December – February), and moderate (in March – April) solar UVR in conditions of polar winter and spring.

SOC registration on two altitudes (1.7 and 17 m) is curried out by chemilumenescent ozonometers made in Polar Geophysical Institute. Nitrogen dioxide concentration is measured in period 29.01- 12.02.2004, on the site of location of the lower ozonometer, at the level 1.7 m. The temperature and humidity of air, atmospheric pressure on the ground level, velocity and direction of wind at altitude 10 m are determined by standard meteorological devices.

Characteristic feature of SOC behavior at the atmospheric station is appearance of ozone concentration disturbances, which represent ozone depressions which amount right up to 30 ppb and can last from one hour to tens hours. The disturbances contemporize with the stagnation periods often as it is shown by ozone measurements on one altitude (Beloglazov et al., 2002). Fast increases of nitrogen dioxide concentration take place simultaneously with ozone depressions as in (Beloglazov et al., 2002), being an evidence of chemical origin of ozone decreases. The observations on two levels show that the disturbance at the upper level does not ever accompany the disturbance at the bottom level. The change of SOC takes place under the decrease of wind velocity to small values, down to zero. The manifold of disturbances can divide to three types: 1) SOC behaviors in the lower and upper ozonometers are practically near in the disturbance period; 2) the disturbance takes place at the bottom but it is absent or is very weak at the top; 3) SOC behaviors have intermediate character when the disturbances at the top and bottom are practically

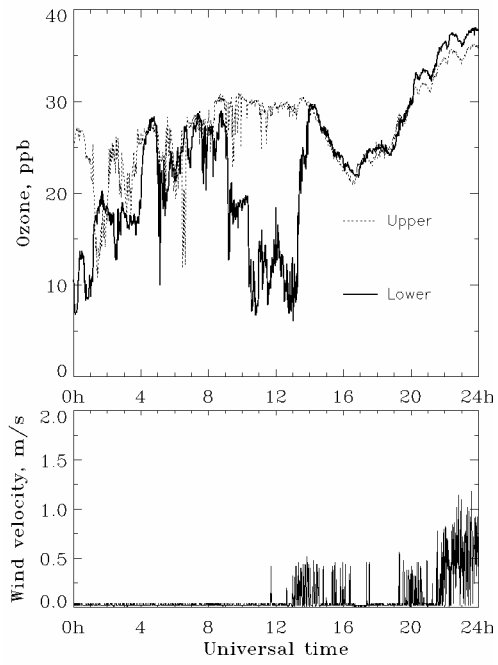

Figure2. As in Figure 1 for 3 January 2004.

near in a part of time but the disturbance at the top is weak during the rest of the time, or the disturbance at the top is distinctly less than the one at the bottom.

There were registered 118 events with duration from 1.5 to 20 hours for the observational period including 46 ones of first type, 23 of second type and 48 – of third type. Some of them are shown on Figures 1-3 in concordance with accepted classification. Figure 1 presents the case of December 19, 2003 when the event of type 1 happened about 0500-1130 UT. The ozonometer records are shown in the upper part of the Figure, the measurements results of the lower ozonometer are indicated with a thick solid line, and the results of the upper one are indicated with a thin point line. The results of wind velocity measurements are shown in lower part of the Figure. It is seen that the ozonometer records do not differ much for this disturbance; the disturbance occurs in the period, when wind velocity goes down to small values. The course of the disturbance of the second type is shown in Figure 2 for January 3, 2004. It is seen from Figure 2 that SOC at the lower level decreases to about 20 ppb at 0900-1400 UT, at the same time SOC changes weakly at the upper level. The SOC disturbance occurs in calm condition. The event of type 3 is analogously shown in Figure 3 for February 11, 2004. The deep bay to 30 ppb is observed at 1300 – 1400 UT at the lower ozonometer; this bay is recorded at the upper one only partially. The record of the upper ozonometer is nearing to the record of the lower one under small values of SOC. Wind velocity is insignificant and is less 1.5 $m \cdot s^{-1}$ at this time.

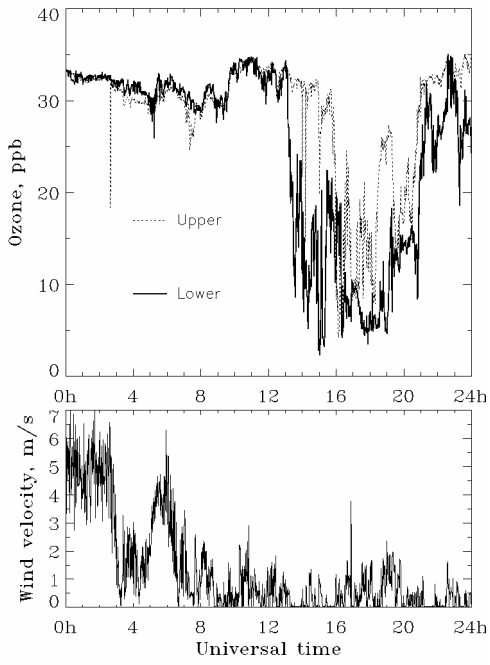

Figure 3. As in Fig. 1 for 11 February 2004.

4. DISCUSSION

Both meteorological and photochemical conditions exert some influence on the appearance of SOC disturbances. On the one hand, the meteorological factors determines the origin of areas with low values of the wind velocity, down to stagnation, in which atmospheric pollution is accumulated and ozone disappears; on the other hand, the appearance of SOC disturbances are determined also by the

photodissociation intensity preventing SOC from decrease. Monthly distributions of summary disturbance duration in local time are evidence of their gradual evolution from monotonic ones in December – January to ones with appearance of deep minimum near the noon in February; this minimum goes down to zero of duration in March – April. It demonstrates the growing importance of the photodissociation in formation of SOC disturbances.

For 81 events it is possible to determine the wind direction just before the disturbance and to find, which direction the air arrives from prior to the beginning. The distribution of different types of disturbances on wind directions befor the beginning of events is shown in Figure 4. Thick solid line represents the results for type 1, thin solid line marked by rhombus – for type 2 and dotted – for type 3. One can see that the disturbances of type 1 are connected mainly with the eastern wind, the disturbances of type 2 are absent at this wind, and the contribution of the disturbances of type 3 is not large at this wind. One could say that ozone disturbances in the air from the eastern sector take place only as registered at two levels (types 1 and 3).

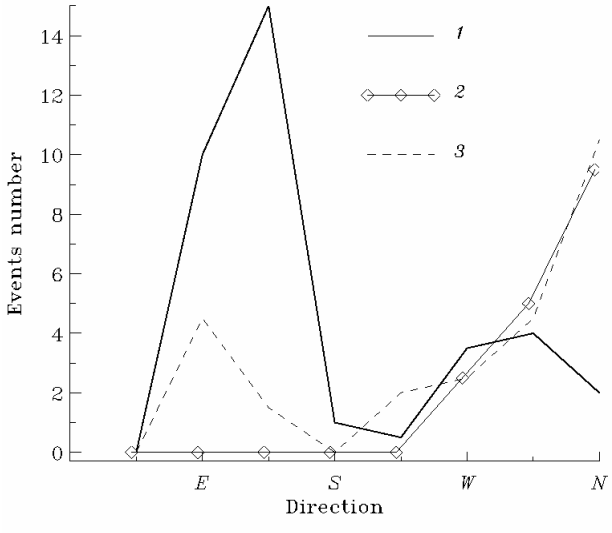

Figure 4. Distributions of ozone disturbances on wind directions.

From the northwestern sector the air is brought in which both disturbances occur, the ones of types 1 and 3 and the ones, registered by the lower ozonometer only (type 2). The disturbances of types 1and 3 can be connected in this sector with three pointed sources i.e. Apatity town, motorway and towns of Monchegorsk and Olenegorsk.

It seems at the disturbances of type 2, the pollutions are registered, which arrive from motorway, located in the north, west and north – east. In this case the source of pollutions is situated near the ground surface. Pollutions have not time to rise up to 17 m level because of the small distance from the motorway to the registration site, and to have an effect upon ozone at this level. The thickening of pollutants near the ground is seen from NO_2 measurements, the results of which are given at (Pundt, 2003). In accordance with them the thickness of NO_2 layer makes up to 20 m leeward. It confirms the results of (Shagapov and Galiaskarova, 2002) about the smog height when his source is on the surface. Nitrogen oxide, incoming from the motorway in thin layer, affects the ozone at the lower ozonometer level only giving rise to ozone disturbance; nitrogen oxide is absent at the upper ozonometer level. In this case the disturbance of type 2 arises. It can explain nearly 20 % of all events. If the upper border of NO layer is cut and its altitude is changed, nitrogen oxide arrives to the upper ozonometer or does not arrive and the disturbance of type 3 arises. These disturbances can originate from the source, situared near the ground surface, under conditions that the altitude of the upper border of pollution layer is variable.

Then the upper ozonometer gets or does not get into the pollution layer. So nearly 40 % of all events can be explained. In these cases the pollution layer is thin and it is adjacent to the surface. The disturbances of type 1, representing about 40 % of the events, originate from either the high source or the remote source, pollution from which is spread along the vertical in the atmosphere.
Very few disturbances occur in air from south. They are related to types 1 and 3.

5. CONCLUSION

It is shown in principle the possibility of pollution monitoring in the industrial area as the results of surface ozone registration on the base of his interaction with nitrogen oxide and the results of the oxidation of carbon oxide. Ozone measurements at two altitudes (1.7 and 17 m) are curried out at the vicinity of a polar town during winter and spring 2003-2004. Measurements have shown the existence of three types of surface ozone reaction to atmospheric pollution. These three types are interpreted as the result of the chemical impact on ozone by pollution spreading on different altitudes. The pollution type has been chosen, which was thickening near the ground (lower 17 m). It is supposed that motor vehicles are one of sources this low – lying pollution. There are confirmed the conclusions of paper (Beloglazov et al., 2002) about the origins of SOC variations in conditions of weak wind basically.

6. ACKNOWLEGEMENT.

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