ESTIMATION OF THE OZONE SINK ON AEROSOL PARTICLES

B.D. Belan, M.V. Panchenko, S.A. Terpugova, and G.N. Tolmachev

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk
Received March 26, 1992

The contribution of aerosol particles to the destruction of the ozone molecules is estimated. It is shown that under typically optical and meteorological conditions the contribution of the sink on the aerosol particles is not more than 20 % of the total sink. Under conditions of the anomalously large dust content in the atmosphere practically all ozone sinks on aerosol. By way of example, the coefficient of the destruction of the ozone molecules on the surface of dust particles is estimated to be $\gamma = 6 \cdot 10^{-5}$ *from the data of airborne sounding obtained in the course of the joint Soviet–American dust experiment DUNE.*

The mechanism of interaction of gases with aerosol particles is most variable in space and time among the variety of the processes of removal of trace impurities from air.[1,2] On the one hand, this is caused by the spatial and temporal variability of aerosol particles under the impact of a large number of geophysical and weather factors and by the great variety of their physical and chemical properties and, on the other hand, by the complicated dependence of heterogeneous reactions on the particle composition, the amount of the trace impurities and, their qualitative composition.

Before the Pittock's paper[3] the sink of the atmospheric ozone on the aerosol was assumed to be insignificant. Further R. Cadle, P. Crutzen, and D. Ehhalt[4] estimated the effect of aerosol particles on the ozone content in the stratosphere and reported that about 5 % of ozone decrease in the lower stratosphere was due to the ozone sink on aerosol.

Now a number of papers are devoted to the investigation of the interrelation between ozone and aerosol contents. The comprehensive analysis of these papers was made in Ref. 5.

The problem of separation of the aerosol contribution to the variability of the ozone content is the most dificult one in the interpretation of the experimental data obtained in the lower atmosphere. On the one hand, the existence of ozone can promote the formation of aerosol particles while, on the other hand, the aerosol particles can cause the destruction of the ozone molecules. One of the main factors hampering interpretation of data is the atmospheric processes, which simultaneously change the ozone and aerosol contents. In the analysis of the data of the ground layer observations there is a problem of separation of the ozone sink on aerosol particles and on the underlying surface.[4] In this paper we try to estimate the rate of the ozone sink on the aerosol particles from the data of observations performed in the real atmosphere.

The variation of the ozone concentration in the unit volume due to the ozone sink on the surface of the aerosol particles can be described by the relation[2]

$$\frac{dm}{dt} = -\frac{m\bar{\upsilon}}{4} S\gamma , \qquad (1)$$

where m is the ozone mass concentration in g/cm^3, $\bar{\upsilon}$ is the mean velocity of the O_3 molecules in cm/s, S is the total surface area of the aerosol particles in the unit volume in cm^2/cm^3, and γ is the coefficient of the destruction of the ozone molecules on the aerosol surface.

For the interpretation of the experimental data it is convenient to represent Eq. (1) in the form

$$\frac{dm}{dt} = -cS , \qquad (2)$$

where c is the rate of the ozone sink on the unit surface area of aerosol particles in the unit volume.

For the analysis we took the results obtained under dust storm conditions as part of the integrated Soviet–American experiment in Dushanbe performed in September of 1989. Regular airborne sounding of vertical profiles of meteorological parameters, ozone concentration, and optical and microphysical aerosol characteristics in the 0–6 km altitude range was carried out in the course of the experiment from September 14 to September 25, 1989.

The gradual accumulation of ozone had been occuring in the lower atmospheric layers in the days preceding the emission of dust. The ozone variations in the 2–6 km altitude range were insignificant from day to day. The powerful dust emission observed at night from September 19 to September 20, 1989 brought a large amount of dust particles to the region of observations, and with their appearance the ozone content in the lower atmospheric layers began to decrease.

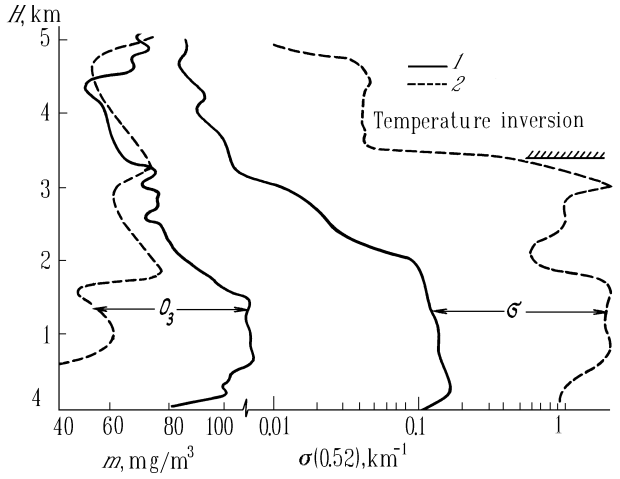

FIG. 1. Vertical profiles of the ozone mass concentration and of the aerosol scattering coefficient: 1) relatively clear air conditions and 2) emission of dust.

0235-6880/92/06 409-03 $02.00

The vertical profiles of the ozone mass concentration and of the aerosol scattering coefficient $\sigma(\lambda = 0.52\ \mu m)$ under relatively clear air conditions (September 18, 1989) and dust storm (September 21, 1989) are shown in Fig. 1 (Unfortunately, during the maximum emission, when the optical depth reached the value $\tau \sim 10$, the flight of the aircraft laboratory was impossible due to the poor visibility conditions at the airport of Dushanbe).

It can be seen from the figure, that with appearance of dust particles in the lower layers the substantial decrease of the ozone content occured, whereas in the layer above the inversion ($H > 3.4$ km) the structure of the vertical profile of O_3 remained practically unchanged. This fact allows us to assume that the advective processes make much less contribution to the variations of the ozone content under dust storm conditions than the aerosol particles.

Large optical depths ($\tau \sim 10$ on September 20, 1989 and $\tau \sim 3$ on September 21, 1989) significantly weakened the radiative and photochemical processes of the ozone formation at that time, and we can ignore them in estimations.

In order to estimate the value of the ozone sink on the aerosol particles, let us consider the variation of the ozone content in the air column with a cross–sectional area of 1 cm^2. The height of the temperature inversion ($H = 3.4$ km) was taken to be its upper boundary. The lower boundary was specified at the altitude H equal to 500 m in order to exclude from the consideration the ozone sink on the surface and the possible effect of the local ozone sources.

During the dust haze in the region of observation (lasting approximately 2 days) the total ozone content in this column decreased by $\Delta m \sim 10$ μg. The mean surface area of the aerosol particles S in the same volume was ~ 10 cm^2. It was calculated from the photoelectric counter data. In contrast to the usual atmospheric state, when the most part of particles with radii $r < 0.2$ μm is outside of the range of measurements of the counter, the usage of the photoelectric counter under the dust haze conditions is quite correct since the majority of particles has the radii $r > 0.2$ μm and is reliably recorded with the counter.[6]

According to Eq. (2) the mean rate of the ozone sink c in the unit volume is estimated to be $5 \cdot 10^{-11}$ g/cm^2·s. We have succeeded in calculating a more exact value of c by considering the shorter time interval in which we could ignore other processes more confidently. The ozone sink rate was estimated over the period of 3:20 between two successive soundings on September 21, 1989.

Since some decrease of the aerosol particles content was observed at that time, the value of c in Eq. (2) was estimated as

$$c = \frac{m_0 - m(T)}{\int_0^1 S(t)dt}, \qquad (3)$$

where S is the surface area of particles.

In this case the value of the sink rate c appears to be equal to $3.9 \cdot 10^{-11}$ g/cm^2·s. Taking into account the data of air temperature sounding and the fact that the mean ozone content $\overline{m}$ varied insignificantly at that period of time, we could estimate the coefficient of the ozone molecule destruction γ in Eq. (1). For a mean ozone content of $60 \cdot 10^{-12}$ g/cm^3 and an average velocity of molecules being equal to $3.9 \cdot 10^4$ cm/s, a value of the coefficient of the ozone molecule destruction is $\gamma = 6 \cdot 10^{-5}$.

According to Refs. 2 and 4, a value of γ for the particles of soil, water–droplet, and crystal aerosol lies within the limits $10^{-4} - 10^{-6}$. Our estimate of γ lies within the same limits and is close to the maximum value.

Thus, the uniqueness of the situation during the entrainment of the dust emissions, when the effect of the sources and other sinks of ozone is insignificant, makes it possible to describe explicitly the aerosol contribution to the ozone destruction and to estimate the coefficient of the ozone molecule destruction on the surface of dust particles quite correctly.

In the case of ozone and aerosol observations in the ground atmospheric layer, which was one of the main purposes of the SATOR program, the above–described quite simple approach to the estimation of the aerosol contribution to the ozone destruction is incorrect.

First, the contribution of the Earth's surface and vegetation to the ozone destruction is getting significant. Second, there are natural independent temporal rhythms of sinks and sources of ozone and aerosols, and, finally, their diurnal variations caused by the effect of the meteorological parameters make the interpretation of the data much more difficult.

The measurements of the summer cycle of the SATOR program were carried out continuously from June 21 to Jule 7, 1991.

In order to estimate the aerosol contribution to the ozone destruction, let us consider the data obtained at night (from 10 p.m. to 6 a.m.), when we can confidently suppose that the photochemical processes of the ozone formation are absent and the effect of industrial ozone sources and ozone–producing substances decreases to the minimum. When interpreting the nighttime data, one should pay attention to the fact that the increase of the aerosol particle content caused by their accumulation in the ground layer (the turbulent and convective removal of aerosols to the upper atmospheric layers slows down with temperature drop) and by the increase in the relative humidity of air, which substantially expands the volume and surface area of aerosol particles, is sharply manifested simultaneously with the ozone content decrease. One can judge about the simultaneity of these processes from the calculated correlation coefficient between the ozone concentration and the scattering coefficient $\rho_{m,\sigma}$. Its value for the nighttime conditions of the summer cycle ρ was found to be equal to ≈ -0.7. Taking into account the large interdiurnal variability of the ozone and aerosol concentration in the measurement cycle as well as the fact that the data were obtained in the local volume and the spatial inhomogenities of the measured parameters strongly affected the results, let us restrict ourselves to the estimate of the averaged data.

The mean values were estimated from the correlation diagram for the values $m_0 - m(T)$ and $\int_0^T S(t)dt$, where the time intervals were taken for different observation hours and varied from 2 to 8 hours.

Under conditions of Tomsk, in contrast to Dushanbe, the fine fraction, which was outside of the sensitivity range of the photoelectric counter, formed the main part of the aerosol. For this reason to estimate the surface area of particles we used the data on the scattering coefficient σ ($\lambda = 0.52$ μm) and its relationship to the surface area of the aerosol particles, which can be approximately written down (within the framework of a single–parameter model[7,8]):

$$S \approx 6 \cdot 10^{-5} \sigma, \qquad (4)$$

where S is the surface area of aerosol particles in cm^2/cm^3 and σ is the scattering coefficient in km^{-1}.

According to the above–described procedure and taking into account Eq. (4), the mean surface area of aerosol particles turned out to be equal to $\overline{S} \sim 6 \cdot 10^{-6}$ cm^2/cm^3. For the mean ozone content $\overline{m} = 25$ μg/m^3 the ozone depletion with the mean rate of ~ 2.5 μg/m^3 per hour was observed at night.

In order to estimate the ozone sink on aerosol particles, let us use two values of the coefficient of the ozone molecule destruction: $\gamma = 10^{-5}$ and $\gamma = 10^{-2}$, which can be considered as its mean value and its maximum, respectively, according to the published data.

Calculation from formula (1) shows that in our experiment for different values of γ the ozone sink can be estimated as $\Delta m = 0.05$ μg/m^3 per hour for $\gamma = 10^{-5}$ and $\Delta m = 0.5$ μg/m^3 per hour for $\gamma = 10^{-4}$.

For the examined conditions of the summer observation cycle only from 2 % to 20 % of the ozone depletion could be caused by its sink on the aerosol particles.

Thus, in order to illustrate the contribution of aerosol particles to the destruction of the ozone molecules, two rather contrast examples have been considered in this paper:

– first, which characterizes the conditions of the anomalously large particle content in the lower 3–km atmospheric layer during the emission of dust, shows the existence of such situations in the real atmosphere, when practically all ozone can sink on the aerosol particles and

– second, which is typical of the ground conditions, when the other processes make the main contribution to the ozone destruction, while the aerosol contributes not more than a few tens of percents of the total sink.

Starting from our analysis and received estimates, we can conclude that under the regular atmospheric conditions the aerosol contribution to the ozone molecule destruction will increase with distance from the ground, and near the sources of aerosol emissions we should apparently expect the complete ozone destruction on the particle surface.

REFERENCES

1. S.I. Rasool, ed., *Chemistry of the Lower Atmosphere* (Plenum Press, New York – London, 1973).
2. S.P. Perov and A.Kh. Khrgian, *Current Problems of the Atmospheric Ozone* (Gidrometeoizdat, Leningrad, 1980).
3. A.B. Pittock, J. Atm. Sci. **23**, No. 5, 538–542 (1966).
4. R.D. Cadle, P. Crutzen, and D. Ehhalt, J. Geophys. Res. **80**, No. 24, 1381–3385 (1975).
5. L.S. Ivlev, in: *Atmospheric Ozone* (Leningrad State University Publishing House, Leningrad, 1988), pp. 63–79.
6. B.D. Belan, A.A. Isakov, V.V. Lukshin, et al., in: *Abstracts of Reports at the 5th All–Union Conference on Atmospheric Optics,* Tomsk (1991), p. 29.
7. M.V. Kabanov, M.V. Panchenko, Yu.A. Pkhalagov, et al., *Optical Models of Coastal Atmospheric Hazes* (Nauka, Novosibirsk, 1988).
8. G.I.Gorchakov, A.S. Emilenko, and M.A. Sviridenkov, Izv. Akad. Nauk SSSR, Fiz. Atmos. Oceana **17**, No. 1, 39–49 (1981).