Seasonal variations of ground ozone concentration over East Sayan

V.L. Potemkin[1] and E.V. Shultais[2]

[1] *Limnological Institute, Siberian Branch of the Russian Academy of Sciences, Irkutsk*
[2] *Institute of Solar-Terrestrial Physics, Siberian Branch of the Russian Academy of Sciences, Irkutsk*

Received January 29, 2004

The paper presents experimental data on long-term variations of total ozone concentration (TOC) in the atmosphere and variations of ground ozone concentration (GOC) over East Sayan region. We discuss the seasonal and diurnal variations of ground ozone. It is found that the ground ozone maximum is delayed (by 42 days, on average, with a correlation coefficient of 0.8) with respect to the maximum of TOC, consistent with Petsold theory on vertical ozone motion, stating that the rate of ozone settling from the stratosphere is less than 1 cm/s.

Study of minor atmospheric constituents like ozone provides an important information for modeling and prediction of future state of the earth climate system. Ozone is also of interest from the biological viewpoint due to its high toxicity and chemical activity. The issue of the tropospheric ozone still does not go beyond the scope of urban problems. In contrast to the stratospheric ozone, ground ozone concentrations increase at a rate of 1–2% per year.[1] In this work, we analyze variations of total and ground ozone concentrations over East Sayan using data of observations at Mondy site.

The TOC in the atmospheric column is a key characteristic of the atmospheric ozone. The stratospheric ozone is monitored by a network of ground-based ozonometric stations (Global Ozone Network) and Total Ozone Mapping Spectrometer (TOMS) measurement systems operating since 1978 on Nimbus-7 and Meteor-3 (NASA) satellites. In Siberian region, this activity is fairy well represented.[2–4] The TOC data are systematically published, they are available to all scientific community and discussed quite extensively. For latitude and longitude of the Mondy site (51.6°N, 101°E), the daily values were sampled for reconstruction of time series from November 1978 to December 2001; the length of the series was 22 years.[5]

Ground ozone concentration (GOC) is characterized by strong spatial and temporal variations. Whereas for urban conditions the growth and sink of ozone are associated with local pollutants, for background regions natural causes become most important. Despite a great body of data, the causes of ground ozone variations are still not fully understood. Therefore, in 1996 the Russian Academy of Sciences in collaboration with the Research Center of Science and Technology in Tokyo University have organized a background ozone station.[6]

Organization of this station is motivated by the need to clarify seasonal and diurnal variations of GOC under background conditions of continental climate. The station is situated on the territory of Sayan Solar Observatory at Institute of Solar-Terrestrial Physics SB RAS in Mondy village (East Sayan, 2010 m above sea level). Located in a valley, the station is few tens of kilometers away from the nearest settlements, separated by more than 300 km from large industrial centers (Irkutsk and Baikalsk), and shielded by Khamar-Daban and East Sayan ridges. It is supplied with industrial electrical power and has no own atmospheric pollution sources. Continuous observations of aerosol chemical composition have been conducted at the station for seven years. It is shown that, with respect to aerosol mass concentration and elemental composition, the Mondy site can be considered as a background station for conditions of Eastern Siberia.[7]

The ozone measurements in the ground atmospheric layer were performed using the ozonometer Dylec, Model 1007-AHJ, with a 1-min averaging. The measurement error of the instrument does not exceed 10%. Simultaneously, we recorded the atmospheric pressure and air temperature inside the building where the instrument was located. The measurements and data registration were fully computed.

1. Diurnal variations of ground ozone

The diurnal data on GOC were used to calculate the variability and diurnal behavior for central (most characteristic) months of the seasons (Fig. 1). In all cases, minimal concentrations are observed at nighttime and in the morning, maximal ones at day and evening hours. In the absence of anthropogenic sources of atmospheric pollution, the character of diurnal ozone variations is governed by intradiurnal behavior of the mixing layer and nighttime temperature inversion layer near the ground surface, as well as by high location of the station. This, for example, explains

0235-6880/04/04 279-04 $02.00

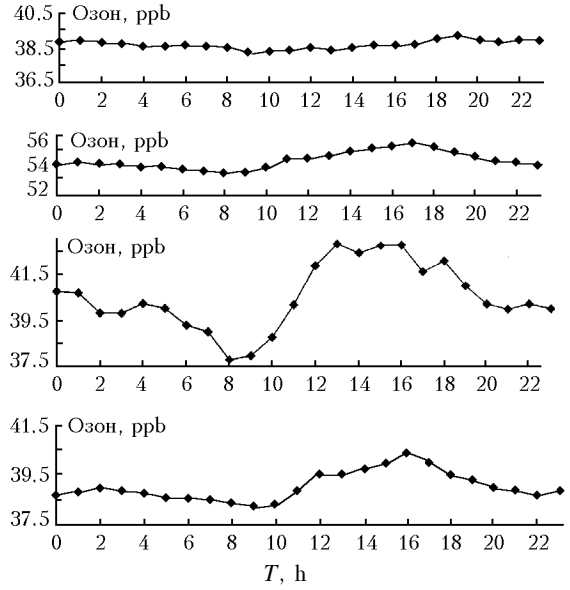

Fig. 1. Duirnal average behavior of GOC.

weak ozone decrease at night hours. Diurnal ozone variations are 2–4 ppb in spring and 4–8 ppb in summer. The diurnal ozone maximum is caused by photochemical processes due to an enhanced insolation in this region and high vegetation productivity of ozone-bearing gases (nitrogen oxides and carbon). The diurnal variations of GOC in winter are insignificant. This is because local ozone sources are absent in this period and the ozone replenishment is through its constant influx from upper atmospheric layers (see Section 4).

2. Annual variations of GOC

To study the annual variations of ground ozone concentration, we used a series of observations from November 1, 1996 to December 18, 2001. The series includes 1792 data points (for technical reasons like electricity interruptions during thunderstorms and storm winds, the series have gaps). The annually mean ground ozone is 43.2 ± 5.2 ppb. This is somewhat higher than the values observed in Europe (30–34 ppb)[8,9] and Western Siberia (20–30 ppb).[10] However, it should be kept in mind that Mondy is a more elevated site. Taking this into account, the ozone measurements closer agree with observations in clean mountain regions of Europe[11–13] (the ozone station in Arosa, the Alpes, 1840 m above see level, where the annually mean ground ozone is 42–43 ppb; and the Kislovodsk high-mountain station, 2070 m above see level, where the ozone concentration in spring is 45–60 ppb). These values are consistent with the corresponding measurements in Eastern Asia[14] (Happo station, 1820 m above see level, where annual mean ground ozone is 46 ± 4 ppb). In the mountains of Spitsbergen archipelago, the August variations of GOC are 30 ppb in the average with a possible growth to 120% at wind changes.[15]

The annual behavior of the ground ozone (Fig. 2) displays a single well-defined maximum in the late April – early May (in different years of the observation period under study, the dates of the ozone maxima varied from April 22 to May 9). For the entire measurement period, the absolute maximum of the ground ozone of 72.7 ppb was observed on May 6, 1999; the long-term mean maximum is 58 ppb.

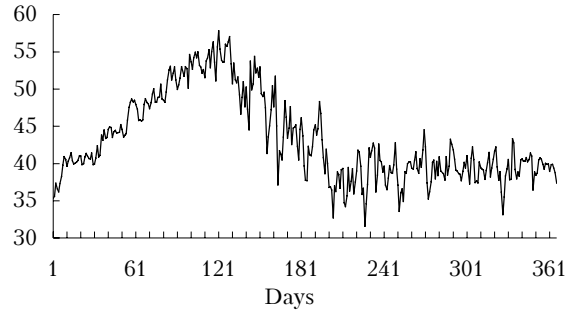

Fig. 2. Long-term mean annual behavior of the ground ozone concentration.

The annual behavior of the ground ozone has no well defined minimum. The spring maximum is followed by the concentration fall continuing until mid-summer. Then, GOC varies around some average value (31–34 ppb) without any well-defined maxima or minima until the cold period. This period is characterized by very high diurnal variability (5–8 ppb) (Fig. 3); in winter, the interduirnal amplitude does not exceed 1 ppb.

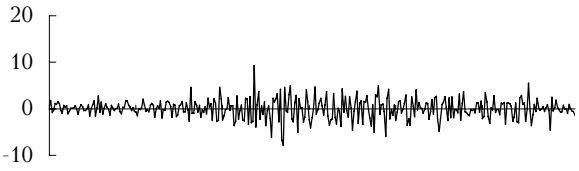

Fig. 3. Long-term mean interduirnal GOC variability.

The annually mean amplitude of ozone variations is 26 ppb, though the maximal observed amplitude for the period under study is 45.3 ppb (season of 2001).

3. Other periodicities in ground ozone variations

The preformed spectral analysis has revealed several principal periods in the ground ozone variations. Most significant is found for 22.8-day period (which is close to 21.3-day period for TOC); also it is possible to see oscillations of a synoptic character with length of 12.8 and 7.1 days. However, these periods have a low spectral density relative to large-period variations (annual and semiannual). With a long time series of uniform observations, it is always interesting to perform correlation analysis to reveal tendencies in evolution of the parameter. For January, the autocorrelation curve monotonically decreased, indicating the random distribution of

daytime ground ozone concentrations without evident sources. Starting from April, the curves had a secondary maximum for a time lag of 22–24 hours, suggesting persistence of a permanent source during the day (insolation). April is the transitional month of decay of the Siberian anticyclone. This period is characterized by a presence of low-gradient pressure field and fair weather. These days, there is a constant circulation between valley and surrounding ridges in the mountain regions, with well defined diurnal periodicity. In August, the autocorrelation curve of the ground ozone concentration also has a 20–24 hour lag maximum.

4. TOC dependence of ground ozone concentration

As is well known, the maximal ozone concentration is observed at altitudes between 20 and 30 km (i.e., in the stratosphere where 85–89% of all ozone resides[16]); therefore, the variations of TOC can be conventionally considered as variations of stratospheric ozone. The existing hypothesis states that the main source of ground ozone is the stratospheric ozone, therefore, a relationship must exist between TOC and ground ozone. Using the 30-day moving averaging (to remove small-scale periodicities associated, in particular, with synoptic-scale processes), we performed a cross-correlation analysis of TOC and GOC series.

In joint analysis of the TOC and GOC variations it was determined that the maxima and minima of GOC, as compared to TOC, occur with some delay, ranging from 33 to 52 days, an average being 42 days (for 30-day averaging and time lag of 42 days, the correlation coefficient was found to be 0.79) (Fig. 4). This confirms the theory on ozone concentration as a conservative property of atmospheric masses, as well as Petsold hypothesis on the rate of vertical ozone motion, which is approximately 0.5–1 cm/s at altitudes below 25 km.[17]

5. Relationship between ground ozone and meteorological parameters

Many authors alluded a relationship between ground ozone and meteorological factors. As early as in 1945, Dobson wrote that during thunderstorm the total ozone may double. For instance, Khrgian[16] points out to a 2–10-times increase of ground ozone prior to thunderstorm. On days with increased air transmittance, a 1.5–2-fold increase of the ground ozone is possible. Front passages and changes of wind direction can also bring ground ozone increase; whereas precipitation, on the contrary, favors a decrease ozone concentration through ozone sink on the surface of precipitation particles.[18] To study this issue, a few days with precipitation and wind, when instrumental and direct visual observations complement each other, were selected from the observation series.

The observations made during a thunderstorm on June 26, 1999 (Fig. 5), have confirmed the hypothesis of preceding growth of the ozone concentration. Thunderstorm with hail (up to 5 mm), and squally wind up to 15 m/s was observed between 13:30 and 14:00 LT; but approximately 2 hours before the thunderstorm start (at about 11:30 LT), the ozone augmentation began (with only a slight reversal at about 12:30 LT) and continued until the thunderstorm onset. Then a decrease of the ozone concentration was

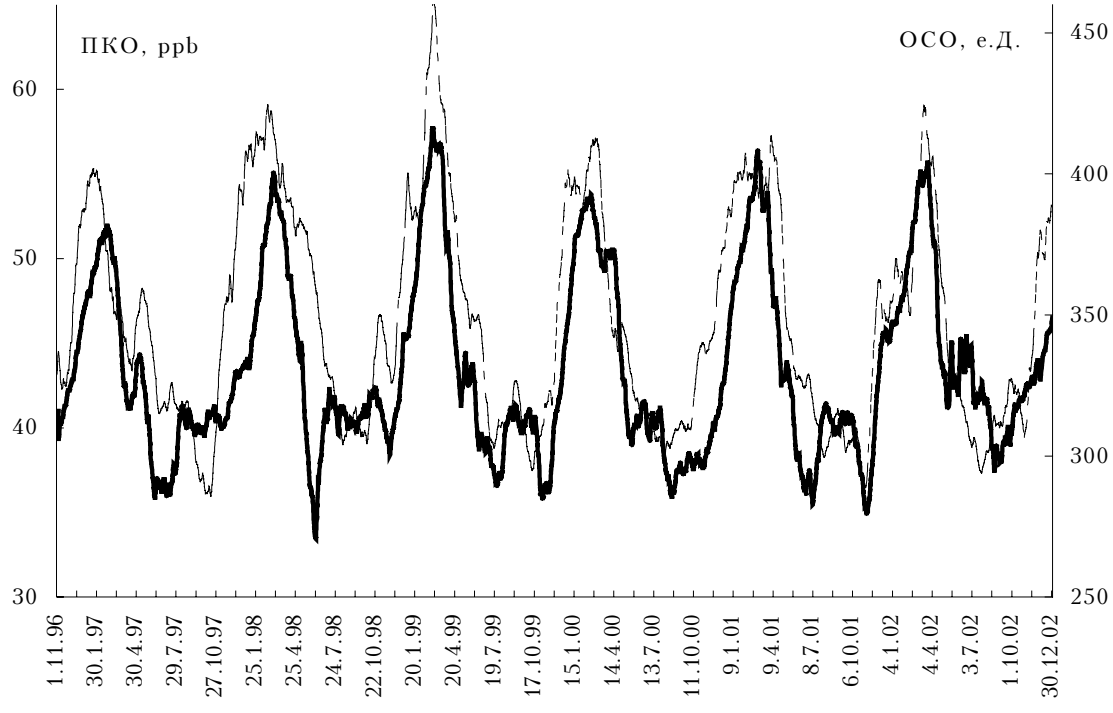

Fig. 4. Comparison of TOC (thin curve) and GOC (bold curve) series with a 42-day lag.

observed throughout the thunderstorm and for a half an hour after, until recovery of mean values. Maximal ground ozone content of 62 ppb was observed at the thunderstorm onset.

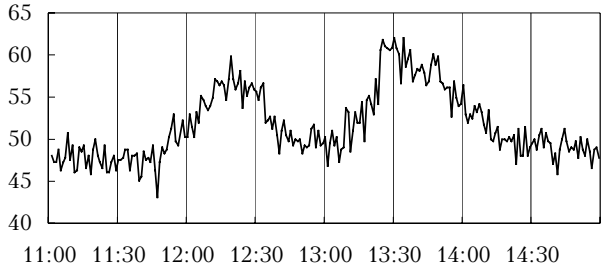

Fig. 5. Ozone variations during thunderstorm on June 26, 1999.

On April 27, 2000 the southern wind of 5–10 m/s was observed until 18:00 LT; then it began to decrease and by 18:45 LT it changed to north-western whose speed has reached 15–20 m/s by 19:30 LT. Then, after 18:00 LT the ground ozone concentration began to decrease (Fig. 6) and continued until 18:30 LT, when a minor increase occurred, seemingly, due to a change of wind direction, followed by further ground ozone reduction until 19:00 LT. The abrupt drop at about 21:00 LT is due to the snowfall onset. The ozone concentration has decreased from 61 ppb at 18:00 to 37 ppb at 21:00 LT.

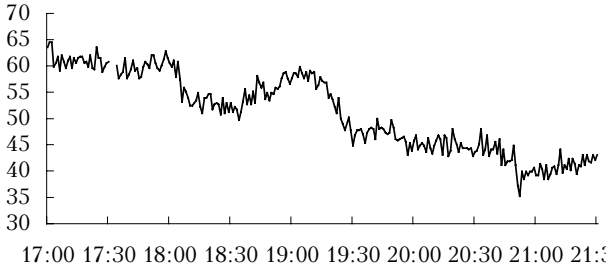

Fig. 6. Variation of GOC at change of wind and snow on April 27, 2000.

Observations on October 11, 2001 during snowfall, also agree with the hypotheses of Ref. 18 (Fig. 7). The ozone reduction started almost simultaneously with snowfall.

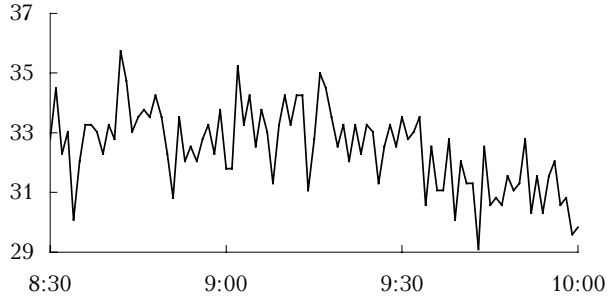

Fig. 7. Fall of the ground ozone concentration during snowfall on October 11, 2001 (snowfall started at 9:30).

Conclusion

Five-year observations of atmospheric ozone variations in the mountain region have allowed identification of the sources affecting the ozone behavior. Variability of the ground ozone concentration mainly depends on meteorological conditions, aggravated in mountains by local circulations. Statistically significant correlation between ground ozone concentration and TOC throughout the year was found, ensuring higher ozone concentrations as compared to flat areas.

References

1. F.Ya. Rovinsklii and V.I. Egorov, *Ozone and Nitrogen and Sulfur Oxides in the Lower Atmosphere* (Gidrometeoizdat, Leningrad, 1986), 183 pp.
2. V.V. Zuev, Atmos. Oceanic Opt. **9**, No. 9, 745–753 (1996).
3. G.A. Zherebtsov, E.S. Kazimirovskii, V.D. Kokourov, and V.V. Koshelev, Atmos. Oceanic Opt. **9**, No. 9, 801–805 (1996).
4. B.D. Belan, V.V. Zuev, T.K. Sklyadneva, S.V. Smirnov, and G.N. Tolmachev, Atmos. Oceanic Opt. **13**, No. 10, 860–864 (2000).
5. Website NASA ftp://toms.gsfc.nasa.gov/pub/eptoms/data/.
6. V.L. Potemkin, O.G. Netsvetaeva, T.V. Khodzher, H. Akimoto, Y. Kaji, and P. Pochanart, Sibirskii Ekologicheskii Zhurnal, No. 6, 601–603 (1999).
7. T.V. Khodzher, V.L. Potemkin, V.A. Obolkin, and O.G. Netsvetaeva, Atmos. Oceanic Opt. **11**, No. 6, 550–552 (1998).
8. T. Laurila and H. Lattila, Atmos. Environ. **28**, 103–112 (1994).
9. P.G. Simmonds, S. Seuring, G. Nickless, and R.G. Derwent, J. Atmos. Chem. **28**, 45–65 (1997).
10. M.Yu. Arshinov, B.D. Belan, V.E. Zuev, O.A. Krasnov, V.A. Pirogov, T.K. Sklyadneva, and G.N. Tolmachev, Atmos. Oceanic Opt. **15**, No. 11, 896–901 (2002).
11. T. Cvitas, N. Kezele, and I. Klasinc, J. Atmos. Chem. **28**, 125–141 (1997).
12. P. Pochanart, H. Akimoto, S. Maksyutov, and J. Staehelin, Atmos. Environ. **35**, 5553–5566 (2001).
13. I.N. Kuznetsova, N.F. Elanskii, I.Yu. Shalygina, E.N. Kadygrov, and A.D. Lykov, Meteorol. Gidrol., No. 9, 40–51 (2002).
14. Y. Kajii, K. Someno, H. Tanimoto, J. Hirokawa, H. Akimoto, T. Katsino, and J. Kawara, Geophys. Res. Lett. **25**, 3505–3508 (1998).
15. O.I. Shumilov, E.A. Kasatkina, O.M. Raspopov, and I.V. Mingalev, Geomagn. Aeron. **42**, No. 6, 798–804 (2002).
16. A.Kh. Khrgian, *Physics of Atmospheric Ozone* (Gidrometeoizdat, Leningrad, 1973), 289 pp.
17. I.A. Khvostikov, *Upper Atmospheric Layers* (Gidrometeoizdat, Leningrad, 1964), 605 pp.
18. V.V. Lunin, M.P. Popovich, and S.N. Tkachenko, *Physical Chemistry of Ozone* (Publishing House of Moscow State University, Moscow 1998), 480 pp.