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Problems in Global Atmospheric Energetics of the Atmosphere

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Abstract—Changes in the Earth's atmosphere that affect its energetics are analyzed. The results of NASA programs on carbon dioxide monitoring in the atmosphere and the evolution of the global temperature, as well as data on measurements of the evolution of local temperature in the past, are presented. Global power processes are analyzed on the basi of contemporary information both for: natural processes and those resulting from human activity. The channels of establishment of an equilibrium between the change in the mass of atmospheric carbon dioxide and that in global temperature are considered. They include decrease of the total rate of photosynthesis as a result of deforestation, combustion of fossil fuels and the greenhouse effect. Based on current information, it is shown that none of these channels explains the observed accumulation of carbon dioxide in the atmosphere. The inconsistency of climatological models of changes in the global temperature as a result of an increase in the concentration of carbon dioxide, which are the basis of the Paris Agreements on Climate, has been demonstrated. The use of these models is based on the assumption that the spectra of carbon dioxide and water molecules do not overlap, which contradicts both the data resulting from measurements with NASA programs and calculations based on the spectroscopic parameters of molecules from the HITRAN data bank. The Pauling concept, which is based on the thermodynamic equilibrium between free atmospheric CO_2 molecules in the atmosphere and bound carbon at the Earth's surface, is presented. Based on this concept, the different nature of the past and current equilibrium is shown. Thus, in the past, the slowest process of oxidation of the bound carbon at the Earth's surface was the evaporation of carbon dioxide molecules dissolved in the ocean, while the limiting process at present is oxidation of carbonates in the oceans.

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INTRODUCTION

The problem of atmospheric carbon dioxide is to determine the reason for its accumulation in the atmosphere. Indeed, the continuous monitoring of atmospheric carbon dioxide carried out at the Mauna Loa observatory in Hawaii United States, which is part of NASA program, shows that the concentration of carbon dioxide molecules in the atmosphere has been monotonically increased since the foundation of this observatory in 1959 (if seasonal oscillations are not taken into account). During the observation period, this value increased from 316 ppm in 1959 to 411 ppm in 2019 [1]. As a unit for the measurement of the molecular concentration, 1 ppm is used, that is equal to one molecule per million air molecules, or 1 GtC, which refers to the mass of carbon in the atmosphereof a gigaton, or 10^{15} g. The connection of these units is 1 ppm = 2.1 GtC; the contemporary atmosphere contains approximately 880 GtC.

Carbon dioxide is in equilibrium with the Earth's surface, which assimilates carbon dioxide, converting it into solid forms of carbon as a result of the photosynthesis. When the resulting carbon compounds are decomposed in plants and the nutrient medium, this carbon returns into the atmosphere in the form of carbon dioxide. The current value of the rate of photosynthesis on Earth is in the range between 150 and 175 GtC/year [2]. Therefore, the average residence time of a carbon dioxide molecule in the atmosphere is 5–6 years. During this time, carbon dioxide is mixed with atmospheric air. Thus, the concentration of carbon dioxide in the atmosphere does not depend on the place of observation if it is located far from sources and sinks of carbon dioxide.

The concentration of carbon dioxide in the atmosphere increases monotonically since the beginning of the industrial period, and it was (277 ± 3) ppm in 1750 and (288 ± 3) ppm in 1870 [3]. One can believe that the concentration of carbon dioxide at the beginning of the industrial period was about 280 ppm, and it increases with an acceleration, being increased by almost one and a half now. If the growth rate observed in the last forty years will be conserved in future, then the doubling time for the concentration of carbon dioxide in the atmosphere will be 120 years.

One can seem that there are two mechanisms of the increase in the concentration of carbon dioxide. First, as a result of the extraction and use of fossil fuels, carbon from the Earth's interior is included in the balance between atmospheric carbon dioxide and bound carbon at the Earth's surface. Therefore, the total mass of carbon involved in the equilibrium increases, and,

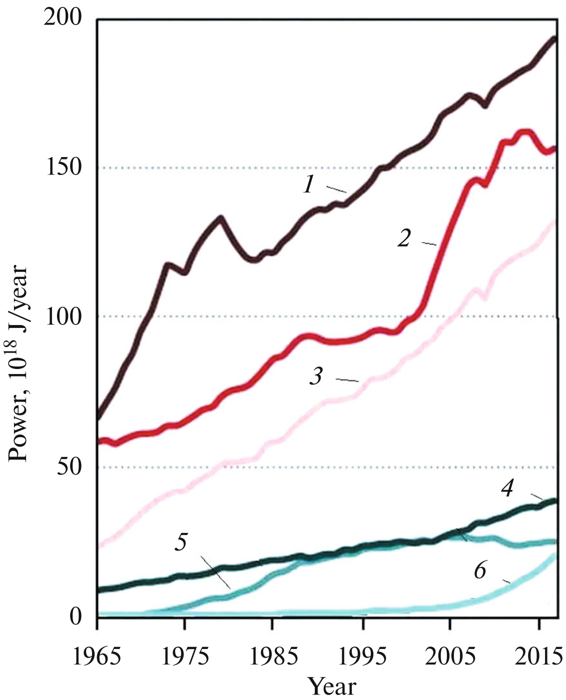

Fig. 1. Types of modern energy and their capacity [4, 5]: (*1*) oil; (*2*) coal; (*3*) gas; (*4*) hydroelectric power plants; (*5*) nuclear power plants; (*6*) solar energy and wind power.

with it, the mass of carbon dioxide in the atmosphere also increases. Second, the deforestation and burning of forests leads to a decrease in the photosynthesis rate and, accordingly, to an increase in the mass of carbon dioxide in the atmosphere.

The changes in the atmospheric carbon dioxide concentration and global temperature are connected with each other due to the equilibrium between atmospheric carbon dioxide and bound carbon in compounds located on the surface of land and ocean. The purpose of this paper is to analyze this connection.

GLOBAL ENERGY OF THE PLANET

Figure 1 shows the capacities of various types of contemporary power engineering [4, 5]. The main contribution to the total world power (more than 80%) is due to fossil fuels. Most of them are used in power plants, where they are eventually converted into carbon dioxide, which passes into the atmosphere and is partially absorbed immediately by the Earth's surface. Since the fluctuations in the rates of these processes are large and can distort the idea of the ratio of the rates of competing processes, their values below are averaged over a decade, from 2008 to 2017 [4, 5].

Thus, in accordance with [4, 5], the carbon flux due to fossil fuel combustion is 9.4 GtC/year, and 1.5 GtC/year enters into circulation as a result of agricultural human activity. Next, 4.7 GtC/year is absorbed by the ocean, 2.4 GtC/year is absorbed by land, and 3.8 GtC/year remains in the atmosphere. This carbon is redistributed between these channels, but this occurs at times exceeding a pical photosynthetic time $t_{ph} = 5$ years. Note that there is no balance between the given flows, since it is also established at the expense of natural flows for the considered channels.

The total power consumed by a person at the present time does not exceed 2×10^{13} W, if we include here the organic mass obtained as a result of the human agricultural activity (Fig. 1). This value is four orders of magnitude less than the total power of solar radiation entering the Earth's atmosphere. Hence, we can conclude that, globally, human energy activity does not manifest itself in the surrounding nature.

Local energetics, however, can be noticeable. For assessment, the consumed power can be attributed to the number of people, which gives slightly less than 3 kW per person. If we assume that this power is consumed where a person resides, it turns out that the specific power of local energy release in cities and megalopolises is two orders of magnitude less than that given by solar energy or thermal radiation from the Earth's surface. If we add this power to the power of the Earth's thermal radiation, it turns out that the local temperature of the Earth in the area of human habitation will increase by several degrees compared with surrounding areas due to the energy associated with a person. Indeed, this is observed for large cities and megacities. As megacities grow, this can be a problem.

Figure 2 shows the evolution of the rate of carbon dioxide emission in the atmosphere as a result of the burning of fossil fuels [4, 5]. Since the fluctuations in changes in this value are noticeable, only the average value should be used to increase the rate of this process. Let [6] the doubling of the rate of the studied process be 40 years. Based on this, the total mass of carbon M may be determined. It is taken from the Earth's interior and included in the carbon located on

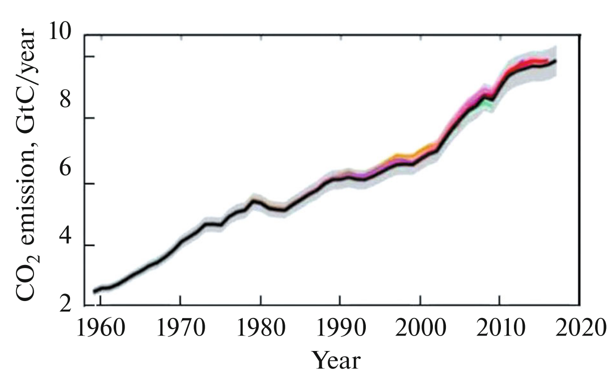

Fig. 2. Total carbon dioxide emissions in the atmosphere as a result of the burning of fossil fuels [4, 5].

the Earth's surface and in the atmosphere, between which an equilibrium is maintained:

$$M = \frac{9.4 \times 40}{\ln 2} = 540,$$

where the mass of carbon introduced into the atmosphere and onto the Earth's surface is expressed in GtC.

Obviously, some of this mass of carbon is transferred to the atmosphere as a result of equilibrium between the atmosphere and the Earth's surface. This part leads to an increase in the concentration of carbon dioxide in the atmosphere, which changed by 220 GtC from 1959 to 2019. Thus, the Earth's surface accounts for 320 GtC. It would seem that from this it is possible to obtain a typical time of the transition of carbon from the Earth's surface to the atmosphere from the equilibrium between them, which is 7–8 years if a time of assimilation of atmospheric carbon dioxide as a result of photosynthesis is t_{ph} = 5 years. However, the result is contradictory. First, such a short time of residence of the bound carbon on the Earth's surface raises doubts. However, the main objection is related to the different times of increase in the concentration of carbon dioxide in the atmosphere and the carbon emission from the interior of the planet into the atmosphere–surface system of the Earth. A time for the mass of carbon in the Earth's atmosphere to double in the composition of carbon dioxide is now about 120 years, and a time for the doubling of the mass of carbon injected into the atmosphere as a result of the burning of fossil fuels is approximately 40 years. This means that, the lifetime of the bound carbon on the Earth's surface decreases significantly during the doubling of the injected carbon mass.

This fact may be associated with a decrease in the forest area on the Earth's surface and, accordingly, a decrease in the rate of photosynthesis, as a result of which atmospheric carbon is converted into bound forms on the Earth's surface. Indeed, forest burning and deforestation have been taking place on a large scale in recent decades [6, 7].

The change in the forest area is relatively small (Fig. 3) [8]. In this case, the main contribution to the process of photosynthesis on the Earth's surface, which is several percent [9, 10], is made by tropical forests. Nevertheless, according to Fig. 3, this change is small. Indeed, first, the most efficient photosynthesis, which is seasonal, takes place at a certain stage of forest development. Second, along with countries of forest mismanagement, in which the forests burn every year, there are other countries in which the forest is being renovated and planted. Figure 3 reflects the average situation, in which the forest area has decreased by 3% in 26 years, i.e., a typical time in which the forest area is halved is hundreds of years. Therefore, the subsequent change in the contribution

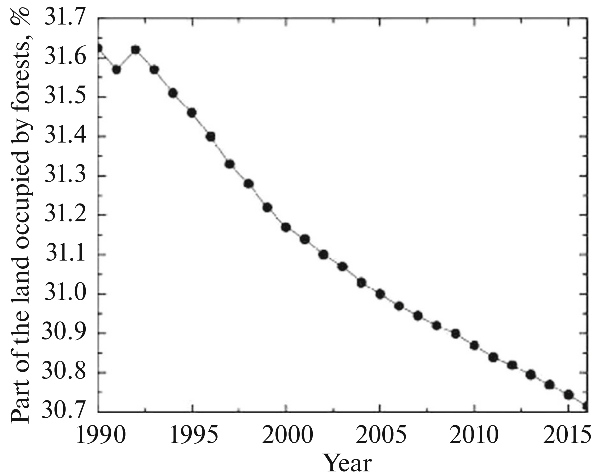

Fig. 3. World Bank data on the share of land occupied by forests [8].

of forests to the change in the mass of carbon dioxide in the atmosphere can be ignored.

PRESENT AND PAST GLOBAL TEMPERATURE

A change in the mass of atmospheric carbon dioxide may be associated with the change in the global temperature, i.e., the temperature of the Earth's surface, averaged over the geographic coordinates, time of day, and season. The global temperature characterizes the state of the Earth as a planet as a whole, so the change in global temperature over the years indicates the evolution of the thermal state of the planet. The most suitable method to determine the evolution of global temperature is based on a comparison of the temperature difference for a given point on the Earth's surface but at the same time of day and season, followed by averaging over the geographic coordinate and time [11], rather than a comparison of the average global temperatures. This makes it possible to reduce fluctuations in the change in global temperature by an order of magnitude.

Figure 4 shows the change in global temperature over the past 150 years. It follows from these and other data that the first hundred years of this time interval were characterized by a slight change in the global temperature, while the last forty years there has seen a sharp change in this parameter by about 0.6 K. Fluctuations amounting to 0.1–0.2 K are observed during the evolution of the global temperature. In addition to this, Table 1 contains the considered changes in average temperature in recent years for land and oceans, as well as for the Northern and Southern Hemispheres [13, 14]. This implies a substantially nonuniform change in the global temperature, which sharply depends on local conditions. Therefore, all conclu-

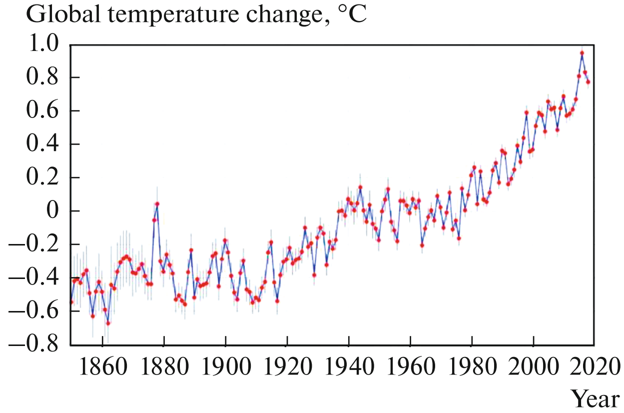

Fig. 4. Change in the global temperature of the Earth, where the average temperature for 1951–1980 is taken as zero [12].

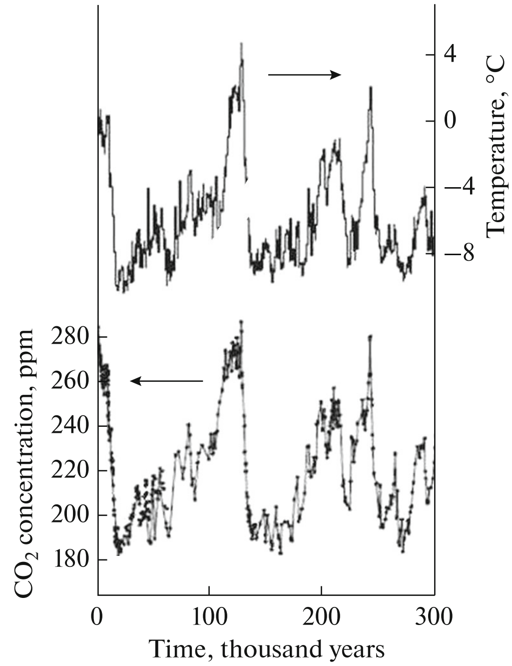

Fig. 5. Evolution of local temperature in the area of Vostok station (Antarctica) and concentration of carbon dioxide in this area [15].

sions about the nature of the evolution of global temperature are rather qualitative.

The evolution of the global temperature correlates with changes in the concentration of carbon dioxide in the atmosphere, which primarily follows from the correlation of the evolution of these parameters in the past. In particular, Fig. 5 shows the evolution of the local temperature of Antarctica and the concentration of carbon dioxide in this region based on data obtained from the analysis of air bubbles in ice deposits extracted in the area of the Vostok meteorological station [15]. In this case, the resulting concentration of carbon dioxide corresponds to its concentration in the bubbles, and the temperature is determined based on the population of the oxygen isotope ^{18}O.

Along with the correlation between changes in the temperature and concentration of atmospheric carbon dioxide, Fig. 5 shows that there have been sharp changes in temperature in the past, at the end of the ice age. They are similar to those observed for global temperature in lastdecades. However, the temperature jump in the past was an order of magnitude higher than that in the present time. Conversely, the concen-

Table 1. Change in the global temperature of the Earth, where the average temperature for the 20th century is taken as zero [13, 14]

	Earth	Northern Hemisphere	Southern Hemisphere
	May 2018		
Land	1.21	1.27	1.06
Oceans	0.60	0.69	0.54
Land + oceans	0.77	0.91	0.62
	May 2019		
Land	1.16	1.25	1.13
Oceans	0.73	0.81	0.69
Land + oceans	0.85	0.93	0.77

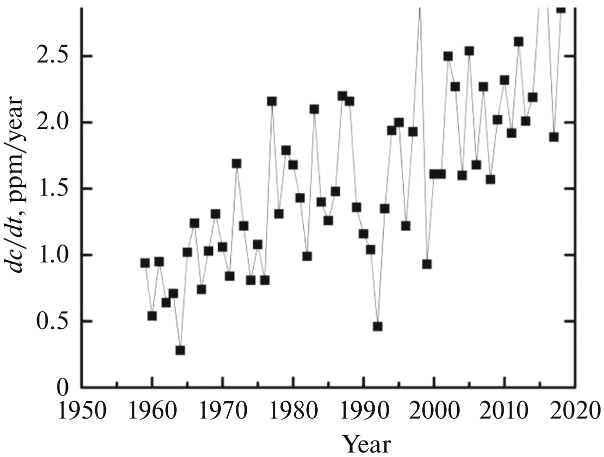

Fig. 6. Annual changes in the concentration of carbon dioxide in the Earth's atmosphere according to the monitoring carried out at the Mauna Loa observatory [1, 16].

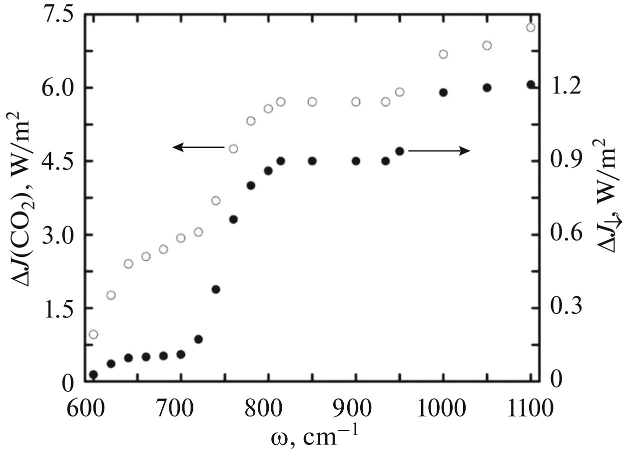

Fig. 7. Changes in the radiation flux created by carbon dioxide molecules $\Delta J(CO_2)$, and change in the total infrared radiation flux $\Delta J\downarrow$ as a result of the doubling of the concentration of carbon dioxide in the atmosphere as the radiation frequency increases [18, 19] for the standard atmosphere model.

trations of atmospheric carbon dioxide molecules in the past (Fig. 5) were 1.5 to two times lower than those at present. This fact may be associated with human industrial activity.

At the same time, the annual changes in the concentration of atmospheric carbon dioxide molecules undergo to large fluctuations, as follows from Fig. 6 [1, 16], which presents the results of measurements at the NASA structure. Based on measurements made within the framework of the NASA program, it is also possible to determine the change in global temperature when the concentration of atmospheric carbon dioxide molecules doubles, which is [17]

$$\Delta T = 2.5 \pm 0.4 \text{ K}. \quad (1)$$

This expression continues the measurement results for the evolution of global temperature and atmospheric carbon dioxide concentration in last decades and therefore uses the assumption that, along with the doubling of the mass of atmospheric carbon dioxide, there is a proportional increase in the content of other components.

One of the channels causing an increase in global temperature as a result of changes in the composition of the atmosphere is the greenhouse effect. Indeed, an increase in the concentration of greenhouse components of the atmosphere causes an increase in the flux of infrared radiation from the atmosphere to the Earth's surface and, consequently, an increase in the global temperature. The goal of the subsequent analysis is to find out how the increase in carbon dioxide concentration contributes to this change.

GREENHOUSE EFFECT IN GLOBAL-TEMPERATURE CHANGE

An increase in the concentration of carbon dioxide in the atmosphere causes an increase in the flux of infrared radiation to the Earth's surface, which in turn leads to an increase in the global temperature. Figure 7 shows the character of the change of radiation fluxes to the Earth's surface with a doubling of the carbon dioxide concentration as the radiation frequency increases [18, 19] due to carbon dioxide molecules and the change in the total radiation flux within the framework of the standard atmosphere model. Based on these data, it is possible to follow the character of the increase in the radiation flux to the Earth as a result of changes in the concentration of a greenhouse gas. The basic absorption band of carbon dioxide includes three vibrational transitions with a change by one of the deformation vibrational number. This band ranges from about 580 to 750 cm^{-1}.

The change in the radiation flux is determined by the range of the spectrum near the band boundary, where the optical thickness of the atmosphere is on the order of one. Indeed, for the main part of the absorption band, where the optical thickness is much greater than one, the radiation temperature corresponds to the temperature of the atmospheric region near the surface. The radiation from this region can reach the Earth's surface without aborption on the way. An increase in the radiation flux created by carbon dioxide molecules at each boundary of the absorption band changes by about 3 W/m^2 (Fig. 7). However, at the red boundary of the absorption band, a decrease in the radiation flux created by water molecules compensates to a noticeable degree for this increase in the total radiation flux. Thus, the change in the total radiation flux due to this part of the spectrum is about 0.1 W/m^2. In the range of the blue boundary of the absorption band of carbon dioxide molecules, the compensation is less

Table 2. Changes in partial fluxes of atmospheric radiation to the Earth's surface due to different greenhouse components of the atmosphere

Frequency range, cm^{-1}	$\Delta J(CO_2)$, W/m^2	$\Delta J(H_2O)$, W/m^2	ΔJ_{cl}, W/m^2	ΔJ_t, W/m^2
580–660	2.55	–2.38	–0.07	0.10
660–740	1.15	–0.46	–0.42	0.27
740–800	1.88	–0.14	–1.25	0.49
800–1000	1.11	–0.04	–0.77	0.30
1000–1100	0.55	0	–0.39	0.16
Amount	7.24	–3.02	–2.90	1.32

due to water molecules and water microdroplets that form clouds. Therefore, the change in the total flux near this boundary of the absorption band is much larger and is approximately 0.8 W/m^2.

Note that a remarkable contribution to the change in the radiation flux of the spectral range near the laser lines of 9.4 and 10.6 microns, which is about a quarter of the total change of the flux. The optical thickness of the atmosphere due to carbon dioxide molecules in this spectrum range is less than one at existing temperatures, and this range of the spectrum givesa small contribution both to the radiation flux created by carbon dioxide molecules and to the change in this flux when the concentration of these molecules changes. However, there is no absorption by water molecules in this range of the spectrum.

A more detailed understanding of the role of the greenhouse effect in the Earth's thermal balance follows from the data in Table 2 [20], which shows the partial changes in radiation fluxes from the atmosphere to the Earth's surface created by carbon dioxide molecules $\Delta J(CO_2)$, water molecules $\Delta J(H_2O)$, and water microdroplets ΔJ_{cl} that constitute clouds, as well as the total change in the radiation flux of the atmosphere to the Earth's surface ΔJ_t as a result of a doubling of the concentration of carbon dioxide molecules in the atmosphere. These values for the frequency interval between ω_1 and ω_2 are introduced as

$$\Delta J = \int_{\omega_1}^{\omega_2} \Delta J_\omega d\omega, \qquad (2)$$

where ΔJ_ω is the change in the radiation flux due to a given greenhouse component per unit of frequencies. In addition, the following relation holds true:

$$\Delta J_t = \Delta J(CO_2) + \Delta J(H_2O) + \Delta J_{cl}.$$

Let us consider the sensitivity of the change in the total radiation flux to the Earth's surface as a result of the doubling the concentration of carbon dioxide to the model used to calculate this value. This analysis is presented in Table 3, which gives the values of the change in the flux calculated on the basis of different models. At the same time, in all of the used models, the total absorption coefficient is the sum of the absorption coefficients for three greenhouse components. The energy balance of the Earth and of its atmosphere is taken as the basis for the current content of greenhouse components in the atmosphere in accordance with the energy balance, according to which the total radiation flux to the Earth's surface is $J = 327$ W/m^2.

Table 3. Changes in partial fluxes of atmospheric radiation to the Earth's surface calculated with different models

Model	ΔJ, W/m^2
1 [20]	1.3 ± 0.1
2 [21]	1.3 ± 0.3
3 [18, 22]	1.4 ± 0.3
4 [19]	1.3 ± 0.1

In this case, the model in [20] assumes that the absorption coefficient due to water molecules and microdroplets is averaged over the spectrum, and the absorption coefficient of carbon dioxide molecules is averaged over the oscillations for transitions between neighboring rotational states, whereas there is no the latter averaging in the model in [21]. In these cases, the absorption-band model is valid. According to this model, the absorption for frequencies within this band is determined by carbon dioxide molecules. Outside the band, carbon dioxide molecules do not contribute to the radiation of the atmosphere. This absorption band is in the frequency range of 580–750 cm^{-1}, while the laser frequency range contributes about 30% to the change in the atmospheric radiation flux. To account for this fact, the values obtained on the basis of models 1 and 2 are increased by 30%.

Model 3 [18, 22] accounts for the spectrua of water molecules and carbon dioxide molecules which are taken from the HITRAN spectroscopic data bank, while a uniform distribution of water microdroplets over heights is used. Model 4 [19] assumes that clouds containing water microdroplets form a dense layer starting from a certain height. This height is determined from the condition that the total radiation flux to the Earth's surface at the current content of greenhouse components in the atmosphere is $J = 327\ \text{W/m}^2$.

The considered models (Table 3) give nearby values of changes in the total radiation flux to the Earth's surface as a result of the doubling of the carbon dioxide concentration, despite the significantly differences in the model assumptions. This change can be into a change in the global temperature, which is called the equilibrium climate sensitivity, and is [21]

$$EA = 0.6 \pm 0.3\ \text{K}. \quad (3)$$

A large error in the transition to the global temperature is associated with the uncertainty of the conversion factor between the change in the radiation flux and that for the global temperature, which is called the climate sensitivity [23]. This value depends on a number of factors and is sensitive to their changes.

Let us determine to which the change in the global temperature led to the change in the concentration of carbon dioxide from the end of the 19th century, when it was equal to 288 ppm [3], to the value of 411 ppm in 2019 [1]. This leads to a change in the global temperature of

$$\Delta T = 0.30 \pm 0.15\ \text{K}. \quad (4)$$

The real change in global temperature during this time is

$$\Delta T = 0.8 \pm 0.1\ \text{K}. \quad (5)$$

According to climatological computer programs, the statistical averaging of the equilibrium climate sensitivity corresponds to [24]

$$EA = 3.0 \pm 1.5\ \text{K}. \quad (6)$$

This leads to the following change in global temperature from the end of the 19th century to the present time, as a result of an increase in the concentration of carbon dioxide molecules in the atmosphere

$$\Delta T = 1.5 \pm 0.8\ \text{K}. \quad (7)$$

This value is in some contradiction with the value (4), which characterizes the real change in global temperature, especially since there are other factors responsible for the change in the global temperature. Nevertheless, let us analyze the reason for such a strong discrepancy in the values of the equilibrium climate sensitivity, i.e., the differences between (3) and (6).

If we consider the contradiction between data (3) and (6) from the standpoint of Table 2, there is a suspicion that, instead of the change the total radiation flux ΔJ_t, the change in the flux due to the emission of carbon dioxide molecules $\Delta J(CO_2)$ is used in computer climatological programs. In other words, climatological calculations which are presented in the form of complex computer programs with using the concept of Arrhenius from his paper [25] of the late 19th century. At that stage of understanding the processes of atmospheric emission, Arrhenius identified a change in the radiation flux from the atmosphere due to a change in the concentration of carbon dioxide molecules with a change in the radiation flux from the atmosphere created by carbon dioxide molecules. This means that the absorption spectra for carbon dioxide and water molecules are separated. This was correct for the resonance transitions considered by Arrhenius, which are different from the transitions responsible for the thermal radiation of the atmosphere.

A more careful analysis of this problem was carried out in 1956 in a series of papers (in particular, [26]) based on the that information on the spectroscopy of carbon dioxide and water molecules. It was concluded in [25] that the interaction of the spectra of water and carbon dioxide molecules leads to a 20% decrease in the change in the thermal radiation flux of the atmosphere. This was further included in contemporary climatological programs. In fact, the flux of thermal radiation from the atmosphere as a result of this effect is reduced by a factor of 5–6, which radically changes the practical significance of this effect.

NATURE OF EQUILIBRIUM FOR ATMOSPHERIC CARBON DIOXIDE

The above analysis shows, in accordance with formulas (1) and (2), that the greenhouse effect due to an increase in the mass of atmospheric carbon dioxide cannot be responsible for the observed heating of the planet, but it does affect it. It is difficult to associate the observed increase in the concentration of carbon dioxide in the atmosphere in the 20th century with the decrease in the rate of global photosynthesis or the burning of fossil fuels, although this seems to be the most appropriate explanation for the accumulation of carbon dioxide in the atmosphere. Thus, let us analyze the change in the concentration of carbon dioxide in the atmosphere and attract other facts to explain it.

The concentration of carbon dioxide in the atmosphere is established as a result of processes that balance the carbon content on the Earth's surface and in the atmosphere. Indeed, as a result of photosynthesis processes, carbon dioxide is converted into solid carbon, which is a part of organic compounds on the Earth's surface and as a result of oxidation processes, solid carbon is transferred in the atmosphere in the form of carbon dioxide. Figure 8 gives the rates of the corresponding processes for the end of the 20th century. As is seen, the contribution of human activity to the flux of carbon dioxide into the atmosphere was about 5%. Although the revision of the photosynthesis

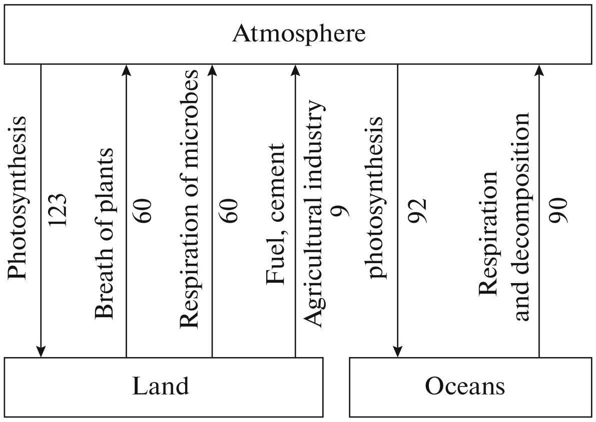

Fig. 8. Carbon balance resulting from the chemical equilibrium between the atmosphere and the Earth's surface [27]; the numbers show fluxes between the Earth's atmosphere and its surface in GtC/year.

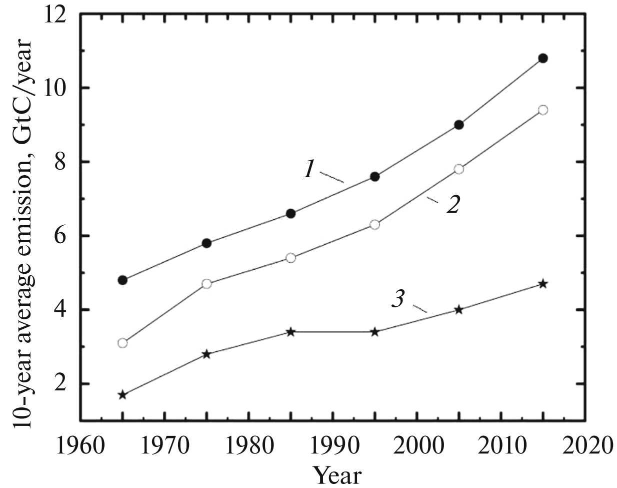

Fig. 9. Global, 10-year average emission of carbon dioxide into the atmosphere: (*1*) total; (*2*) due to the burning of combustible fuel; (*3*) remaining in the atmosphere [4, 5].

rate [2] leads to a decrease in this value and the carbon dioxide emissions in the atmosphere as a result of human industrial activity have increased from that time, the conclusion that humans give a small contribution to carbon fluxes conserves..

In order to understand how carbon dioxide emissions in the atmosphere form, we present the values of these fluxes in Fig. 9. The total flux of carbon dioxide into the atmosphere (Fig. 9, curve *1*) is a sum of fluxes due to industrial and agricultural human activities; the industrial contribution (Fig. 9, curve *2*) is mainly determined by combustion of fossil fuels. This carbon dioxide is then converted into solid carbon as a result of the photosynthesis or it remains in the atmosphere as carbon dioxide. Figure 9, curve *3*, shows the rate of accumulation of carbon dioxide in the atmosphere. As is seen, more than 40% of carbon dioxide emissions remain in the atmosphere.

The contribution of human agricultural activitiy to atmospheric carbon dioxide emissions decreases in time. According to [4, 5], emissions of carbon dioxide into the atmosphere for the period from 1750 to 2017 due to industrial (combustion of fossil fuels), agricultural activities, and total emissions amounted to 430 ± 20, 235 ± 95 and 680 ± 95 GtC/year, respectively. For the period 1959–2017, these values corresponded to 350 ± 20, 80 ± 40, and 430 ± 45 GtC/year. As can be seen, the role of the agriculture in the studied processes falls noticeably with the development of civilization. For comparison, we also note that the current carbon content in the atmosphere in the form of carbon dioxide is about 900 GtC. Thus, although there is a noticeable change in the content of carbon dioxide in the atmosphere over the industrial period, it is not so great.

EVOLUTION OF ATMOSPHERIC CARBON DIOXIDE CONTENT

In order to understand the character of human influence on accumulation of carbon dioxide in the atmosphere, let us construct a simple mathematical scheme that connects the concentration of atmospheric carbon dioxide and the global temperature. Let A denote the mass of carbon in atmospheric carbon dioxide. Let us join the ocean and land by introducing the mass of carbon m, which is located on the Earth's surface and participates in the exchange of carbon between the Earth's surface and the atmosphere. It can be considered that $m \gg A$, since there is a large amount of bound carbon on the Earth's surface. In particular, the mass of carbon dissolved in the ocean and stored there in the form of carbon compounds is approximately 380000 GtC.

Introducing the oxidation rate of carbon j, located in a bound state on the Earth's surface, where the oxidation rate is normalized to the carbon concentration, we obtain the balance equation for the concentration of atmospheric carbon dioxide molecules c:

$$\frac{dc}{dt} = j - \frac{c}{t_{\rm ph}}.$$

From this it follows , for the concentration of carbon dioxide molecules in equilibrium with bound carbon on the Earth's surface

$$c = jt_{\rm ph}.$$

This relation is valid if the scale of the considered times significantly exceeds a typical time $t_{\rm ph}$ of residence of the carbon dioxide molecule in the atmosphere. In fact, this relation describes the balance between the carbon, which is located in the atmosphere in the form of carbon dioxide, and the bound carbon, which is part of organic compounds on the Earth's surface. It can be represented as

$$\frac{A}{t_{\rm ph}} = \frac{m}{t_{\rm oxid}},$$

where $t_{\rm oxid}$ is the oxidation time of bound carbon on the Earth's surface.

Let an equilibrium be established between atmospheric carbon dioxide and bound carbon, which is on the Earth's surface in the form of carbon compounds. In this case, the flux of carbon dioxide into the atmosphere is created as a result of the slow oxidation of these compounds. Obviously, this process has a thermal nature. Then one can use the Pauling's concept [28, 29], according to which a thermodynamic equilibrium is established between the bound and free carbon dioxide. Since the mass of carbon in the atmosphere is small, the dependence of the concentration of carbon dioxide on the global temperature has the form

$$c \sim \exp\left(-\frac{\Delta H}{T}\right), \quad \frac{dc}{dt} = c\frac{\Delta H}{T^2}\frac{dT}{dt},$$

where ΔH is the enthalpy of the transition of a carbon atom from the Earth's surface to the atmosphere. Hence, we obtain the following relation between the transition enthalpy and changes in the considered values:

$$\Delta H = T^2\frac{d\ln c}{dT}.$$

Let us check within the framework of this formula the data of Fig. 6 for Antarctica in the past with this formula, as well as the current data. According to data for Antarctica, on the basis of Fig. 5, in the region of a strong warming when the average temperature increases by $\Delta T = 12$ K, the average temperature was $T = 271$ K and the concentration of carbon dioxide changed from 180 to 280 ppm. This gives $\Delta H = 0.21$ eV for the enthalpy of solid carbon oxidation, which roughly corresponds to the dissolution energy of carbon dioxide molecules in water.

Now let us consider from the same positions the change in global temperature, as well as the concentration of atmospheric carbon dioxide. In this case

$$\frac{d\ln c}{dt} = (5.02 \pm 0.06)\times 10^{-3}\ 1/\text{yr},$$

$$\frac{dT}{dt} = 18 \pm 3\ \text{mK/yr}.$$

This gives $\Delta H = 2.0 \pm 0.2$ eV, which corresponds to the formation of carbonates in seawater. Thus, in the past and at the present, a different character of the equilibrium is observed between atmospheric carbon dioxide and the bound carbon on the Earth's.

As follows from the comparison, the character of establishment of the equilibrium between bound carbon on the Earth's surface and carbon dioxide of the atmosphere is now fundamentally different from what it was in the past. For the sake of definiteness, let us take the ocean as the Earth's surface that partakes in the carbon equilibrium, and, judging by the value of the enthalpy of carbon oxidation, the bound carbon in the past was in the form of carbon dioxide dissolved in the ocean, while the bound carbon forms carbonates dissolved in the ocean at present. If we accept this point of view, we can assume that a sufficient amount of catalyst in the form of radicals is currently dissolved in the ocean and that it converts the dissolved carbon dioxide into carbonates. Thus, the difference between the past and the present is the relatively high density of radicals in nature, which is the result of human activity.

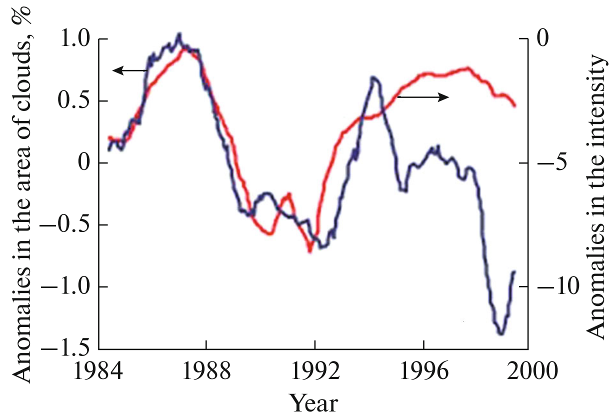

Fig. 10. Correlation between the intensity of cosmic rays and the area of the lower layer of clouds [30–33].

One can expect that a remarkable increase in the concentration of chemically active compounds, which change the character of chemical processes and are responsible for the state of the atmosphere, occurred at the end of the 20th century. Indeed, according to data of Figure 4, a high rate of the change of the global temperature was established in the 1980s. Figure 10 gives another example of this kind. It shows the evolution of the area of the lower layer of clouds and the intensity of cosmic rays [30–33]. Anomalies are associated with the part of cosmic rays that are created by the Sun or pass through it. Cosmic rays which enter in the Earth's atmosphere partake into a nuclear reaction in the upper tropopause and cause atmospheric ionization. Ions formed under the action of cosmic rays are the nuclei of condensation in the atmosphere.

As follows from the data of Fig. 10, the influence of changes in the intensity of cosmic rays on the average cloudiness was manifested in the 22nd circle of 11-year solar cycles, while no correlation between these values was observed in the 23rd solar cycle. This fact can be explained by the appearance in the atmosphere a sufficient density of chemically active molecules, which also become condensation nuclei and compete in this process during the 23rd solar cycle with the atmospheric ions which are formed under the action of cosmic rays.

It follows from the above analysis that global changes on Earth and in the atmosphere occur due to chemically active compounds in the atmosphere, which, despite their relatively small amount in the atmosphere, affect various atmospheric processes, such as smog formation, condensation processes, the greenhouse effect, and others. These compounds and radicals are formed as a result of the economic or mismanagement human activity. As it is shown above, the carbon dioxide produced in the power processes of the burning of fossil fuels is mainly absorbed by plants and oceans as a result of the photosynthesis, and the observed increase in the concentration of atmospheric carbon dioxide over time accordis with the Pauling's concept, is associated with the heating of the Earth, which in turn is determined by more subtle processes. All of this requires a more detailed study.

ANALYSIS RESULTS

According to the above results, there is a global warming, as well as an increase in the concentration of carbon dioxide in the atmosphere, which significantly exceeds the corresponding values in the preindustrial period. It is necessary to understand the reasons for these changes, as well as the degree of this danger. It would seem that one can obtain the cause of these changes in a simple way based on the changes that resultts from the human economic activity.

First, the forest mismanagement in a number of countries is accompanied by deforestation and burning, and the reduction of the forest area reduces the rate of photosynthesis on the Earth's surface and, consequently, the rate of removal of carbon dioxide from the atmosphere. However, measurements show that the forest area decreases too slowly in time. Thus, the increase of the atmospheric carbon dioxide concentration is not associated with the forest problem.

Second, the increase in the concentration of carbon dioxide molecules in the atmosphere may be associated with the "carbon energetic" , which is which is associated with fossil fuels extracted from the Earth's interior. They are involved in the processes that establish an equilibrium between atmospheric carbon dioxide and bound carbon on the Earth's surface. Over the past century, as a result of burning of fossil fuels, approximately 540 GtC have been released into the Earth's atmosphere, i.e., the carbon in the composition of carbon dioxide molecules, and the amount of carbon in the atmosphere in these molecules has increased by about 200 GtC. Since the carbon dioxide injected into the atmosphere, in accordance with the proportions of carbon in the atmosphere and on the Earth's surface, then mainly passes to the surface, such a mechanism for the accumulation of carbon dioxide in the atmosphere is not realized. An even stronger argument against this mechanism is that the time for the doubling of the mass of carbon dioxide in the atmosphere (about 120 years) is noticeably is longer than the time to double the mass of combustible fossil fuels per unit of time (40 years), which rules out this mechanism.

Third, the greenhouse effect may be responsible for the increase in global temperature if the increase in the mass of atmospheric carbon dioxide is anthropogenic. However, the current increase in the mass of atmospheric carbon dioxide causes an increase in global temperature as a result of the greenhouse effect, which is four to five times lower than the observed one. Thus, it is necessary to abandon from this mechanism as responsible for the observed increase of the global temperature.

Thus, the analysis of contemporary information complels us to refuse from simple mechanisms of the relationship between the increase in the mass of carbon dioxide in the atmosphere and the global temperature. It is more likely that the equilibrium between atmospheric carbon dioxide and bound carbon on the Earth's surface changes as a result of changes in the processes responsible for this equilibrium. In particular, based on obtained values of the effective enthalpy of solid carbon oxidation in the past and the present, one can assume that this occurred earlier through the carbon dioxide dissolved in the ocean, and it was the release of this carbon dioxide into the atmosphere that limited the total process of carbon oxidation. Currently, this happens directly with the participation of carbonates in the ocean, and the pollution of the ocean as a result of human activity creates catalysts that become crucial for the main channel of oxidation.

Next, let us analyze the dangers associated with the changes under consideration. As for warming, then, as follows from Fig. 5, in the past, the temperature increase was an order of magnitude higher than that observed in the last hundred fifty years. These changes can be associated with a turn of the Earth's axis as a result of interaction with the environment, which follows from the Milankovich theory [34]. Moreover, in the recent past, there was a similar warming and then a cooling. Vikings occupied the Greenland in the 11th century and left it in the 14th century because of a cooling. As you can see, this continent was free of ice at that time, although the current melting of the Greenland glacier worries climatologists.

The recent change in the concentration of atmospheric carbon dioxide does not pose a danger to humans, since exhaled air contains 5–8% of carbon dioxide. It can only cause concern in general terms. At the same time, some channels of pollution of the atmosphere and the Earth's surface are dangerous to humans, especially the photochemical smog observed in industrial southern cities over the past century. In this case, toxic substances are formed in the Earth's atmosphere under the influence of solar radiation, in addition to organic substances, industrial products, and ozone, which affect human's health.

Thus, the analysis shows that the observed increase in the concentration of carbon dioxide in the atmosphere is not explained by standard methods of exposure to the atmosphere. Apparently, environmental pollution creates new channels to establish a balance between atmospheric carbon dioxide and bound carbon on the Earth's surface, which explains the above changes.

CONCLUSIONS

According to the data underlying the Paris Climate Agreements, which ignore the overlaping of spectra of carbon dioxide and water molecules, an increase in the global temperature with the observed change in the concentration of carbon dioxide molecules since the end of the 19th century is 1.5°C (equality (7)). According to detailed calculations [19] based on information from the HITRAN databank [35, 36], this value is 0.3°C (expression (4)). These data refer to the part of the global temperature change that is due to carbon dioxide molecules, while the total value of this value is 0.8°C (5) in accordance with the data of several thousand meteorological stations. Hence, the assumption underlying the Paris Climate Agreements, as well as the predictions based on them, is fallacious.

According to data for last decades, approximately 40% of the carbon dioxide emissions in the atmosphere resulted from the burning of fossil fuels remains in the atmosphere. In the case of an equilibrium between the atmosphere and the Earth's surface, carbon of this carbon dioxide passes into a bound state in the upper layers of the land and ocean. The growth rate for the rate land temperature is about twice compared to that of the ocean. These and other facts related to energeitics of the atmosphere characterize its evolution and require an additional analysis.

Let us note one more feature of the problems considered above. While researching a scientific problem, the scientist strives for the truth, while the Paris Climate Agreements are initiated by an international financial group with the goal of making a profit. Due to its high business organization, this group has influence on the main informational resources, as well as on a number of the country's leading climate scientists, who can find and reject publications that do not comply with the Paris Climate Agreements. The possibility of this financial group can be seen in the example of pressure on President Trump, who, after consulting with leading American scientists, withdrew the United States from the Paris Climate Agreements. All of this should be taken into account in the analysis of publications related to atmospheric carbon dioxide.

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