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ATMOSPHERIC RADIATION, OPTICAL WEATHER, AND CLIMATE

The Scale of Ozone Destruction in Clouds

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Abstract—Changes in the concentration of tropospheric ozone in clouds were investigated based on aircraft sensing data. Three ozonometers were used for the measurements—one chemiluminescent 3-02P and two UV 49C (Thermo Environment Inc., United States). The following types of clouds were studied: *Cu*, *Cu* med., *St*, *Sc*, *As*, and *Ac*. The thickness of the cloud layers was 1.5 km on average and varied from 0.4 to 4.5 km. The ozone destruction in clouds was 11–15 ppb on average and ranged from 3 to 34 ppb; it changed nearly twofold depending on the cloud type. The estimation of the annual runoff of ozone in clouds has shown that it is close to the annual ozone balance in the troposphere.

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INTRODUCTION

Tropospheric ozone interacts directly with life forms, revealing its toxicant properties especially in the surface air layer. In large concentrations, it strongly inhibits the vital activity of plants and affects the human body in many ways. According to biological and medical investigations [1], ozone in the troposphere is a virulent poison; in addition to systemic toxicity, it exhibits such properties as mutagenicity, oncogenicity, and a radiomimetic effect (an effect on blood similar to ionizing radiation). Ozone exceeds such a well-known poison as hydrocyanic acid in its toxicity level. In addition to the impact on people and plants, ozone is an all-powerful oxidizer that damages rubber and oxidizes many metals, even of the platinum family [2].

Having a long lifetime in the atmosphere (from several days to several months) and strong absorption lines, tropospheric ozone can play a significant role in the greenhouse effect. According to [3], it contributes more than 8% to the total warming of the air caused by the absorption of solar radiation by greenhouse gases. Later estimates have shown that the contribution can be even larger.

Everything said requires a more detailed study of the balance of the ozone concentration in the troposphere. We considered the input part of the balance in previous works [4–7]. In addition, there is also the output part; together they form the ozone balance in the troposphere. Ozone runoff from the troposphere can result from the following processes: ozone photolysis, ozone interaction with gas components (ozonolysis), ozone interaction with aerosols, ozone sedimentation to the underlying surface, and precipitation erosion. The interaction of ozone with cloud aerosol is the least understood. These questions were studied theoretically in [8–14]. The number of experimental works is far less [15–17]; therefore, the aim of this work is to estimate the ozone destruction in clouds from experimental data.

1. INSTRUMENTS AND TECHNIQUES

The measurements were carried out from onboard the "Optik-E" AN 30 aircraft during cloud crossing, climb, and descent.

The problem of ozone measurements in conditions deviating from the background ones was earlier discussed in [18–23]. In view of this, three onboard ozonometers operated simultaneously—one chemiluminescent 3-02P, designed at ZAO OPTEC (St. Petersburg, Russia), and two UV 49C (Thermo Environment Inc., United States). The ozonometers were calibrated using a GS-2 ozone generator (ZAO OPTEC). Air venting of the devices was carried out via Teflon tubes. Cloud crossing was controlled visually as well as by records of the meteoparameters and aerosol number density.

Examples of the recording of the ozone concentration by the devices are shown in the figure (X corresponds to the chemiluminescent ozonometer, and TEI_1 and TEI_2 correspond to the UV ones). The distribution of the temperature and relative air humidity is shown in the left part of the figure; the cloud layer is grey.

As is seen from the Fig. 1, the ozone concentration either decreases inside the cloud layer or remains invariable up to the upper boundary. The concentration increases near the upper boundary. This seemingly occurs due to the involvement of air richer in ozone in the environmental exchange. The dashed lines show the deviation of the real distribution from

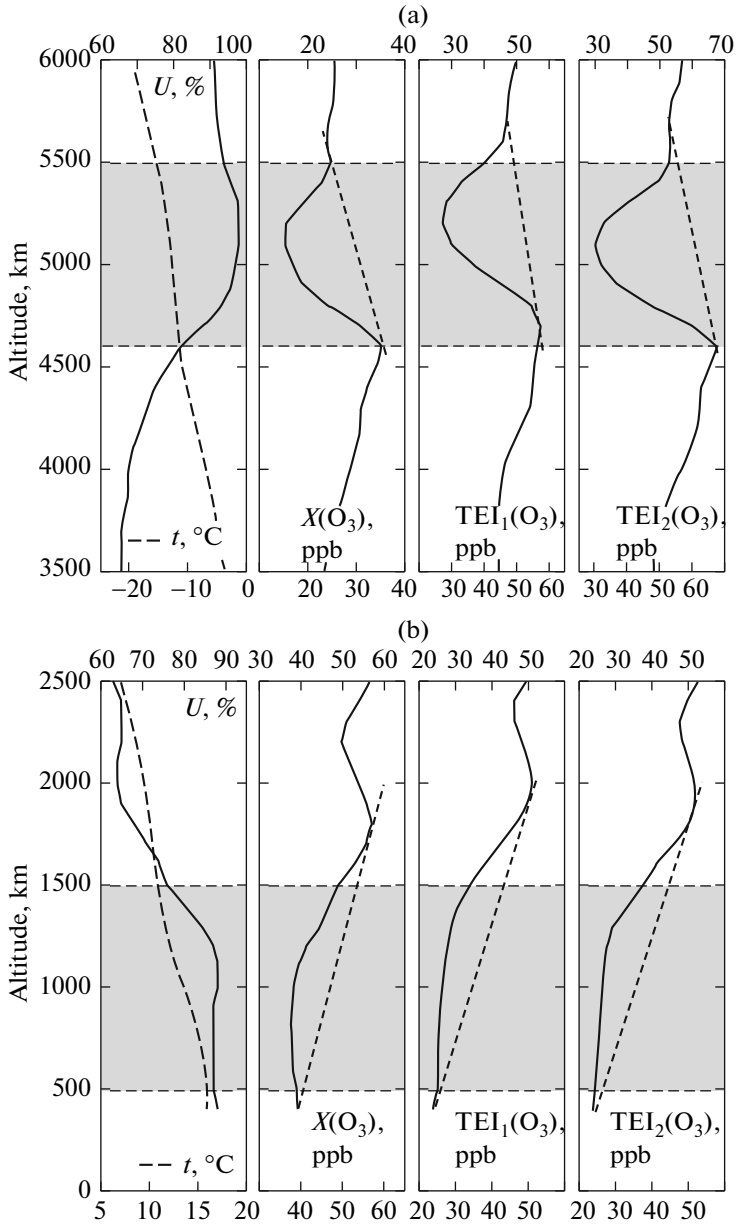

Fig. 1. Variations of the ozone concentration while crossing clouds: *As* near Khatanga on July 8, 2008 (a) and *Cu* near Yakutsk on July 23, 2008 (b).

the probable one in the case of the absence of the cloud layer.

The Fig. 1 also shows a good qualitative agreement between the readings of the three ozonometers. The quantitative criteria for 158 cases of cloud crossing by the aircraft are given in Table 1.

The single-shot accuracy of the 3-02P ozonometer is 15% and of the Thermo Environment Inc. (Model-49C) ozonometer is ±1 ppb; in view of this, the mean deviations in Table 1 perfectly fall within the error range. In addition, the measurements can differ profoundly in certain cases. This especially concerns the X-TEI_2 pair, where the difference in the readings reached +6 and −19 ppb. We will not dwell on this fact, because it is not the subject of our study. Let us assume that the above three ozonometers satisfactorily reflect the ozone distribution in the cloud layers.

2. MEASUREMENT RESULTS AND DISCUSSION

First, consider the measurements of the ozone concentration in the cloud layer independently of the cloud type (Table 2).

As follows from Table 2, the measurements were carried out in clouds from 0.4 to 4.5 km in thickness at

Table 1. Deviations (ppb) between the readings of the ozonometers while crossing clouds

Deviation	X–TEI_1	X–TEI_2	TEI_1–TEI_2
Average	2.6	4.7	2.2
Rms	1.4	1.4	1.0
Minimum	–12	–19	–10
Maximum	6	6	1

Table 2. Variations of the ozone concentration while crossing clouds

Deviation	Variation of the ozone concentration, ppb			Cloud layer thickness, km
	Ozonometer			
	X	TEI_1	TEI_2	
Average	11	12	15	1.5
Rms	5	6	8	0.8
Minimum	3	3	6	0.4
Maximum	25	24	34	4.5

Table 3. Relative variation of the ozone concentration in clouds

Ozonometer	X	TEI_1	TEI_2
Relative variation, %	22	24	27

an average value of 1.5 km. The average decrease in the ozone concentration in a cloud was 11, 12, and 15 ppb for each ozonometer, respectively; the coefficient of the variation reached 50%. The obtained values are significantly higher than in [15–17]. This can very well be due to the physical and geographical features of the region under study, as well as the experimental periods.

To partly exclude the climatic effect, we give the relative variations of the ozone concentration in clouds (Table 3). Here, the variation value is normalized to the average ozone concentration in the cloud marked by the dashed line in the Fig. 1.

It follows from Table 3 that the X ozonometer shows the minimum while the TEI_2 shows the maximum values; the relative ozone variation is 22–27% of its atmospheric concentration.

Variations of the ozone concentration in certain types of clouds can be inferred from Table 4 built on the basis of the 3-02P ozonometer data.

It is seen from Table 4 that the decrease in the concentration in *Cu* med. is larger than that in *Ac* clouds by 1.75 times. The widest variation range of the ozone concentration is also in *Cu* med. The relative variation is the highest in *As* clouds—it reaches 27%. The minimum one (17%) has been fixed in *Cu*, *St*, and *Ac* clouds; this is seemingly caused by their water content.

Table 4. Variations of the ozone concentration in clouds of different types

Deviation	Cloud type					
	Cu	*Cu* med.	*St*	*Sc*	*As*	*Ac*
Average ± rms, ppb	11 ± 5	14 ± 5	10 ± 5	9 ± 2	11 ± 5	8 ± 2
Relative, %	17	25	17	27	27	17
Range, ppb	7–16	8–25	4–15	7–11	3–18	5–10
The number of events	13	26	25	13	30	26

Table 5. Estimates of the power of the sources and ozone runoff in the troposphere (10^{12} g/year) and budget (10^{12} g)

Components	The Northern Hemisphere	The Southern Hemisphere	Earth
Inflow from the stratosphere	420 430	230 220	650 650
Photochemical formation	770–2050 330–1240	320–450 180–690	990–2500 310–1930
Photochemical runoff	1330	1110	2440
Runoff to the Earth's surface	940–1300 650	360–760 430	1300–2100 1080
Budget	94 158	47 83	141 241

3. ESTIMATE OF THE SCALE OF THE CLOUD EFFECT ON THE OZONE BALANCE IN THE TROPOSPHERE

The data given above regarding the variations of the ozone concentration in clouds allow for an estimation of the scale of ozone runoff from the troposphere when interacting with cloud aerosol in the first approximation.

According to [24], the average annual amount of clouds on the Earth is 5.8, i.e., 58% of the surface is covered by clouds. The area of the Earth is 5.1×10^{14} m^2. Again, multiplying the thickness of the cloud cover (it equals 1.5 km in our experiments) by the area, we obtain a volume of 4.44×10^{17} m^3 where ozone runoff occurs.

According to Table 2, the variation of the ozone concentration is 11 ppb by the "minimum" and 15 ppb by the "maximum" ozonometers, or 22 and 30 μg/m^3. Multiplying the volume by the concentration, we obtain 97.6 and 133.1 Tg of ozone precipitating on aerosol particles in clouds. The thus obtained estimate is close to the values of the annual ozone balance in the troposphere given in [25, 26] equal to 141 and 241 Tg per year, respectively (Table 5).

CONCLUSIONS

Ozone destruction on cloud aerosol has been revealed from the results of the experiments carried out with the help of three ozonometers mounted onboard the "Optik-E" An-30 aircraft laboratory. The following types of clouds were studied: *Cu*, *Cu* med., *St*, *Sc*, *As*, and *Ac*. The thickness of the cloud layers was 1.5 km on average and varied from 0.4 to 4.5 km.

Ozone destruction in clouds was 11–15 ppb on average and ranged from 3 to 34 ppb; it varied nearly twofold depending on the cloud type.

The estimation of the annual runoff of ozone in clouds has shown that it is close to the annual ozone balance in the troposphere.

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