Two types of diurnal variation of ozone in the boundary atmospheric layer

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The measurement results on the ozone diurnal variation in the near-water atmospheric layer in the off-shore (50–100 km far from a shore) regions are generalized for the mid-latitude summer. Two periods of O_3 accumulation (during a day and in the evening) in the near-water atmospheric layer are revealed. Accumulation culminates in the fast decay of O_3 in the later half of night. Analysis of simplest three-reservoir scheme of the O_3 diurnal behavior shows that not only diurnal variation in the generation of O_3, but also diurnal variations of the sink rate are characteristic of the near-water atmospheric layer.

The nature of ozone (of its sources and sinks) in the lower part of the troposphere has been the subject of long discussions. In the Junge models tropospheric ozone is considered as a result of O_3 transfer from the stratosphere[1]; according to other models, ozone in the troposphere and boundary atmospheric layer is formed as a result of photochemical processes.[2,3] One salient feature of the temporal behavior of O_3 density in the lower near-ground part of the atmosphere is its diurnal variation. It is a subject of numerous experimental studies,[4,5] which show high variability in the behavior and absolute values of O_3. Generalization and systematization of experimental data on diurnal variations of O_3, in a permanent sequence of days, may allow one to better understand the mechanisms of formation of the tropospheric ozone.

At present numerous measurement results on O_3 in the boundary tropospheric layer indicate that diurnal variation of ozone in the boundary layer follow the diurnal solar cycle. The common property of diurnal variation of O_3 is its minimum density in the morning, while the maximum ozone density not always coincides with the maximum solar radiation flux. With the altitude, starting from about 50 m, the amplitude of variation decreases, and no diurnal variation is observed at altitudes above 300 to 500 m.

However, other "strange" types of diurnal variation[4] not associated, at first sight, with diurnal variation of the solar radiation flux are observed in the boundary layer. These variations may have several peaks, peaks may fall on nighttime, an so on.

We have conducted numerous observations of ozone variations at different geographic sites on land and on seas. Measurements were carried out in summer, as a rule, in July and August in the mid-latitudes with a chemiluminescent ozonometer (Fig. 1). A sampler was set at the altitude of 1 to 10 m above the sea level or the surface. Measurements were conducted near Tomsk, in Russian sea ports, as well as from onboard a ship 50 to 100 km far from the shore. The troposphere near Tomsk is a typical example of the continental troposphere. In the sea ports the troposphere experiences the influence of the land or sea depending on the direction of air mass transport; in the mid-latitudes the troposphere is subjected to breeze either. On the sea 50 to 100 km far from the shore, the atmosphere, in relation to O_3, can be considered as marine one, because the time of air mass transport across such distances at the standard wind situation (~5 m/s) equals about half a day.

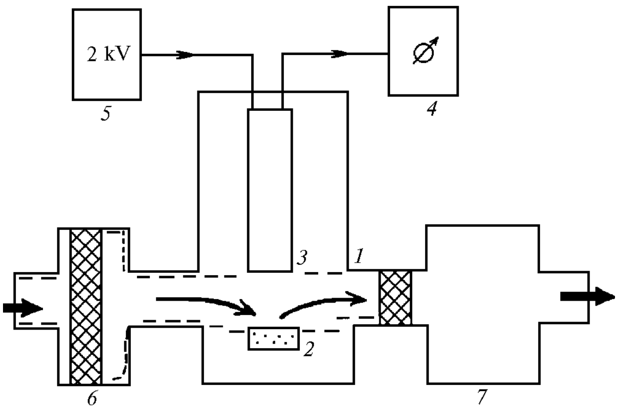

Fig. 1. Block-diagram of the ozonometer: container (*1*), dye tablet (*2*), PMT (*3*), photon counter (*4*), PMT power supply (*5*), filters (*6*), initiator (*7*).

In Fig. 2 curves *1–5* are examples of records of diurnal variation of the ozone: in Tomsk (curve *1*), in " lack and Japan Seas (curves *2* and *4*), in the port near Vladivostok (curve *5*), and in the Pacific Ocean near Petropavlovsk-Kamchatskii (curve *3*). As seen from the records, the curves characterizing the diurnal behavior of O_3 on seas (" lack Sea, 30 km to the west from Pitsunda; Avachinskaya " ay, 50 km to the east from Petropavlovsk-Kamchatskii; Japan Sea, 100 km to the east from Vladivostok) have no any peculiar structure; peaks of O_3 density fall on night hours of the local summer time. The diurnal behavior of O_3 deep in the continent contains, as a rule, components of different time scales, which manifest themselves on the records as a significantly high noise.

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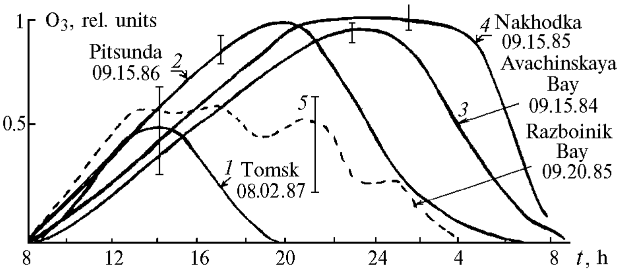

Fig. 2. Records of diurnal variation of n_3 at different geographical sites.

As seen from the records shown in Fig. 2, differences in the diurnal variation of the tropospheric O_3 on the sea and land are of principal character. In this connection it is worth calling them the marine and continental types of the ozone diurnal variation. Their generalized presentations are shown in Fig. 3. Visually, they differ in the position of the maximum of ozone density: in the boundary layer of the continental troposphere the maximum falls on 12:00–13:00 L.T., that is, near the diurnal maximum of the solar radiation flux; for the boundary layer of the marine troposphere the maximum of O_3 is shifted by about 12 hours, that is, it falls on the evening and night time. We often observed, for example, diurnal variation of O_3 with peaks, at 02:00–03:00 L.T. The common feature of the ozone diurnal variation in the lower layer of the marine and continental troposphere is the peak of ozone density in the morning hours, usually about 06:00–08:00 L.T. It should be noted that maximum and medium values of O_3 density in the near-water boundary layer of the troposphere are, as a rule, higher than those in the same atmospheric layers over the continent. We believe that various types of diurnal variation of O_3 in the boundary layer of the troposphere during mid-latitude summer are derivatives of the two types mentioned above.

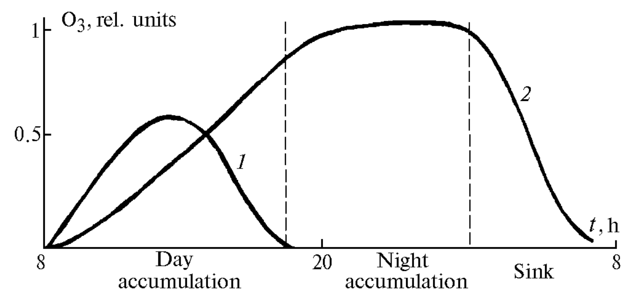

Fig. 3. Generalized curves of the continental (*1*) and marine (*2*) types of diurnal variation of the ozone.

For example, diurnal variation of O_3 in ports are mainly of the marine type, but the cases of mixed temporal distribution were also observed (see curve *5* in Fig. 2). In this connection, it should be noted that the diurnal variation of O_3 in Crimea[4] and on the shore of Italy[6] are typical cases of the continental, marine, and mixed behavior of O_3 concentration. It is natural that the examples of diurnal ozone variation that we have observed in our study correspond to a warm season in the mid-latitudes of the Northern Hemisphere.

The question on the influence of bounded land areas, such as islands, on the spatial distribution of ozone in the atmosphere of their off-shore water areas is very interesting and informative. To answer it, we recorded the variation of O_3 as the ship moved in nighttime near islands of different area. We have selected the nighttime because in this time the continental diurnal behavior of O_3 concentration reaches its minimum, while the marine one is close to its maximum, so the difference between the continental and marine concentrations of O_3 is the largest.

As a result of these experiments, it was found that on the windward side of islands the O_3 density in the boundary atmospheric layer is typical of this time of day, while on the leeward side the O_3 concentration is lower and characterized by a significant spatiotemporal variability, that is, the mixed type of diurnal variation takes place. In these experiments, the spatiotemporal variations of O_3 content connected with the air mass passage over the land were observed at a distance up to 1 km from the island shore. Figure 4 shows a typical experimental scheme and examples of records of ozonometer signals as the ship passed by the island. As seen from the records, deep variations of O_3 density take place in the wind shadow of an island.

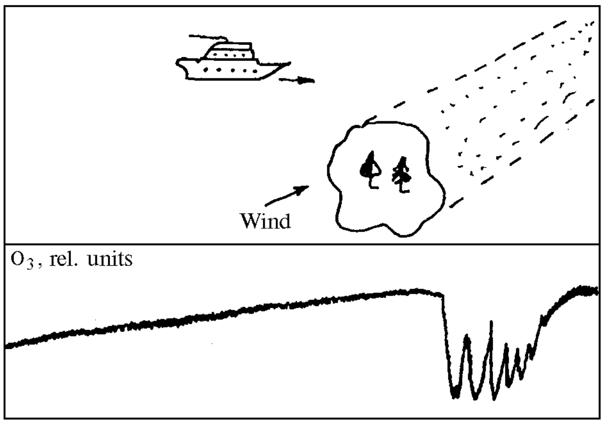

Fig. 4. Scheme of the experiment and the record of the ozone density spatial distribution.

These experiments clearly confirm the repeatedly advanced assumption that O_3 destruction in the surface layer of the troposphere is the result of O_3 interaction with the elements of the underlying surface. In this respect, the above-mentioned classification of diurnal variation into the marine and continental types is rather natural.

Let us note some distinctive properties of the marine type of diurnal variation of O_3. The first property is accumulation of O_3 in the near-water atmospheric layer in the later half of a day, i.e., during the time when the solar activity decreases. The second property is the existence of the period of slow accumulation of O_3 after sunset. The period of evening and night accumulation of O_3 lasts 5 to 10 hours. The third property is relatively fast decay of O_3 upon completion of the accumulation periods; the characteristic time of this decay is 2 to 3 hours. Similar marine diurnal variation of O_3 has also been recorded by other authors.[6–8]

As known, the values of O_3 "sink" to the land and water are different: the O_3 sink to water surface is several times less efficient.[9] However, the principal differences in the diurnal behavior of O_3 on the sea and land discussed above cannot be explained by the difference in sink power.

Assume, for example, the processes of generation and destruction of O_3 as a three-reservoir scheme shown in Fig. 5: reservoir of the source (troposphere) (*3*), reservoir of the current values of O_3 (near-surface layer of the troposphere) (*2*), reservoir of sink (the underlying surface) (*1*); α_2 and α_3 are the rates of O_3 generation in reservoirs *2* and *3*, τ_{32} and τ_{21} are the times of the processes of O_3 transport from reservoir *3* to reservoir *2* and from reservoir *2* to reservoir *1*, respectively. Such schemes are well known; they are used for description of the processes of isotope accumulation, build-up of luminescence, and others. In particular, on the assumption that from the time $t = 0$ the processes of ozone generation are turned off, that is, $\alpha_3 = \alpha_2 = 0$, the system of kinetic equations of O_3 density in reservoir *2* has the following solution:

$$N_2 = N_{20}\,[(\gamma + 1)\exp(-t/\tau_{21}) - \gamma\exp(-t/\tau_{32})],$$

where $\gamma = (N_{30}/N_{20})\,[\tau_{21}/(\tau_{21} - \tau_{32})]$, and N_{20} and N_{30} are the densities of O_3 in reservoirs *2* and *3* at time $t = 0$.

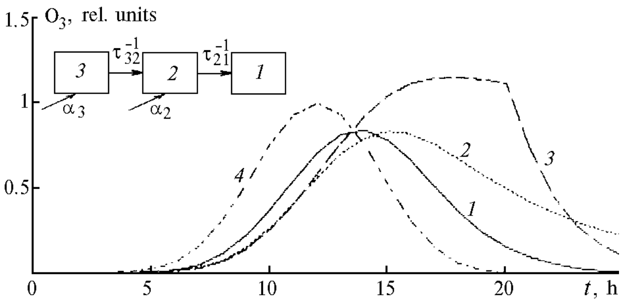

Fig. 5. Three-reservoir scheme of formation of diurnal ozone variation and the calculated results: diurnal variation over the continent (curve *1*), illustration of deformation of the diurnal variation at three times increase in τ_{21} (*2*), curve presenting the diurnal variation at time-separation of processes of the ozone generation and destruction (*3*), process of ozone generation (*4*).

Figure 5 shows the version of numerical solutions of the equations of the three-reservoir scheme on the assumption that photochemical processes of ozone generation in the troposphere over both the land and sea have the same rate and can be simulated by the sinusoidal function (curve *4*) with the half-period about 12 hours. Other sources of ozone, such as ozone descent from the upper layers of the troposphere, were ignored. The values of τ_{21} and τ_{32} were fitted for both the sea and land by the criterion of the closest agreement between the calculated curve and the experimentally measured ones. As seen from the solutions (curve *1*), we have managed to find such values of τ_{21} and τ_{32} that the behavior of O_3 in the continental troposphere is well described by this model. However, for the near-water troposphere this model fails to describe the above-mentioned most important features of diurnal variations at any τ_{21} and τ_{32}. If, for example, it is taken that the characteristic time of O_3 destruction by the sea water is three times longer than that for the land,[9] then the solution has the form shown by curve *2* in Fig. 5, which does not reproduce the experimental curve.

More complex models describe the experimental diurnal behavior of O_3 on the sea significantly better; for example, curve *3* corresponds to the model of time-separation of the processes of generation and sink, namely, the absence of sink between 08:00 and 22:00, while from 22:00 to 08:00 the sink is being equal to the sink onto the land.

The search for solutions well describing the temporal behavior of O_3 in the marine troposphere (see, for example, curve *3* in Fig. 5) has shown that the experimentally observed diurnal behavior of O_3 with the maximum in the nighttime may be formed by the following processes, which result in the variable, in time, ozone sink in the troposphere over sea: breeze, if the "continental" troposphere can achieve the region of measurements in 6 to 8 hours after sunset; the presence, in the marine troposphere, of the ozone source having the diurnal behavior of O_3 generation shifted by 6 to 8 hours relative to the photochemical process of O_3 generation in the atmosphere; the existence of the particular diurnal behavior of the ozone sink in the troposphere over sea with the maximum falling on the later half of a night.

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