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ORIGINAL ARTICLE

Greenhouse gases and greenhouse effect

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Abstract Conventional theory of global warming states that heating of atmosphere occurs as a result of accumulation of CO_2 and CH_4 in atmosphere. The writers show that rising concentration of CO_2 should result in the cooling of climate. The methane accumulation has no essential effect on the Earth's climate. Even significant releases of the anthropogenic carbon dioxide into the atmosphere do not change average parameters of the Earth's heat regime and the atmospheric greenhouse effect. Moreover, CO_2 concentration increase in the atmosphere results in rising agricultural productivity and improves the conditions for reforestation. Thus, accumulation of small additional amounts of carbon dioxide and methane in the atmosphere as a result of anthropogenic activities has practically no effect on the Earth's climate.

Keywords Adiabatic model · Climate change · Carbon dioxide · Methane · Troposphere · Anthropogenic effect

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Introduction

For comprehensive analysis of the influence of increasing concentration of the greenhouse gases on the global temperature of atmosphere, one needs to develop an advanced physicochemical theory of mass—energy redistribution among the Earth's systems. This advanced theory should include: (1) evolution of the composition of atmosphere, (2) evolution of the geological conditions, (3) data on changing solar radiation, (4) the Earth's revolution precession, (5) oceanological data, and (6) multiple feedbacks between the atmosphere and ocean.

The authors investigate the greenhouse effect using the adiabatic model, which relates the global temperature of troposphere to atmospheric pressure and allows one to analyze the temperature changes due to variations in mass and chemical composition of the atmosphere. The existing feedbacks between atmosphere and ocean are intentionally neglected in the article with the focus on the atmospheric temperature changes due to anthropogenic greenhouse gases emission.

Evaluating the temperature distribution in atmosphere

The adiabatic theory of greenhouse effect (Sorokhtin 2001, 2006; Sorokhtin et al. 2007; Khilyuk and Chilingar 2003, 2004, 2006; Chilingar and Khilyuk 2007) shows that the temperature distribution in planet's troposphere (including the Earth's troposphere) at pressure >0.2 atm (2.0265×10^1 kPa) under the greenhouse effect theory can be determined using the following equation:

$$T = b^{\alpha}\left[\frac{S(1-A)}{\sigma\left(\frac{\pi/2-\psi}{\pi/2}\times 4+\frac{\psi}{\pi/2}\times 2\times\frac{2}{1+\cos\psi}\right)}\right]^{1/4}\left(\frac{p}{p_0}\right)^{\alpha} \qquad (1)$$

where S (=1.367 × 10^6 erg/cm^2 s) is the solar constant (flow of the solar energy reaching the Earth); σ (=5.67 × 10^{-5} erg/cm^2 s °C^4) is the Stefan–Boltzmann constant; A is the planet's reflectivity (albedo) (for the Earth $A \approx 0.3$); b is a scaling factor; α is the adiabatic exponent, $\alpha = (\gamma - 1)/\gamma$; $\gamma = c_p/c_v$, where c_p and c_v are the specific heats of gas at constant pressure and constant volume, respectively; ψ is the precession angle of the revolving planet (for the present-day Earth, $\psi = 23.44°$). At $\psi = 23.44°$, the denominator in Eq. 1 is equal to 3.502 rather that 4.0 in the classic format at $\psi = 0$.

According to current measurements, average near-surface Earth temperature at $p = p_0 = 1$ atm (1.01324 × 10^2 kPa) is approximately equal to 288 K or +15°C (Bachinsky et al. 1951). Factor b can be found under condition that the present-day average Earth's surface temperature is equal to 288 K at $\alpha = 0.1905$. In such a case $b = 1.597$, and for the nitrogen–oxygen atmosphere composition, $b^\alpha = 1.093$. For a different composition of troposphere, the factor b remains the same, but the b^α value changes depending on the adiabatic exponent α (Sorokhtin 2006).

If the specific heat at a constant pressure (c_p) is expressed in cal/g °C, and the universal gas constant $R = 1.987$ cal/mol °C, the relationship between the adiabatic exponent α and the composition and humidity of troposphere can be presented by the following equation:

$$\alpha = \frac{R}{\mu\left(c_p + C_w + C_r\right)} \tag{2a}$$

$$c_p = \frac{p_{N_2}c_p(N_2) + p_{O_2}c_p(O_2) + p_{CO_2}c_p(CO_2) + p_{Ar}c_p(Ar)}{p} \tag{2b}$$

where $R = 1.987$ cal/mol °C is the gas constant; μ is the molar weight of atmospheric mixture (for the Earth, $\mu \approx 28.9$); $p_{N_2} = 0.7551$; $p_{CO_2} = 0.00046$ $p_{N_2} = 0.7551$ and $p_{Ar} = 0.0128$ atm are the partial pressures of the corresponding gases (Voitkevich et al. 1990); $p \approx 1$ atm is the total atmospheric pressure at sea level; $c_p(N_2) = 0.248$, $c_p(O_2) = 0.218$ cal/g °C, $c_p(CO_2) = 0.197$ cal/g °C, $c_p(Ar) = 0.124$ cal/g °C are specific heats of nitrogen, oxygen, carbon dioxide, and argon at constant pressure (Naumov et al. 1971); C_w and C_r are the correction factors with the dimension of specific heat (taking into account total heating effect of the water vapor condensation process C_w in a humid atmosphere and the absorption of heat from the Earth and Sun C_r by greenhouse gases).

From Eq. (2a):

$$C_w + C_r = \frac{R}{\mu\alpha} - c_p \tag{3}$$

At $\psi = 23.44°$ and $A \approx 0.3$, the best fit of the theoretical temperature distribution (Eq. 1) within the Earth's troposphere to the averaged empiric data occurs at $\alpha = 0.1905$ and $b^\alpha = 1.093$. For a dry air mixture of the Earth's atmosphere, $c_p = 0.2394$ cal/g °C. Thus, using Eq. 3 for the absorbing-infrared-radiation humid air of the troposphere with the temperature gradient of 6.5°/km, the $C_r + C_w = 0.1203$ cal/g °C. For planets with the atmospheres of a different composition these parameters should be understood as the description of any thermophysical or chemical processes resulting in the heat release (at $C_r + C_w > 0$) or absorption (at $C_r + C_w < 0$) within the troposphere.

To determine the C_r and C_w factors, it is necessary to involve the characteristic temperatures T_s and T_e of a planet (Sorokhtin 2001):

$$C_r = \frac{R}{\mu\alpha}\left(\frac{T_s - T_e}{T_s}\right) \tag{4a}$$

$$C_w = \frac{R}{\mu\alpha}\frac{T_e}{T_s} - c_p \tag{4b}$$

On substituting the values of Earth's atmospheric parameters into Eqs. 4a and 4b ($\alpha = 0.1905$, $\mu = 28.9$, $c_p = 0.2394$ cal/g °C, $T_s = 288$ K, $T_e = 263.5$ K and $R = 1.987$ cal/mol °C), one obtains $C_r = 0.0306$ cal/g °C; $C_w = 0.0897$ cal/g °C; and $C_r + C_w = 0.1203$ cal/g °C. Equation 3 gives the same results.

The adiabatic model (Eq. 1) was verified by comparing it with the standard temperature distribution in the Earth's troposphere (Bachinsky et al. 1951). The results of the comparison [at $\psi = 23.44°$ and $p_0 = 1$ atm (1.01324 × 10^2 KPa)] are presented in Fig. 1.

A much more stringent check of the universality of the derived patterns is a computation of temperature distribution in the troposphere of Venus. It is performed based on the given pressure of 90.9 atm (92.1035 × 10^2 kPa), solar constant $S = 2.62 \times 10^6$ erg/cm^2 s, precession angle $\psi \approx 3.18°$, and the molecular weight $\mu = 43.5$ (Marov 1986; Venus 1989). The results are also presented in Fig. 1. The best fit of the theoretical temperature distribution with its empirical values occurs at the adiabatic exponent $\alpha = 0.1786$ and b^α factor of 1.429 ($b = 7.37$). For Venus, $c_p = 0.2015$ cal/g °C, $T_s = 735.3$ K and $T_e = 230.5$ K. Then, $C_r = 0.1756$ cal/g °C, $C_w = 0.1213$ cal/g °C and $C_q = C_r + C_w = 0.0543$ cal/g °C. The C_r parameter determines the absorption of the planet's heat radiation by atmosphere. Its relatively elevated value is apparently due to a high atmospheric pressure and very hot troposphere. Inasmuch as $C_w < 0$ for Venus troposphere (especially in its lower and middle layers), endothermic reactions predominate (dissociation of some chemical compounds, for instance, dissociation of the sulfuric acid into SO_3 and water). For the upper layer of the Venetian troposphere (at the elevations between 40 and 60 km) $C_w > 0$. There, the

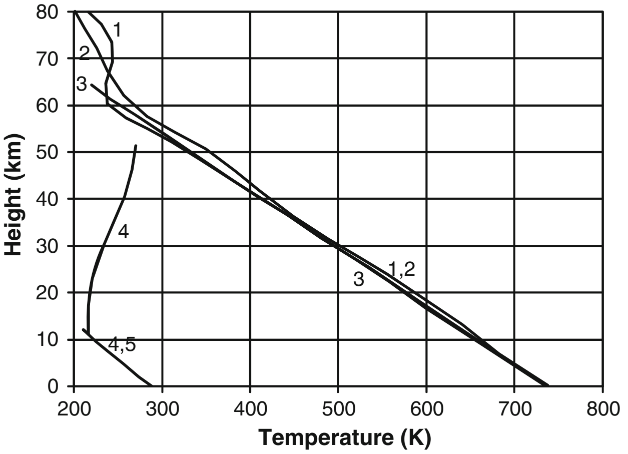

Fig. 1 Distribution of experimentally determined temperature within the Earth's troposphere and stratosphere (*curve* 4; Bachinsky et al. 1951) and within the Venetian troposphere (*curves* 1 and 2; Venus 1989) as compared to the theoretical distributions (*curves* 5 and 3). Constructed in accordance with the adiabatic theory of the greenhouse effect. Temperatures are in Kelvin

exothermic chemical reactions (such as the reduction of sulfuric acid) and condensation of water vapor in the clouds prevail.

As Fig. 1 shows, theoretical temperature distribution in the Venetian troposphere, which is completely different from the one on Earth, fits quite well to the empirical data quoted in Venus (1989). The range of relative error through the elevations up to 40 km is 0.5–1.0%. Theoretical temperatures at the elevations ranging from 40 to 60 km are positioned between two series of empirical data corresponding to the measurement at the Venetian high and low latitudes. At the higher altitudes where $p < 0.2$ atm (Venetian tropopause), the presented theory is not valid. This cannot be accidental and most likely this is an indication of the validity of the presented theory for the troposphere layer.

The temperature distributions presented in Fig. 1 were constructed based on the adiabatic theory of temperature distribution and are in effect the first ever theoretical models of the Earth's and Venus's tropospheric heat regime, i.e., the models for the planets with totally different atmospheric parameters. The obtained close fit of the theoretical model to experimental data is a strong testimony on the validity of the adiabatic theory of greenhouse effect. The results of comparison indicate that the average temperature distribution in a planetary troposphere is determined by the solar constant, the planet's albedo, the mass (pressure) of atmosphere, heat-absorbing capacity of its gaseous mixture, and the planet's precession angle.

By definition, the greenhouse effect ΔT is the difference between the planet's surface average temperature T_s and its effective temperature T_e:

$$\Delta T = T_s - T_e \tag{5}$$

Average temperature for the entire Earth's surface is approximately 288 K or +15°C. Its effective temperature (at $\psi = 0$) is $T_e = 255$ K or −18°C. Thus, the present-day value of the greenhouse effect for the Earth is +33°C. If we take into account that the present-day Earth's precession angle is $\psi = 23.44°$, then the effective temperature of Earth turns out to be $T_e = 263.49$ K (Sorokhtin 2006), and the corresponding greenhouse effect is 24.5°C.

The adiabatic model allows one to estimate the effect of so-called "greenhouse gases" on the temperature regimes of the Earth troposphere and its greenhouse effect. For asymptotic estimates, the writers assumed that the nitrogen–oxygen Earth's atmosphere is completely replaced by a carbon dioxide one and, then, by a methane one, with the same atmospheric pressure $p_s = 1$ atm $(1.01324 \times 10^2$ KPa). The adiabatic exponents are determined from Eq. 2a and 2a at $\mu_{CO_2} = 44$, and $c_p = 0.197$ cal/g °C, and $\mu_{CH_4} = 16$, and $c_p = 0.528$ cal/g °C. Thus, $\alpha_{CO_2} = 0.1423$ and $\alpha_{CH_4} = 0.1915$. Substituting these α values into Eq. 1 with the same b factor value of 1.597, one can construct the temperature distribution in the hypothetical carbon dioxide and methane atmospheres. The corresponding near-surface temperature of the hypothetical carbon dioxide atmosphere will be 281.5 K (6.4°C) lower than that at the nitrogen–oxygen composition of the atmosphere, and for the methane atmosphere it will be 288.1 K, which is just 0.1°C above the usual average Earth's temperature of 288 K. One needs to remember, however, that the carbon dioxide atmosphere is denser, whereas the methane atmosphere is lighter so that the same pressures in these atmospheres will be reached at different elevations than those in the nitrogen–oxygen atmosphere

$$h_{CO_2} = h_{N_2+O_2}\frac{\mu_{N_2+O_2}}{\mu_{CO_2}} \text{ and } h_{CH_4} = h_{N_2+O_2}\frac{\mu_{N_2+O_2}}{\mu_{CH_4}} \tag{6}$$

where $\mu_{N_2+O_2}$ (=28.9) is the molar weight of the nitrogen–oxygen atmosphere, and μ_{CO_2}(=44) and μ_{CH_4}(=16) are the molecular weights of carbon dioxide and methane, respectively. The constructed temperature distributions within the hypothetical totally carbon dioxide and totally methane atmospheres are shown in Fig. 2 together with the already presented (Fig. 1) temperature distribution in the existing nitrogen–oxygen atmosphere.

Thus, for the hypothetical carbon-dioxide atmosphere with the same near-surface pressure of 1 atm, the average Earth's surface temperature declines by approximately 6.5°C (and not increases significantly as commonly believed). Besides, due to a higher molecular weight of carbon dioxide, temperature within the entire thickness of such a troposphere is always lower than in the nitrogen–oxygen troposphere.

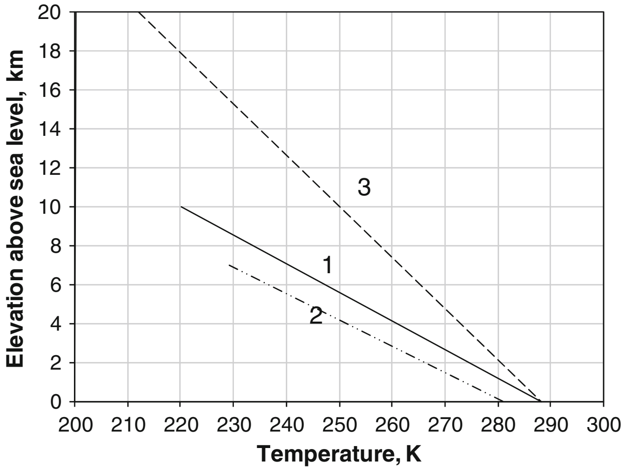

Fig. 2 Averaged temperature distributions in the Earth's troposphere using Eq. 1. *1*, for the Earth's troposphere with a nitrogen–oxygen air; *2*, for a model Earth's atmosphere composed totally of carbon dioxide; *3*, for a model Earth's atmosphere composed totally of methane (all other parameters of Models 2 and 3 are the same as in case 1)

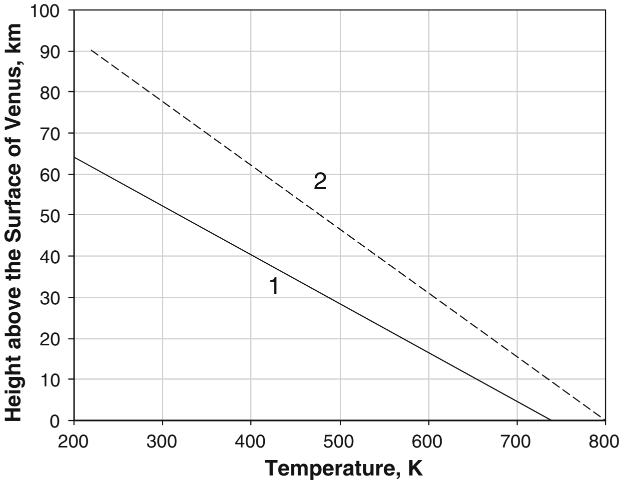

Fig. 3 Averaged temperature distributions in the Venetian troposphere based on Eq. 1: *1*, for the Venus's carbon dioxide troposphere; *2*, temperature distribution for a hypothetical model of the nitrogen–oxygen troposphere of Venus with all other conditions being equal

For a hypothetical methane atmosphere, the near-surface temperature at sea level remains almost unchanged, because $\alpha_{N_2+O_2} = 0.1905 \approx \alpha_{CH_4} = 0.1915$. At the same time, in the troposphere it is higher than that for the nitrogen–oxygen atmosphere, inasmuch as $\mu_{CH_4}(= 16) < \mu_{N_2+O_2}(= 28.9)$, because the methane atmosphere is much thicker than the nitrogen–oxygen one. That is why in the mountainous areas surface temperature may significantly increase under such atmosphere.

Similarly, for a hypothetical nitrogen—oxygen Venetian atmosphere at the same pressure of 90.9 atm, its surface temperature will rise from 735 to 795 K (462–522°C; see Fig. 3).

These estimates show that saturation of the atmosphere with carbon dioxide, with all other conditions being equal, results not in an increase but in a decrease of the greenhouse effect and average temperature within the entire layer of planet's troposphere. This happens despite intense absorption of the heat of radiation by CO_2. The physical explanation of this phenomenon is clear: molecular weight of carbon dioxide is 1.5 times higher and its heat-absorbing capacity is 1.2 times lower than those of the Earth's air. As a result (see Eq. 2a and 2b), the adiabatic exponent for a carbon dioxide atmosphere, at the same all other conditions, is about 1.34 times lower than that for a nitrogen–oxygen humid air: $\alpha_{(N_2O_2)} = 0.1905$ On Venus, the correction factors C_w and C_r are different from those on Earth, and α parameter is different from the carbon dioxide adiabatic exponent. Thus, a carbon dioxide atmosphere may be compared with a thin, dense blanket with a lower heat-absorbing capacity, whereas a nitrogen–oxygen atmosphere is like a downy (fluffy) blanket, characterized by a higher heat-absorbing capacity.

From the thermodynamic viewpoint, the explanation of this phenomenon consists in the fact that the heat release from the troposphere occurs mostly due to the air mass convection, which is a much more efficient mechanism than the heat transfer by radiation. After the greenhouse gases absorb the heat of radiation, the energy of this radiation is converted into energy of thermal oscillations of gas molecules. This, in turn, leads to the expansion of gas mixture and its rapid rise to the stratosphere where, due to rarified nature of the stratosphere, the excess heat is radiated into space. Therefore, in a troposphere with elevated carbon dioxide content the convection of the atmospheric gases will accelerate substantially.

Besides, there are direct experimental data indicating that the fluctuations of the carbon dioxide partial pressure are the effect, and not a cause, of the temperature changes (Khilyuk and Chilingar 2003; Chilingar and Khilyuk 2007). Based on the data obtained from the Antarctic ice cores (Fig. 4), there is a correlation between temperature fluctuations and changes in the partial pressure of carbon dioxide obtained from the air bubbles in the Antarctic ice sheets of Vostok Station: these atmospheric parameters are closely related. However, a detailed study of the Vostok Station ice cores showed that the temperature fluctuations preceded the corresponding changes in CO_2 concentration in the cores (Monin and Sonechkin 2005). Fischer et al. (1999) and Mokhov et al. (2003) showed that the changes in CO_2 concentration occur after the temperature changes, on average by about 500–600 years. This is the time needed for a complete stirring of the upper (active) oceanic

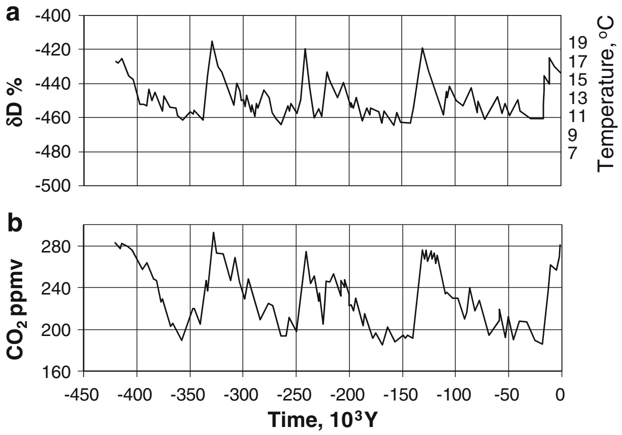

Fig. 4 Correlation between the isotopic air temperature (**a**) and carbon dioxide concentration changes (**b**) over the recent 420,000 years at the Antarctic Vostok Station. The data on CO_2 concentrations and temperature were obtained from the cores of the well drilled in the ice to a depth of 3,623 m, kindly provided by Kotlyakov 2000. The scale of Earth's average temperatures represents the interpretation by the writers

layer, which is the main "controller" of carbon dioxide partial pressure in the atmosphere.

Thus, the data derived from the Antarctic core studies indicate that the temperature changes over the recent 420,000 years had always preceded the corresponding changes in the CO_2 concentrations of ice cover. This is indisputable evidence to the fact that the changes in CO_2 concentrations of the atmosphere are the effect of the global temperature changes, and not their cause.

Figure 2 shows the temperature distributions in totally carbon dioxide and totally methane tropospheres. The temperature effects of the greenhouse gases emission are in the same direction (but much lower in value) in proportion to the concentrations of these gases in the nitrogen–oxygen atmosphere ($CO_2 \approx 4.6 \times 10^{-4}$ and $CH_4 \approx 1.2 \times 10^{-6}$). For instance, the cooling effect for carbon dioxide will be about 2,200 times, and the heating effect for methane, 800,000 times smaller. Therefore, saturation of the atmosphere with carbon dioxide can result only in the accelerated convective mass exchange in the troposphere, and lead to climate cooling (not heating), whereas an increase in methane concentration in the atmosphere practically has no effect on the Earth's climate.

Evaluation of the anthropogenic effect on the Earth's climate

The human effect on the Earth's climate is usually evaluated based on the emotional perception of the fact that greenhouse gases absorb heat of radiation. One can estimate the quantitative effect of anthropogenic carbon dioxide releases into the Earth's atmosphere on the climate applying the adiabatic theory of the greenhouse effect. Various estimates of the current carbon dioxide releases due to burning of natural fuels are on the order of 7–10 billion tons or 1.9–2.7 billion tons of carbon per year. This large amount of CO_2 not only changes the composition of the atmospheric gas mixture and decreases its heat-absorbing capacity, but also slightly increases the atmospheric pressure. These two factors operate in the opposite directions. As a result, the average atmospheric temperature of the Earth is barely affected. From Eq. 1, after differentiation and transition to finite differences (see also Khilyuk and Chilingar 2003), and assuming that $p_s \approx 1$ atm, one can obtain the following equation:

$$\Delta T_s \approx T_s \alpha \Delta p_s \tag{7}$$

where ΔT_s is the change in temperature at sea level attributed to the corresponding change in atmospheric pressure Δp_s (average Earth's temperature $T_s = 288$ K) and the adiabatic exponent $\alpha = 0.1905$. For instance, under the doubled carbon dioxide concentration in the Earth's atmosphere from 0.046 to 0.092 mass % (as anticipated by the year 2100), the pressure increase Δp_s would reach 0.46 mbar. Using Eq. 7, $\Delta T_s \approx +0.025$°C. This temperature rise is not associated with the change in the atmosphere's composition, but only with some increase in the atmospheric pressure. Thus, the anthropogenic carbon dioxide releases into the atmosphere have no practical influence on the greenhouse effect in the atmosphere.

According to Henry's law, most of the carbon dioxide released into the atmosphere is dissolved in the oceanic water, and upon hydration of the oceanic crust it is bound in carbonates (some CO_2 is taken up by plants). Part of the atmospheric oxygen, together with carbon, is also fixed in carbonates.

Therefore, instead of some increase in the atmospheric pressure one may expect its slight decrease, which results in a slight climate cooling (rather than its significant warming as suggested by some ecologists). In addition, upon hydration of oceanic crust rocks, part of carbon dioxide is reduced to methane. Currently, due to formation of carbonates and methane generation, 2.3×10^8 tons/year of carbon dioxide are removed from the ocean, and, therefore, from the atmosphere. The potential of this CO_2 removal mechanism, however, is much higher. Although the period of this geochemical cycle is over 100 years, the effect is cumulative over the time.

Together with the man-made carbon dioxide, some oxygen is removed from the atmosphere. Based on the CO_2 molecular stoichiometry, almost 2.3 g of oxygen is removed from the atmosphere with each gram of carbon. Provided the ocean and vegetation absorb all excessive CO_2 after the year 2100, this should result in a decline of

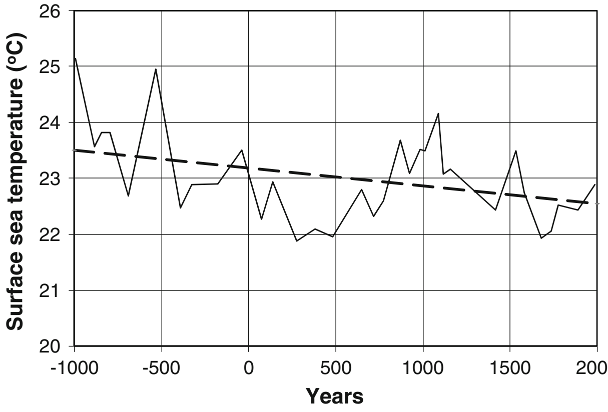

Fig. 5 Surface temperatures of the Sargasso Sea (averaged over 50 years) determined from isotopic ratios of oxygen in plankton remains buried in the bottom deposits (Keigwin 1996). Dashed line is the cooling temperature trend (about 3.3×10^{-4} °C/year)

atmospheric pressure approximately by 0.34 mbar and, therefore, in the additional climate cooling by -8.2×10^{-3} K ≈ -0.008°C. In reality, however, life activity of the plants should almost completely restore the equilibrium distorted by humans (accelerated biomass growth), which would restore the climatic balance.

From the above estimates, one can conclude that even significant releases of anthropogenic carbon dioxide into the Earth's atmosphere practically do not change average parameters of the Earth's heat regime and the greenhouse effect. Moreover, accumulation of CO_2 in the Earth's atmosphere is, no doubt, a useful factor increasing the productivity of the agriculture and facilitating more efficient re-growth of the plants in the deforested areas.

Geologic data testify to the oscillatory changes of Earth's climate under a general cooling trend. Oxygen isotopic shifts in the planktonic foraminifera remains from the Sargasso Sea indicate a steady, although fluctuating, decrease in the surface water temperature over the last 3,000 years (Fig. 5). As shown in this figure, we are currently near the maximum of a warm-up (although far from the strongest one) period, which began centuries ago when there was no massive technogenic carbon dioxide releases into the atmosphere. That is why it may be expected that a new climate cooling-down phase will begin soon (possibly by 2012).

The earth is now in the period of the latest interglacier stadial that began about 12,000 years ago after the Wurm ice age. Sorokhtin et al. (2007) showed that a series of past climatic processes was associated with the periodic changes of Earth's precession angle. The changes were caused by the Lunar–Solar interaction with the excess mass of the equatorial swelling of Earth's rotational ellipsoid and by glaciations emerging over the northern continents as a result of this interaction. Such self-oscillatory processes with the period of $100–120 \times 10^3$ years will continue in the future. About 12,000 years ago new cooling-down cycle began, a harbinger of a new glaciation period (Fig. 6).

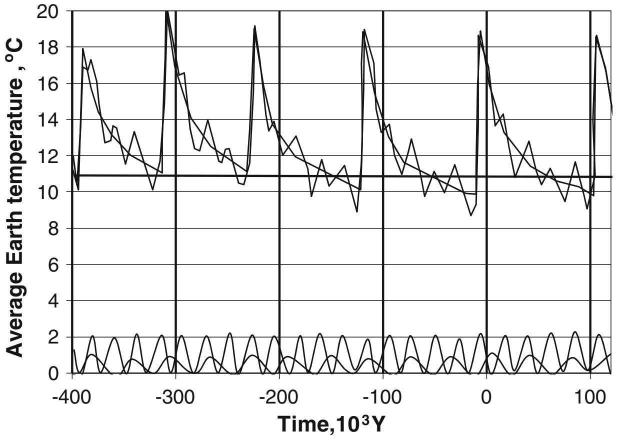

Fig. 6 Average Earth's temperature. The forecast region for the next 120 thousand years (to the *right* of 0)

Conclusions

Occurring (and future) climate cooling-down is quite natural. It is caused by a decrease in Earth's precession angle and by a decline in the atmospheric pressure due to life activity of the nitrogen-consuming bacteria, which continuously remove nitrogen from the atmosphere and transfer it to sediments. As follows from Eq. 1, either of these processes cause cooling-down. For this reason, the future decline in the Earth's surface average temperature may turn out to be more profound than all previous ones. These processes are way beyond the human control, and humans are absolutely powerless to do anything to stop them because the effect of available human controls is negligible in comparison with the global forces of nature.

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