Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. pp. 304-312, 26-30 September 2005, Istanbul – Turkey

ORIGIN OF DIURNAL VARIATION OF SURFACE OZONE IN KOLA PENINSULA AND FINLAND

Sergey Rumyantsev[1], Valentin Roldugin[1] and Tuomas Laurila[2]

[1]Polar Geophysical Institute, Fersman str., 14, Apatity, Murmansk region *Russia 184209* rumyantsev@pgi.kolasc.net.ru, roldugin@pgi.kolasc.net.ru
[2]Finnish Meteorological Institute, Air Quality Research, Sahaajankatu 22E SF-00880 Helsinki, Finland, Tuomas.Laurila@fmi.fi

ABSTRACT

The monthly average daily courses of surface ozone concentration (SOC) at the Lovozero in the Kola peninsula and at four stations in Finland are investigated. The seasonal behavior of the amplitude of SOC daily variations are determined. The role of factors, having an influence on the ozone daily variations, has been investigated by numerical modeling using the simple one–box photochemical model. It is shown that mainly the average SOC daily variation is caused by dry deposition and destruction of ozone by nitrogen oxide at night, and by changing both photodissociation of nitrogen dioxide and concentration of the organic peroxyradicals.

Key Words: surface ozone, diurnal course, ultraviolet, peroxyradicals, mixing layer.

1. INTRODUCTION

Surface ozone can strongly influence the state of biological and technical objects. The ozone near terrestrial surface originates in transport from the upper layers of the atmosphere, where it is formed by rigid solar ultra-violet radiation (UVR), and in local generation by soft solar UVR from the ozone precursors. As shown at airplane investigation (Mauzerall et al., 1996), in summer in northern region the local photochemical processes give the main part of the ozone, contained in the boundary layer of the atmosphere; the second important source is the transfer from the upper troposphere.

Variations of SOC are caused by both change of solar radiation and by change of conditions of ozone penetration from the upper troposphere to the surface. The ground SOC observations give information on the proportion of two sources on the surface through a daily course of SOC. In Northern Europe the diurnal variations have been studied experimentally in Finland (Hakola et al.,1991; Laurila and Lättilä,1994; Laurila, 1996, 1999) and the Kola peninsula (Larin et al.,1997). In these studies, no theoretical investigations of the problem, permitting to connect experimental characteristics of the variations with parameters of atmospheric environment, have been carried out. In the present study, the SOC in the Kola peninsula and Finland is investigated.

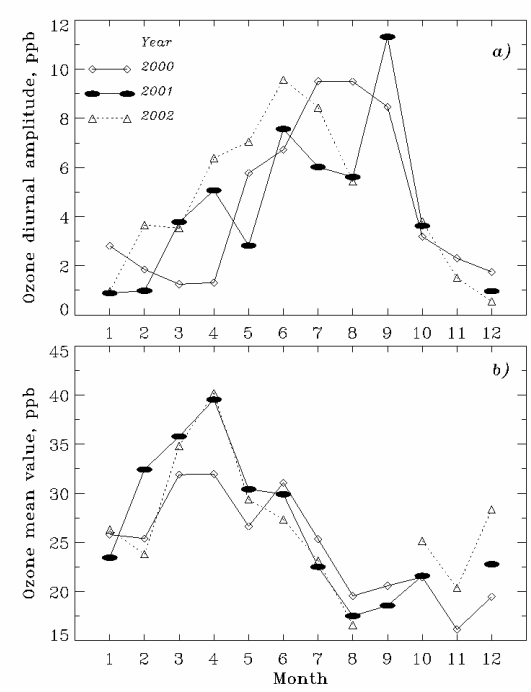

Figure 1. Monthly mean values of amplitude of ozone diurnal variation (top) and its average value (bottom) in Lovozero.

2. OBSERVATIONS

The results of SOC measurements in Lovozero in the Kola peninsula in 2000-2002 are used for the research. There is no industrial activity near the Lovozero settlement. The every minute ozone measurements are made by DASIBI - 1008 AH device and are registered to a data gathering system together with meteoparameters. The SOC data, measured at the station, represent background values for the high-latitude atmosphere with a small level of industrial pollution.

The found daily curves for all months are approximated by the sum of two first diurnal harmonics. The amplitude of daily variation, defined as difference of the approximation for concrete month, is shown in Fig. 1a. The daily variation is maximal in June – September in different years, amounting to 10 ppb, and is minimal in winter months, 1-3 ppb. The seasonal variation of mean SOC value, defined as half-sum of the maximum and minimum values of the approximation, is shown in Fig. 1b. As a whole, the monthly change of a daily variation corresponds to the change of solar light exposure.

3. THE PROBABLE REASONS OF DAILY VARIATIONS

The content of the surface ozone undergoes the influence of many factors. A daily SOC variation may be caused by: a) the daily change of solar UV intensity, b) the change of ozone precursors concentration; c) the change of thermodynamic parameters of air; d) the change of height of mixing layer; e) the daily change of dry deposition velocity, most appreciable in summer time; f) the daily variations of ozone transport rate. The role of these factors is apparently different. The results of (Belan and Sklyadneva, 2001) indicate a significant role of solar radiation flux in the formation of SOC daily course. As it is qualitatively noted in (Rovinskii and Egorov, 1986), the height change of mixing layer in the atmosphere, connected with sunrise and sunset, can cause daily SOC changes. It is shown in (Roldugin et al., 2004), that the change of ozone precursor concentration from spring to autumn results in a significant change of daily SOC variation amplitude. There are only theoretical estimations of the daily change of dry deposition velocity in summer in the high latitudes (Ganzveld and Lellieveld, 1995), and there is known practically nothing about daily variations of ozone transport.

To find out the contribution of the a-e factors into daily SOC variation, we use numerical modeling of generation and destruction processes of ozone.

4. MODEL CHARACTERISTICS

To solve this problem, we use the simple one–box photochemical model (Rumyantsev and Roldugin, 2003), which suggests that the concentrations of trace gases are homogeneous in the mixing layer. This model describes adequately some basic characteristics of ozone distribution in the background and polluted conditions (Roldugin et al., 2003).

The model characteristics are given in (Rumyantsev and Roldugin, 2003) in a most detailed form. The model describes the chemical transformation of 9 trace gases: O_3, NO, NO_2, NO_3, N_2O_5, HNO_3, CH_2O_3, PAN and HO_2 in the mixing layer, where the concentrations of these gases are supposed constant in height. They react with each other and with solar UVR in 33 reactions, presenting the basic interactions, which are realized in the near-surface atmosphere. It is supposed that the formed atomic oxygen transforms to ozone right away. The following gas species take into account as given: molecular hydrogen, aqueous vapor, hydroxyl, carbon oxide, formaldehyde, methane, organic peroxyradicals RO_2, including peroxyacetyl radical $CH_3C(O)O_2$. The formative ozone compounds, named as ozone precursors, include the hydroperoxyl HO_2 and organic peroxyradicals. The sources of HO_2 are reactions of hydroxyl OH. Methylperoxy radical CH_3O_2 is formed at the oxidation of methane by hydroxyl. Sources of HO_2 and CH_3O_2 are known more or less.

The photodissociation rates of NO_2, NO_3, the concentrations of hydroxyl OH and important ozone precursors $CH_3C(O)O_2$, RO_2 are given as the following function of local time: positive branch of sinusoidal function, when Sun is above the horizon, and it is equal to zero, when Sun is below the horizon. In the light period the bulk of the volatile organic compounds (VOC) is injected, and hydroxyl is generated. Organic peroxyradicals are originated in reactions of hydroxyl with VOC (Isidorov, 2001). Dry deposition velocities for different species are taken from the references. They are independent from daytime and season except for ozone. For ozone the velocities are taken from (Ganzveld and Lellieveld, 1995) and (Markova, 2002). In summer months, the model for Alaska, depending on daytime, was used too with the minimal value $v(O_3) = 0.004$ m/s at night, and maximal value 0.01 m/s at daytime using the results of (Ganzveld and Lellieveld, 1995). The simple model of the mixing layer height h, typical for the middle latitude atmosphere (Honore et al., 2000), is used: $h = h_{min}$ for $t \le t_r$; $h = h_{min} + (h_{max} - h_{min})(t - t_r)/t_0$ for $t_r \ge t \ge (t_r + t_0)$; $h = h_{max}$ for $(t_r + t_0) \le t \le t_d$; $h = h_{min}$ for $t \ge t_d$. Here t_r and t_d – the times of sunrise and sundown, $t_0 = 6$ hours, h_{min}, and h_{max} – minimal and maximal values of the mixing layer height. The maximal value of the photodissociation rate of nitrogen dioxide, that has been taken equal to $6 \cdot 10^{-3}$ s^{-1}, resulted from the measurements in Spitzbergen (Beine et al., 1999).

The model permits to research diurnal SOC variations, caused by factors a – e.

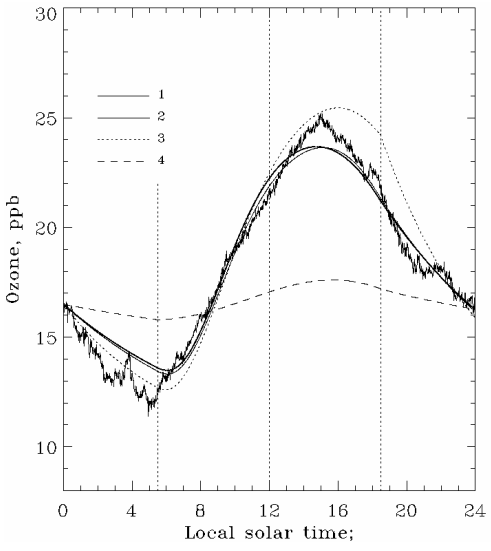

Figure 2. Mean daily variation of surface ozone concentration in Lovozero in September 2001 (uneven curve) and simulation curves 1 – 4, calculated for different chemical and meteorological conditions, see the text. The vertical dotted lines show sunrise, noon and sunset times.

5. COMPARISON OF MODELING WITH EXPERIMENT

The described model calculations have been compared with the experimental data obtained in Lovozero. The diurnal SOC variations, averaged for one month, are taken as experimental data. The modeling was carried out with alternating change of parameters, managing by the factors a – e, to single out the parameters, whose changes cause diurnal SOC variation. At first, the calculations were realized for conditions, when the temperature is taken equal to a mean value for the month; then the calculations are made for the case with observed daily distribution of temperature. Further, the SOC is calculated in the situation, when the concentrations of organic peroxyradicals $CH_3C(O)O_2$ and RO_2 are equal to zero. In this case the ozone generation takes place only from the precursors HO_2 and CH_3O_2, which are always present in the model and are being for it as the components of internal origin in contrast to $CH_3C(O)O_2$ and RO_2, taken from outside. At these calculations, the height of the mixing layer has always been accepted $h_{max} = h_{min} = 1000$ m. Then the calculations were carried out for a varying configuration of the mixing layer with $h_{min} = 300$ m, $h_{max} = 1000$ m. In summer months, the SOC was calculated for time-dependent dry deposition velocity with height of the mixing layer $h = 1000$ m. At such sequence of calculations the role of the factors, influencing the ozone content, is ascertained in turn: photodissociation rate, temperature, concentration of organic peroxyradicals, configuration of the mixing layer and changing of dry deposition velocity.

In Fig. 2 the monthly mean experimental values of diurnal SOC variation for September, 2001 and the results of calculations with average temperature of air is 4.5º C and the maximal value of NO_2 photodissociation rate is equal to 0.003 s^{-1}. The maximal concentration of the basic ozone precursors, organic peroxyradicals RO_2, is equal to 0.03 ppb. Line 1 shows the result of computation for the case, when solar UVR and organic peroxyradical concentration change only. All other parameters, which can determine the SOC are constant during the day. The daily SOC variation in the calculations is produced by those parameters, which vary with time, i.e. by photodissociation intensity and concentration of the ozone precursors in this case. Line 2 shows the results for the case, when the temperature of air varies within the day according to observations. It is obvious, that the distinction of this case from the previous one (line 1), is insignificant. Line 3 describes the case of varying mixing layer height: $h_{min} = 300$ m, $h_{max} = 1000$ m with other parameters as for the line 2. The

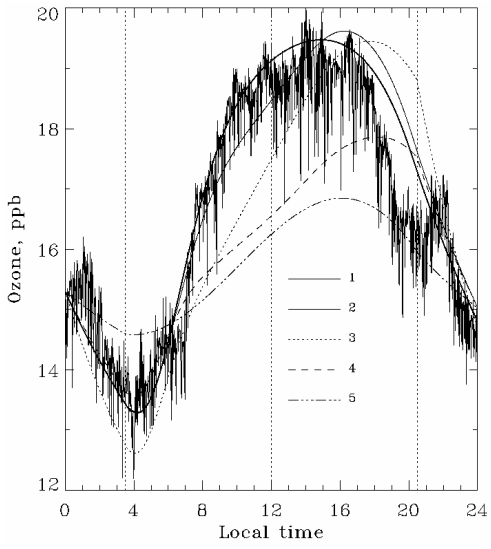

Figure 3. As in Fig.2 but for August 2002.

incorporation of the dependence of the mixing layer height on time *h(t)* increases ozone absorption due to dry deposition. Line 4 represents the results of calculations, when the concentrations of RO_2 and $CH_3C(O)O_2$ are equal to zero, and the ozone generation occurs only from the HO_2 and CH_3O_2 precursors at NO_2 photodissociation. One can see, that the amplitude of diurnal variation strongly decreases, the concentrations of generated hydroperoxyl and of peroxymethyl radical are insufficient for an explanation of the observable change of SOC variation. The comparison of curves 1 and 3, 1 and 4 shows, that the influence of change of the mixing layer height on SOC is appreciable enough, but strongly concedes to the influence of the organic peroxyradicals content. As it follows from computation, the night decrease of SOC in September, caused by dry deposition and destruction of ozone by nitrogen oxide, is ceding place, approximately at 5 - 6 h of local solar time (LST), to the growth caused by the strengthening of photodissociation at the increase of solar UVR. The beginning of growth approximately coincides with the sunrise. At about 14 h LST the recession of SOC (caused by reduction of photodissociation) starts, which is influenced insignificantly by the collapse of the mixing layer at 18.5 hours.

In Fig. 3 the mean SOC values in August, 2002 are given. Line 1 represents the results of modeling for the average temperature of this month 7.5º C. Values of other parameters are the following: the maximal RO_2 concentration is equal to 0.02 ppb, the maximal NO_2 photodissiciation rate is equal to $6 \cdot 10^{-3}$ s^{-1}. Line 2 illustrates the calculation for the observed change of diurnal temperature in August. The appreciable difference of daily ozone variation (lines 1 and 2) in the results of modeling during 08 - 20 h LST in this case is caused by the growth of air temperature in daytime, which brings changes of chemical reactions rates and reduction of ozone loss. Line 3 represents the case of varying mixing layer height with h_{min} = 300 m, h_{max} = 1000 m, and with values of other parameters as for line 2. The time distribution of SOC in this case appreciably differs from the one, presented by lines 1 and 2 because of additional ozone absorption at dry deposition. Line 4 illustrates calculation for the changing mixing layer and varying dry deposition velocity, taken, as in (Ganzveld and Lellieveld, 1995), instead of average dry deposition velocity, used at computations of lines 1 - 3 in this Figure. It is clear from comparison of the curves 3 and 4, that the difference between these cases is essential, except for the night hours. At last, line 5 shows what the daily variation would be in the absence of organic peroxyradicals, provided other conditions are the same, as for line 2. In this case SOC variations are noticeably less than for lines 1-3, reflecting the fact, that the ozone generation is weak at small amount of the precursors. The

influence of change of the parameters of the mixing layer and dry deposition velocity on diurnal SOC variation can be appreciable for the chosen conditions.

In Fig. 4 the comparison of the experimental data with the calculated ones for the period with a small daily variation about 4 ppb in March, 2001 is shown. Lines 1 and 2 show results of calculations for constant temperature T = -14° C and for variable atmospheric temperature correspondingly. The modeling curves pass closely to each other and to experimental data. Curve 3 illustrates the results of computations under condition of equality to zero of organic peroxyradicals concentration, when only photodissociation change takes place.

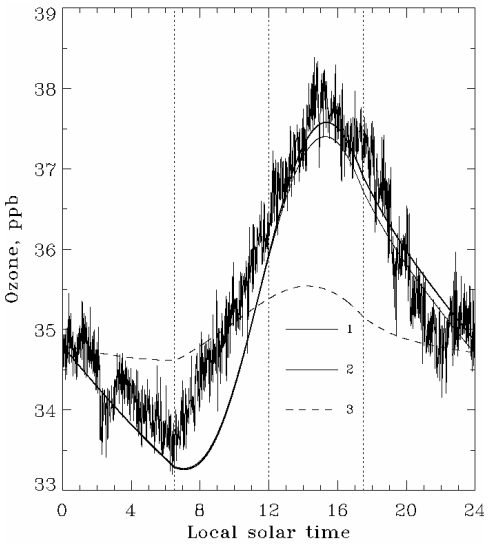

Figure 4. As in Fig.2 but for March 2001.

Thus, it is seen from figures 2 - 4 that the basic variation of the ozone content at this time is caused by the dry deposition, destruction by nitrogen oxide and joint change of solar UVR and concentration of organic peroxyradicals. The influence of changes of the mixing layer height is most appreciable in the periods, when the light and dark periods of day are close in duration, then the small heights of mixing layer and, as a consequence, large values of dry deposition rate, result in appreciable variations of ozone concentration. In summer months, the role of changes of temperature within a day becomes more appreciable.

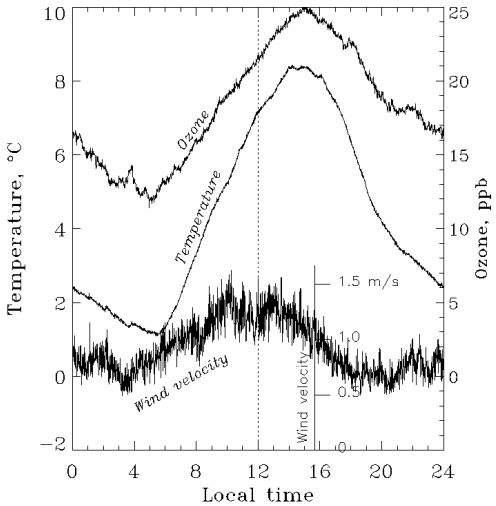

Figure 5. Mean daily variations of surface ozone concentration, temperature and wind velocity in Lovozero in September, 2001.

As it is noted, one of the reasons of diurnal SOC course can be the daily variation of velocity of ozone transportation, both vertical, and horizontal. First of all this transportation is connected with wind, which not only transfers ozone from other areas, but also mixes the air along vertical.

In Fig. 5, as a typical example, the diurnal variations in September, 2001 of SOC, already considered in Fig. 2, and of wind, and also of temperature are shown as functions of LST. One can see the distinct daily course of wind, but it differs from the ozone daily course: the maximum is achieved near the local noon, but not 3 hours after it, as for ozone, there is no characteristic minimum at 5 hour. Therefore, it is possible to make a conclusion, that wind does not play a determining role in the formation of the diurnal course of SOC.

6. DIURNAL SOC VARIATION IN FINNISH OBSERVATORIES

The ideas, used above for the explanation of daily SOC course in Lovozero, were applied for analysis of daily courses at four Finnish stations: Oulanka, Ähtäri, Virolahti and Utö. The most northern station Oulanka settles near the Polar circle in a wood at the height of 300 m, far from sources of pollution. The station Ähtäri is located in the central Finland, at the height of 180 m, also in a woody district. Virolahti lays on the coast of the Finnish gulf eastwards of Helsinki, and the air is subjected to industrial pollution from large seaports of the gulf. The station Utö is located on a rocky woodless island in the Baltic sea at the height of 7 m. The atmosphere in Finland is exposed to the influence of pollution both from their own industry, and from transboundary transport of industrial air pollution from Western Europe.

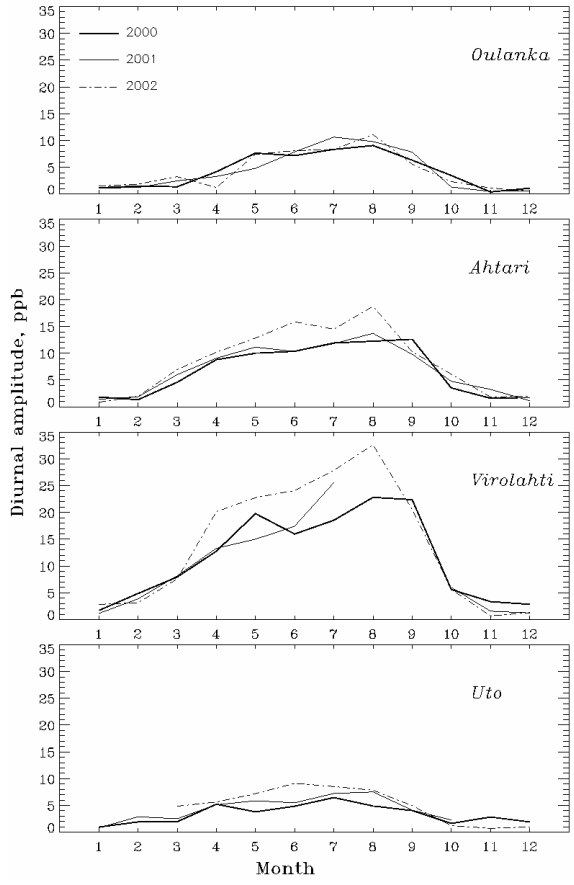

Figure 6. Monthly mean values of diurnal amplitudes of surface ozone variations in 2000 – 2002 at four Finnish observatories.

The hourly average ozone data for these stations for 1997 - 2002 are taken on the site http://www.nilu.no/projects/ccc/mnetwork/index.html.

Comparing the daily courses of the geographically closest stations Lovozero and Oulanka, a close resemblance of both forms and amplitudes of daily courses for most of months is detected. The SOC values in Lovozero are a little bit lower, than in Oulanka, that is, probably, connected to the prevalence of westerlies, and to industrial air pollution from the Western Europe.

The amplitudes of diurnal SOC variations for different months for finnish stations are found and shown in Fig. 6. The maximal amplitudes of average diurnal variations in Lovozero and Oulanka, equal at these stations, make up about 10 ppb, see Fig. 1a and Fig. 6. The results of paper (Laurila, 1999) for 1990-1996 are the similar.

The comparison of results of observations in Lovozero and at the Finnish stations shows, that the distribution of the daily variation of surface ozone within a year and in different geographical areas is determined by the basic rules about generation, absorption and transport of ozone, which are known now and realized in the submitted model.

A daily ozone variation is weak from November till February at all stations, it becomes appreciable in March and grows, reaching the maximum in June - September, and then goes down to small values in October (Fig. 6). In various years, the maximal value of a daily variation is reached in different months. In March - September the solar UV flux and intensity of VOC emissions vary strongly during an intensive growth and decay of vegetation. Increase and decrease of UVR flux and of VOC concentration results in increase and decrease of the contents of the ozone precursors. The ozone concentration increases and decreases during this time accordingly. The structure of the observed daily variations is the same at examined stations: a drop in night hours with a minimum in the morning, caused by night ozone destruction by trace gases and by dry deposition, then growth with a maximum at afternoon hours, caused by increase of a solar UV flux and VOC concentration at the sunrise, and a reduction connected with the lowering of the Sun and ozone generation weakening. A certain contribution into amplitude of the daily variation can be brought by anthropogenic pollution of air, which strengthens or decreases the ozone generation by UV radiation.

The amplitude of daily variation increases from north to south for continental stations (except for Utö), i.e. the ozone generation amplifies in this direction, in which both UVR flux and VOC emission are increased. It is evident from Fig. 6, in which the maximal values of average diurnal amplitude amount to 10 ppb for Oulanka, 19 ppb - for Ähtäri , 32 ppb - for Virolahti ; 9 ppb - for Utö. The Utö sea station surroundings are poor in vegetation and, as a consequence, the VOC concentration is lower there, than in woody areas of Finland

7. CONCLUSIONS

The average daily SOC variation in Lovozero is caused by dry deposition and destruction of ozone by nitrogen oxide at night, and by change of both photodissociation of nitrogen dioxide and concentration of the organic peroxyradicals during daylight hours. Amount of hydroperoxyle and peroximethyl radical, formed in the atmosphere and being a part of precursors, is not enough for explanation of the observed SOC variability. The peroxyradical concentrations, which are necessary for SOC variations, have to been created by growth in the vegetation period. The contribution of change of a mixing layer height and variability of dry deposition velocity is a small value and can be noticeable only in summer months. The contribution of the horizontal ozone transport into the appearance of diurnal variation seems to be not to amount to much.

The temporary distribution of SOC at four stations in Finland has been investigated, the average SOC values and the amplitude of diurnal variations of ozone concentration are found. The increase of the amplitude of diurnal SOC variation from north to south at continental stations of Finland is obtained. The comparison with results of observations in the Kola peninsula is made. On the basis of the considered chemical model, which has been applied quantitatively to the Lovozero data, the qualitative explanation of behaviour of diurnal variations in Finland is given.

8. ACKNOWLEDGEMENT
This research was partially supported by RFBI under Grants 05-05-64271, 02-05=64114.

REFERENCES
Beine, H., Dahlback, A., J.B. Ørbæk, 1999. Measurements of J(NO_2) at Ny – Ålesund, Svalbard. J. Geophys. 104, D13, 16009-16019.
Belan, B.D., Sklyadneva, T.K., 2001. Diurnal course of surface ozone concentration near Tomsk. Meteorology and Hydrology. 5, 50-60 (in Russian)
Ganzveld, L., Lellieveld, J., 1995. Dry deposition parametrization in a chemistry general circulation model and its influence on the distribution of reactive trace gases. J. Geophys. Res. 100, D10, 20999-21012.
Hakola, H., Joffre, S., Lättilä, H., Taalas H., 1991. Transport, formation and sink processes behind surface ozone variability in North European conditions. Atmos. Environ. 25A, 1437-1447.
Honore, C., Vautard, R., Beekman, M., 2000. Photochemical regimes in urban atmospheres: the influence of dispersion. Geophys. Res. Lett. 27, 15, 1895-1898.
Isidorov, V.A., 2001. Organic chemistry of the atmosphere. S.-Petersburg. Himizdat, 352 p. (in Russian).
Larin, V.F., Beloglazov, M.I., Vasil'ev, A.N., Roumiantsev, S.A., 1997. Diurnal variations of surface ozone on Kola peninsula: preliminary results. Ann. Geophysicae 15, 1615-1616.
Laurila, T., 1996. Effects of environmental conditions and transport on surface ozone concentrations in Finland. Geophysica. 32, 1-2, 167-193.
Laurila, T. 1999. Observational study of transport and photochemical formation of ozone over northern Europe. J. Geophys. Res. 104, D21, 26,235-26,243.
Laurila, T., Lättilä, H., 1994. Surface ozone exposures measured in Finland. Atmos. Environ. 28, 1, 103-114.
Markova, T.A., 2002. Spatial and temporal variability of ozone concentration in surface layer of the atmosphere. Abstract of the dissertation. Moscow, MSU (in Russian).
Mauzerall, D. L., Jacob, D. J., Fan, S.-M., Bradshaw, J. D., Gregory, G. L., Sachse, G. W., Blake, D. R., 1996.Origin of tropospheric ozone at remote high northern latitudes in summer. J. Geophys. Res. 1996, 101, D2, 4175-4188.
Roldugin, V.C., Rumyantsev, S.A., Karpechko, A.Yu., Beloglazov, M.I., 2003. Influence of solar UV radiation on surface ozone in background and polluted conditions on the Kola peninsula. In: Kashulin, N.A., and Vandysh, O.I. (Eds.) "Kola peninsula on the threshold of the third millennium: ecological problems" Apatity, 248 p. (in Russian).
Roldugin, V.C., Rumyantsev, S.A., Karpechko, A.Yu., Beloglazov, M.I., 2004. Surface ozone variations and UV radiation intensity on the Kola peninsula. Optika atmosfery i okeana. 17, 7, 598-604 (in Russian)
Rovinskii, F.Y., Egorov, V.I., 1986. Ozone, sulfur and nitrogen oxides in the lower atmosphere. Leningrad, Gidrometeoizdat, 183 p. (in Russian)
Rumyantsev, S.A., Roldugin, V.C., 2003. Interaction of trace atmospheric gases with air anthropogenic pollution in the high – latitude industrial area. Ecologicheskaya himiya. 12, 2, 69-78 (in Russian).