

# Carbon Dioxide Exchange Between Atmosphere and Ocean and the Question of an Increase of Atmospheric CO<sub>2</sub> during the Past Decades

Roger Revelle & Hans E. Suess

To cite this article: Roger Revelle & Hans E. Suess (1957) Carbon Dioxide Exchange Between Atmosphere and Ocean and the Question of an Increase of Atmospheric CO<sub>2</sub> during the Past Decades, Tellus, 9:1, 18-27, DOI: [10.3402/tellusa.v9i1.9075](https://doi.org/10.3402/tellusa.v9i1.9075)

To link to this article: <https://doi.org/10.3402/tellusa.v9i1.9075>



© 1957 The Author(s). Published by Taylor and Francis Group LLC



Published online: 15 Dec 2016.



Submit your article to this journal [↗](#)



Article views: 1351



View related articles [↗](#)

# Carbon Dioxide Exchange Between Atmosphere and Ocean and the Question of an Increase of Atmospheric CO<sub>2</sub> during the Past Decades

By ROGER REVELLE and HANS E. SUESS, Scripps Institution of Oceanography, University of California, La Jolla, California

(Manuscript received September 4, 1956)

## *Abstract*

From a comparison of C<sup>14</sup>/C<sup>12</sup> and C<sup>13</sup>/C<sup>12</sup> ratios in wood and in marine material and from a slight decrease of the C<sup>14</sup> concentration in terrestrial plants over the past 50 years it can be concluded that the average lifetime of a CO<sub>2</sub> molecule in the atmosphere before it is dissolved into the sea is of the order of 10 years. This means that most of the CO<sub>2</sub> released by artificial fuel combustion since the beginning of the industrial revolution must have been absorbed by the oceans. The increase of atmospheric CO<sub>2</sub> from this cause is at present small but may become significant during future decades if industrial fuel combustion continues to rise exponentially.

Present data on the total amount of CO<sub>2</sub> in the atmosphere, on the rates and mechanisms of exchange, and on possible fluctuations in terrestrial and marine organic carbon, are inadequate for accurate measurement of future changes in atmospheric CO<sub>2</sub>. An opportunity exists during the International Geophysical Year to obtain much of the necessary information.

## **Introduction**

In the middle of the 19th century appreciable amounts of carbon dioxide began to be added to the atmosphere through the combustion of fossil fuels. The rate of combustion has continually increased so that at the present time the annual increment from this source is nearly 0.4 % of the total atmospheric carbon dioxide. By 1960 the amount added during the past century will be more than 15 %.

CALLENDAR (1938, 1940, 1949) believed that nearly all the carbon dioxide produced by fossil fuel combustion has remained in the atmos-

phere, and he suggested that the increase in atmospheric carbon dioxide may account for the observed slight rise of average temperature in northern latitudes during recent decades. He thus revived the hypothesis of T. C. CHAMBERLIN (1899) and S. ARRHENIUS (1903) that climatic changes may be related to fluctuations in the carbon dioxide content of the air. These authors supposed that an increase of carbon dioxide in the upper atmosphere would lower the mean level of back radiation in the infrared and thereby increase the average temperature near the earth's surface.

Subsequently, other authors have questioned Callendar's conclusions on two grounds. First, comparison of measurements made in the 19th century and in recent years do not demonstrate that there has been a significant increase in

Contribution from the Scripps Institution of Oceanography, New Series, No. 900. This paper represents in part results of research carried out by the University of California under contract with the Office of Naval Research.

Table 1. CO<sub>2</sub> added to atmosphere by consumption of fossil fuels

Decade	Average amount added per decade Measured		Cumulative total added			
	10 <sup>18</sup> gms	% Atm CO <sub>2</sub>	10 <sup>18</sup> gms	% Atm CO <sub>2</sub>	10 <sup>18</sup> gms	% Atm CO <sub>2</sub>
1860—69	0.0054	0.23	0.0054	0.23		
1870—79	0.0085	0.36	0.0139	0.59		
1880—89	0.0128	0.54	0.0267	1.13		
1890—99	0.0185	0.79	0.0452	1.92		
1900—09	0.0299	1.27	0.0751	3.19		
1910—19	0.0405	1.72	0.1156	4.91		
1920—29	0.0470	2.00	0.1626	6.91		
1930—39	0.0497	2.11	0.2123	9.02		
1940—49	0.0636	2.71	0.2759	11.73		
Forecast						
Assuming fossil fuels are used to meet future requirements of fuel and power as estimated by UN (1955)					Assuming fossil fuel consumption remains constant at estimated 1955 rate	
1950—59	0.091	3.9	0.367	15.6	0.367	15.6
1960—69	0.128	5.4	0.495	21.0	0.458	19.5
1970—79	0.176	7.5	0.671	28.5	0.549	23.4
1980—89	0.247	10.5	0.918	39.0	0.640	27.2
1990—99	0.340	14.5	1.258	53.5	0.731	31.1
2000—09	0.472	20.0	1.730	73.5	0.822	35.0

atmospheric CO<sub>2</sub> (SLOCUM, 1955; FONSELIUS *et al.* 1956). Most of the excess CO<sub>2</sub> from fuel combustion may have been transferred to the ocean, a possibility suggested by S. ARRHENIUS (1903). Second, a few percent increase in the CO<sub>2</sub> content of the air, even if it has occurred, might not produce an observable increase in average air temperature near the ground in the face of fluctuations due to other causes. So little is known about the thermodynamics of the atmosphere that it is not certain whether or how a change in infrared back radiation from the upper air would affect the temperature near the surface. Calculations by PLASS (1956) indicate that a 10 % increase in atmospheric carbon dioxide would increase the average temperature by 0.36° C. But, amplifying or feed-back processes may exist such that a slight change in the character of the back radiation might have a more pronounced effect. Possible examples are a decrease in albedo of the earth due to melting of ice caps or a rise in water vapor content of the atmosphere (with accompanying increased infrared absorption near the surface) due to increased evaporation with rising temperature.

During the next few decades the rate of

combustion of fossil fuels will continue to increase, if the fuel and power requirements of our world-wide industrial civilization continue to rise exponentially, and if these needs are met only to a limited degree by development of atomic power. Estimates by the UN (1955) indicate that during the first decade of the 21st century fossil fuel combustion could produce an amount of carbon dioxide equal to 20 % of that now in the atmosphere (Table 1).<sup>1</sup> This is probably two orders of magnitude greater than the usual rate of carbon dioxide production from volcanoes, which on the average must be equal to the rate at which silicates are weathered to carbonates (Table 2). Thus human beings are now carrying out a large scale geophysical experiment of a kind that could not have happened in the past nor be reproduced in the future. Within a few centuries we are returning to the atmosphere and oceans the concentrated organic carbon stored in sedimentary rocks over hundreds of millions of years. This experiment, if adequately

<sup>1</sup> World production of CO<sub>2</sub> from the use of limestone for cement, fluxing stone and in other ways was about 1 % of the total from fossil fuel combustion in 1950.

documented, may yield a far-reaching insight into the processes determining weather and climate. It therefore becomes of prime importance to attempt to determine the way in which carbon dioxide is partitioned between the atmosphere, the oceans, the biosphere and the lithosphere.

The carbon dioxide content of the atmosphere and ocean is presumably regulated over geologic times by the tendency toward thermodynamic equilibrium between silicates and carbonates and their respective free acids, silica and carbon dioxide (UREY, 1952). The atmosphere contains and probably has contained during geologic times considerably more  $\text{CO}_2$  than the equilibrium concentration (HUTCHINSON, 1954), although uncertainties in the thermodynamic data are too great for an accurate quantitative comparison. Equilibrium is approached through rock weathering and marine sedimentation. Estimated rates of these processes give a very long time constant of the order of magnitude of 100,000 years. Rapid changes in the amount of carbon dioxide produced by volcanoes, in the state of the biosphere, or as in our case, in the rate of combustion of fossil fuels, may therefore cause considerable departures from average conditions.

**Table 2. Estimated present annual rates of some processes involving atmospheric and oceanic carbon dioxide, in part after HUTCHINSON (1954)**

	$10^{18}$ gms	In units of atm $\text{CO}_2(A_0)$
Consumption of fossil fuels— $\text{CO}_2$ produced. Bicarbonate and carbonate added to ocean by rivers (as $\text{CO}_2$ ) <sup>1</sup> . .	0.0091	0.0039
Photosynthesis on land — $\text{CO}_2$ consumed . . . .	0.00103	0.0004
Photosynthesis in ocean — $\text{CO}_2$ consumed . . . .	$0.073 \pm 0.018$	0.031
	$0.46 \pm 0.3$	0.20

<sup>1</sup> According to CONWAY (1942) and HUTCHINSON (1954) 87 % of the river borne bicarbonate and carbonate comes from weathering of carbonate rocks, the remainder from weathering of silicates.

The answer to the question whether or not the combustion of coal, petroleum and natural gas has increased the carbon dioxide concentration in the atmosphere depends in part upon

the rate at which an excess amount of  $\text{CO}_2$  in the atmosphere is absorbed by the oceans. The exchange rate of isotopically labeled  $\text{CO}_2$  between atmosphere and ocean, which, in principle, could be deduced from  $\text{C}^{14}$  measurements, is not identical with the rate of absorption, but is related to it.

### Notations and geochemical constants

In our discussion of exchange and absorption rates we shall use the following notations:

$S_0$ :	Total carbon of the marine carbon reservoir at equilibrium condition, at time zero.
$A_0$ :	Atmospheric $\text{CO}_2$ carbon at time zero.
$i$ :	Annual amount of industrial $\text{CO}_2$ added to the atmosphere.
$t$ :	Time in years.
$s = S_t - S_0$ :	Amount of $\text{CO}_2$ derived from industrial fuel combustion in the sea at time $t$ .
$r = it - s$ :	Amount of $\text{CO}_2$ derived from industrial fuel combustion in the atmosphere at time $t$ .
$r^*$ :	Observed decrease in $\text{C}^{14}$ activity.
$\tau(\text{atm})$ :	Average lifetime of a $\text{CO}_2$ molecule in the atmosphere, before it becomes dissolved in the sea.
$\tau(\text{sea})$ :	Average lifetime of carbon in the sea, before it becomes atmospheric $\text{CO}_2$ .
$k_1 = 1/\tau(\text{atm})$ :	Rate of $\text{CO}_2$ transfer per year from the atmosphere to the sea.
$k_2 = 1/\tau(\text{sea})$ :	Rate of $\text{CO}_2$ transfer per year from the sea to the atmosphere.
$P_{\text{CO}_2}$ :	Partial $\text{CO}_2$ pressure in the atmosphere.

Table 3 gives the amount of carbon, expressed in  $\text{CO}_2$  equivalents, in the various geochemical reservoirs on the surface of the Earth.

The symbols  $S^*$  and  $A^*$  shall be used for denoting respective "effective" reservoirs.

### Rate of $\text{CO}_2$ exchange between sea and atmosphere

Two types of  $\text{C}^{14}$  measurements independently allow calculation of the exchange rate

**Table 3. Amount of carbon, computed as CO<sub>2</sub>, in sedimentary rocks, hydrosphere, atmosphere and biosphere from data given by RUBEY (1951), HUTCHINSON (1954), and SVERDRUP et al. (1942)**

	Total on Earth: 10 <sup>18</sup> gms	In units of A <sub>0</sub>
Carbonate in sediments...	67,000	28,500
Organic carbon in sediments	25,000	10,600
CO <sub>2</sub> in the atmosphere (A <sub>0</sub> )	2.35	1
Living matter on land <sup>1</sup> ....	0.3	0.12
Dead organic matter on land.....	2.6	1.1
CO <sub>2</sub> + H <sub>2</sub> CO <sub>3</sub> in ocean <sup>2</sup> ....	0.8	0.3
CO <sub>2</sub> as HCO <sub>3</sub> <sup>-</sup> in ocean <sup>2</sup> ...	114.7	48.7
CO <sub>2</sub> as CO <sub>3</sub> <sup>=</sup> in ocean <sup>2</sup> ....	14.2	6.0
Total inorganic carbon in ocean.....	129.7	55.0
Dead organic matter in ocean.....	10	4.4
Living organic matter in ocean.....	0.03	0.01
Total carbon in ocean (S <sub>0</sub> )	140	59.4

<sup>1</sup> Living organic matter on land estimated from assays of standing timber in the world's forests. 30 % of land surface is relatively thick forest, averaging about 5,000 board feet/acre of commercial size timber or 0.26 gm CO<sub>2</sub>/cm<sup>2</sup> of forest. Assuming that total living matter in forests is twice the amount of timber, and that other components of the biosphere are 1/3 of total gives 0.34 × 10<sup>18</sup> gm CO<sub>2</sub> in land biosphere.

<sup>2</sup> Carbon dioxide components in sea water are assumed to be in equilibrium with a CO<sub>2</sub> partial pressure of 3 × 10<sup>-4</sup> atmospheres; chlorinity: 20 ‰; temperature: 10° C; alkalinity: 2.46 × 10<sup>-3</sup> meq/L. Under these conditions pH = 8.18. Volume of the Ocean = 1.37 × 10<sup>24</sup> cm<sup>3</sup>. This is probably an underestimate, because the water below the thermocline contains CO<sub>2</sub> produced by oxidation of organic matter, and the average temperature of the ocean is somewhat less than 10° C.

through the sea-air interface, if assumptions are made with respect to mixing rates of the water masses in the oceans: (a) the apparent C<sup>14</sup> age of marine materials and (b) the effects of industrial coal combustion on the C<sup>14</sup> concentration in the atmosphere (Suess 1953). Experimental data on these two subjects are inadequate for rigorous quantitative interpretation but are sufficiently accurate to allow estimates of the order of magnitude of the rate constant for the exchange.

Considering the combined marine and atmospheric carbon reservoir as a closed

system in equilibrium, the following relation holds by definition:

$$\frac{\tau(\text{sea})}{\tau(\text{atm})} = \frac{k_1}{k_2} = \frac{S_0}{A_0} \quad (1)$$

$\tau(\text{sea})$ , the average lifetime of a carbon atom as a member of the marine reservoir, is equal to the average apparent C<sup>14</sup> age of marine material.

An apparent C<sup>14</sup> age of marine material is obtained by comparison of the C<sup>14</sup> activity with that of a wood standard corrected for isotopic fractionation effects in nature or in the laboratory by mass spectrometric measurement of the C<sup>13</sup>/C<sup>12</sup> ratios. In marine carbonate the C<sup>13</sup>/C<sup>12</sup> ratio is about 2.5 % higher than in land plants (NIER and GULBRANSEN, 1939 and CRAIG 1953, 1954). Because of the double mass difference the effect for C<sup>14</sup> should be twice as large as that for C<sup>13</sup>, if the isotopic distribution is established sufficiently rapidly so that radioactive decay of C<sup>14</sup> can be neglected. If, after normalizing to equal C<sup>13</sup>/C<sup>12</sup> ratios, a lower C<sup>14</sup> concentration is found than that of the wood standard, then this difference is attributed here to the effect of radioactivity, and is expressed as apparent age. A detailed study of the expected relationship between the isotopic fractionation factors for C<sup>13</sup> and C<sup>14</sup> in the bio-geochemical cycle of carbon has been made by CRAIG (1954).

Assuming from the then available C<sup>14</sup> measurements that shell and wood have the same specific C<sup>14</sup> activity, CRAIG (1954) attributed this unexpected result to slow transfer of CO<sub>2</sub> across the ocean-atmosphere interface resulting in a radiocarbon age of 400 years for surface ocean bicarbonate. Since then, more precise C<sup>14</sup> measurements, supplemented by mass spectroscopic C<sup>13</sup> determinations, have been published by SUESS (1954, 1955) and by RAFTER (1955) (see also HAYES ET AL., 1955). The standard error of about 0.5 % corresponds to an uncertainty in the age values of about 40 years. The apparent ages calculated from the published measurements are as follows:

Atlantic: (SUESS, 1954).

<i>Mercenaria mercenaria</i>	Shells 440 yrs.
Nantucket sound (from under 45 ft of water)	Flesh 540 yrs.
Sargassum weed from sea surface, 36°24' N, 69°37' W	320 yrs.

New Zealand area: (RAFTER, 1955).

Pauna Shells	350 yrs.
Limpet shells	360 yrs.
Cockle shells	280 yrs.
Pauna flesh	290 yrs.
Limpet flesh	140 yrs.
Seaweed	250 yrs.
Seawater (East Cape area)	370 yrs.

The average of the ages given here is 430 yrs. for the Atlantic samples and 290 yrs. for the New Zealand samples. The difference of 140 yrs. is due to the fact that the ages of the first group were calculated using wood grown in the 19th century as standard, whereas contemporaneous wood was used as standard for the New Zealand samples.<sup>1</sup>

Assuming that these apparent ages for marine surface materials are representative for the average age of marine carbon, or in other words, that mixing times of the oceans are short compared to the ages measured, an apparent age of about 400 years for marine carbon corresponds, according to Eq. (1), to an exchange time  $\tau$  (atm) of about 7 years.

This lower limit for the exchange time of  $\text{CO}_2$  between the atmosphere and the sea can now be compared with computations of this quantity from the observed effect of industrial fuel combustion on the specific  $\text{C}^{14}$  activity of wood. This second way, however, will lead to an upper limit for the exchange time if rapid mixing in the oceans is assumed.

At present  $9.1 \times 10^{15}$  grams of  $\text{C}^{14}$  free  $\text{CO}_2$ , or a fraction of  $3.9 \times 10^{-3}$  of the atmospheric  $\text{CO}_2$ , is added per year to the atmosphere by artificial burning of fossil fuels. The total amount added during the 100 years prior to 1950 corresponds to about 12 % of the atmospheric carbon reservoir.

Neglecting any effect of the industrial  $\text{CO}_2$  on the rate constants  $k_1$  and  $k_2$  one obtains:

$$\frac{ds}{dt} = k_1(it - s) - k_2s \quad (2)$$

and integrated:

$$s = it \frac{k_1}{k_1 + k_2} - i \frac{k_1}{(k_1 + k_2)^2} (1 - e^{-(k_1 + k_2)t}) \quad (3)$$

<sup>1</sup> See FERGUSSON and RAFTER. These authors have now found that 110 years should be added to all of their previous age determinations to correct for the difference of the standards.

for the amount of industrial  $\text{CO}_2$  in the sea at the time  $t$ . As  $k_1 \approx 60 k_2$ , we may neglect  $k_2$  as small compared to  $k_1$ . We then obtain:

$$s = it - \frac{i}{k_1} (1 - e^{-k_1 t}) \quad (4)$$

or

$$r = it - s = \frac{i}{k_1} (1 - e^{-k_1 t}) \quad (5)$$

Expressing  $i$ ,  $s$ , and  $r$  in units of the atmospheric  $\text{CO}_2$ , we obtain with  $i = 0.25$  % (corresponding to the value during the 1940's) and  $t = 40$  years, the following values of  $r$  for exchange times  $\tau$  (atm) =  $\frac{1}{k_1}$  as listed:

Table 4

$1/k_1 = \tau$ (atm) years	$r$ %
5	1.2
10	2.5
20	4.4
30	5.5
40	6.3
100	8.3
$\infty$	10.0

Empirical values for the decrease in the specific  $\text{C}^{14}$  activity  $r^*$  were obtained by comparing  $\text{C}^{14}$  activities of wood samples grown in the 19th century with those grown more recently, taking into account isotope fractionation effects by  $\text{C}^{13}$  measurements and correcting for the  $\text{C}^{14}$  decay by normalizing to equal age (SUESS 1955).

With the assumption that the total atmospheric carbon reservoir is only negligibly greater than the amount of  $\text{CO}_2$  in the atmosphere,  $r^*$  will be equal to  $r$ .

Table 5

Tree	Years of growth from annual rings	$r^*$ %
Spruce, Alaska . . . .	1945—1950	1.77
White Pine, Massachusetts	1936—1946 1946—1953	3.40 2.90
Incense Cedar, California	1940—1944 1950—1953	1.85 1.05
Cedrela, Peru	1943—1946 1948—1953	0.05 1.05

It might be tempting to assume that the effects found in the samples investigated and their individual variations are due to local contamination of air masses by industrial CO<sub>2</sub> and that the world-wide decrease in the C<sup>14</sup> activity of wood is practically zero. This, however, implies a too fast exchange rate and is inconsistent with the lower limit of  $\tau$  (atm) given above. By coincidence, it so happens that taking the average of the  $r^*$  values listed, 1.73 %, an exchange time  $\tau$  (atm) of 7 years is obtained as an upper limit, identical with the lower limit obtained previously from the C<sup>14</sup> age of marine surface material. An exchange time of 7 years, however, makes it necessary to assume unexpectedly short mixing times for the ocean.<sup>1</sup>

By reconsidering the relative size of the marine and atmospheric carbon reservoirs, and the assumptions necessary for treating the combined reservoirs as a closed system, we may approximate more closely to the conditions prevailing in nature. First, it seems possible that some of the organic matter and carbonate present in soils may have to be added to the carbon that constitutes the atmospheric carbon reservoir. Practically nothing is known about the C<sup>14</sup> age of soils and it may be that some of the soil carbon, partly through bacterial action, is in more rapid isotopic exchange with atmospheric CO<sub>2</sub> than the data on plant assimilation and biological oxidation indicate. The total amount of carbon in soils may be equal to, or larger by as much as a factor of two than that in the CO<sub>2</sub> of the atmosphere. Rapid exchange with such carbon would decrease the change in C<sup>14</sup> activity resulting from industrial fuel combustion by a factor equal to the ratio of the total "effective" atmospheric carbon reservoir to the atmospheric CO<sub>2</sub>. However, the overturn time of the atmospheric CO<sub>2</sub> through the terrestrial biological cycle and the soil is probably at least several decades and it therefore seems improbable that a mechanism exists that might

account for an atmospheric reservoir of more than 1.5 times the CO<sub>2</sub> in the atmosphere.

Nevertheless, it is interesting, in order to demonstrate how the uncertainty in the size of the atmospheric carbon reservoir affects our results, to introduce "effective" reservoirs  $A^*$  and  $S^*$ , so that  $A^* > A$ , because of exchange with soil carbon, and  $S^* < S$ , because of incomplete mixing in the oceans.  $A^*$  and  $S^*$  are defined in such a way that Eq. (1) becomes

$$\frac{k_1}{k_2} = \frac{S^*}{A^*} \quad (1a)$$

For Eq. (5):

$$r^* = \frac{A}{A^*} \frac{i}{k_1} (1 - e^{-k_1 t}) \quad (5a)$$

is to be substituted.

Then the relationships of the three unknown quantities  $k_1$ ,  $S^*$  and  $A^*$  according to the two equations (1a) and (5a) are shown graphically in figure 1.

With an average age of surface sea carbon of 400 years, i.e.,  $k_2 = 1/400$ , one finds, even with an improbably large  $A^*$  equal to 3  $A$ , that  $S^*$  is only 10 to 30 % smaller than  $S$ , so that the resulting mixing times of the oceans cannot be larger than a few 100 years.

The overturn time for the marine carbon through rock weathering and precipitation can be estimated to be of the order of 100,000 years (table 3). During an average lifetime of sea carbon of 400 years an amount corresponding to 0.3 % of the marine reservoir will be added to the oceans through rock weathering in the form of C<sup>14</sup> free carbon and be precipitated after isotopic equilibration. On the average, this will cause the C<sup>14</sup> age of sea carbon to appear about 35 years older. Locally, and especially along shores, the effect may well be considerably greater, so that the ages measured so far may, on the average, be too great by as much as 100 years. In figure 1, solutions are shown for  $1/k_2 = 300$  years, indicating a value of  $S^*/S$  of about  $2/3$  for acceptable values of  $A^*$ .<sup>1</sup>

A possibility that the addition of C<sup>14</sup> free CO<sub>2</sub> to the atmosphere from volcanic eruptions in the 19th century may obscure the

<sup>1</sup> In a separate paper in this issue, H. Craig evaluates the exchange time by considering present data on the C-14 production rate by cosmic rays, and obtains a value of  $7 \pm 3$  years. He further finds that a more detailed model of ocean mixing gives the same value. An earlier estimate of 20 to 50 years (Suess 1953) was based on C-14 measurements of woods grown in an area of industrial contamination.

<sup>1</sup> For a discussion of the physical significance of  $S^*/S$  in terms of mixing times in the ocean see H. Craig's paper in this issue.

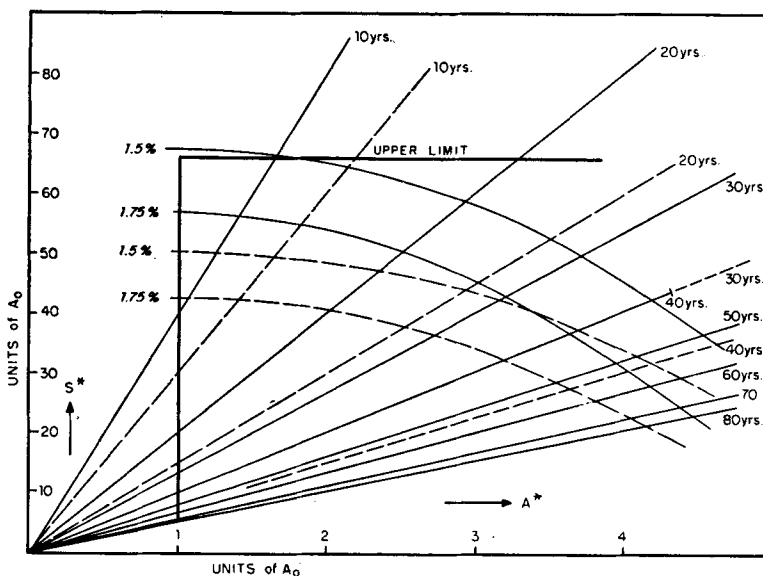


Fig. 1. Graphic solutions of Eq. (1 a) for values  $1/k_1$  ranging from 10 to 80 years (straight lines), and of Eq. (5 a) for  $r^* = 1.5\%$  and  $1.75\%$  (curved lines), for average apparent  $C^{14}$  age of sea water  $1/k_2 = 400$  years (solid lines) and 300 years (broken lines). Points of intersection of straight lines and curves are possible solutions of the two equations for effective reservoirs  $A^*$  and  $S^*$ .

effect from industrial fuel combustion needs further experimental investigation.

We conclude that the exchange time  $\tau$  (atm) =  $1/k_1$ , defined as the time it takes on the average for a  $CO_2$  molecule as a member of the atmospheric carbon reservoir to be absorbed by the sea, is of the order of magnitude of 10 years. This corresponds to a net exchange rate of the order of  $10^{-7}$  mol  $CO_2$  per second and square meter of the ocean surface, larger by a factor of 100 than that postulated by PLASS (1956) and smaller by a factor of 10,000 than that deduced by DINGLE (1954) as a lower limit from numerical values of the various rate controlling constants. These are, as HUTCHINSON (1954) has forcefully pointed out, too uncertain to allow any definite conclusions. On the other hand, our exchange data give a value for the "invasion coefficient" of carbon dioxide close to that determined experimentally by BOHR (1899) for a stirred liquid surface.

#### Secular variation of $CO_2$ in the atmosphere

In the preceding section of this paper, two simplifying assumptions were made when

estimating the exchange rate of  $CO_2$  between the atmosphere and the oceans: (1) that the rate constants  $k_1$  and  $k_2$  were not affected by a small increase of the exchangeable carbon reservoir such as that from industrial fuel combustion, and (2) that, except for that increase, no other changes in the sizes of the oceanic and atmospheric carbon reservoirs have taken place. If these assumptions were rigorously correct, the increase in atmospheric  $CO_2$  due to an addition of  $C^{14}$  free  $CO_2$  would be nearly equal to  $r$ , as given by Eq. (5) and in table 4, and equal to the decrease in the specific  $C^{14}$  activity  $r^*$ , multiplied by a factor  $A^*/A$ .

Because of the peculiar buffer mechanism of sea water, however, the increase in the partial  $CO_2$  pressure is about 10 times higher than the increase in the total  $CO_2$  concentration of sea water when  $CO_2$  is added and the alkalinity remains constant (BUCH, 1933, see also HARVEY, 1955), so that under equilibrium conditions at a given alkalinity

$$\frac{r}{A_0} = \frac{\gamma s}{S_0} \text{ or } \frac{A_0}{S_0} = \frac{k_1}{k_2} = \frac{r}{\gamma s},$$

$\gamma$  being a numerical factor of the order of 10



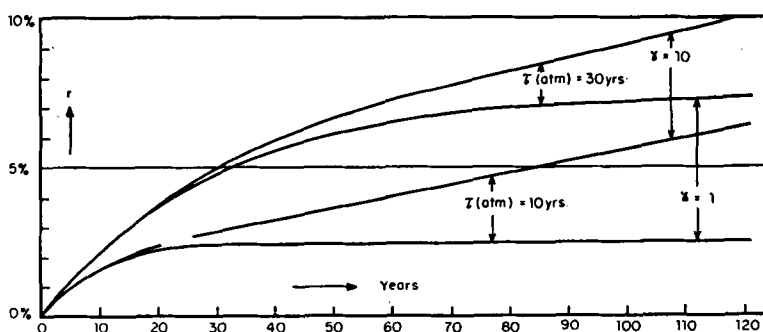


Fig. 2. Expected secular increase in the CO<sub>2</sub> concentration of air ( $r$ ) according to Eq. (7), for average lifetimes of CO<sub>2</sub> in the atmosphere  $\tau(\text{atm}) = 10$  years and 30 years, with and without correction for the increase in the partial CO<sub>2</sub> pressure with total CO<sub>2</sub> concentration of sea water (curves for  $\gamma = 10$  and  $\gamma = 1$  respectively), for a constant rate of addition of industrial CO<sub>2</sub> of  $i = 2.5 \cdot 10^{-3} \times A_0$ .

for  $r$  and  $s$  small compared to  $A_0$  and  $S_0$  respectively.

As a reasonable approximation we may write instead of Eq. (3):

$$s = it \frac{k_1}{k_1 + \gamma k_2} - i \frac{k_1}{(k_1 + \gamma k_2)^2} (1 - e^{-(k_1 + \gamma k_2)t}) \quad (6)$$

or

$$r = it \frac{\gamma k_2}{k_1 + \gamma k_2} + i \frac{k_1}{(k_1 + \gamma k_2)^2} (1 - e^{-(k_1 + \gamma k_2)t}) \quad (7)$$

Figure 2 shows  $r$  as a function of time calculated from Eq. (7) for two values of  $k_1$  corresponding to an exchange time of 10 and 30 years respectively, assuming constant addition of industrial CO<sub>2</sub> equal to 0.25 % of the CO<sub>2</sub> in the atmosphere per year. At present the integrated amount of industrial CO<sub>2</sub> corresponds to about 40 to 50 years of addition at this constant rate. The increase in CO<sub>2</sub> in the atmosphere plus biosphere and soil due to industrial fuel combustion should therefore at present amount to 3 to 6 %, depending on the assumptions made with respect to the size of the "effective" atmospheric carbon reservoir that exchanges with the ocean.

Eq. (7) and figure 2 show that addition of industrial CO<sub>2</sub> at a constant rate should eventually lead to a situation in which the secular increase in CO<sub>2</sub> in the atmosphere plus biosphere and soil equals  $\frac{iyk_2/k_1}{1 + \gamma k_2/k_1}$  per year.

With  $S_0/A_0 = k_1/k_2 \approx 60$  and  $i = 0.25$  an increase of 3.6 % per century is obtained. We have neglected the present rate of increase in alkalinity, which is small compared to the rate

of CO<sub>2</sub> production from fossil fuels. However, over a sufficiently long period of time the alkalinity of the ocean must be expected to rise more rapidly as a consequence of the higher total CO<sub>2</sub> concentration in the atmosphere and ocean which will tend to increase the rate of rock weathering and to decrease the rate of deposition of CaCO<sub>3</sub>. The secular increase in  $r$  should therefore be less than that calculated from Eq. (7) with  $\gamma = 10$  and somewhere between the curves shown in figure 2 for  $\gamma = 10$  and  $\gamma = 1$ .

It seems therefore quite improbable that an increase in the atmospheric CO<sub>2</sub> concentration of as much as 10 % could have been caused by industrial fuel combustion during the past century, as Callendar's statistical analyses indicate. It is possible, however, that such an increase could have taken place as the result of a combination with various other causes. The most obvious ones are the following:

- 1) Increase of the average ocean temperature of 1°C increases  $P_{\text{CO}_2}$  by about 7 %. However, such increase would also raise the sea level by about 60 cm, due to thermal expansion of the ocean water. Actually, according to MUNK and REVELLE (1952), although the sea level has risen about 10 cm during the last century, this rise can be accounted for almost quantitatively by addition of melt water from retreating glaciers and ice caps. The increase in the average ocean temperature is probably not more than 0.05°C, which corresponds to an increase in  $P_{\text{CO}_2}$  of 0.35 %. In the case of slow oceanic mixing, the increase could be somewhat larger, if only

the top layers of the sea were affected by a rise in temperature.

2) Decrease in the carbon content of soils: HUTCHINSON (1954) considers this the most probable additional cause of the Callendar effect. The increase in arable lands of about  $4 \times 10^{16}$  cm<sup>2</sup> since the middle of the 19th century has resulted in a corresponding decrease of forest land of about 10 %. Assuming that 70 % of all the soil carbon is in forests (probably a considerable over-estimate), and that cultivation reduced this by 50 %, the total decrease in soil carbon would correspond to  $9 \times 10^{16}$  gms of CO<sub>2</sub> which is 4 % of that in the atmosphere. At least four-fifths of this amount should have been transferred to the ocean.

3) Change in the amount of organic matter in the oceans. About 7 % of the marine carbon reservoir consists of organic material. The amount of organic matter must depend on the balance between the rates of reduction of CO<sub>2</sub> by photosynthesis and of production of CO<sub>2</sub> by oxidation. As pointed out previously, a change in the CO<sub>2</sub> content of sea water by a certain factor without a corresponding change in alkalinity changes  $P_{CO_2}$  by about 10 times this factor. Therefore a 1 % change in the concentration of organic material in the sea will change the partial CO<sub>2</sub> pressure and hence the atmospheric CO<sub>2</sub> by roughly 1 %. During the past 50 years, the increase in marine carbon from absorption of industrial CO<sub>2</sub> of about 0.2 % might have increased the rate of photosynthesis without a corresponding change in the rate of oxidation per unit mass of organic matter, and thus decreased  $P_{CO_2}$ . An increase in the temperature of surface water might have increased the rate of oxidation per unit mass of organic matter, and hence increased  $P_{CO_2}$ . We suspect that fluctuations in the amount of organic marine carbon might be an important cause for changes in the atmospheric CO<sub>2</sub> concentration.

ERIKSON and WELANDER (1956) have discussed a mathematical model of the carbon cycle between the atmosphere, the land biosphere and dead organic matter, and the ocean, in which it is assumed that the rate of input of carbon to the biosphere is directly proportional, not only to the total size of the biosphere but also to the amount of CO<sub>2</sub> in the atmosphere. Their estimate of the land biosphere is 7 times

larger than that given in Table 3. They conclude that most of that part of the CO<sub>2</sub> added by fossil fuel consumption, which has not been absorbed by the ocean, has probably gone into the biosphere. Erikson and Welander's basic assumption that the amount of atmospheric carbon dioxide limits the growth of the terrestrial biosphere seems highly unlikely, in view of the fact that the principal photosynthetic production on land is in forests, where a deficiency of plant nutrients might be expected. In any case as HUTCHINSON (1954) has shown, the amount of carbon in the biosphere and soil humus has probably decreased, rather than increased, during the past century, because of the clearing of forests.

In contemplating the probably large increase in CO<sub>2</sub> production by fossil fuel combustion in coming decades we conclude that a total increase of 20 to 40 % in atmospheric CO<sub>2</sub> can be anticipated. This should certainly be adequate to allow a determination of the effects, if any, of changes in atmospheric carbon dioxide on weather and climate throughout the earth.

Present data on the total amount of CO<sub>2</sub> in the atmosphere, on the rates and mechanisms of CO<sub>2</sub> exchange between the sea and the air and between the air and the soils, and on possible fluctuations in marine organic carbon, are insufficient to give an accurate base line for measurement of future changes in atmospheric CO<sub>2</sub>. An opportunity exists during the International Geophysical Year to obtain much of the necessary information.

#### Acknowledgements

A paper on the same subject by James R. Arnold and Ernest C. Anderson appears in this issue of this journal; we are grateful to Drs. Arnold and Anderson for the opportunity of discussing the problem before publication. We are happy to note that these authors have simultaneously and independently derived essentially the same conclusions as presented in this paper. We hope that the somewhat different approach will make both contributions equally valuable to the reader. We also wish to thank Dr. Carl Eckart for valuable discussions and Dr. Harmon Craig for much constructive criticism. Dr. Craig's own careful analysis of the subject appears in a separate paper in this issue.

## REFERENCES

- ARRHENIUS, SVANTE, 1903: *Lehrbuch der kosmischen Physik* 2. Leipzig: Hirzel.
- BOHR, C., 1899: Die Löslichkeit von Gasen in Flüssigkeiten. *Ann. d. Phys.* **68**, p. 500.
- BUCH, K., 1933: Der Borsäuregehalt des Meerwassers und seine Bedeutung bei der Berechnung des Kohlen-säuresystems. *Rapp. Cons. Explor. Mer.* **85**, p. 71.
- CALLENDAR, G. S., 1938: The artificial production of carbon dioxide and its influence on temperature. *Quarterly Journ. Royal Meteorol. Soc.* **64**, p. 223.
- CALLENDAR, G. S., 1940: Variations in the amount of carbon dioxide in different air currents. *Quarterly Journ. Royal Meteorol. Soc.* **66**, p. 395.
- CALLENDAR, G. S., 1949: Can carbon dioxide influence climate? *Weather* **4**, p. 310.
- CHAMBERLIN, T. C., 1899: An attempt to frame a working hypothesis of the cause of glacial periods on an atmospheric basis. *J. of Geology* **7**, pp. 575, 667, 751.
- CONWAY, E. J., 1942: Mean geochemical data in relation to oceanic evolution. *Proc. Roy. Irish Acad., B.* **48**, p. 119.
- CRAIG, H., 1953: The geochemistry of the stable carbon isotopes. *Geochim. et Cosmochim. Acta* **3**, p. 53.
- CRAIG, H., 1954: Carbon 13 in plants and the relationship between carbon 13 and carbon 14 variations in nature. *Journ. Geol.* **62**, p. 115.
- DINGLE, H. N., 1954: The carbon dioxide exchange between the North Atlantic Ocean and the atmosphere. *Tellus* **6**, p. 342.
- ERIKSON, E., and WELANDER, P., 1956: On a mathematical model of the carbon cycle in nature. *Tellus* **8**, p. 155.
- FERGUSON, G. J., and RAFTER, T. A.: *New Zealand C-14 Age Measurements III*. In press.
- FONSELIUS, S., KOROLEFF, F., and WÄRME, K., 1956: Carbon dioxide variations in the atmosphere. *Tellus* **8**, p. 176.
- HARVEY, H. W., 1955: *The Chemistry and Fertility of Sea Water*. Cambridge: University Press.
- HAYES, F. N., ANDERSON, E. C., and ARNOLD, J. R., 1955: Liquid scintillation counting of natural radiocarbon. *Proc. of the International Conference on Peaceful Uses of Atomic Energy, Geneva*, **14**, p. 188.
- HUTCHINSON, G. E., 1954: In *The Earth as a Planet*, G. Kuiper, ed. Chicago: University Press. Chapter 8.
- MUNK, W., and REVELLE, R., 1952: Sea level and the rotation of the earth. *Am. Journ. Sci.* **250**, p. 829.
- NIER, A. O., and GULBRANSEN, E. A., 1939: Variations in the relative abundance of the carbon isotopes. *Journ. Am. Chem. Soc.* **61**, p. 697.
- PLASS, G. N., 1956: Carbon dioxide theory of climatic change. *Tellus* **8**, p. 140.
- RAFTER, T. A., 1955: C<sup>14</sup> variations in nature and the effect on radiocarbon dating. *New Zealand Journ. Sci. Tech. B.* **37**, p. 20.
- RUBEY, W. W., 1951: Geologic history of sea water. *Bull. Geol. Soc. Amer.* **62**, p. 1111.
- SLOCUM, GILES, 1955: Has the amount of carbon dioxide in the atmosphere changed significantly since the beginning of the twentieth century? *Monthly Weather Rev.* Oct., p. 225.
- Suess, H. E., 1953: Natural Radiocarbon and the rate of exchange of carbon dioxide between the atmosphere and the sea. *Nuclear Processes in Geologic Settings*, National Academy of Sciences — National Research Council Publication, pp. 52—56.
- Suess, H. E., 1954: Natural radiocarbon measurements by acetylene counting. *Science* **120**, p. 5.
- Suess, H. E., 1955: Radiocarbon concentration in modern wood. *Science* **122**, p. 415.
- SVERDRUP, H. U., JOHNSON, M. W., and FLEMING, R. H., 1942: *The Oceans*. New York: Prentice-Hall, Inc.
- UNITED NATIONS, 1955: World requirements of energy, 1975—2000. *International Conference on Peaceful Uses of Atomic Energy, Geneva*, **1**, p. 3.
- UREY, H. C., 1952: *The Planets*. New Haven: Yale Univ. Press.