

## The Possible Global Budget of Carbon Dioxide.

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**Summary.** — The possibility of fixation of excess atmospheric carbon (without its subsequent oxidation) by ocean phytoplankton is considered. This can result in an additional amount of carbon absorbed by the ocean equal to the amount of carbon ejected to the atmosphere at the expense of forest cutting. With the indicated mechanism in action, the concentration of atmospheric carbon dioxide should not exceed the preindustrial level by more than 40%.

### 1. - Introduction.

At present at the expense of mineral-fuel combustion (coal, oil, natural gas) the atmosphere gets 5 Gt C (1 Gt C =  $10^9$  t C gigaton of carbon) <sup>(1-3)</sup> as carbon dioxide. 2.3 Gt C/y of this amount are accumulated in the atmosphere, and about an equal amount is absorbed by the ocean as an inorganic substance <sup>(1,4,5)</sup>. The speed of inorganic carbonate accumulation on land remains, apparently, at the preindustrial level and is small (about 0.1 Gt C/y <sup>(6)</sup>).

(1) W. S. BROECKER, T. TAKAHASHI, H. J. SIMPSON and T.-H. PENG: *Science*, **206**, 409 (1979).

(2) G. M. WOODWELL, R. H. WHITTAKER, W. A. REINERS, G. E. LIKENS, C. C. DELWICHE and D. B. BOTKIN: *Science*, **199**, 141 (1978).

(3) G. M. WOODWELL: *Sci. Am.*, **238**, 34 (1978).

(4) H. OESCHGER, U. SIEGENTHALER, U. SCHOTTERER and A. GUGELMAN: *Tellus*, **27**, 168 (1975).

(5) U. SIEGENTHALER and H. OESCHGER: *Science*, **199**, 388 (1978).

(6) A. B. RONOV: *Geochimia*, **8**, 1252 (1976) (in Russian).

In the first approximation, the given estimates provide for the balance of carbon based on the law of conservation of matter. However, the analysis of the data on world forest cutting shows that an additional amount of carbon equal to  $(2 \div 18)$  Gt C/y (8 Gt C/y on the average) is ejected to the atmosphere <sup>(2,3,7)</sup>. But the ocean cannot absorb this additional amount of carbon in inorganic form <sup>(4,5)</sup>. If the latter estimate holds, a more effective mechanism for absorption of CO<sub>2</sub> from the atmosphere should exist as compared to the absorption of inorganic carbon by the ocean <sup>(2,3)</sup>.

Such a mechanism could be an enhancement of the synthesis of organic matter by marine phytoplankton at its constant oxidation by heterotrophs which takes place due to increasing concentration of CO<sub>2</sub> in the atmosphere and ocean surface layer with a fixed content of oxygen in them. With growing concentration of CO<sub>2</sub> in the atmosphere, the productivity of land and aquatic plants grows proportionally <sup>(8,9)</sup>. In the last hundred years, the CO<sub>2</sub> concentration in the atmosphere has increased by about  $(15 \div 20)$  % <sup>(1,2,10)</sup> (from  $(268 \div 290)$  p.p.m. in 1850 to 335 p.p.m. nowadays). The total production of marine phytoplankton is estimated to be  $(30 \div 50)$  Gt C/y <sup>(11-14)</sup>. An additional  $(15 \div 20)$  % increase of production constitutes  $(4 \div 10)$  Gt C/y and coincides with the amount of carbon ejected to the atmosphere due to forest cutting <sup>(2)</sup>. Increment of phytoplankton cell production may take place with simultaneous increase of consumption of other nutrient elements, nitrogen and phosphorus, in particular. An increase in extracellular excretion of phytoplankton, consisting mainly of carbohydrate organic compounds, can take place in oligotrophic waters even without any increase of phosphorus, nitrogen and silicon consumption.

## 2. - Reduction of the biomass of forests.

From statistical data, the global consumption of timber does not exceed 1 Gt C/y <sup>(2)</sup>. This quantity cannot indicate the amount of carbon received by

<sup>(7)</sup> R. A. KERR: *Science*, **208**, 1358 (1980).

<sup>(8)</sup> A. H. LAISK: *Kinetics of Photosynthesis and Photorespiration of C<sub>3</sub>-plants* (Moscow, 1977) (in Russian).

<sup>(9)</sup> V. LARCHER: *Ökologie der Pflanzen* (Stuttgart, 1976).

<sup>(10)</sup> M. STUIVER: *Science*, **199**, 253 (1977).

<sup>(11)</sup> S. V. BRUEVICH and V. J. IVANENKOV: *Okeanologia*, **11**, 835 (1971) (in Russian).

<sup>(12)</sup> C. G. N. DE VOOGS: *Primary production in aquatic environments*, in *The Global Carbon Cycle*, edited by B. BOLIN, E. T. DEGENS, S. KEMPE and P. KETNER (New York, N. Y., 1979), p. 259.

<sup>(13)</sup> G. E. FOGG: *Biochemical path ways in unicellular plants*, in *Photosynthesis and Productivity in Different Environments*, edited by J. P. COOPER (London, 1975), p. 437.

<sup>(14)</sup> T. PLATT and D. V. S. RAO: *Primary production of marine microphytes*, in *Photosynthesis and Productivity in Different Environments*, edited by J. P. COOPER (London, 1975), p. 249.

the atmosphere as a result of the reduction of forest areas. If total consumption took place in forest areas exploited for a long period by continuous cutting of rising trees, the biomass of forests would remain stable. The biomass is reduced only due to the expansion of exploited forest areas and their transformation into cultivated pastures and arable lands. When virgin forests are subjected to continuous all-round cutting of rising trees, the biomass of forests averaged over the period of ripening is halved<sup>(15)</sup>. With substitution of forests by arable lands and pastures having a 40-fold lesser biomass<sup>(16)</sup>, the total carbon of the forest biomass goes irretrievably to the atmosphere. Both these processes are accompanied by a decrease in the carbon content of the soil<sup>(2)</sup>. According to rather approximate global data, the forest areas have been reduced from  $(4.4 \div 4.9) \cdot 10^9$  hectares in 1950-1958<sup>(16,17)</sup> to  $(2.8 \div 3.0) \cdot 10^9$  hectares in 1978<sup>(2,18)</sup>, *i.e.* by  $(1.4 \div 2.1) \cdot 10^9$  hectares for the period 20  $\div$  30 years or at an average rate of  $(0.5 \div 1.1) \cdot 10^8$  hectares/y. An average biomass of forests constitutes 150 t C/hectare<sup>(2,3,16,17)</sup>. Transformation of virgin forests into cultivated lands would give a reduction of the forest biomass by  $(7.5 \div 11)$  Gt C/y, and into exploited forests by  $(4 \div 5)$  Gt C/y, *i.e.* the rate of enrichment of the atmosphere by carbon lies within  $(4 \div 11)$  Gt C/y (without regard to the reduction in the carbon content of soils). This estimate coincides with direct calculations of forest biomass reduction carried out by WOODWELL *et al.*<sup>(2)</sup>.

In the middle of our century, forest production constituted 70% of the total production on land<sup>(2,16)</sup>. Virgin forests' productivity is twice as high as compared to cultivated land<sup>(2,16)</sup>. Substitution of half the forest areas with half-productive plants has led to a 20% decrease of the total production on land, which could have been compensated with an increase in land production at the expense of atmospheric CO<sub>2</sub> concentration increased by the same amount.

However, even with the total increase of land production, its biomass does not grow, since an increase in production is totally compensated by its increasing oxidation due to excess atmospheric oxygen. Even extremely productive forests with their stable biomass are neither source nor sink of oxygen or carbon dioxide. The entire oxygen released by plants is immediately expended on plants and heterotrophs' respiration.

Extermination of all the forests will not change the oxygen content in the atmosphere, since the total amount of living biomass of the planet does not exceed  $10^3$  Gt C<sup>(2,16)</sup>, and the atmospheric oxygen supply constitutes  $10^6$  Gt O<sub>2</sub>.

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<sup>(15)</sup> F. H. BORMANN and G. E. LIKENS: *Pattern and Process in a Forested Ecosystem* (New York, N. Y., 1979).

<sup>(16)</sup> R. H. WHITTAKER: *Communities and Ecosystem* (New York, N. Y., 1975).

<sup>(17)</sup> P. DUVIGNEAND: *La synthèse écologique* (Paris, 1974).

<sup>(18)</sup> N. A. OSARA: *Trends and prospect of the world forests as renewable resources, IUBS XX General Assembly, Helsinki, August 19-27, 1979, KO250-26/G.*

There would not be a marked change in the oxygen content even upon combustion of all the fossil resources reaching  $10^4$  Gt C (<sup>5,19</sup>). Only oxidation of all the organic matter dispersively distributed in sedimentary rocks ( $\sim 5 \cdot 10^6$  Gt C) (<sup>6</sup>) can bound the entire atmospheric oxygen. Therefore, there is no oxygen problem. Only the  $\text{CO}_2$  problem exists.

### 3. - Primary production of the ocean.

The fixation reaction for carbon and other biogenes (bound nitrogen, phosphorus, silicon) is of fermentative character. It has been established empirically that the fixation rate for all the plants practically increases with increasing concentration of each biogene and carbon dioxide, with all the rest needed biogenes in excess (<sup>8,9</sup>). It means that saturation concentrations (Muchealis-Menten constants (<sup>8</sup>)) exceed those of corresponding substances in the environment. Therefore, for each limiting biogene the rates of its fixation in natural conditions obey simple laws of diffusion and can be represented as (<sup>8</sup>)

$$(1) \quad \left\{ \begin{array}{l} p = v^e([Y^e] - [Y^i]) = v^i([Y^i] - [Y^f]) = v^f[Y^f], \\ \text{or} \\ p = \frac{[X^e]}{R} = \frac{[X^e] - [X^i]}{r^e} = \frac{[X^i]}{r^i}, \quad R = r^e + r^i, \\ r^i = r^e + r^f, \quad r^{e,t} = \frac{\xi \zeta}{v^{e,t}}, \quad r^f = \frac{1}{v^f}, \quad v^{e,t} = \frac{D^{e,t}}{L^{e,t}}, \\ p = j(1 - \eta), \quad \zeta = \frac{\Delta \ln [X]}{\Delta \ln [Y]}, \quad \xi = \frac{[X]}{[Y]}, \quad \mathcal{P} = pS, \end{array} \right.$$

where  $p$ ,  $j$  and  $\eta$  are net, gross primary productivity and the ratio of plants respiration to gross productivity;  $S = 3.6 \cdot 10^{14}$  m<sup>2</sup> and  $\mathcal{P}$  are the aquatic area and net primary production of the world ocean; indices e, i and f characterize the external medium beyond functioning of all living organisms (e), on the outer surface of an aquatic plant (i) and in the centres of biochemical assimilation of elements (f);  $[Y]$  is the concentration of a compound which propagates in the external medium and inside the aquatic plant and contains the main part of the absorbed chemical element  $X$ ;  $[X]$  is the concentration of absorbed compound;  $D$ ,  $L$ ,  $v$  and  $r$  are diffusion coefficients (diffusivity), length, conductance and effective resistance, respectively (with e-index for the external medium,

(<sup>19</sup>) C. D. KEELING and R. B. BACASTOW: *Impact of industrial gases on climate*, in *Energy and Climate* (Washington, D. C., 1977).

with indices i, t, f inside an aquatic plant). An internal resistance  $r^i$  is the sum of the transport resistance of molecular diffusion  $r^t$  and (usually smaller in value) (\*) the resistance of biochemical assimilation of an element  $r^f$  (carboxylation resistance in the case of  $\text{CO}_2$  fixation).

During the synthesis of phytoplankton cell production, carbon, nitrogen and phosphorus are absorbed in the following ratio (20):

$$(2) \quad \text{C/N/P} = 106/16/1.$$

Concentrations of N (without the  $\text{N}_2$  dissolved gas) and P in the ocean, for which  $[Y] = [X]$ , decrease several times beginning from the depth of several hundred metres towards the surface (approximately tenfold for N and fivefold for P) (20). It means that the zone of oxidation of phytoplankton production by heterotrophs is hundreds of metres far from the surface zone of photosynthesis, and the main diffusion resistance is the external resistance  $r_N^e \simeq r_P^e \simeq L^e/D^e$ , which turns out to be much greater than the internal one ( $r_N^i \sim 0.1r^e$ ,  $r_P^i \sim 0.2r^e$ ). The  $[\text{N}]/[\text{P}]$  concentration ratio is 16 in deep ocean (20), therefore, the ratio of diffuse fluxes of these biogenes is close to the ratio in their absorption by phytoplankton (\*).

The mechanism for photosynthesis is the same for the plants of both the land and the ocean, and, therefore, the oceanic phytoplankton should absorb, like land plants, rather  $\text{CO}_2$  than the more numerous  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  ions (15,21).  $\text{CO}_2$  molar concentrations in the ocean are 3 times less than those of N (20), therefore, according to eq. (2), with diffusion of only  $\text{CO}_2$  molecules, carbon would have been the most deficient element in the ocean. Actually, the propagation of carbon from the oxidation zone to that of photosynthesis occurs by way of diffusion of all dissolved carbon-containing compounds:

$$[Y] = [\sum \text{CO}_2] = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2].$$

Therefore, the external and internal transport resistances to the effective propagation of molecules  $X = \text{CO}_2$ , in accordance with formula (1), happen

(20) A. IVANOV: *Introduction à la océanographie*, Vol. 1 (Paris, 1972), Vol. 2 (1975).

(\*) The difference in surface «pre-form» concentrations of N and P due to different internal resistances of their propagations in aquatic plants changes the total diffuse fluxes by values not exceeding twenty per cent:

$$(p_N/[N^e])/(p_P/[P^e]) = 1 + (r_P^i - r_N^i)/r^e \simeq 1 + 0.2$$

(note that phytoplankton absorbs more N, the relative concentration  $[\text{N}^i]/[\text{N}^e]$  of which near the surface is less than that of P).

(21) V. G. GORSHEKOV: *The possible balance of the carbon cycle*, *Collection of papers presented at the X Leningrad Workshop on Cosmophysics* (Leningrad, 1979).

to be  $(\xi\zeta)^{-1} = 20$  times less (the value of  $r_C^e$  being much greater than that of  $r_C^i$ , as in the case of N and P) (\*).

As a result, the ratio of diffuse fluxes  $p_C/p_N/p_P$  becomes close to relationship (2) needed to construct the cell production of phytoplankton, which in the process of species formation has adapted itself to the chemical possibilities of the ocean.

With excess  $\text{CO}_2$  concentration as compared to other biogenes, plants should possess the mechanism for liquidation of an excess synthesized primary organic product or for blocking its synthesis. Apparently, such a mechanism is photorespiration<sup>(22)</sup> for  $\text{C}_3$ -land plants and extra-cellular organic excretions for unicellular aquatic plants<sup>(13)</sup>. Both these mechanisms are additional energy expense on a plant. Therefore, the plant adapts itself to existing natural conditions in such a way that this expense be minimized. Most favourite is a situation in which all the elements are absorbed by plants in proportions provided for by the environment. In this case all the biogenes are similarly limiting, there is no need of the blocking mechanism and the assimilation of elements obeys the laws of diffusion (1).

At the expense of variations in cells' geometry during a time period needed for species formation, an internal resistance  $r_C^i$  can be selected, which would provide for equilibrium between the amounts of surface and atmospheric carbon dioxide ( $[\text{CO}_2^i] = \beta[\text{CO}_2]_{\text{atm}}$ ,  $\beta$  is  $\text{CO}_2$  solubility) and the absence of  $\text{CO}_2$  fixation flux from the atmosphere (otherwise, all the carbon could have left the atmosphere). The condition of the absence of net  $\text{CO}_2$  flux from the atmosphere

(\*) The amount of ocean primary production is totally determined by deep-water concentrations of  $[\text{CO}_2]$  or  $[\sum \text{CO}_2]$ ,  $[\text{N}]$  and  $[\text{P}]$ , and by the external resistance  $r^e = L^e/D^e$ , *i.e.* by the distance of the oxidation zone from that of photosynthesis  $L^e$ , minus a 75 m well-mixed surface layer, and the deep-water eddy diffusivity  $D^e$ . Measurements have given the following:

$$\begin{aligned} [\sum \text{CO}_2] &= 2.3 \text{ mol C/m}^3, & [\text{CO}_2^i] &= 1.2 \cdot 10^{-2} \text{ mol C/m}^3, \\ \xi = [\text{CO}_2^i]/[\sum \text{CO}_2] &= 0.5 \cdot 10^{-2}, & \zeta = d \ln [\text{CO}_2]/d \ln [\sum \text{CO}_2] &\simeq 10, \\ [\text{N}] &= 4 \cdot 10^{-2} \text{ mol N/m}^3, & [\text{P}] &= 2.5 \cdot 10^{-3} \text{ mol P/m}^3 \text{ (6,20)}, \\ L^e &= (75 \div 125) \text{ m}, & D^e &= 4 \cdot 10^3 \text{ m}^2/\text{y} \text{ (1,4,5,20)}, \end{aligned}$$

from which, using (1) and (2) in approximation of  $r_X^i = 0$ , we obtain

$$\begin{aligned} p_C/p_N/p_P &= [\sum \text{CO}_2] \xi^{-1}/[\text{N}]/[\text{P}] = 100/16/1, \\ r_C^e &= \xi h r^e \simeq r_C^i = r^e X [\text{CO}_2^i]/C[X], \quad X = \text{N, P} \end{aligned}$$

independent of  $r^e$ ,

$$p_C = [\text{CO}_2^i] D^e / L^e \xi \zeta = (8 \div 13) \text{ mol C/m}^2 \text{ y}$$

*i.e.*  $\mathcal{P}_O = (30 \div 50) \text{ Gt C/y}$  for all the aquatic area, which fits direct measurements of ocean production<sup>(11-14,16)</sup>. In the region of shelf and upwellings an increase in production is connected with decreasing  $r^e$  (*i.e.* decreasing  $L^e$  or increasing  $D^e$ ) and  $r_C^i$ .  
(22) I. ZELITCH: *Science*, **183**, 626 (1975).

to the ocean is provided for by the equality of interior ( $p_c^i$ ) and deep-water ( $p_c^e$ ) fluxes of carbon (1), which relates the atmospheric concentration of  $[\text{CO}_2]_{\text{atm}}$  to the deep-water concentrations of  $[\text{N}^e]$  and  $[\text{P}^e]$  in the following way:

$$[\text{CO}_2]_{\text{atm}} = [\text{N}^e] \frac{r_c^i}{\beta r^e} \left( \frac{\text{C}}{\text{N}} \right) = [\text{P}^e] \frac{r_c^i}{\beta r^e} \left( \frac{\text{C}}{\text{P}} \right),$$

where C/N and C/P are the ratios of the contents of elements in phytoplankton cells. This relationship should have been also preserved in the period of paleoclimate.

#### 4. - Possible atmospheric $\text{CO}_2$ flux sinking to the ocean in organic form.

With a sudden increase of  $[\text{CO}_2]_{\text{atm}}$  the flux of  $\text{CO}_2$  fixation by phytoplankton should increase at the expense of  $\text{CO}_2$  flux from the atmosphere expressed as follows:

$$(3) \quad \delta p_c^a = \frac{\beta}{r_c^a + r_c^i} \delta [\text{CO}_2]_{\text{atm}},$$

where  $r_c^a$  is the external resistance of  $\text{CO}_2$  coming from the atmosphere. The main part of  $r_c^a \simeq L^a/D^a$  is the resistance of molecular diffusion ( $D^a \simeq 3 \cdot 10^{-2} \text{ m}^2/\text{y}$ ) through the surface film  $L^a \simeq 30 \mu\text{m}$  thick<sup>(1,23)</sup>. An increase in  $\text{CO}_2$  flux from the oxidation zone due to the accelerated destruction of organic matter is impossible because of the stationary character of the oxygen flux to the oxidation zone. Additionally produced oxygen, due to photosynthesis enhancement, propagates deep into the ocean ( $\delta p_o^e = \delta [\text{O}_2]/r_o^e$ ,  $r_o^e = r^e$ ) and in the atmosphere ( $\delta p_o^a = \delta [\text{O}_2]/r_o^a$ ,  $r_o^a \sim r_c^a$ <sup>(\*)</sup>). Due to the relationship  $\delta p_o^e/\delta p_o^a = r_o^a/r_o^e \ll 1$ , practically all the additionally produced oxygen will come to the atmosphere.  $L^e$  is assumed to remain constant with changing  $[\text{CO}_2]_{\text{atm}}$ .

The value  $2r_o^a \simeq r_c^e = r^e \xi \zeta \simeq r_c^i$ <sup>(\*)</sup>,  $\beta \sim 1$ <sup>(23)</sup>, therefore, according to eqs. (1) and (3), the following relationship holds:

$$(4) \quad \delta p_c^a/p_c = \varepsilon \frac{\delta [\text{CO}_2]_{\text{atm}}}{[\text{CO}_2]_{\text{atm}}}, \quad \varepsilon = \frac{r_c^i}{r_c^a + r_c^i} \sim 1,$$

which provides for a proportional increment of production with increasing content of atmospheric carbon dioxide.

Formation of additional  $\text{CO}_2$  flux from the atmosphere leads to breaking the relationships  $p_c/p_N/p_P$  (3). The primary carbohydrate product of photo-

<sup>(23)</sup> W. S. BROECKER and T.-H. PENG: *Tellus*, **26**, 21 (1974).

<sup>(\*)</sup> This relationship comes from the fact that the maximum possible carbon flux from the atmosphere, with the existing  $[\text{CO}_2]_{\text{atm}}$  equal to  $19 \text{ mol C/m}^2$ <sup>(6)</sup>, coincides with the doubled magnitude of the ocean production; probably, this coincidence determines the order of magnitude of  $L^e$  in the ocean.

synthesis  $p_c$  breaks into two parts:  $p_c^{\text{cell}} + p_c^{\text{excr}}$ . The  $p_c^{\text{cell}}$  part corresponding to eq. (3) is used for cell production. Another part,  $p_c^{\text{excr}}$ , for which stationary N and P fluxes are insufficient, should excrete from an aquatic plant and increase the amount of dissolved and particulate organic carbon (DOC and POC) in the ocean. Estimates show that at present the excreted production of oceanic phytoplankton constitutes  $\sim 20\%$  of the total production (<sup>12,13</sup>). With growing concentration of  $\text{CO}_2$  in the ocean, under the influence of increasing concentration of atmospheric carbon dioxide and with constant concentrations of N and P, the production of phytoplankton should increase proportionally (1), (4) at the expense of the increasing share of excretions (\*). Probably, excretions in the preindustrial time period had been zero, and the presently observed share of excretions ( $\sim 20\%$ ) results from the rise of atmospheric  $\text{CO}_2$  by  $(15 \div 20)\%$ .

With decreasing  $[\text{CO}_2]_{\text{atm}}$  the production of phytoplankton decreases, and heterotrophs (apparently, mainly bacterioplankton that should be depressed by other heterotrophs in the abundance of primary production) must compensate for the shortage in primary production by oxidation of DOC, which leads to conversion of a share of DOC to the atmospheric  $\text{CO}_2$ . Thus DOC, with life existing in the ocean, is functioning as an organic buffer smoothing  $\text{CO}_2$  variations in the atmosphere.

## 5. - Carbon isotopic budget.

As a result of growing concentration of atmospheric carbonic acid, the additionally synthesized organic carbon (ASOC) should have been transformed into oceanic DOC and POC. The recent data on the age and distribution of DOC and POC do not contradict the existence of an organic sink of atmospheric  $\text{CO}_2$  to the ocean (<sup>25-28</sup>). During the last 20 years about  $10^2$  Gt C of ASOC,

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(\*) Generally, it is possible an increase in cell production (not more than by  $(10 \div 20)\%$ ) with growing  $[\text{CO}_2]$  and constant  $[\text{N}]$  and  $[\text{P}]$  on the rather artificial assumption (though not contradictory to the available factors) that  $r_{\text{N,P}}^1$  and, consequently,  $[\text{N}^1]$  and  $[\text{P}^1]$  decrease by  $(2 \div 3)$  times with  $[\text{CO}_2]$  increasing by  $10\%$  (<sup>21,24</sup>).

(<sup>24</sup>) V. G. GORSHKOV: *On the role of the terrestrial and marine biota in the global carbon budget*, Leningrad Nuclear Physics Institute, No. 534 (November, 1979).

(<sup>25</sup>) M. E. ARHELGER, P. J. KINNEY, T. LINICK and P. M. WILLIAMS: *The radiocarbon activity of the dissolved and particulate organic carbon in the Northeastern Pacific ocean*, UCSB 10P20-169, IMR Prog. Res. on Mar. Food Ch. (June, 1974).

(<sup>26</sup>) K. MOPPER and E. T. DEGENS: *Organic carbon in the ocean: nature and cycling*, in *The Global Carbon Cycle*, edited by B. BOLIN, E. T. DEGENS, S. KEMPE and P. KETNER (New York, N. Y., 1979).

(<sup>27</sup>) R. NYDAL, K. LÖVSETH and S. GULLIKSEN: *A survey of radiocarbon variation in nature since the Test Ban Treaty*, in *Proceedings of the IX International Radiocarbon Conference, University of California, Los Angeles and San Diego, June 20-26, 1976*.

(<sup>28</sup>) P. W. WILLIAMS, M. C. STEINHOUSE, E. U. DRUFFEL and M. KOIDE: *Nature (London)*, **276**, 698 (1978).



young as for the content of  $^{14}\text{C}$ , should have been accumulated, which constitutes about 10% of the total DOC, whose pool and age are  $1 \cdot 10^3$  Gt C and  $3 \cdot 10^3$  years, respectively ( $^{25,28}$ ) (\*).

The balance of carbon isotopes  $^{13}\text{C}$  and  $^{14}\text{C}$  gives additional information about the rate of change of the biomass of the biosphere and carbon fluxes to the ocean. This information can be obtained from measurements of the difference of the isotope contents in various objects. Let us consider the content ( ${}^iC_i$ ) of isotopes (i) in three reservoirs (l): the atmosphere (a), the biosphere (b), and the fossil fuel (f). The relative difference between the isotopic ratio of sample  $R^i$  and that of the international standard  $R_s^i$  is determined by the quantities ( $^{10,25}$ )

$$\delta^i C = \frac{R^i - R_s^i}{R_s^i}, \quad R^i = \frac{{}^iC}{{}^{12}C}, \quad \delta^i C_a - \delta^i C_b = \sigma^i \ll 1.$$

Let the preindustrial  ${}^iC_a$  content in the atmosphere be  ${}^iC_{a0}$ :

$${}^{12}C_{a0} = 590 \text{ Gt C } (\approx 280 \text{ p.p.m.}) \text{ } (^{1,10}).$$

We determine the amount of carbon isotopes ejected from reservoirs l and accumulated in atmosphere ( $\Delta^i C_i$ ) in the following way:

$$(5) \quad \Delta^{12} C_i \equiv \varepsilon_i {}^{12}C_0, \quad \Delta^i C_i \equiv R_i^i \varepsilon_i {}^{12}C_0, \quad \varepsilon_i \ll 1.$$

Here we may neglect temporal variations of  $R_b^i$ , since it is a quantity of higher order of smallness. There is no  $^{14}\text{C}$  isotope in the fossil fuel, and, therefore,  $\Delta^{14} C_f = R_f^{14} = 0$ . The present-day value of  $R_a^{14}$  for the atmosphere is determined from the relationship

$$(6) \quad R_a^{14} = \frac{{}^{14}C_0 + \Delta^{14} C_b}{{}^{12}C_0 + \Delta^{12} C_b + \Delta^{12} C_f} = \frac{{}^{12}C_0 R_0^{14} + {}^{12}C_0 \varepsilon_b R_b^{14}}{{}^{12}C_0 + \varepsilon_b {}^{12}C_0 + \varepsilon_f {}^{12}C_0} = \\ = R_0^{14} \frac{1 + \varepsilon_b - \varepsilon_b \sigma_{14}}{1 + \varepsilon_b + \varepsilon_f} \approx R_0^{14} (1 - \varepsilon_f).$$

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(\*) In the 75 m surface mixed layer, concentration  $[\text{DOC}]_s \approx 0.9 \text{ gC/m}^3$ , the content is about 25 Gt C, the age is about 200 y ( $^{25,26,28}$ ). At a depth of 200 m  $[\text{DOC}]_d = 0.6 \text{ gC/m}^3$  ( $^{25,26}$ ). The amount of pure DOC flux into deep waters is  $([\text{DOC}]_s - [\text{DOC}]_d)/r^o \approx (4 \div 8) \text{ Gt C/y}$ , which is close to the flux of ASOC. The total flux of « young » DOC to deep waters can reach  $[\text{DOC}]_s/r^o = (10 \div 20) \text{ Gt C/y}$ , it can be substantially compensated for by the flux of « old » DOC from deep waters, which leads to an old age of DOC in the surface layer. The relationship C/N/P (2) for DOC has not yet been established ( $^{26}$ ), C/P varies from 100 to 600 (1). With the above-mentioned mechanism in action, the share of carbon in DOC should be several tens of per cent greater than in the cells of phytoplankton (2).

The latter equation is written to an accuracy of the first order for small values  $\sigma_i \sim \varepsilon_i \ll 1$ . As is seen from eq. (6), the  $R_a^{14}$  value decreases due to ejection into the atmosphere of fossil carbon, which does not contain  $^{14}\text{C}$  (Suess effect) <sup>(1,10,29)</sup>. The value of  $\varepsilon_t$  (in 1950  $\varepsilon_t = (2 \pm 0.3)\%$  and in 1970  $\varepsilon_t = 3.9\%$  <sup>(10)</sup>) corresponds to the share of fossil carbon preserved in the atmosphere. With the known total content of carbon ejected to the atmosphere as a result of fossil-fuel combustion,  $^{12}\text{C}_t = E_t \cdot ^{12}\text{C}_{a0}$  ( $^{12}\text{C}_t = 60 \text{ Gt C}$  in 1950,  $^{12}\text{C}_t = 120 \text{ Gt C}$  in 1970 <sup>(10)</sup>), we can find the exchange coefficient  $\kappa$

$$(7) \quad \kappa = \frac{E_t}{\varepsilon_t} = \frac{E_b}{\varepsilon_b} \simeq 5,$$

which determines what amount of atoms of carbon ejected to the atmosphere remains there considering the exchange with the ocean and the biosphere. The exchange processes are similar for carbon of any source, and, therefore, the amount of carbon ejected from the biosphere ( $^{12}\text{C}_b = E_b \cdot ^{12}\text{C}_{a0}$ ) is connected with the amount of carbon accumulated in the atmosphere ( $^{12}\text{C}_b = \varepsilon_b \cdot ^{12}\text{C}_{a0}$ ) with the same exchange coefficient  $\kappa$  (7). With the  $\kappa$ -coefficient known, one can determine the value of  $E_b$  from measured  $\varepsilon_t$  and known  $E_t$ , if one succeeds in determining the  $\varepsilon_b$  value. The latter can be found from measurements of the present-day value of  $R_a^{13}$ . Similarly to (6), we obtain

$$(8) \quad R_a^{13} = \frac{^{13}\text{C}_0 + \Delta \cdot ^{13}\text{C}_b + \Delta \cdot ^{13}\text{C}_t}{^{12}\text{C}_0 + \Delta \cdot ^{12}\text{C}_b + \Delta \cdot ^{12}\text{C}_t} = R_0^{13} \frac{1 + \varepsilon_b + \varepsilon_t - (\varepsilon_b + \varepsilon_t)\sigma_{13}}{1 + \varepsilon_b + \varepsilon_t} = R_0^{13} [1 - (\varepsilon_b + \varepsilon_t)\sigma_{13}].$$

Bearing in mind that at constant  $\sigma_{13}$  (5)  $R_a^{13} - R_0^{13} = R_b^{13} - R_{b0}^{13}$ , where  $R_{b0}^{13}$  is the preindustrial biospheric value, relationship (8) in the first nonvanishing approximation can be rewritten as <sup>(10,30)</sup>

$$(9) \quad \delta^{13}\text{C}_b - \delta^{13}\text{C}_{b0} = \frac{R_b^{13} - R_{b0}^{13}}{R_0^{13}} = -(\varepsilon_b + \varepsilon_t)\sigma_{13}.$$

Direct measurements of the left-hand part of (9) in tree rings and the known  $\varepsilon_t$  value permit the determination of  $\varepsilon_b$  from (9).

The analysis performed by STUIVER <sup>(10)</sup> shows that  $\varepsilon_b \geq \varepsilon_t$  up to the middle of our century, and  $\varepsilon_b < \varepsilon_t$  at present.

<sup>(29)</sup> C. D. KEELING: *The carbon dioxide cycle*, in *Chemistry of the Lower Atmosphere* (New York, N. Y., 1973), p. 251.

<sup>(30)</sup> C. D. KEELING, W. G. MOOK and P. P. TANS: *Nature (London)*, **277**, 121 (1979).

The above-given considerations hold only in the case in which carbon ejected to the atmosphere continues the free circulation through all the reservoirs and does not leave the cycle as fixed formations. It is clear that, when organic matter is simply transferred from terrestrial biota into the deep sea without entering the atmosphere, the latter will not evidently contain any information about the process involved. This hypothetical case differs from that under consideration (biospheric carbon comes to the atmosphere, then is fixed by phytoplankton and deposits in deep ocean) by the fact that in the first case the ocean contains a transferred organic pool with a preindustrial value of  $R_{b0}^{13}$ , and in the second case it would contain the absorbed organic matter with the present value of  $R_b^{13}$ . In both cases the content of  $^{12}\text{C}$  isotope does not vary, and the denominator in (8) is also the same. The difference of the  $^{13}\text{C}$  isotope contents in the additional organic matter of the ocean in both these cases is  $(R_b^{13} - R_{b0}^{13}) E_b^{12} C_{a0}$ . The latter value should be added to the numerator in the first equation of (8). This leads in (9) to an additional term  $(R_b^{13} - R_{b0}^{13}) \varepsilon_b / R_{a0}^{13}$  of a higher order of smallness, which has been neglected. Therefore, the proposed mechanism for carbon uptake from the atmosphere by phytoplankton should not affect variations of the isotope content in tree rings.

## 6. – Forecasting the change of carbon-dioxide concentration in the atmosphere.

The existence of the sink of organic carbon to the ocean changes the available forecasts of  $\text{CO}_2$  content variations in the atmosphere<sup>(5,19,31)</sup>.

Variations of the content of carbon dioxide in the atmosphere are described by the relationship

$$(10) \quad \frac{dC}{dt} = A - J,$$

where  $A$  is the source and  $J$  is the sink of carbon dioxide. Combustion of fossil fuel and reduction of unexploited forest areas are the source of carbon dioxide<sup>(2)</sup>. The energy of fossil fuel is spent on consumption of biosphere's resources which approaches saturation<sup>(32)</sup>. Regardless of fossil-fuel supplies, the energy consumption should approach saturation, and the extrapolation of the observed exponential increase to the future<sup>(5,19,31,33)</sup> is groundless. An increase of exploited forest areas is limited due to the limited stock of forest. Therefore, the temporal de-

<sup>(31)</sup> R. REVELLE and W. MUNK: *The carbon dioxide cycle and the biosphere*, in *Energy and Climate* (Washington, D. C., 1977).

<sup>(32)</sup> V. G. GORSHKOV and V. R. DOLNIK: *Sov. Phys. Usp.*, **23**, 386 (1980).

<sup>(33)</sup> M. I. BUDYKO, E. N. BYUTNER, K. YA. VINNIKOV, G. S. GOLITSYN, O. A. DROZDOV and I. A. KAROL: *Meteorol. Gidrol.*, **8**, 5 (1981) (in Russian).

pendence of the source  $A$  should be naturally described by a logistic curve

$$(11) \quad A = \frac{A_{\max}}{1 + \exp[-\alpha t]}, \quad A_{\max} = 21 \text{ Gt C/y}, \quad \alpha = 0.031 \text{ y}^{-1},$$

where the point  $t = 0$  corresponds to 1970 (it is chosen from the coincidence of the solution for (10) with the observed value — 322 p.p.m.); a saturation value of  $A_{\max}$  is chosen from  $A(0) = A_{\max}/2 = 10.5 \text{ Gt C/y}$  (4.0 Gt C/y from fossil-fuel combustion<sup>(5,19,31)</sup> and 6.5 Gt C/y from forest area reduction<sup>(2)</sup>, the latter figure is equal approximately to  $0.15 \cdot 43 \text{ Gt C/y}$  (0.15 is increment of carbon-dioxide concentration<sup>(1,2,10)</sup>, 43 Gt C/y is the primary production of the ocean<sup>(12)</sup>); the  $\alpha$ -parameter at fixed  $A(0)$  has been found from the observed derivative of the solution at  $t = 0$ , it is close to the rate of exponential increase of the use of wood timber, which at present, apparently, determines the greater portion of carbon ejection to the atmosphere.

The sinking of atmospheric carbon dioxide is determined by  $\text{CO}_2$  absorption by the ocean

$$(12) \quad J = \mathcal{P}_0 \frac{C - C_0}{C_0}, \quad \mathcal{P}_0 = 55 \text{ Gt C/y}, \quad C_0 = 590 \text{ Gt C} (= 280 \text{ p.p.m.}),$$

where  $C_0$  is the preindustrial  $\text{CO}_2$  content in the atmosphere (the average of two published extreme values 268 p.p.m.<sup>(10)</sup> and 292 p.p.m.<sup>(1,5)</sup>; 1 p.p.m. corresponds to 2.1 Gt C);  $\mathcal{P}$  is the sum ( $\mathcal{P}_0^{\text{org}} + \mathcal{P}_0^{\text{inorg}}$ ) of ocean primary production ( $\mathcal{P}_0^{\text{org}} = 43 \text{ Gt C/year}$ <sup>(12)</sup>) and a portion

$$\mathcal{P}_0^{\text{inorg}} = C_0 J^{\text{inorg}} / (C - C_0) \simeq 12 \text{ Gt C/y} \sim [\text{CO}_2] S / r_c^*, \quad r_c^* \simeq \xi h / \sqrt{D^*} \alpha,$$

corresponding to the absorption of  $\text{CO}_2$  by the ocean as inorganic matter (obtained from the present value of inorganic absorption 2.0 Gt C/y<sup>(1,5,10,19)</sup> and the present—1978—18% excess of carbon dioxide above the preindustrial level<sup>(1,5,10)</sup> in the approximation that absorption increases proportionally to the excess  $\text{CO}_2$  concentration).

Using eqs. (11), (12) and (10), we obtain

$$(13) \quad \left\{ \begin{array}{l} \frac{dx}{dt} = \frac{a}{1+z} - bx, \quad x = \frac{C - C_0}{C_0}, \\ a = \frac{A_{\max}}{C_0} = 0.036 \text{ y}^{-1}, \quad b = \frac{\mathcal{P}_0}{C_0} = 0.093 \text{ y}^{-1} \simeq 3\alpha, \\ z = \exp[-\alpha t], \\ x = \frac{a}{b} \left\{ 1 - \frac{3}{2}z + 3z^2 \left[ 1 - z \ln \left( 1 + \frac{1}{z} \right) \right] \right\}, \quad \frac{a}{b} = 0.38. \end{array} \right.$$

Figure 1 shows the time behaviour of the solution of eq. (13) and the source function of (11). An asymptotic value of concentration corresponds to a 40% increment, *i.e.*  $C_{\max} = 390$  p.p.m. Values close to this figure will be reached in the next century (\*).

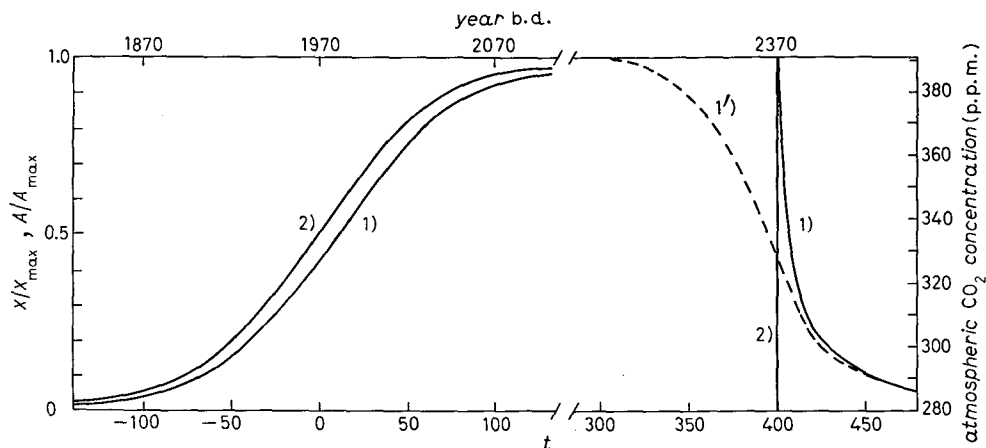


Fig. 1. — Temporal variations of carbon dioxide concentration in the atmosphere.  $t = \text{year b.d.} - 1970$ . Curve 1) the relative increment of atmospheric carbon dioxide (left scale of ordinates), the relative atmospheric  $\text{CO}_2$  concentration (right scale of ordinates); curve 2) the relative temporal variation of the source  $A$  (11) (left scale of ordinates). The end of curves 1) and 2) is obtained for constant source function  $A$  at its asymptotic value till depletion of exploitable fossil fuel and wood reserves estimated as  $7 \cdot 10^3$  GtC and  $8 \cdot 10^3$  GtC, respectively. Broken line 1) is the possible real behaviour of curve 1).

Upon depletion of fossil-fuel deposits, *i.e.* in several hundreds of years, the  $A$ -function (11) should become zero, and the concentration of atmospheric carbon dioxide should return to the preindustrial value, since the DOC supply in the ocean can easily increase several times. On the contrary, when the ocean

(\*) For  $b \neq n\alpha$  ( $n$  is an integer number), the solution is expressed with the hypergeometric function without changing the characteristic pattern shown in fig. 1. With a fixed parameter of the source's increase  $\alpha$ , the values  $A_{\max} = 21$  Gt C/y and  $t = 0$  (1970) give the observed value of the present concentration (335 p.p.m. in 1978) and the mean rate of concentration growth (0.3%/y in 1965-1975). The time period needed to reach equilibrium and determined by the  $\alpha^{-1}$ -parameter grows shorter with increasing  $\alpha$ . At fixed observed  $x(0)$  and  $x'(0)$ ,  $A_{\max}$  should decrease with increasing  $\alpha$ . When  $\alpha < 0.03 \text{ y}^{-1}$ , it leads to highly over-estimated values of  $A(0) = A_{\max}/2$ . For  $\alpha = 0.045 \text{ y}^{-1}$  (the rate of increase of energy consumption) we obtain  $A_{\max} = 16$  Gt C/y,  $t = 0$  (1955),  $a/b = 0.30$ ,  $C_{\max} = 360$  p.p.m. Therefore,  $C_{\max} = 390$  p.p.m. given in fig. 1 should be considered as an upper limit.

absorbs only inorganic carbon, about 20% of ejected carbon remains for ever in the atmosphere due to the buffer nature of absorption of inorganic carbon by the ocean <sup>(4,22,24)</sup> (\*).

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(\*) Carbon supply in the ocean ( $C_{oc}$ ) is 60 times greater than that in the atmosphere ( $C_a$ ). When an amount  $\delta C = \delta C_a + \delta C_{oc}$  is ejected to the atmosphere, upon reaching the stationary state the ocean should receive  $\delta C_{oc} = \zeta^{-1}(C_{oc}/C_a) \delta C_a \sim \zeta^{-1} 60 \delta C_a \sim 4 \delta C_a$  (for  $\zeta \sim 15$  <sup>(5)</sup>), i.e. 80% of the ejected carbon is absorbed by the ocean, and 20% remains in the atmosphere.

● RIASSUNTO (\*)

Si considera la possibilità di fissazione di carbone atmosferico in eccesso (senza successiva ossidazione) mediante il fitoplancton dell'oceano. Questa può risolversi in una quantità addizionale di carbone assorbito dall'oceano uguale alla quantità di carbone espulso nell'atmosfera a causa del disboscamento. Con il meccanismo indicato in azione, la concentrazione di anidride carbonica atmosferica non dovrebbe eccedere il livello preindustriale più del 40%.

(\*) *Traduzione a cura della Redazione.*

**Резюме.** — Рассмотрена возможность фиксации избытка атмосферного углерода (без его последующего окисления) морским фитопланктоном. Показано, что этот процесс может дать величину добавочного поглощения углерода океаном, совпадающего с количеством углерода, выбрасываемого в атмосферу вследствие сокращения лесов. При действии этого механизма концентрация атмосферной двуокиси углерода не должна превысить преиндустриальный уровень более, чем на 40%.