

# Changes in the Global Carbon Cycle: Evidence from the Measurements of $O_2/N_2$ in the Atmosphere and $CO_2$ Partial Pressure at the Ocean–Atmosphere Boundary

V. G. Gorshkov and A. M. Makar'eva

*Institute of Nuclear Physics, Russian Academy of Sciences,  
Orlova roshcha, Gatchina, Leningrad oblast, 188300 Russia*

*e-mail: elba@infopro.spb.su*

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**Abstract**—The global carbon budget includes inorganic and organic constituents. The rates of fossil fuel combustion and inorganic carbon accumulation in the atmosphere and the ocean are known. The organic constituents include changes in the abundance of organic matter in ocean and land areas. Proceeding from changes in  $CO_2$  content and  $O_2/N_2$  concentration ratio in the atmosphere and the known stoichiometric proportions of oxygen binding at organic matter decomposition, changes in the masses of organic substances were quantified in terrestrial and marine environments. The resulting values of organic constituents of the carbon budget are consistent with independent estimates based on the data on anthropogenic land cultivation and the concentration ratio  $^{14}C/^{12}C$  in the dissolved organic carbon of the ocean. We took into account an increase with time in the rate of concentration changes of dissolved inorganic carbon in the ocean inferred from  $^{13}C/^{12}C$  measurements. Profiles were constructed for changes in  $CO_2$  partial pressure and  $\delta^{13}C$  through the atmosphere–ocean boundary, which correspond to the obtained values of the total carbon uptake by the ocean in inorganic and organic forms.

## INTRODUCTION

The investigation of the atmospheric  $CO_2$  budget is among the major problems of global changes. Since 1958, the rate of carbon accumulation in the atmosphere has been documented in many regions of the Earth's surface [1–4]. The main source of increases in atmospheric carbon dioxide is the combustion of fossil fuel. Variations in the rate of carbon discharge from this source are well known from the beginning of the industrial era [1]. It is traditionally believed that the oceanic reservoir of dissolved inorganic carbon is the main absorber of excess atmospheric carbon [2]. According to ice core data [3, 4], the atmosphere–ocean physicochemical system has been in equilibrium through the past several thousand years. The anthropogenic disturbance of atmospheric carbon dioxide is many times higher than any occasional fluctuations of the equilibrium preindustrial state [3, 4]. Owing to the tendency of the atmosphere–ocean system to the equilibrium state, the rate of atmospheric carbon uptake by the inorganic oceanic system should increase proportionally to the departure of atmospheric  $CO_2$  concentration from the preindustrial equilibrium level [5]. The rate of inorganic carbon accumulation in the ocean was determined from the data on changes in  $^{13}C/^{12}C$  between 1970 and 1990 [2] and corresponds to the average rate up to 1980. Up to now, the increment in atmospheric  $CO_2$  content increased by approximately 30% in com-

parison with 1980. The increase in the rate of carbon uptake by the inorganic ocean system should be the same.

Many details of the organic constituent of the carbon budget are still not fully understood both in terrestrial and marine areas [5–11]. New data on changes in the atmospheric  $O_2/N_2$  ratio [6] contribute substantially to the solution of this problem. The requirement of the closeness of the global carbon and oxygen budgets defines two equations with two unknown constituents of these budgets: changes in organic matter contents in terrestrial and marine environments (next section). Taking into account differences in the available estimates of carbon uptake by the ocean in inorganic form [6–8], we can solve the equations of carbon and oxygen budgets as two separate dependencies of the rates of change in organic matter contents in terrestrial and marine environments on the rate of carbon uptake by the ocean in inorganic form.

In any case, it is hardly possible to correlate all diverse pieces of evidence without accounting for the compensating response of marine biota slightly disturbed by the anthropogenic activity to an increase in the concentration of atmospheric carbon dioxide. This response occurs in accordance with negative feedback and tends to decrease the gain in the concentration of atmospheric carbon dioxide through its transformation into dissolved organic carbon. On the other hand, ter-

restrial biota is significantly disturbed by anthropogenic activity and could lose its compensation capacity and begin functioning in accordance with positive feedback enhancing atmospheric disturbances together with fossil fuel combustion.

An independent method for the determination of the total absorption of atmospheric carbon by the ocean is the measurement of carbon flux through the ocean-atmosphere boundary. This method requires no knowledge of the internal ocean structure nor information on the presence and changes in the masses of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). However, in order to determine the flux of carbon uptake by the ocean using this method, it is necessary to know precisely changes in CO<sub>2</sub> partial pressure on a microscopic scale near the interface boundary. Modern measurement techniques rely on data on the differences of CO<sub>2</sub> partial pressure on a macroscopic scale in the atmosphere and the mixed ocean layer. This results in the loss of some information on possible extrema of CO<sub>2</sub> concentration on a microscopic scale and CO<sub>2</sub> uptake by phytoplankton organisms near the interface boundary.

The use of various methods for the determination of carbon uptake by the ocean has resulted in significantly diverging estimates of the gross flux of atmospheric carbon uptake [12–15]. In this work, we determined time- and ocean surface-averaged profiles of <sup>12</sup>CO<sub>2</sub> and <sup>13</sup>C/<sup>12</sup>C changes at microscopic distances from the interface boundary. Taking into account these changes, we demonstrated that the three methods currently employed for the assessment of the total uptake flux of atmospheric carbon to the ocean (the use of data on changes in CO<sub>2</sub> concentration and O<sub>2</sub>/N<sub>2</sub> in the atmosphere, see the next section; the use of data on changes in <sup>13</sup>C/<sup>12</sup>C in DIC [2, 7] and <sup>14</sup>C/<sup>12</sup>C in DOC [5]; and the measurement of CO<sub>2</sub> flux through the ocean-atmosphere interface boundary, see the third section) resulted in the same gross carbon uptake fluxes by the ocean.

#### GLOBAL CARBON BUDGET FROM THE DATA ON CO<sub>2</sub> AND O<sub>2</sub>/N<sub>2</sub> CHANGES IN THE ATMOSPHERE

Global changes in carbon mass in the biosphere are related either to organic matter oxidation from the combustion of fossil fuel and deforestation or to the synthesis of additional masses of organic matter by terrestrial and marine biota. These processes are accompanied by opposite changes in the mass of atmospheric oxygen. The molecular stoichiometric ratios O<sub>2</sub>/CO<sub>2</sub> from the synthesis and decomposition of organic matter should be equal in a steady-state environment. The reciprocal value CO<sub>2</sub>/O<sub>2</sub> is known as the respiratory ratio and is reliably estimated for the majority of biochemical processes in the biosphere.

During the decomposition or synthesis of organic matter in terrestrial and marine systems, the main changes in oxygen content occur in the atmosphere, because oxygen solubility in the ocean is low and the oxygen abundance of the ocean is two orders of magnitude lower than that of the atmosphere. The amount of oxygen in the atmosphere is higher than that of carbon by a factor of 1000. Thus, an increase in CO<sub>2</sub> concentration of 30% is accompanied by a decrease in oxygen concentration of about 0.05%. New techniques of O<sub>2</sub>/N<sub>2</sub> measurement in the atmosphere [6] allow changes in oxygen concentration to be determined with sufficient accuracy.

The equations of the closing of the global carbon and oxygen budgets (mass conservation laws) can be written as

$$f_C + a_C + b_C + s_C = 0, \quad s_C = s_C^+ + s_C^- \quad (1)$$

and

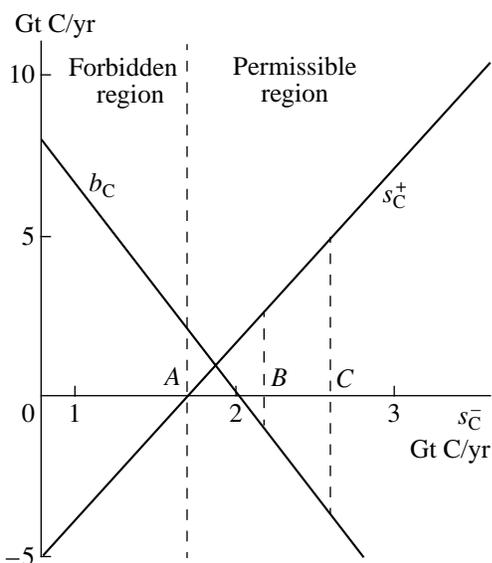
$$f_O + a_O + b_O + s_O = 0, \quad s_O = s_O^+ + s_O^-, \quad (2)$$

where the subscripts C and O refer to carbon and oxygen, respectively, and the symbols of budget constituents correspond to the global rates of changes in the amount of matter in fossil fuel due to its combustion ( $f$ ), atmosphere ( $a$ ), terrestrial biota ( $b$ ), and ocean ( $s^+$  organic matter and  $s^-$  inorganic matter). Sources appear in Eqs. (1) and (2) with the minus sign and sinks, with the plus sign. Fossil fuel combustion and organic matter decomposition (sources of atmospheric carbon) are accompanied by oxygen binding (sinks of atmospheric oxygen). Because of this, all the terms of Eq. (2) have opposite signs in comparison with the respective terms of Eq. (1).

The term  $a_O$  of Eq. (2) can be calculated from changes in the atmospheric O<sub>2</sub>/N<sub>2</sub> ratio [6]. Other terms are calculated from given dimensionless stoichiometric proportions  $\alpha = O_2/CO_2$ . Fossil fuel combustion gives a value of  $\alpha = \alpha_f = 1.38$  [6]. The synthesis of organic substances by marine biota occurs at the Redfield ratio,  $\alpha = \alpha_s^+ = 1.30$  [16, 17]. The synthesis of long-lived terrestrial organic substances (mainly wood) occurs at  $\alpha = \alpha_b = 1.10$  [6]. Thus, Eq. (2) transforms into

$$-\alpha_f f_C \left(1 - \frac{a_O}{f_O}\right) - \alpha_b b_C - \alpha_s^+ s_C^+ = 0, \quad (3)$$

which takes into account the fact that the carbon uptake by the ocean in inorganic form does not result in a change in the concentration of atmospheric oxygen,  $\alpha_s^- = 0$  [6]. The atmospheric component in Eq. (3) is written as  $a_O(\alpha_f f_C/f_O)$ , which transforms the measurement units of the rate of oxygen concentration changes,  $a_O$  and  $f_O$ , into the units of the rate of carbon concentration changes,  $f_C$ .



**Fig. 1.** Dependence of the rates of mass changes of organic carbon in oceanic ( $s_C^+$ ) and land ( $b_C$ ) areas on the rate of mass changes of inorganic carbon in the ocean ( $s_C^-$ ) according to Eqs. 5 and 6.

The rates of fossil fuel combustion averaged over 1991–1994,  $f_C$ ; corresponding oxygen uptake,  $f_O$ ; carbon accumulation,  $a_C$ ; decrease in the atmospheric oxygen content,  $a_O$ ; and the values of stoichiometric coefficients,  $\alpha$  [6, 16, 17], were estimated by Keeling *et al.* [6] as<sup>1</sup>

$$\begin{aligned} f_C &= (-5.9 \pm 0.3) \text{ Gt C/yr,} \\ f_O &= (57 \pm 3) \text{ per meg,} \\ a_C &= (2.2 \pm 0.2) \text{ Gt C/yr,} \\ a_O &= (-42 \pm 6) \text{ per meg,} \\ \alpha_f &= 1.38 \pm 0.04 [6], \quad \alpha_b = 1.10 \pm 0.05 [6], \\ \alpha_s^+ &= 1.30 \pm 0.03 [16, 17]. \end{aligned} \quad (4)$$

The dimension “per meg” refers to a change in the relative difference of the concentration of atmospheric oxygen ( $O_2 - O_{2\text{ref}}/O_{2\text{ref}}$ ) multiplied by  $10^6$ , where  $O_{2\text{ref}}$  is the standard initial concentration of oxygen in the atmosphere [6]. All the uncertainties in Eq. (4) are standard deviations. The relative errors in the values  $f$  and  $a$  are about 10%. The relative errors in the stoichiometric

<sup>1</sup> There is inconsistency in [6] between the  $f_C$  and  $f_O$  values reported in the diagram and the text. We used the data from the diagram, because only these values are consistent with the condition of budget closeness and the solutions of Eq. (1) provided in [6] at  $s_C^+ = 0$  for the uptake by marine ( $s_C^- = 1.7$  Gt C/yr) and terrestrial ( $b_C = 2$  Gt C/yr) biota. The use of values from the diagram was approved by M. Heimann, one of the authors of [6].

coefficients are no higher than 5%. Substitution of Eq. (4) into Eqs. (1) and (3) and the solution of these equations with respect to  $s_C^+$  and  $b_C$  yield the following relationships:

$$\begin{aligned} s_C^+ &= -9.4 \text{ Gt C/y} + 5.5s_C^-, \\ b_C &= 13 \text{ Gt C/y} - 6.5s_C^-. \end{aligned} \quad (5)$$

Similar to Eq. 4, the relative errors of all values in Eq. (5) are about 10%. Figure 1 shows a graphical solution of Eq. (5).

Equation 3 establishes a direct connection between the rates of change in the masses of organic carbon in terrestrial ( $b_C$ ) and marine environments ( $s_C^+$ ), which could be also obtained through eliminating the value  $s_C^-$  from Eq. (5),

$$b_C = 2.0 \text{ Gt C/yr} - 1.2s_C^+. \quad (6)$$

Note that the possibility of solving Eqs. (1) and (3) with respect to the organic contributions of terrestrial ( $b_C$ ) and marine areas ( $s_C^+$ ) depends on the reliable difference between the stoichiometric coefficients for land ( $\alpha_b$ ) and ocean areas ( $\alpha_s^+$ ) (see Eq. (4)). If these coefficients were identical, the determinant of the system of equations with respect to the unknowns  $b_C$  and  $s_C^+$  would be zero with any given inorganic components in Eqs. (1) and (3). In such a case, the two equations ((1) and (3)) would determine only the sum of the organic components of the budget and should be identical; i.e., the data on oxygen concentration measurement would not provide any additional information on the carbon budget components. If the synthesis and decomposition of organic substances occurred similarly in land and ocean areas, changes in  $CO_2$  and  $O_2$  concentrations in the atmosphere would obviously have no bearing on the problem of whether organic substances are efficiently transported from terrestrial to marine environments or whether this flux of synthesis and decomposition of organic matter is closed within particular land areas.

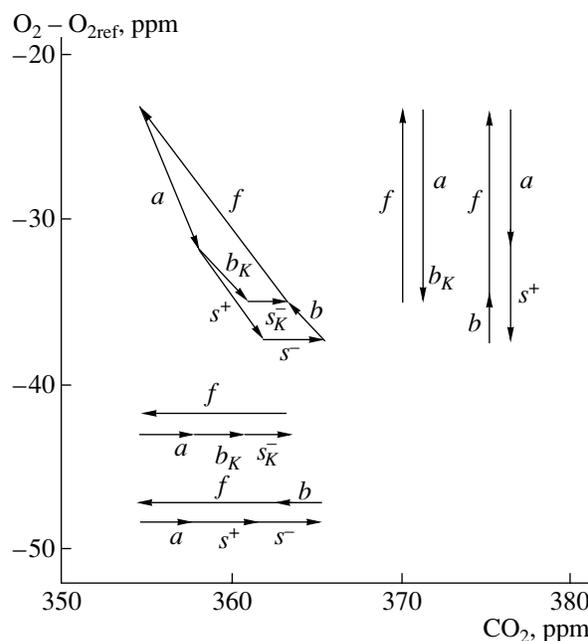
The marine biota is slightly disturbed by anthropogenic activity. Taking into account the existence of the preindustrial stable equilibrium state of the global environment, it can be stated that this biota cannot emit carbon into the atmosphere and respond to an anthropogenic impact in accordance with a positive feedback. Because of this, the region left of point A in Fig. 1, where  $s_C^+ < 0$ , is forbidden (Eq. (6)). This also means that the terrestrial biota cannot consume carbon at a rate higher than 2 Gt C/yr. In particular, the estimates of the rate of carbon uptake by terrestrial environments of 3.5 Gt C/yr [10] are in conflict with the mass conservation law (Eqs. (1), (2)).

If there is no change in the mass of organic matter in the ocean, which corresponds to point A in Fig. 1, we obtain a result identical to that of Keeling *et al.* [6] (Fig. 2). This result is unsatisfactory for two reasons. First, it corresponds to carbon uptake by the terrestrial biota at a rate of 2 Gt C/yr, which is in conflict with the estimate of changes in carbon content in usable (cultivated) land territories, according to which the terrestrial biota of these territories emits carbon at a rate of 1.6 Gt C/yr [4, 9]. Consequently, there must be a compensating carbon sink on uncultivated territories with an intensity of 3.6 Gt C/yr. There is no feasible candidate among terrestrial ecosystems for such a sink [9–11]. Second, the average rate of carbon uptake by the ocean, 1.7 Gt C/yr, which was estimated for 1991–1994, is lower than 2.0 Gt C/yr, which was obtained by the method of  $^{13}\text{C}/^{12}\text{C}$  measurement in the earlier period of 1970–1990 [2, 7]. If the ocean uptake rate increased proportionally to an increase in atmospheric  $\text{CO}_2$  concentration relative to the preindustrial equilibrium concentration, this rate should have attained a value of 2.6 Gt C/yr [5] (table).

If we accept a rate estimate of 1.1 Gt C/yr for the resulting decrease in the mass of organic carbon in terrestrial areas (mass reduction in the tropical zone at a rate of 1.6 Gt C/yr [4, 9] and increment in the boreal forest zone at 0.5 Gt C/yr [4, 9]), which corresponds to point B (Fig. 1), the values  $s_c^+ = 2.6$  and  $s_c^- = 2.2$  Gt C/yr can be obtained for the rates of carbon uptake by the ocean in organic and inorganic forms, respectively. These values are consistent within errors with independent estimates based on  $^{14}\text{C}/^{12}\text{C}$  [5] and  $^{13}\text{C}/^{12}\text{C}$  measurements [2] accounting for the growth of the rates with time [5] (Fig. 2, table).

The main source of error in the value of carbon uptake rate by marine biota,  $s_c^+$ , which is calculated from  $^{14}\text{C}/^{12}\text{C}$  ratios, is the uncertainty in the total mass of DOC in the ocean. The rate of carbon uptake by marine biota is proportional to the mass of DOC [5]. The universally accepted estimate for the mass of DOC is 700 Gt C [3, 18]. This mass corresponds to a present-day value of  $s_c^+ = 2.3$  Gt C/yr. The rate  $s_c^+ = 2.6$  Gt C/yr corresponds to a DOC mass of 790 Gt C, which is within the uncertainty limits of the traditional estimates of this value [3, 18].

Furthermore, a value of  $s_c^- = 2.6$  Gt C/yr [5] can be accepted as a true estimate for the carbon uptake rate in inorganic form accounting for its increase with time, which is shown by point C in Fig. 1. In such a case, we obtain a decrease in the mass of terrestrial organic carbon at a rate of  $b_c = -3.8$  Gt C/yr and an increase in the mass of marine organic carbon at a rate of  $s_c^+ = 4.9$  Gt C/yr. The former value is consistent with the previous estimates of the reduction of terrestrial organic carbon resources [19, 20]. The latter value corresponds to a



**Fig. 2.** Reduction of  $\text{O}_2$  concentration as a function of an increase in  $\text{CO}_2$  concentration in the atmosphere; the volume is ppm for dry air and  $\text{O}_{2\text{ref}}$  is the initial fixed  $\text{O}_2$  concentration in the atmosphere.

The vectors and their projections on the ( $\text{CO}_2$ ) axis connect values corresponding to July 1991 and July 1994;  $a$  is the vector of observations in the atmosphere, and other vectors are calculated from the known rates of emission (absorption) of carbon from the relation 1 ppm = 2.1 Gt C and the slope  $R = \alpha^{-1} \equiv \text{CO}_2/\text{O}_2$  (respiration ratio):  $f$  refers to fossil fuel,  $R_f = 1/1.4$  [6];  $b$ , terrestrial biota,  $R_b = 1/1.1$  [6];  $s^-$ , inorganic carbon of the ocean,  $R_s^- = 1/0$  [6]; and  $s^+$ , marine biota,  $R_s^+ = 1/1.3$  (Redfield ratio [16, 17]). The closing of the vector diagram (sum of all vectors is zero) corresponds to the balance of carbon and oxygen. The vectors  $s_K^-$  and  $b_K$  were calculated [6] with a zero marine biota response ( $s_c^+ = 0$ ). The vectors  $s^-$  and  $s^+$  were calculated at a given resulting rate of carbon uptake by terrestrial biota (table). The balances of projections on the  $\text{CO}_2$  and  $\text{O}_2$  axes are shown in the lower and right linear diagrams, respectively.

DOC mass of 1500 Gt C, which is near the upper boundary of estimates for this value [21–23].

### OCEAN ABSORPTION FLUX OF ATMOSPHERIC CARBON THROUGH THE WATER–AIR INTERFACE

The net flux of atmospheric  $^{14}\text{C}$  isotope uptake,  $^{14}F$ , through the water–air interface boundary is the difference of the gross  $^{14}\text{CO}_2$  flux from the atmosphere to the ocean,  $^{14}G_a$ , which is proportional to  $^{14}\text{CO}_2$  concentration in the atmosphere near the boundary, and the opposite gross  $^{14}\text{CO}_2$  flux from the ocean to the atmosphere,  $^{14}G_s$ ,

Global carbon budget, Gt C/yr\*

Source	IPCC 95 1980–1989 [4]	Measurements	Calculated to 1991–1994**	1991–1994	This work, 1991–1994
1. Fossil fuel, cement	$-5.5 \pm 0.5$			$-5.9 \pm 0.5$ [6, 8]	$-5.9 \pm 0.5$ [6]
2. Atmosphere	$3.3 \pm 0.2$			$2.2 \pm 0.3$ [6, 8]	$2.2 \pm 0.3$ [6]
3. Ocean (inorganic)	$2.0 \pm 0.8$	$2.0 \pm 0.8$ 1970–1990 [2, 7]	$2.6 \pm 1.0$ [2, 5, 7]	$1.7 \pm 1.0$ [6, 8]***	$2.2 \pm 1.0$ ****
4. Organic carbon (4) = –[(1) + (2) + (3)]	$0.2 \pm 0.5$			$2.0 \pm 1.0$ [6, 8]***	$1.5 \pm 0.5$ ****
4a Ocean	0	$1.4 \pm 0.6$ [5] 1955–1986	$2.3 \pm 1.0$ [5]	0	$2.6 \pm 1.0$ ****
4b Land (4b) = (4) – (4a)	$0.2 \pm 0.5$			$2.0 \pm 1.0$ ***	$-1.1 \pm 0.9$ [4]
4b <sub>1</sub> Tropical zone	$-1.6 \pm 1.0$			$-1.6 \pm 1.0$ [4]	$-1.6 \pm 1.0$ [4]
4b <sub>2</sub> Boreal zone	$0.5 \pm 0.5$			$0.5 \pm 0.5$ [4]	$0.5 \pm 0.5$ [4]
4b <sub>3</sub> Residual (4b <sub>3</sub> ) = (4b) – (4b <sub>1</sub> ) – (4b <sub>2</sub> )	$1.3 \pm 1.5$			$3.1 \pm 1.5$	0

\* All data are average rates of carbon emission for the specified time period. The rates are positive for sources and negative for sinks. Similar to [4, 6, 8], all the errors (standard deviations multiplied by 1.645) correspond to a confidence level of 90%.

\*\* Recalculated assuming a linear increase in the rate proportional to the increment of CO<sub>2</sub> concentration in the atmosphere relative to the equilibrium preindustrial value [5].

\*\*\* Calculated from Fig. 1 at zero carbon absorption by marine biota, (4a) = 0 [6].

\*\*\*\* Calculated from Fig. 1 at given rates of carbon absorption by terrestrial biota,  $4b_1 + 4b_2$ , on condition of the closeness of carbon budget in terrestrial environments, (4b<sub>3</sub>) = 0.

which is proportional to <sup>v</sup>CO<sub>2</sub> concentration in the ocean near the boundary [12]. The net flux of <sup>v</sup>CO<sub>2</sub> uptake is proportional to the difference of the concentration of <sup>v</sup>CO<sub>2</sub> dissolved in water directly below the interface boundary in equilibrium with atmospheric concentration and the minimum concentration, [<sup>v</sup>CO<sub>2</sub>]<sub>min</sub>, in the microscopic water layer below the interface boundary, where the distribution of carbon dioxide is controlled by molecular diffusion,

$${}^vF = K([\text{}^v\text{CO}_2]_s - [\text{}^v\text{CO}_2]_{\min}). \quad (7)$$

The flux <sup>v</sup>F is usually measured as the rate of <sup>v</sup>C mass absorption per year and the unit area of oceanic surface and has the dimension g C m<sup>-2</sup> yr<sup>-1</sup>. The values [CO<sub>2</sub>] are measured in molar concentration units for dry air,  $n_a$ , mol/m<sup>3</sup>; [CO<sub>2</sub>] =  $n_c/n_a$  in ppm, where  $n_c$  is the molar carbon concentration in mol C/m<sup>3</sup>. The coefficient  $K = v\rho_a(\mu_c/\mu_a)$ , where  $\rho_a$  is the air density in g/m<sup>3</sup>;  $\mu_a = 29$  g/mol is the molecular weight of air;  $\mu_c = 12$  g/mol is the molecular weight of carbon; and  $v$  is the coefficient having the dimension of velocity (m/yr) and defining the velocity of CO<sub>2</sub> molecule movement through the water–air interface boundary. The concentrations [CO<sub>2</sub>] are usually determined from the partial pressure of CO<sub>2</sub> in the atmosphere,  $[\text{CO}_2]_s = \alpha_{ml}(p\text{CO}_2)_a$ , and the mixed upper layer of the ocean,  $[\text{CO}_2]_{\min} = \alpha_{ml}(p\text{CO}_2)_{ml}$ , where  $\alpha_{ml}$  is the CO<sub>2</sub> solubility (ratio of equilibrium

CO<sub>2</sub> molar concentrations in water and air) in the mixed layer and  $(p\text{CO}_2)_a$  and  $(p\text{CO}_2)_{ml}$  are the CO<sub>2</sub> partial pressures in the atmosphere above the interface boundary and in the air volume in equilibrium with water from the mixed layer. The values  $p\text{CO}_2$  are measured in atmospheric pressure units,  $p_a$ , and coincide in the atmosphere with the above-defined concentrations [CO<sub>2</sub>],  $p\text{CO}_2 = p_c/p_a = n_c/n_a$ ,  $p_a = n_aRT$ , and  $p_c = n_cRT$ , where  $R$  is the gas constant,  $T$  is the absolute temperature of air, and  $p_c$  is the CO<sub>2</sub> partial pressure. The dimension of  $p\text{CO}_2$  is the same as that of [CO<sub>2</sub>], i.e., ppm. Then, the net absorption flux of atmospheric carbon by the ocean is written as [14, 24]

$${}^vF = K\alpha_{ml}\{(p\text{}^v\text{CO}_2)_a - (p\text{}^v\text{CO}_2)_{ml}\}. \quad (8)$$

Robertson and Watson [24] noted that Eq. (8) contained a small error in comparison with Eq. (7) related to the temperature dependence of  $\alpha_{ml}$  and the existence of a temperature difference between the microscopic surface film and the mixed layer.

However, Eq. (8) can differ from Eq. (7) more significantly, because the thickness of the near-surface layer of molecular CO<sub>2</sub> diffusion is comparable with the size of phytoplankton cells, about 50 μm, and CO<sub>2</sub> consumption by phytoplankton cells can significantly impoverish this zone in CO<sub>2</sub> relative to the bulk concentration in the mixed layer. The use of Eq. (8) also results in a significant contradiction of estimates obtained by

other methods for the flux of atmospheric carbon uptake by the ocean, which are based on measurements of the distribution of the ratio  $^{13}R \equiv ^{13}C/^{12}C$  in DIC [2, 7].

With an accuracy of 0.1%, the coefficient  $K$  in Eqs. (7) and (8) and solubility  $\alpha_{ml}$  in Eq. (8) are identical for  $^{13}C$  and  $^{12}C$  [25]. In the preindustrial era, the ocean was in chemical equilibrium with the atmosphere, and the partial pressures ( $pCO_2$ )<sub>0</sub> in the atmosphere and the mixed ocean layer were equal. Let us introduce the differences between partial pressures and its equilibrium value,

$$\Delta(pCO_2)_i \equiv (pCO_2)_i - (pCO_2)_0, \quad i = a, ml,$$

and take into account the following relation for the rates of change in carbon isotope masses,  $^{13}M$  and  $^{12}M$  in the ocean with time:

$$\frac{d}{dt} ^{13}M = \frac{d}{dt} (^{13}R ^{12}M) = ^{13}R \frac{d}{dt} ^{12}M + ^{12}M \frac{d}{dt} ^{13}R,$$

$$^{13}R \equiv ^{13}M / ^{12}M.$$

The right subscripts are used to denote the atmosphere (*a*), ocean (*s*), and mixed ocean layer (*ml*). The subscript 0 denotes preindustrial values, and right superscripts + and -, values related to organic and inorganic oceanic carbon, respectively. The value of preindustrial gross equilibrium carbon flux from the atmosphere into the ocean is  $G_{a0} = G_{s0} \equiv G_0 = (S_s/S_a)K\alpha_{ml}M_{a0} = 74 \text{ Gt C/yr}$  [3, 4], where  $S_s$  and  $S_a$  are the total areas of the ocean and the Earth, respectively. The present-day value of  $G_0$  is higher by 30%,  $G_a = 92 \text{ Gt C/yr}$  [3, 4]. Constructing dimensionless ratios from  $G_a$  and denoting the masses of DOC and DIC in the ocean as  $M_s^+$  and  $M_s^-$ , respectively, we get the following relations equivalent to Eq. (8) for two carbon isotopes,  $^{12}C$  and  $^{13}C$  (see Appendix):

$$\begin{aligned} & \bar{M}_s^- / G_0 + \dot{M}_s^+ / G_0 \\ &= \Delta(pCO_2)_a / (pCO_2)_0 - \Delta(pCO_2)_{ml} / (pCO_2)_0 \quad (9) \\ & 0.03 + [0.02] = 0.25 - 0.22 \pm 0.10. \end{aligned}$$

$$\begin{aligned} & \sigma_{s,a}^- \bar{M}_s^- / G_0 + M_s^+ \dot{\delta}_s^- / G_0 \\ &+ \sigma_{s,a}^+ \dot{M}_s^+ / G_0 + M_s^- \dot{\delta}_s^+ / G_0 = \Delta\delta_a - \Delta\delta_{ml} \quad (10) \\ & 0.40 - 1.5 + [-0.3] - 0.06 = -1.14 + 0.50\%. \end{aligned}$$

Here, we use the following designations

$$\delta_i \equiv \delta^{13}C_i \equiv ^{13}R / ^{13}R_B - 1;$$

$$\sigma_{i,a} = \delta_i - \delta_a, \quad \dot{x} \equiv dx/dt,$$

where  $^{13}R_B$  is  $^{13}C/^{12}C$  for the PDB standard [26]. All values for which uncertainties are not shown have standard deviations no higher than 15%. Numerals below the respective dimensionless terms in the formulas are the measured values of these quantities. Numerals in

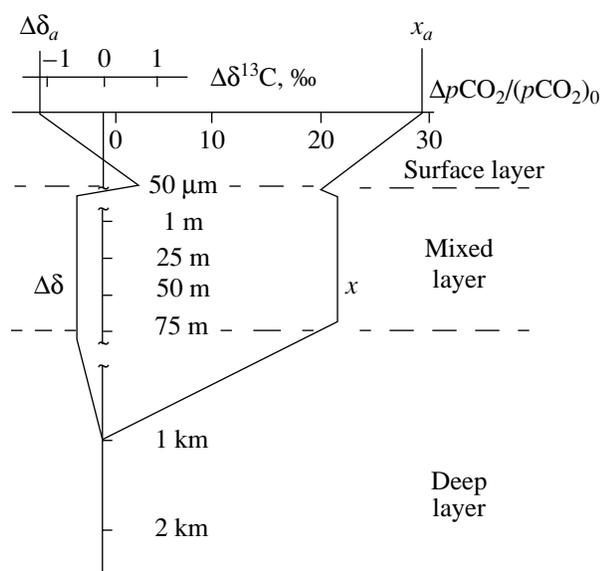
brackets are the values of carbon uptake by marine biota obtained from the results of Gorshkov [5] (table). The first term of Eq. (9) was determined in [2, 7]. The second term of Eq. (9) was obtained by Gorshkov [5]. The first term on the right-hand side of Eq. (9) is known from the measurements of  $CO_2$  content in ice cores [3, 4]. The last term on the right-hand side of Eq. (9) is known with very poor accuracy from the data on the  $CO_2$  partial pressure difference between the atmosphere and the mixed layer averaged over the whole ocean area [12–14]. This difference has opposite signs in polar and equatorial waters. Some controversial issues related to the use of Eqs. (8) and (9) were discussed in [12–14, 24].

The first two terms of Eq. (10) were determined in [2, 7], the third term was calculated using our previous results [5], and the fourth term was also estimated by us and is small compared with the other values. ( $\dot{\delta}_s^+ \sim \dot{\delta}_s^- \sim 0.02\% \text{ yr}^{-1}$  [2]. According to [2], a change in  $^{13}C$  mass occurred in 14% of the DIC mass. Assuming that  $^{13}C$  changed in 20% of the DOC mass, we obtain the above estimate for the last term on the left-hand side of Eq. (10)). The values on the right-hand side of Eq. (10) were determined from the data of [2, 4, 7, 27, 28].

Within the error of the last term of Eq. (9), the two sides of the equality are consistent with each other both at a zero value of the second term and at its value shown in brackets. However, the nonzero magnitude of the second term increases the difference between the left-hand and right-hand sides of Eq. (9).

The left-hand and right-hand sides of Eq. (10) for  $^{13}C$  differ by about a factor of 2 even at the zero value of the third term, which takes into account the response of marine biota. This difference is higher than the experimental errors of all the quantities. Accounting for the zero value of the third term increases the difference between the right-hand and left-hand sides of Eq. (10).

This discrepancy could be explained by the incorrect use of  $pCO_2$  values in the mixed ocean layer in Eqs. (7) and (8) for microscopic distances from the interface boundary. This was also noted in [24]. The discrepancy can be eliminated by supposing the existence of a small minimum in the  $pCO_2$  profile and a maximum in the  $\delta^{13}C$  profile at microscopic distances of about 50  $\mu\text{m}$  from the water–air interface boundary, which correspond to the size of phytoplankton cells. These extrema must result from the activity of marine biota, which forms a resulting sink of atmospheric  $CO_2$  into the dissolved organic carbon of the ocean [5], and from the effect of  $^{13}C$  discrimination at the absorption of inorganic carbon by phytoplankton cells [25, 29]. In Eqs. (9) and (10), the equality of right-hand and left-hand sides is restored if we assume that  $\Delta(pCO_2)/(pCO_2)_0 = 0.20$  in the near-surface minimum as compared with the observed value (0.22) in the mixed layer [12–14], and  $\Delta\delta^{13}C_s = +0.5\%$  in the near-



**Fig. 3.** Profiles of changes in  $\text{CO}_2$  concentrations and  $\delta^{13}\text{C}$  at the transition from the atmosphere to ocean depth.

surface maximum as compared with  $-0.5\text{‰}$  in the mixed layer [28] (Fig. 3).

The formation of such extrema could be attained if a mere 5% of oceanic gross primary production were due to phytoplankton in direct contact with the interface boundary. This does not contradict the measured distribution of phytoplankton biomass with depth in the euphotic ocean layer [30, 31]. These extrema must be manifested after averaging the primary ocean productivity over seasonal changes and global ocean area, which is difficult to achieve at direct measurements of productivity. Because of this, the methods that are used for the determination of carbon uptake by the ocean from measurements of the difference of partial pressures in the atmosphere and the upper mixed layer of the ocean (which ignore the influence of marine biota and changes in the real  $\text{CO}_2$  profile at microscopic distances from the interface boundary) result in large errors and an underestimation of the total oceanic sink of carbon by several orders of magnitude.

## CONCLUSIONS

The global carbon budget was never obtained in a closed form with an adequate degree of reliability [4]. The influence of terrestrial and marine biota on the  $\text{CO}_2$  concentration in the atmosphere remained unknown [4, 6]. Ignoring the influence of marine biota resulted in the appearance of a "missing carbon sink" problem [2–4]. It was shown that the cultivation of land territories is an extensive carbon source for the atmosphere because of the excess of the decomposition of organic matter over its synthesis (primary production) [4, 11]. Less assimilated territories, which are represented mainly by the

boreal forests of Russia and Canada, are, according to direct estimates, capable of absorbing no more than one third of carbon emitted in habituated (cultivated) areas [4, 6, 9, 10].

Fossil fuel is burnt mainly in the northern hemisphere. This results in a concentration gradient in atmospheric carbon dioxide between the two hemispheres. The observed gradient is lower than that predicted by the models of interhemispheric mixing in the atmosphere and ocean [6]. This contradiction is eliminated in [6, 10] by the assumption of the existence of additional biotic carbon sinks in the northern hemisphere. These sinks are assigned to unknown terrestrial regions, whose absorption capacity is twice as high as the carbon emission in habituated (cultivated) territories [10]. However, there is no indication of specific terrestrial ecosystems that could be responsible for such a considerable value of atmospheric carbon uptake [11]. Thus, the extent of interhemispheric mixing is probably higher than that predicted by the models of [6, 10].

In general, marine biota is much less disturbed by anthropogenic activity than terrestrial biota. The reliably known stability of the global environment in the past millennia, when the anthropogenic impact was weak, means that the marine biota together with the undisturbed terrestrial biota of the past contributed comparably to the stabilization of the global environment [3, 4]. The cultivation of terrestrial biota could only decrease its compensation capacity of environmental disturbances. The present-day response of marine biota to the increase in the concentration of atmospheric  $\text{CO}_2$  cannot be much lower than that of terrestrial biota, which is strongly distorted by anthropogenic activity. This is supported by our studies.

Our study demonstrated the consistency of recent  $\text{CO}_2$  and  $\text{O}_2$  measurement in the atmosphere with the value of carbon uptake by the ocean in organic and inorganic forms obtained from  $^{13}\text{C}/^{12}\text{C}$  [2, 7] and  $^{14}\text{C}/^{12}\text{C}$  values [5]. The carbon uptake is twice as high as the estimated total carbon discharge by terrestrial biota (emission in cultivated areas minus uptake in boreal forests). The total ocean uptake of atmospheric carbon (abiotic owing to the tendency toward physicochemical equilibrium and biotic owing to the response of marine biota) increases proportionally to the departure of the atmospheric  $\text{CO}_2$  concentration from the equilibrium preindustrial level. Now, it has attained a value comparable with carbon discharge due to fossil fuel combustion. Accounting for the influence of marine biota closes the global carbon budget and resolves the dilemma of the "missing carbon sink."

The traditional estimates of carbon flux on the basis of measurements of the difference of  $\text{CO}_2$  partial pressures and  $\delta^{13}\text{C}$  in the atmosphere and the surface mixed oceanic layer do not account for the biotic changes in the profiles of  $\text{CO}_2$  and  $\delta^{13}\text{C}$  in the microscopic near-surface layer. This results in contradictions between the

changes in the concentration of dissolved organic and inorganic carbon in the ocean calculated from measured  $^{13}\text{C}/^{12}\text{C}$  and  $^{14}\text{C}/^{12}\text{C}$  values. Accounting for carbon absorption by marine biota reveals small extrema of  $p\text{CO}_2$  and  $\delta^{13}\text{C}$  at microscopic distances from the interface boundary comparable with the size of phytoplankton cells. The existence of these extrema, which are difficult to detect, eliminates the contradictions between the results obtained by various techniques for the determination of atmospheric carbon uptake by the ocean. The necessary magnitudes of the extrema are attained if 5% of oceanic gross primary production is produced by phytoplankton cells in direct contact with the interface boundary. This is consistent with the observed distribution of the phytoplankton biomass with depth in the euphotic layer of the ocean.

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### APPENDIX

The rate of  $^{12}\text{C}$  and  $^{13}\text{C}$  mass changes in the ocean depths must be equal to the net flux of these isotopes from the atmosphere to the ocean (or vice versa) through the interface boundary (Eq. (8)). This yields the following relations:

$$\frac{d}{dt}({}^vM_s^- + {}^vM_s^+) = {}^vG_{a0} \left\{ \frac{(p^v\text{CO}_2)_a}{(p^v\text{CO}_2)_{a0}} - \frac{(p^v\text{CO}_2)_{ml}}{(p^v\text{CO}_2)_{ml0}} \right\}, \quad (\text{A1})$$

$${}^vG_{a0} = S_s K \alpha_{ml} (p^v\text{CO}_2)_{a0}, \quad (\text{A2})$$

where  ${}^vM_s^-$  and  ${}^vM_s^+$  are the masses of the isotope  ${}^v\text{C}$  in DIC and DOC, respectively;  $(p^v\text{CO}_2)_a$  and  $(p^v\text{CO}_2)_{ml}$  are the  ${}^v\text{CO}_2$  partial pressures in the atmosphere and the mixed ocean layer, respectively;  $(p^v\text{CO}_2)_{a0} = (p^v\text{CO}_2)_{ml0}$  are the equilibrium preindustrial values of these parameters;  ${}^vG_{a0}$  is the equilibrium gross flux of carbon isotopes from the atmosphere to the ocean (and back);  $S_s$  is the ocean surface area (interface boundary);  $K$  is the coefficient of  $\text{CO}_2$  passage through the interface boundary; and  $\alpha_{ml}$  is the  $\text{CO}_2$  solubility in the upper mixed layer.

In order to derive Eq. (10) for  $^{13}\text{C}$ , let us introduce the following designations:

$$\Delta(p^v\text{CO}_2)_k \equiv (p^v\text{CO}_2)_k - (p^v\text{CO}_2)_{k0}, \quad k = a, ml, \quad (\text{A3})$$

$$\delta_k \equiv \frac{(^{13}\text{C}/^{12}\text{C})_k}{(^{13}\text{C}/^{12}\text{C})_B} - 1, \quad R_B \equiv \left( \frac{^{13}\text{C}}{^{12}\text{C}} \right)_B, \quad (\text{A4})$$

$$\Delta\delta_k \equiv \delta_k - \delta_{k0}, \quad (\text{A5})$$

where the subscript 0 denotes the equilibrium value and  $(^{13}\text{C}/^{12}\text{C})_B$  is the isotope ratio in the PDB standard.

Omitting the index  $v = 12$  for the main isotope  $^{12}\text{C}$ , we obtain for an equilibrium state

$$(p\text{CO}_2)_{a0} = (p\text{CO}_2)_{ml0} \equiv (p\text{CO}_2)_0, \quad (\text{A6})$$

$$(p^{13}\text{CO}_2)_{a0} = (p^{13}\text{CO}_2)_{ml0}. \quad (\text{A7})$$

Equations (A6) and (A7) yield for the equilibrium  $\delta_{k0}$  values (Eq. (A4))

$$\delta_{a0} = \delta_{ml0}. \quad (\text{A8})$$

Using the notation of Eq. (A3), Eq. (A1) for the main isotope can be presented in the form of Eq. (9):

$$(\dot{M}_s^- + \dot{M}_s^+)/G_{a0} = \frac{\Delta(p\text{CO}_2)_a}{(p\text{CO}_2)_0} - \frac{\Delta(p\text{CO}_2)_{ml}}{(p\text{CO}_2)_0}. \quad (\text{A9})$$

Using designations (A3)–(A5) and Eqs. (A6) and (A8) for the right-hand side of Eq. (A1) for the isotope  $^{13}\text{C}$ , we have the following relation:

$$G_{a0} R_B \left\{ (1 + \delta_{a0} + \Delta\delta_a) \left( 1 + \frac{\Delta(p\text{CO}_2)_a}{(p\text{CO}_2)_0} \right) - (1 + \delta_{ml0} + \Delta\delta_{ml}) \left( 1 + \frac{\Delta(p\text{CO}_2)_{ml}}{(p\text{CO}_2)_0} \right) \right\}. \quad (\text{A10})$$

Omitting terms that are quadratic in increments of Eqs. (A3) and (A5), relation (A10) becomes

$$G_{a0} R_B \left\{ \Delta\delta_a - \Delta\delta_{ml} + (1 + \delta_{a0}) \left[ \frac{\Delta(p\text{CO}_2)_a}{(p\text{CO}_2)_0} - \frac{\Delta(p\text{CO}_2)_{ml}}{(p\text{CO}_2)_0} \right] \right\}. \quad (\text{A11})$$

The left-hand side of Eq. (A1) for  $^{13}\text{C}$  is written as

$$\frac{d}{dt} R_B \{ (1 + \delta_s^-) M_s^- + (1 + \delta_s^+) M_s^+ \} = R_B \{ (1 + \delta_s^-) \dot{M}_s^- + (1 + \delta_s^+) \dot{M}_s^+ + M_s^- \dot{\delta}_s^- + M_s^+ \dot{\delta}_s^+ \}. \quad (\text{A12})$$

Expressing the latter term of Eq. (A11) through the left-hand side of Eq. (A9) and equating (A11) and (A12), we obtain Eq. (10).

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