
“OXYGEN STARVATION” OF THE ATMOSPHERE

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Abstract. Since the discovery of the phenomenon of abnormal cooling and sinking of the middle and upper atmosphere in 1993–1998, two concepts have developed which explain its origin by man-made processes. Both focus on different consequences arising from one common cause — the burning of carbon fuels on an industrial scale. The first concept is based on the hypothesis about the key role of the decrease in oxygen content in the atmosphere in this process. The second model, which emerged a little later, attributes the observed effects to the growth of greenhouse gases in the atmosphere, primarily CO₂. Over the years, numerous attempts have been made to confirm the assumption of the dominance of the second mechanism in the excitation of the long-term trend of the climate of the middle and upper atmosphere. However, all of them turned out to be futile. At the same time, today, firstly, the validity of the first proposed hypothesis is justified which recognizes the leading role of oxygen in climate change in the upper atmosphere, and secondly, errors that cause the

erroneous rejection of this conclusion are revealed. It becomes obvious that man-made processes affecting the atmosphere lead to two multidirectional phenomena: a) global warming of the troposphere; b) global cooling of the thermosphere: an extreme increase in the mass of CO₂ heats the lower layers of the atmosphere, and its upper layers are cooled even by an inconspicuous decrease in part of O₂ relative to the total mass. Since nothing indicates a decline in the man-made activity of the world civilization in the coming years, in order to adequately predict the consequences of an increase in atmospheric pollution the effect of a decrease in oxygen content on the state of near-Earth outer space should probably be taken into account.

Keywords: oxygen, carbon dioxide, long-term trends, global cooling, global warming, meso-thermosphere, ionosphere.

INTRODUCTION

The first reference to climate change in the upper atmosphere, which has occurred since the middle of the XX century and is not related to solar activity, was based on the analysis of long-term data from vertical sounding of the ionosphere [Givishvili, Leshchenko, 1993b]. Over the past 30 years, many facts of man-induced impact on almost all parameters of neutral and charged components of the middle and upper atmosphere have been revealed. Key mechanisms of their excitation were identified and analyzed in publications and international symposia results of which were presented in [Givishvili, Golitsyn, 1999], and then in reviews [Danilov, 1997, 2012; Danilov, Konstantinova, 2020]. At the same time, two interpretations of the source of the detected phenomenon were first proposed. The former, described in [Givishvili, Leshchenko, 1993b] and developed in a series of articles [Givishvili, Leshchenko, 1993; Givishvili, Leshchenko, 1994, 1995; Givishvili, Shubin, 1994], was based on the hypothesis about a sharp drop in the content of free oxygen in the thermosphere, caused by burning of carbon fuels on an industrial scale. The latter, presented in [Danilov, 1997, 2012; Danilov, Konstantinova, 2020], suggests the primacy of an increase in greenhouse gases in the atmosphere, which is caused by the same man-made impact.

In fact, both concepts arose from a common premise — burning of carbon fuels. Carbon burns in a cycle of many reactions, which are finally reduced to the formula $C+O_2=CO_2+Q$, where Q is the thermal effect of the reaction. The difference between the interpretations was the emphasis on the final outcome of this reaction. In the first case, the emphasis is on decreasing O₂; in the second, on increasing CO₂. The second concept is based on the theoretical model of the reaction of the atmosphere to the hypothetical twofold increase in CO₂ content in it [Roble, Dickinson, 1989] and to ionospheric consequences of this effect [Rishbeth, 1990]. As can be seen from the conclusions drawn in [Danilov, Konstantinova, 2020], despite all the efforts of theorists to explain the observed processes in some way by a direct increase in CO₂ in the atmosphere, the results remain completely unsatisfactory. The increase in CO₂ since the middle of the last century was not 100, but only 10–15 %, whereas changes in the parameters of the meso-thermosphere and ionosphere significantly exceed errors in their measurements.

The purpose of our work is: 1) to describe the technique that allows us to assess local, regional, and global changes in the oxygen content in the upper atmosphere; 2) to prove that the total content of free oxygen in the atmosphere is subject to decrease due to man-made factors; 3) to identify the reasons why empirical evidence documenting this process is somehow ignored.

1. TECHNIQUE FOR ESTIMATING THE O₂ CONTENT AT HEIGHTS OF THE E LAYER OF THE IONOSPHERE

The empirical database the analysis is based on contains data from ionospheric monitoring by vertical sounding (VS) performed at the station Moscow since 1943. The emphasis is on the results of measurements of E-layer characteristics. There are two reasons. First, the influence of wind transport, diffusion, and electric field processes in this layer at midlatitudes is insignificant; therefore, vertical distribution of the electron density N_e in it is determined mainly by fluxes of solar ionizing radiation forming free electrons and aeronomy that controls the rate of their losses in recombination reactions. Accordingly, the range of possible natural external sources of uncertainties causing N_e variations significantly narrows, and anthropogenic factors of disturbances of this parameter are typically left.

Second, the key characteristics of the layer — the critical frequency f_oE [MHz] and the height of maximum h_mE [km], which define the vertical profile of N_e in the height range 100–130 km — are determined with unprecedentedly high accuracy for geophysics. The frequency f_oE is found with an error not exceeding $\pm 1\%$ in the absence of interference and underlying sporadic E layers (E_s); and h_mE , which, in fact, is the virtual height $h'E$, with an error of $\pm 2\%$.

Under quasi-equilibrium conditions, which occur within 2–4 hours near the local noon, the equality holds

$$N_e = (q/\alpha)^{0.5}, \quad (1)$$

where q is the ionization rate; α is the effective electron loss coefficient in reactions with positive ions. At the height of the layer maximum, the peak value of N_e :

$$N_mE = 1.24 \cdot 10^4 f_oE^2. \quad (2)$$

Ionization here is driven mainly by solar X-ray (8–165 Å) and ultraviolet (977–1037 Å) radiation. In this case, ultraviolet radiation interacts only with O₂ (with efficiency q_U), whereas the X-ray flux ionizes all gas components, including three main ones — O₂, O, and N₂ (with efficiency q_X). Hence, the total ionization rate $q_\Sigma = q_U + q_X$, where q_U corresponds to [O₂]; and q_X , to [O₂]+[O]+[N₂]. Due to the high radiation flux density in the ultraviolet spectrum, $q_U > q_X$.

Since there are no direct methods for monitoring the molecular oxygen content in the lower thermosphere, an indirect method for its estimation was proposed in [Ivanov-Kholodny et al., 1976]. It is based on the fact that during a flare q_U changes slightly, whereas q_X often increases by two or more orders of magnitude. In other words, during flares there is a sharp imbalance in the contribution of these two portions of spectrum to the total ionization rate due to an abrupt increase in q_X . Their ratio during a flare can be estimated from the equation

$$q_X/q_\Sigma = \{ [f_oE^f / f_oE]^4 - 1 \} / \{ [J_{1-8}^f / J_{1-8}]^p - 1 \}, \quad (3)$$

where the index "f" corresponds to the moment of the flare; J_{1-8} is the intensity of the radiation flux in the range 1–8 Å; $p = 0.25 \pm 0.1$.

It is recognized that the total content of O₂, O, and N₂ in the lower thermosphere remained stable for at least the entire XX century. Long-term synchronous series of ground-based measurements by the VS method and satellite recording of X-ray fluxes can therefore provide insight not only into the variability in [O₂] depending on coordinates, season, and solar cycle, but also into its long-term dynamics over the given VS station.

Using data from ground-based ionosphere monitoring (station Moscow) and satellite measurements of solar X-ray flux, Givishvili et al. [2005] have shown that from 1969 to 1994 the ratio q_X/q_Σ increased from 1.4 to 2.2. Since the total concentration of neutral components of the lower thermosphere remained stable during this time, it was suggested that for 25 years of observations in the latter half of the XX century [O₂] decreased 2–4 times at the height of the E-layer maximum over the observation station.

Givishvili and Leshchenko [2022a] have also analyzed the results of measurements at five Japanese VS stations. In addition, the time range of data was expanded: in Moscow from 1969 to 2017; in Japan, from 1969 to 2000. This made it possible to evaluate not only temporal, but also spatial characteristics of the ionospheric E layer's response to X-ray flares. It turned out that in the entire analyzed space-time range, firstly, latitude-longitude effects are insignificant; secondly, the ionosphere responds to flares almost uniformly, thereby confirming effectiveness of the method [Ivanov-Kholodny et al., 1976]. The close similarity between the values of q_X/q_Σ , found from the annual average solar activity index $F10.7$ for Moscow and Japan, allowed us to present a general formula for the long-term positive trend in this parameter as follows:

$$q_X/q_\Sigma(t) = 0.0072 \text{ Year} + 0.0012 F10.7 - 4.139, \quad (4)$$

where $\text{Year} = 1969, 1970, \dots$

2. PRELIMINARY CALCULATIONS OF f_oE , h_mE , AND q_X/q

Equinoctial periods are most convenient for recording the E-layer characteristics. In winter, the duration of its existence is several hours shorter, f_oE is significantly lowered, and absorption of sounding signals in the underlying D-region is often increased (the so-called winter anomaly). In summer, the sporadic E layer (E_s) shields the regular E layer for most of the day. Moreover, in order to calculate long-term trends in ionization rates, it is necessary to exclude the influence of not only seasonal, but also cyclical factors on them. The average solar activity for the entire 71-year observation period $F10.7 = 148$. We have therefore used data from the NRLMSIS model [Emmert et al., 2020] corresponding to noon on March 15, 1970 at $F10.7 = 158$ as a reference model for calculating the ionization rates q_X and q_U .

Height profiles of the ionization rates [$\text{cm}^{-3} \text{ s}^{-1}$] were calculated by formulas:

$$q_U(h) = \sigma_i [O_2] J_U \times \exp \left\{ -2\sigma_{\alpha 90} \int^\infty [O_2] dh Ch(R, \chi) \right\}, \quad (5)$$

$$q_X(h) = \sigma_i [X] J_X \times \exp\left\{-2\sigma_{\alpha 90} \int^{\infty} [X] dh Ch(R, \chi)\right\}, \quad (6)$$

where $X=O, O_2, N_2$; σ_i and σ_{α} are cross-sections of their ionization and absorption respectively; $Ch(R, \chi)$ is the Chapman function.

Table 1 lists values of σ_i and σ_{α} , as well as intensities of solar radiation fluxes at different wavelengths.

Table 1
Cross-sections of ionization σ_i and absorption σ_{α} , as well as solar radiation fluxes J_U and J_X at different wavelengths

$\lambda, \text{\AA}$	$[O_2]$		
	σ_i, cm^{-2}	$\sigma_{\alpha}, \text{cm}^{-2}$	$J_U, \text{cm}^{-2} \text{s}^{-1}$
977	$2.5 \cdot 10^{-18}$	$4.0 \cdot 10^{-18}$	$5 \cdot 10^9$
1026	$1.0 \cdot 10^{-18}$	$1.5 \cdot 10^{-18}$	$4 \cdot 10^9$
	$[X]$		
	σ_i, cm^{-2}	$\sigma_{\alpha}, \text{cm}^{-2}$	$J_X, \text{cm}^{-2} \text{s}^{-1}$
110	$5.3 \cdot 10^{-18}$	$1.4 \cdot 10^{-18}$	$1.8 \cdot 10^8$
80	$3.7 \cdot 10^{-18}$	$8.0 \cdot 10^{-19}$	$2.6 \cdot 10^8$
63	$2.4 \cdot 10^{-18}$	$4.2 \cdot 10^{-19}$	$1.7 \cdot 10^8$
50	$1.7 \cdot 10^{-18}$	$2.2 \cdot 10^{-19}$	$1.7 \cdot 10^8$
37	$1.1 \cdot 10^{-18}$	$1.0 \cdot 10^{-19}$	$9.0 \cdot 10^7$

The information on the intensity of ionizing radiation fluxes J_U and J_X , as well as on the corresponding ionization and absorption cross-sections, was taken from [Ivanov-Kholodny, Firsov, 1964; Ivanov-Kholodny, Mikhailov, 1980]. To estimate the total ionization rate ($q_{\Sigma}=q$) at a known electron density value under quasi-equilibrium conditions, it is necessary to know the effective electron loss rate α in recombination reactions with NO^+ and O_2^+ prevailing at heights of the E-region. According to laboratory measurements [Mehr, Biondi, 1969]:

$$\alpha_{NO^+} = 4.1 \cdot 10^{-7} (300/T)^{0.5} \text{ cm}^3 \text{ s}^{-1}, \quad (7)$$

$$\alpha_{O_2^+} = 2.2 \cdot 10^{-7} (300/T)^{0.5} \text{ cm}^3 \text{ s}^{-1}, \quad (8)$$

so that

$$\alpha = \alpha_{O_2^+} \left\{1 + 2\phi^+ / (1 + \phi^+)\right\}, \quad (9)$$

where $\phi^+=[NO^+]/[O_2^+]$.

According to NRLMSIS, at equinoctial noon at the latitude and longitude of Moscow during the period of interest the temperature in the height range 105–115 km $T \approx 200$ K [Emmert et al., 2020]. Hence, on the assumption of the approximate equality in the content of NO^+ and O_2^+ near the height of the E-layer maximum [Danilov et al., 1981], we can take the effective coefficient of recombination (loss) $\alpha \approx 3.8 \cdot 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. Thus, under quasi-equilibrium conditions, according to Formulas (1) and (9) the total initial ionization rate should be close to $5.4 \cdot 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ (Table 2, column 1).

The results of our calculations with parameter values [Ivanov-Kholodny, Nusinov, 1979] ([Iv-Kh, N]) and [Ivanov-Kholodny, Firsov, 1974] ([Iv-Kh, F]) are presented in columns 3–6 of Table 2. Calculations of $q_U(h)$ and $q_X(h)$ taking into account J_U and J_X from [Ivanov-Kholodny, Firsov, 1974; Ivanov-Kholodny, Mikhailov, 1980] led to a paradoxical conclusion. It turned out that, firstly, in the entire range of heights from 100 km and higher the contribution of X-rays to the total ionization rate exceeds that of ultraviolet radiation (Figure 1) so that near the layer maximum $q_X/q_U=1.23$ (see Table 2, column 4). This contradicts conclusions based on empirical data, including those drawn in [Ivanov-Kholodny et al., 1977], which argued quite the opposite (column 3), namely, that in the entire E-region the contribution of X-rays is obviously lower than that of ultraviolet radiation; therefore, the ratio q_X/q_U during the year varies from a minimum (0.15) to a maximum (0.32) with an average of 0.28 at the equinox (column 1). Both the ionization rate q_m , and accordingly, the electron density $N_m E$ at the maximum of the layer, as well as the layer height and the critical frequency $f_o E$, reduced to $F10.7=150$ (column 4), turned out to be significantly lower than the empirical values (column 1).

The accuracy of estimating the E-layer parameters by the VS method is unprecedented. The reliability of the constants of reactions (7) and (8) detected in laboratory conditions is also beyond doubt. It remains to assume that all the identified errors are due to a single reason —

Table 2

Experimental and calculated values of the basic characteristics of the ionospheric E layer

Parameter	Experiment		[Iv-Kh, N]	[Iv-Kh, F]	[Iv-Kh, F]*	[Iv-Kh, F]*
	1	2	$\chi=60^\circ$	MSIS	MSIS	MSIS**
	1946	2017	1977	1946	1946	2017
$(f_o E)_{150}, \text{MHz}$	3.12	3.21	2.62–2.15	2.7	3.16	3.4
$N_m E, \text{cm}^{-3}$	$1.2 \cdot 10^5$	$1.3 \cdot 10^5$	$7.6 \cdot 10^4$ – $6.15 \cdot 10^4$	$9.5 \cdot 10^4$	$1.24 \cdot 10^5$	$1.43 \cdot 10^5$
h_m, km	116.5	113	105–109	107	116.5	111.5
$q_m, \text{cm}^{-3} \text{s}^{-1}$	$5.4 \cdot 10^3$	$6.6 \cdot 10^3$	$1.95 \cdot 10^3$ – $1.58 \cdot 10^3$	$3.4 \cdot 10^3$	$5.8 \cdot 10^3$	$7.8 \cdot 10^3$
q_X/q_U	0.28	0.82	0.16–0.37	1.23	0.45	0.84

Note: * — the flux intensity J_{977} increased 3 times; and J_{1026} , 2 times; ** — the concentration of O_2 decreased 3.9 times at a height of 110 km.

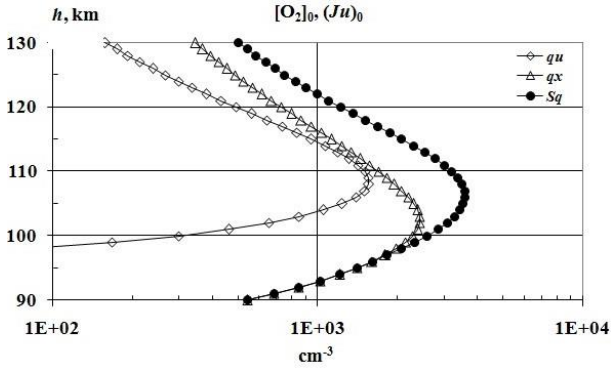


Figure 1. Calculated height profiles q_U , q_X , and q determined from data on $[O_2]$, $[N_2]$, and $[O]$ from the NRLMSIS model and the intensities of solar X-ray and ultraviolet radiation fluxes from [Ivanov-Kholodny, Firsov, 1974; Ivanov-Kholodny, Mikhailov, 1980]

a significant underestimation of the data on flux intensities in the 977 Å and 1026 Å lines tabulated in [Ivanov-Kholodny, Firsov, 1974].

3. CORRECTED CALCULATIONS

In order for the calculated estimates of $q(h)$ to satisfy the results of the estimates of f_oE and N_mE , determined by the VS method, and laboratory data on the electron loss rates in recombination reactions with NO^+ and O_2^+ , we had to artificially increase the intensity of radiation fluxes in the 977 Å line three times, and in the 1026 Å line two times (since the height of the peak value of $q_U(h)$ in the 977 Å line is 3–4 km higher than the maximum of $q_X(h)$ and closer to the actual height of the E-layer maximum). The calculation results are presented in Figure 2. Now, first, the total ionization rate runs to $5.8 \cdot 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ (see Table 2, column 5), which even slightly exceeds the empirical initial value of q_m and hence the frequency $(f_oE)_{150}$ for 1946.

Second, at $h_mE=116.5$, $q_X/q_U=0.45$. Third, the height of the maximum ionization rate $h(q_m)$ remained practically unchanged, as expected.

We managed to achieve a synchronous increase in f_oE and a simultaneous decrease in h_mE by the required 3.5 km for 2017 only with a radical decrease in the

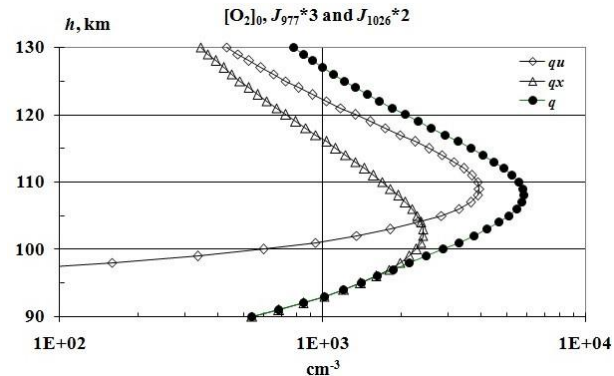


Figure 2. Calculated height profiles q_U , q_X , and q , found from data on $[O_2]$, $[N_2]$, and $[O]$ from the NRLMSIS model. Fluxes are increased 3 times in the 977 Å line, 2 times in the 1026 Å line

molecular oxygen content at heights exceeding the height of the turbopause (~ 100 km). The start height from which we artificially reduced the molecular oxygen content was 90 km. Figure 3 exhibits the height profiles of the concentration of $[O_2]$ for the coordinates of Moscow: $[O_2]_0$ according to the NRLMSIS model; $[O_2]_1$ and $[O_2]_2$ with a 2.1- and 3.9-fold decrease at 10 km respectively.

A satisfactory result was obtained by reducing the concentration of O_2 to ~ 4 times. In this case, the height profiles $q_X(h)$, $q_U(h)$, and $q(h)$ had the form shown in Figure 4. At the same time, $h(q_m)$ — the calculated height of maximum $q(h)$ — decreased by 5 km, and the peak value of q_m ran to $7.8 \cdot 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ (column 6). With the effective loss coefficient unchanged, this would be equivalent to $N_mE=1.43 \cdot 10^5 \text{ cm}^{-3} \cdot (f_oE=3.4 \text{ MHz})$, which would significantly exceed the desired value $N_mE=1.2 \cdot 10^5 \text{ s}^{-3}$. Meanwhile, the ratio q_X/q_U increases to 0.84 at $h_mE=113$ km (column 6). This fulfills both requirements for the calculated profiles $q_U(h)$ and $q_X(h)$: a) $q_U(h) > q_X(h)$; b) $q_U(h) + q_X(h) \geq 5.4 \cdot 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ (see Table 2).

The insignificant actually observed increase in $N_mE(f_oE)$ with the strong increase in q_m can be explained as follows. The content of NO^+ at the height of the E-layer maximum is determined by the ratio [Brasseur, Solomon, 1987]

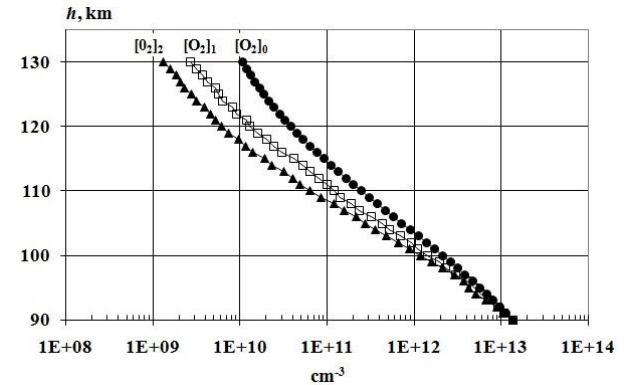


Figure 3. Height density profiles of $[O_2]$: $[O_2]_0$ from the NRLMSIS model; $[O_2]_1$ and $[O_2]_2$ with a 2.1- and 3.9-fold decrease respectively at a height of 110 km

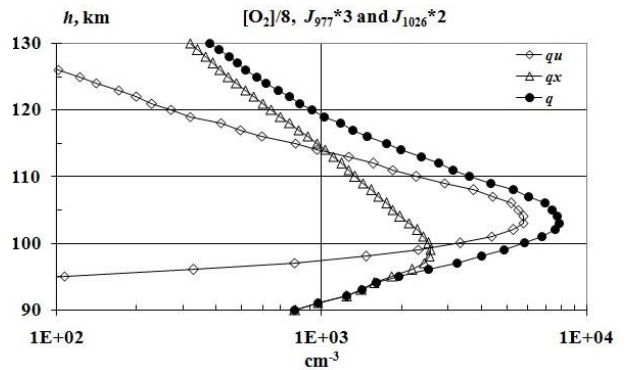


Figure 4. Calculated height profiles q_U , q_X , and q , determined from $[N_2]$ and $[O]$ from NRLMSIS, and $[O_2]$ reduced 3.9 times at 110 km. Fluxes are increased 3 times in the 977 Å line, 2 times in the 1026 Å line

$$[\text{NO}^+] = \left\{ \gamma_1 [\text{NO}] \left[\text{O}^+ \right] + \gamma_2 [\text{N}_2] \left[\text{O}^+ \right] + \gamma_3 [\text{O}] \left[\text{N}_2^+ \right] \right\} / \alpha_{\text{NO}^+} N_e, \quad (10)$$

where $\gamma_1 = 6.3 \cdot 10^{-10}$, $\gamma_2 = 10^{-12}$, $\gamma_3 = 1.4 \cdot 10^{-10}$.

With a multiple reduction in the O_2 and O_2^+ content, the concentration of NO^+ should change less noticeably since it is known that the concentration of $[\text{N}_2]$ in the upper atmosphere is not subject to perceptible long-term changes, and we assumed $[\text{O}^+]$ to be independent of time. (This is not a completely correct assumption, but estimates show that the rate of decrease in $[\text{O}^+]$ as compared to the rate of decrease in $[\text{O}_2^+]$ is really low, which, in particular, is indicated by the data from [Pokhunkov et al., 2003]).

Calculations from Formula (10) for the coordinates of Moscow, the 110 km height, and the conditions on March 15, 1970 ($F 10.7 = 170$), using the MSIS model and data on the concentrations of O_2^+ from [Danilov et al., 1981], and O^+ and N_2^+ from [Koshelev et al., 1983], have revealed that $[\text{NO}^+]_1 = 6.7 \cdot 10^4 \text{ cm}^{-3}$. When $[\text{O}_2]$ decreases four times, $[\text{NO}^+]_2 = 2.1 \cdot 10^4 \text{ cm}^{-3}$. In other words, the decrease in $[\text{NO}^+]$ is 1.25 times slower than the decrease in $[\text{O}_2]$. Accordingly, other factors being equal, there should be a ~ 1.25 -fold increase in the rate of electron recombination compensating for the increase in the ionization rate and leading to a less noticeable increase in $N_m E(f_o E)$ than would be expected with a constant electron loss rate.

The long-running question about the discrepancy between the heights of electron density maxima $h_m E$ and the ionization rate $q_m h(q_m)$, which may be as large as 8–9 km, remains open. This is probably due to the fact that the electron loss rate during the transition from the D-region (60–90 km) to the F1 layer (~ 200 km) varies by about three orders of magnitude. This happens due to a radical change in the composition of positive ions with increasing height: cluster ions C1 predominate in the D-region: $\text{NO}^+(\text{H}_2\text{O})$, $\text{NO}^+(\text{H}_2\text{O})_2$, $\text{NO}^+(\text{H}_2\text{O})_3$ with velocity constants $\alpha_{\text{C1}} = (5-10) \cdot 10^{-6} (300/T)^{0.5} \text{ cm}^3 \text{ s}^{-1}$, whereas in the F1 layer electrons recombine mainly with predominant O^+ at a velocity $\alpha = (5-10) \cdot 10^{-9} \text{ s}^{-3} \text{ s}^{-1}$ [Alpert, 1972]. At the same time, at the heights of E-layer maximum, where NO^+ and O_2^+ dominate, the electron density is very sensitive to variations in $[\text{NO}^+]/[\text{O}_2^+]$ since $\alpha_{\text{NO}^+} \approx 2\alpha_{\text{O}_2^+}$.

4. DISCUSSION

The key mechanism initiating cooling and sinking of the atmosphere has been discussed since the discovery of the influence of anthropogenic activity on the ionosphere and the emergence of our hypothesis about the decisive role of man-made loss of free oxygen in the upper atmosphere during this process [Givishvili, Leshchenko, 1995]. Obviously, the massive release of carbon dioxide in the surface layers of the atmosphere leads to binding of free oxygen in the entire column of the atmosphere. The consequences of this process are such that even a microscopic (by the standards of surface layers) reduction in $[\text{O}_2]$ causes irreversible changes in

the atmosphere as a whole. Moreover, this effect produces the greatest resonance, where the density of the atmosphere is many orders of magnitude lower than in the troposphere.

This raises two questions. First, why have not any noticeable changes in oxygen concentration been observed in the surface layers of the atmosphere so far? Despite the fact that the main source of loss of $[\text{O}_2]$ is anthropogenic activity binding free oxygen to carbon dioxide.

Until the middle of the XX century, emissions of fossil fuel products into the atmosphere were relatively low: in 1960, the total content of $\Sigma(\text{CO}_2)_1$ in the atmosphere was 315 ppm or $1.6 \cdot 10^{12}$ tons. The situation changed dramatically in the second half of the XX century, and by 2010 $\Sigma(\text{CO}_2)_2$ increased to 385 ppm or $2.0 \cdot 10^{12}$ tons [https://techcrunch.com/author/jonathan-shieber /]. Thus, over 50 years, the total mass of $\Delta\Sigma\text{CO}_2 = \Sigma(\text{CO}_2)_2 - \Sigma(\text{CO}_2)_1$ has increased by $4.0 \cdot 10^{11}$ tons. Since the mass fraction of O_2 in CO_2 is 70 %, the observed increase in $\Delta\Sigma\text{CO}_2$ is equivalent to a decrease in the integral mass of $\Delta\Sigma\text{O}_2 = \Sigma(\text{O}_2)_2 - \Sigma(\text{O}_2)_1$ by $3.0 \cdot 10^{11}$ tons over the same time period.

If we assume that the O_2 content remained stable until 1960, its total mass $\Sigma(\text{O}_2)_1$ was as large as $1.3 \cdot 10^{15}$ tons. It follows that the total losses of $\Delta\Sigma\text{O}_2$ over 50 years amounted to 0.0025 % of its total content. In other words, the decrease in the mass of O_2 caused by combustion of carbon fuel has not yet had time to affect its concentration in the surface layers, equal to 20.9488 ± 0.0017 %. These losses are even less noticeable when converted to the annual rate of loss of O_2 : $\Delta\Sigma\text{O}_2/50 = 6 \cdot 10^9$ tons/year. For the total mass of ΣO_2 , this is $6 \cdot 10^9 / 1.3 \cdot 10^{15} = 4.6 \cdot 10^{-6}$ tons/year. No existing instrument or sensor has the sensitivity to detect such changes in oxygen content as long as the gas components are completely mixed in the atmosphere. However, what went unnoticed in the absolute O_2 losses proved to be conspicuous in the relative losses for the atmospheric layers above the turbopause (~ 100 km). Because here, firstly, vertical distribution of each atmospheric component becomes independent of the others, and secondly, the density of the atmosphere is 6–7 orders of magnitude lower than the surface one.

If we assume that until the middle of the XX century the mass of $\Sigma(\text{O}_2)_1$ remained unchanged, then, according to MSIS, in 1946 above 100 km $\Sigma(\text{O}_2)_1 = 5 \cdot 10^8$ tons. According to our estimates based on ionosphere monitoring data, for 71 years above 100 km $\Sigma(\text{O}_2)_2$ decreased by $3.8 \cdot 10^8$ tons, which is equivalent to ~ 75 %. Thus, despite the sources of O_2 loss in the thermosphere being located mainly in the troposphere, their effect on the atmosphere is much stronger at the heights where its density is many orders of magnitude lower than in the surface layers.

In [Givishvili, Leshchenko, 2022b], attention was drawn to the fact that noticeable disturbances in the ionosphere and especially in the E layer began to manifest themselves after 1957–1958. The effect was explained by the beginning of a rapid increase in the number of ground-based nuclear tests and ballistic missile launches during these years. By injecting a mass of radioactive aerosols and isotopes of dozens of different elements into the middle and upper atmosphere,

they played the role of a catalyst for disturbances in these media. At the same time, the shock wave spreading over hundreds and thousands of kilometers horizontally should also have contributed to the abrupt increase in the intensity of turbulence and the drift of mesospheric air to the heights of the thermosphere. The upward wave of disturbances in the neutral atmosphere should have manifested itself in the ionosphere with a delay: during the transition from the D-region (60–90 km) through the E layer (90–130 km) to the F2 layer (200–400 km). Measurement data from incoherent scatter facilities at Millstone Hill and Saint-Santin suggests that the disturbances reached the heights of the F2 layer circa 1980. Accordingly, they covered ~250 km for ~20 years, i.e. their vertical propagation velocity was ~12.5 km/year, which is four orders of magnitude lower than velocities of the zonal or meridional wind. Given such a low vertical transfer rate with a total mass of O₂ losses of 0.0025 % over 50 years of observations, it is not surprising that these losses are hardly noticeable in direct estimates of [O₂] and can only be fully estimated at heights where photochemical processes prevail over dynamic ones.

5. POSSIBLE EXPLANATION OF REASONS FOR IGNORING THE OXYGEN FACTOR

Why is it that such a clear cause-and-effect relationship between the oxygen content in the atmosphere and its structure is still ignored by most interpreters of the phenomenon of its cooling and sinking? In our opinion, the main reason is that the concept of the dominant role of oxygen has been subjected to unfair criticism from both sides. On the one hand, Danilov and Smirnova [1997] explained this trend by a long-term change in the ionic composition of the E layer. Analyzing data from rocket mass spectrometric measurements of the ionic composition, the authors concluded that from 1957 to 1986 the relation $\phi^+ = [\text{NO}^+]/[\text{O}_2^+]$ decreased 2–4 times at a height of 120 km (Figure 5).

Therefore, in accordance with Equations (1), (2), and (9), the increase in N_e in the E layer, and accordingly, in f_oE was explained by a decrease in $[\text{NO}^+]/[\text{O}_2^+]$ and hence in the electron recombination rate. At the same time, the nature of such a rapid drop in ϕ^+ was not explained by the authors in any way and was accepted as its natural long-term trend.

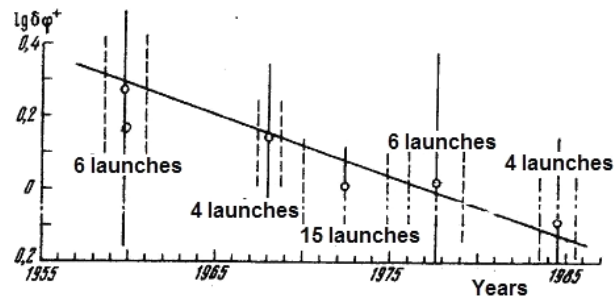


Figure 5. The ϕ^+ values of launches (circles) averaged over several time intervals at 120 km for mid-latitude launches: vertical segments are standard deviations; the solid line is a trend in ϕ^+

The effect was not related to either geomagnetic or solar activity, which was surprising. Because if the content of O₂ and hence O₂⁺ remains unchanged, while maintaining a similar rate of decrease in ϕ^+ , the content of NO⁺ at 110–130 km (as, apparently, at heights of the D-region) in the next 20–30 years should have been reduced to almost zero!

Nevertheless, there is a perfectly natural explanation for their mistake. Analysis of satellite measurements at midlatitudes at heights close to the maximum of the E layer has shown a strong dependence of the NO content on the time of day, geomagnetic activity, and, especially, solar activity [Titheridge, 1997], so that

$$[\text{NO}] = \{14.8 + 0.22(F10.7 - 100) - 0.0008(F10.7 - 100)^2 + 0.1s\Phi\} \cdot 10^6 \text{ [cm}^{-3}\text{]}, \quad (11)$$

where $s=0$ corresponds to the equinox; $s=1$, to the solstice; Φ is latitude.

Taking into account the extreme variability in the NO content at the heights under study, we have analyzed the dependence of $[\text{NO}^+]$ on various factors and have found that the $\delta\phi^+$ variations identified in [Danilov, Smirnova, 1997] turned out to result from its dependence on solar activity level [Givishvili, Leshchenko, 2009]. The fact is that rocket launches were not carried out at a uniform time interval, but were grouped into five large groups, the temporary "epicenters" of which randomly coincided with periods that sharply differed in solar activity levels.

Table 3 lists the years to which the results of these data groups were centered, the annual average solar activity indices corresponding to these years, as well as the values of $[\text{NO}]$ calculated by Formula (11) for equinox conditions ($s=0$). As can be seen, $[\text{NO}]$ and hence the parameter ϕ^+ strictly follow the solar activity (with a correlation coefficient running to 0.996) due to the validity of Expression (10). Thus, neglecting the question about the possible causes of such a strong variability in $[\text{NO}]$, and accordingly, $[\text{NO}^+]$ contributed to the unsubstantiated statement about the ϕ^+ dependence on time. Later, this conclusion served as a reason for Danilov [1997] to put forward a wrong explanation of the long-term increase in f_oE , which was accepted as trustworthy by most researchers of this problem [Laštovička et al., 2008].

Danilov and Smirnova [1999], when analyzing data from rocket measurements of the electron density N_e in the D-region of the ionosphere, stated: "The magnitude of the change in $\lg N_e$ by 80 km over ~25 years (1962–1987) is 0.8. This means that the electron density has increased almost 6-fold over this period!" Nevertheless, even in this case, they see no need to identify the possible causes and consequences of such a staggering rate of

Table 3

Dependence of $[\text{NO}]$ on solar activity					
Years	1960	1968	1972	1977	1985
F10.7	162	149	129	87	75
$[\text{NO}]$	$2.5 \cdot 10^7$	$2.3 \cdot 10^7$	$2.1 \cdot 10^7$	$1.1 \cdot 10^7$	$0.9 \cdot 10^7$

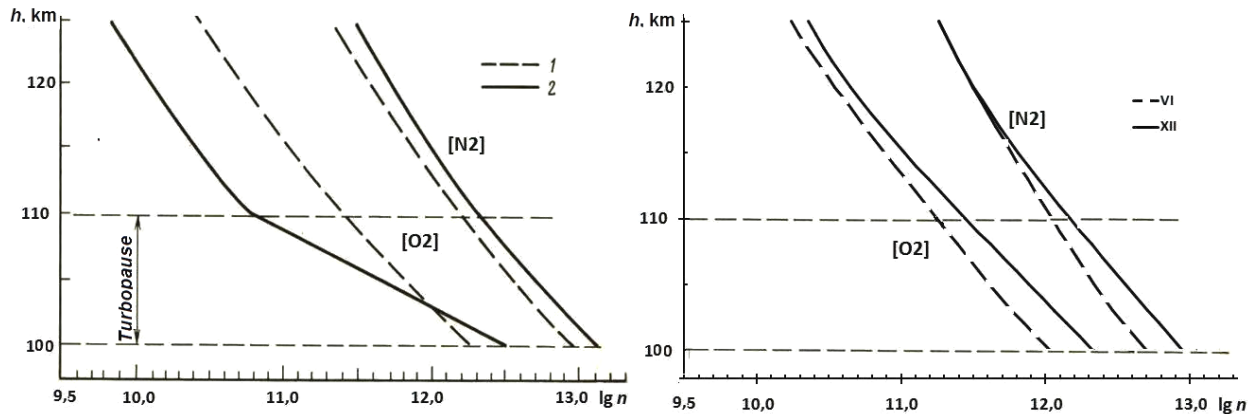


Figure 6. Height profiles of [O₂] for winter (2) and summer (1) according to [Ivanov-Kholodny, Nusinov, 1979] (a); midday height profiles of [O₂] for winter and summer and latitude of Moscow (1983) according to NRLMSIS (b)

electron density increase in the D-region (6 times for less than 30 years!). They did not take into account that if such a trend continued, long-range radio communication in the decameter range would be impossible today since most of radio signals would be absorbed in the lower ionosphere. It should be recognized, however, that later the authors did not refer to such shocking conclusions about the trends in the electron density in the lower ionosphere.

Another obstacle to the recognition of man-made oxygen loss as the main mechanism of atmospheric cooling and sinking was the idea that noticeable changes in [O₂] in the mid-latitude upper atmosphere are caused solely by seasonal variations in this parameter [Ivanov-Kholodny, Nusinov, 1979]. In particular, Ivanov-Kholodny and Nusinov [1979] argued that the winter anomaly (at a fixed solar zenith angle, χ , f_oE is greater in winter than in summer) is explained by a twofold decrease in the O₂ content in the E layer in winter relative to summer (Figure 6, a).

Nonetheless, this hypothesis is erroneous. Because, firstly, according to the NRLMSIS model, seasonal oxygen variations have exactly opposite signs: in the mid-latitude lower thermosphere, [O₂] in winter is higher than in summer (see Figure 6, b). Secondly, as shown by our estimates based on data on summer and winter height profiles of [O₂], presented in Figure 6, a, the calculated values of f_oE in summer and winter proved be by 0.5–1.0 MHz lower than the actual values (see Table 2, column 3). With a measurement accuracy of ± 0.05 MHz for this parameter [URSI, 1978], this discrepancy between theory and experiment is unacceptable: it suggests that the initial data used in the calculations [Ivanov-Kholodny, Nusinov, 1979] is incorrect. This is confirmed by comparing Figures 6, a and b. We can see that at 110 km the value of [O₂] adopted in [Ivanov-Kholodny, Nusinov, 1979] is by an order of magnitude lower in winter than in the MSIS model, and at least three times lower in summer. As a result, the ionization rates calculated by the authors and the summer and winter values of f_oE determined by them are extremely underestimated. Perhaps that is why in order to avoid discussing the issue of

the intolerably large discrepancy between the model and empirical values of f_oE , they are not given in the collected articles cited.

CONCLUSION

1. The phenomenon of long-term cooling and sinking of the upper atmosphere was discovered in 1993–1995 and confirmed in the following years. However, the man-made increase in the carbon dioxide content in the atmosphere cannot be recognized as the main mechanism inducing the climate change in the mesothermosphere, despite numerous studies in this direction.

2. Meanwhile, calculations show that it is possible to obtain an adequate explanation for the long-term changes in the key characteristics, in particular, the ionospheric E layer, only if the fact of a multiple decrease in the molecular oxygen content in the thermosphere on a global scale is recognized. In other words, the cooling and sinking of the atmosphere is caused not so much by an increase in its greenhouse gas content as by a decrease in the mass of free oxygen. Thus, the long-term discussions concerning the main mechanism of the cooling and sinking of the middle and upper atmosphere can be considered completed.

3. The effect of free oxygen on the atmosphere remains the least understood. In order for models to acquire significant predictive value, they must take this into account since anthropogenic impact on the atmosphere increases every year.

4. Ionosphere monitoring can be considered as an effective and sensitive tool for determining the ecological state of the atmosphere as a whole.

REFERENCES

- Alpert J.L. Propagation of electromagnetic waves and the ionosphere. Moscow, Nauka Publ., 1972, 564 p.
- Brasseur G.P., Solomon S. Aeronomy of the Middle Atmosphere. Springer, 1986, 452 p.
- Danilov A.D. Long-period variations in temperature and composition of the mesosphere and thermosphere (Review). *Geomagnetism and Aeronomy*. 1997, vol. 37, no. 2, pp. 1–17.

- Danilov A.D. Long-term trends in the upper atmosphere and ionosphere (a review). *Geomagnetism and Aeronomy*. 2012, vol. 52, no. 3, pp. 271–291. DOI: [10.1134/S0016793212030036](https://doi.org/10.1134/S0016793212030036).
- Danilov A.D., Smirnova N.V. Long-term trends in ion composition in the E region. *Geomagnetizm i aeronomiya* [Geomagnetism and Aeronomy]. 1997, vol. 37, no. 4, p. 43. (In Russian).
- Danilov A.D., Smirnova N.V. Long-term trends in electron concentration in the D region: experimental data. *Geomagnetizm i aeronomiya* [Geomagnetism and Aeronomy]. 1999, vol. 39, no. 2, pp. 107–112. (In Russian).
- Danilov A.D., Konstantinova A.V. Long-term variations of the parameters of the middle and upper atmosphere and ionosphere (Review). *Geomagnetism and Aeronomy*. 2020, vol. 60, no. 4, pp. 397–420. DOI: [10.1134/S0016793220040040](https://doi.org/10.1134/S0016793220040040).
- Danilov A.D., Semenov V.K., Simonov A.G. Model of relative ion composition at altitudes of 60–200 km. *Ionosfernye issledovaniya* [Ionospheric Research]. 1981, vol. 34, pp. 73–97. (In Russian).
- Emmert J.T., Drob D.P., Picone J.M., Siskind D.E., Jones M., Jr., Mlynczak M.G., et al. NRLMSIS 2.0: A whole-atmosphere empirical model of temperature and neutral species densities. *Earth and Space Science*. 2020, vol. 8, no. 3, e2020EA001321. DOI: [10.1029/2020EA001321](https://doi.org/10.1029/2020EA001321).
- Givishvili G.V., Golitsyn G.S. About the International workshop “Cooling and subsidence of the middle and upper atmosphere” (Moscow, July 6–10, 1998). *Geomagnetizm i aeronomiya* [Geomagnetism and Aeronomy]. 1999, vol. 39, no. 3, pp. 139–144. (In Russian).
- Givishvili G.V., Leshchenko L.N. D region depletions about the Persian Gulf. *J. Atmos. Terr. Phys.* 1993a, vol. 55, no. 1, pp. 125–128.
- Givishvili G.V., Leshchenko L.N. Long-term trends in the properties of the ionosphere and thermosphere of the middle latitudes. *Doklady Akademii Nauk*. 1993b, vol. 333, no. 1, pp. 86–89. (In Russian).
- Givishvili G.V., Leshchenko L.N. Possible evidence of the presence of man-made effects on the mid-latitude ionosphere. *Doklady Akademii Nauk*. 1994, vol. 334, no. 2, pp. 213–214. (In Russian).
- Givishvili G.V., Leshchenko L.N. Dynamics of the climatic trend of the mid-latitude region E of the ionosphere. *Geomagnetizm i aeronomiya* [Geomagnetism and Aeronomy]. 1995, vol. 35, no. 3, pp. 166–174. (In Russian).
- Givishvili G.V., Leshchenko L.N. Dependence of the $[NO^+]/[O_2^+]$ ratio in the ionosphere layer E on solar activity. *Solnechno-zemnaya fizika* [Solar-Terr. Phys.]. 2009, iss. 14 (127), pp. 93–96. (In Russian).
- Givishvili G.V., Leshchenko L.N. The long-term trend of the reaction of the E-layer of the ionosphere to solar flares. *Solar-Terr. Phys.* 2022a, vol. 8, no. 1, pp. 51–57. DOI: [10.12737/stp-81202206](https://doi.org/10.12737/stp-81202206).
- Givishvili G.V., Leshchenko L.N. On the causes of cooling and subsidence of the middle and upper atmosphere. *Izvestiya RAS. Physics of the atmosphere and ocean*. 2022b, vol. 58, no. 5, pp. 601–614.
- Givishvili G.V., Shubin V.N. Long-term variations of atomic oxygen content in the upper atmosphere. *Geomagnetizm i aeronomiya* [Geomagnetism and Aeronomy]. 1994, vol. 34, no. 4, pp. 169–173. (In Russian).
- Givishvili G.V., Ivanov-Kholodny G.S., Leshchenko L.N., Tchertoprud V.E. Solar flares and the gas composition of the upper atmosphere. *Geomagnetizm i aeronomiya* [Geomagnetism and Aeronomy]. 2005, vol. 45, no. 2, pp. 263–267. (In Russian).
- Ivanov-Kholodny G.S., Firsov V.V. Spectrum of short-wave solar radiation at various levels of activity. *Geomagnetizm i aeronomiya* [Geomagnetism and Aeronomy]. 1974, vol. 14, no. 3, pp. 393–398. (In Russian).
- Ivanov-Kholodny G.S., Mikhailov A.V. Forecasting the state of the ionosphere (deterministic approach). Leningrad, Gidrometizdat Publ., 1980, 190 p. (In Russian).
- Ivanov-Kholodny G.S., Nusinov A.A. Formation and dynamics of daytime the mid-latitude layer E of the ionosphere. *Proc. Institute of Applied Geophysics*. Moscow, Goskomgidromet Publ., 1979, iss. 37, 129 p. (In Russian).
- Ivanov-Kholodny G.S., Leshchenko L.N., Odintsova I.N. The ratio of X-ray and ultraviolet radiation from solar flares in the ionization of the E-region of the ionosphere. *Geomagnetizm i aeronomiya* [Geomagnetism and Aeronomy]. 1976, vol. 16, no. 2, pp. 246–250. (In Russian).
- Ivanov-Kholodny G.S., Leshchenko L.N., Nusinov A.A., Odintsova I.N. The influence of seasonal variations of the neutral atmosphere on the ionization of the E-region of the ionosphere. *Geomagnetizm and Aeronomy*. 1977, vol. 17, no. 5, pp. 839–846. (In Russian).
- Koshelev V.V., Klimov N.N., Sutyurin N.A. Aeronomy of the mesosphere and lower thermosphere. Moscow, Nauka Publ., 1983, 183 p. (In Russian).
- Laštovička J., Akmaev R.A., Beig G., Bremer J., Emmert J.T., Jacobi C., et al. Emerging pattern of global change in the upper atmosphere and ionosphere. *Ann. Geophys.* 2008, vol. 26, no. 5, pp. 1255–1268. DOI: [10.5194/angeo-26-1255-2008](https://doi.org/10.5194/angeo-26-1255-2008).
- Mehr F.J., Biondi M.A. Electron temperature dependence and recombination of O_2^+ and NO^+ ions with electrons. *Phys. Rev.* 1969, vol. 181, no. 1, pp. 264–269. DOI: [10.1103/PhysRev.181.264](https://doi.org/10.1103/PhysRev.181.264).
- Pokhunkov A.A., Rybin V.V., Tulinov G.F. The trend of atomic oxygen in the thermosphere of middle and equatorial latitudes. *Geomagnetizm i aeronomiya* [Geomagnetism and Aeronomy]. 2003a, vol. 43, no. 5, pp. 688–696. (In Russian).
- Rishbeth H. A greenhouse effect in the ionosphere? *Planet. Space Sci.* 1990, vol. 38, pp. 945–948. DOI: [10.1016/0032-0633\(90\)90061-T](https://doi.org/10.1016/0032-0633(90)90061-T).
- Roble R.G., Dickinson R.E. How will changes in carbon dioxide and methane modify the mean structure of the mesosphere and thermosphere? *Geophys. Res. Lett.* 1989, vol. 16, pp. 1441–1444. DOI: [10.1029/GL016i012p01441](https://doi.org/10.1029/GL016i012p01441).
- Titheridge J.E. Model results for the ionospheric E region: solar and seasonal changes. *Ann. Geophys.* 1997, vol. 15, no. 1, pp. 63–78. DOI: [10.1007/s00585-997-0063-9](https://doi.org/10.1007/s00585-997-0063-9).
- URSI Handbook of Ionogram Interpretation and Reduction. Report UAG-23. 1978, 138 p.
URL: <https://techcrunch.com/author/jonathan-shieber/> (accessed July 5, 2024).
- Original Russian version: Givishvili G.V., Leshchenko L.N., published in *Solnechno-zemnaya fizika*. 2025, vol. 11, no. 1, pp. 41–49. DOI: [10.12737/szf-111202504](https://doi.org/10.12737/szf-111202504). © 2025 INFRA-M Academic Publishing House (Nauchno-Izdatelskii Tsentr INFRA-M)

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