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Radiocarbon Evidence on the Dilution of Atmospheric and Oceanic Carbon by Carbon from Fossil Fuels

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Abstract—The dilution of atmospheric carbon dioxide by carbon dioxide from fossil fuels is estimated to be about 3½ pct, on the basis of radiocarbon assays of tree rings of known ages from several trees of different genera, after allowance has been made for effects attributable to ecological differences. The cumulative mass of fossil carbon dioxide released to the atmosphere is 3.3 x 10^{17} gm, equivalent to about 14 pct of the carbon dioxide in the atmosphere. Based on these data, the fractional part of the atmospheric carbon dioxide which enters the ocean each year is estimated to be 0.062. Radiocarbon assays of several nineteenth-century marine shells and of their modern counterparts indicate a one to two per cent dilution of shallow oceanic carbonates by carbon dioxide from fossil fuels. Use of these data in a simplified mathematical model of atmosphere-ocean yields information on mixing times of the ocean.

Introduction—The effects of addition to the carbon cycle in nature of carbon dioxide from industrial activities have been the subject of speculation in several fields of science. Of particular interest is the fate of the enormous quantity of carbon dioxide which has been introduced into the atmosphere since the beginning of the industrial revolution in the 19th century, and the manner in which the added carbon dioxide has been distributed in the carbon cycle. Although appreciable amounts of carbon dioxide have undoubtedly been added from soils by tilling of land, apparently a much greater amount has resulted from the combustion of fossil fuels.

Callendar [1940] pointed out that direct measurements of the carbon dioxide concentration in air, made over a number of years by various investigators, indicate a significant increase in concentration over the period 1866–1935. From this he concluded that most of the carbon dioxide from the industrial revolution has remained in the air and, consequently, that the rate of absorption of carbon dioxide by the oceans is very slow. *Hutchinson* [1954] suggested that the radiocarbon content of woods from trees which have lived during the industrial revolution might throw light on the dilution of atmospheric carbon dioxide by carbon dioxide from the combustion of fossil fuels. *Suess* [1954] at about the same time determined the radiocarbon content of tree rings of known ages from several trees. These results indicated a dilution of about 3½ pct. In later work *Suess* [1955], on the basis of results on additional samples, revised the probable dilution downward to less than one per cent and ascribed the former higher indicated dilution to localized effects of industrial activity.

Within the last several years there have been rapid advances in the methodology of radiocarbon assay, particularly as it pertains to radiocarbon dating. As a result, it is possible today to make routine radiocarbon assays in which the statistical uncertainty is less than one per cent for contemporary concentrations of natural radiocarbon. In view of such precision, a knowledge of the dilution effect becomes important in the precise radiocarbon dating of carbon-containing materials. It was to gain knowledge of the dilution effect in both plant material and shallow oceanic carbonates that the investigation described in the following sections was undertaken. In all of the experimental work, radiocarbon assays were made by proportional counting of the sample as carbon dioxide gas, contained in the counter under a pressure of five atmospheres absolute [*Brannon, Taggart,* and *Williams,* 1955]. The same counter was used for all assays. In the preparation of each sample the conversion to carbon dioxide and the recovery of the carbon dioxide were virtually complete, assuring an absence of effects due to isotopic fractionation. The results in all cases have been expressed in terms of net counts per minute for the particular counter employed. No attempt has been made to convert the results to a form which would reflect the absolute disintegration rate per unit mass of carbon.

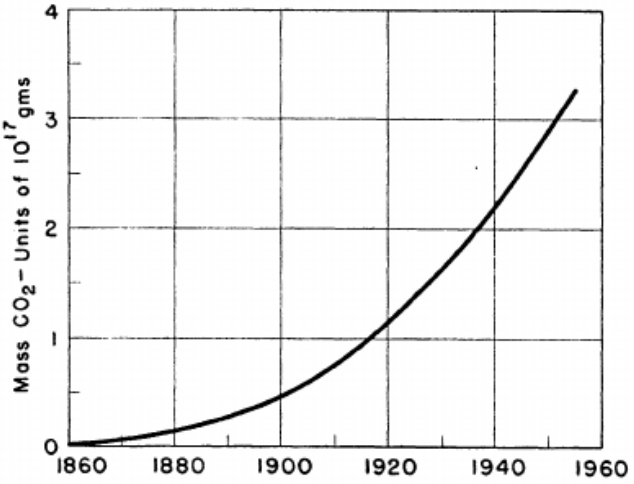

FIG. 1 — Cumulative carbon dioxide released to atmosphere by combustion of fossil fuels

Appraisal of carbon dioxide production from fossil fuels—Although various estimates have been made of the cumulative amount of carbon dioxide released to the atmosphere since the beginning of the industrial revolution by the combustion of fossil fuels, it was deemed desirable to reappraise both the total amount and the rate at which it has been introduced into the atmosphere.

The greater part of this carbon dioxide, by far, has been attributable to the burning of coal. Perhaps the best data suitable for the estimation of the contribution from coal are given by *Putnam* [1953] for world-wide consumption since the year 1860. His values are expressed in terms of heat content of coal consumed, so that proper weight may be considered to have been given to the rank of the coal. The conversion of Putnam's figures for coal consumption to mass of carbon dioxide produced may be accomplished by means of a factor relating carbon content to heat content of coal. Perhaps the most reliable data for the consumption of liquid petroleum are those given in a publication of *DeGolyer* and *MacNaughton* [1955]. The carbon dioxide produced by combustion of petroleum may be estimated by use of an average value for the carbon content of liquid petroleum. Although the mass of carbon dioxide produced by the combustion of natural gas is relatively minor, this may be approximated by use of an average carbon content of natural gas and of a ratio of gas to oil produced. This ratio may be assumed to have increased continuously from about 1910 to the present.

Figure 1 shows an estimate of the cumulative amount of carbon dioxide released to the atmosphere by the burning of fossil fuels made by use of the foregoing data and assumptions. The cumulative production to date, approximately 3.3×10^{17} grams of carbon dioxide, is equivalent to about 14 pct of the total amount of carbon dioxide in the atmosphere. This is somewhat less than an estimate made by *Putnam* [1953], and is slightly higher than an unpublished estimate made by Harrison Brown (private communication). Although no values of carbon dioxide equivalency are contained in a paper on total fossil fuel production by *Hubbert* [1956], application of reasonable carbon contents of coal and of petroleum to Hubbert's estimates of production would likely result in an estimate of total carbon dioxide production which would be slightly higher than that of Figure 1. It may also be noted that the estimate made by *Callendar* [1940] for carbon dioxide production between 1900 and 1935 is somewhat higher than that shown by Figure 1.

The curve of Figure 1 is not of simple exponential form. The portion from 1860 to about 1910 approximates an exponential form, but the part of the curve from 1910 onward deviates progressively from the exponential. The deviation is such that less carbon dioxide has been produced than would be expected from an exponential relation fitted to the early part of the curve. Application to the curve of combustion efficiency factors given by Putnam, however, yields a curve which follows closely an exponential form. From this it may be inferred that improvements in efficiency of utilization of fuels achieved during the last several decades have resulted in appreciably less consumption of fuels than would have been the case otherwise.

Evidence on dilution of atmospheric carbon dioxide—In investigating the dilution of atmospheric carbon dioxide and, consequently, of the carbon contained in vegetation by carbon from fossil fuels, the method of attack was essentially that followed by *Suess* [1954, 1955]. Radiocarbon assays were made of tree rings of known age, including rings of very recent age.

The selection of the woods for investigation posed a problem. Obviously, if an attempt were made to include all types of woody plants from all possible environments in which they are found, the number of samples would be prohibitively large. The decision was made, therefore, to choose only a very limited number of woods, but, in the selection, to attempt to choose samples which might yield definitive results. In particular, the samples were selected to represent extremes in environment and ecology.

The woods investigated were oak, gum, 'cypress' (*Taxodium*), and Douglas fir. The oak and gum samples were obtained from locations in eastern Texas approximately 75 miles north of Houston.

The cypress sample came from the swamps of south Louisiana, and the Douglas fir, kindly furnished by Edmund Schulman, was from the Rocky Mountain region. In all cases the samples were obtained from areas relatively remote from the centers of industrial activity in which there might be abnormally large concentrations of dead carbon released to the atmosphere from the utilization of fossil fuels.

Results of radiocarbon assay of samples of these woods of various ages are given in Table 1. An examination of the results reveals several features of interest. Perhaps the most conspicuous of these is the variation of the extrapolated contemporary assay of the four woods. This variation may be seen more clearly when the averages of the contemporary assay, extrapolated from the actual assays of samples 50 years or more old, are tabulated (Table 2). In the computation of the average extrapolated assay for the cypress, it is probably justifiable to disregard the data obtained from assay of the 600-year ring on the ground that this ring was in close proximity to the central cavity common in the swamp cypress, and therefore was particularly vulnerable to the influence of intrusive carbon. The difference in extrapolated assays of the Douglas fir and cypress is roughly six per cent.

Although the possibility cannot be ruled out that the differences in the extrapolated contemporary assays are attributable to differences in physiological behavior peculiar to the diverse genera, it seems more reasonable that the differences in assays are a reflection of the different ecological conditions under which the trees grew.

The Douglas fir generally grows on a steep and well-drained slope in what *Bannister* and *Smiley* [1955] term, in the sense that the word is used in dendrochronology, a 'sensitive' site, that is, one in which the soil moisture is derived directly from local precipitation. The oak and gum, on the other hand, are inhabitants of a 'complacent' site or one in which moisture is available from a porous subsoil as well as from direct precipitation. The area from which these particular oak and gum samples were obtained is one of moderately heavy forestation, and of clayey soil containing a moderate amount of humus. The environment in which the swamp cypress grows is necessarily one of standing swamp water; cypress swamps contain abundant organic remains in various stages of decay.

If it be assumed that ecological conditions are responsible for the differences observed in the extrapolated contemporary assay, then a reasonable mechanism by which these differences are achieved must be postulated. A mechanism which may be called upon to furnish an explanation is that postulated by *Wickman* [1952] in an attempt to explain variations in the abundance of the stable carbon isotopes in plants. According to Wickman's views, old carbon may be introduced into plants either by uptake of carbon dioxide contained in ground water, or by utilization in photosynthesis of carbon dioxide released from the soil. In corroboration of part of Wickman's postulate and of views expressed by *Godwin* [1951], *Deevey* and others [1954] have demonstrated that vegetation growing in hard-water lakes exhibits a decreased radiocarbon content, presumably by introduction into the plant material of inorganic carbon compounds dissolved in the lake water. *Craig* [1954], on various grounds, has rejected as untenable the idea ex-

TABLE 1 – *Radiocarbon assays of woods*

Sample	Radiocarbon assay	
	Actual	Extrapolated to present
	cpm	cpm
Douglas Fir (*Pseudotsuga taxifolia*)		
Western U.S., 15-yr ring	20.20 ± 0.17[a]	20.24 ± 0.17
Same, 225-yr ring	20.43 ± 0.17[a]	21.00 ± 0.17
Oak (Quercus stellata [?]), Cleveland, Texas, 0–10-yr rings	19.94 ± 0.17	...
Same, 100-yr ring	20.27 ± 0.17	20.52 ± 0.17
Gum (*Liquidamber styraciflua*) Cleveland, Texas, 0–10-yr rings	19.53 ± 0.17	...
Same, 50-yr ring	20.23 ± 0.17[a]	20.36 ± 0.17
Same, 100-yr ring	19.77 ± 0.17	20.02 ± 0.17
Same, 150-yr ring	19.93 ± 0.17	20.31 ± 0.17
Cypress (*Taxodium distichum*) Tangipahoa Parish, La., 0–10-yr rings	19.48 ± 0.17	...
Same, 200-yr ring	19.36 ± 0.17	19.86 ± 0.17
Same, 400-yr ring	18.68 ± 0.17	19.68 ± 0.17
Same, 450-yr ring	18.71 ± 0.17	19.84 ± 0.17
Same, 500-yr ring	18.58 ± 0.17	19.85 ± 0.17
Same, 600-yr ring	17.85 ± 0.17	19.35 ± 0.17

[a] Average of two determinations.

TABLE 2 – *Averages of contemporary assay, extrapolated*

Wood	Assay
	cpm
Douglas fir	21.00 ± 0.17
Oak	20.52 ± 0.17
Gum	20.23 ± 0.17
Cypress (*Taxodium*)	19.81 ± 0.17

TABLE 3 – *Extent of dilution exhibited by the various woods*

Wood	Extrapolated contemporary assay	Dilution
	cpm	pct
Douglas fir	21.00 ± 0.17	3.6 ± 1.1
Gum	20.23 ± 0.17	3.3 ± 1.1
Oak	20.52 ± 0.17	2.8 ± 1.1
Cypress	19.81 ± 0.17	1.7 ± 1.2

pressed by Wickman that there can be appreciable cyclic exchange through the atmosphere of carbon dioxide between plants and the pedosphere which would result in enrichment of the plant in C^{12}.

In an effort to shed light on the mechanism which apparently operated in the case of the four woods examined, $C^{12} - C^{13}$ ratios were determined for several of the same wood samples which had been subjected to radiocarbon assay. Results from these determinations indicate that differences among the $C^{12} - C^{13}$ ratios of the various woods are relatively small, and that the measurements do not serve to clarify the mechanism responsible for the variations in radiocarbon content.

Although the evidence is admittedly very scanty, it appears that the difference in extrapolated contemporary assays of the woods may be explained most reasonably by postulating the introduction of relatively small amounts of dead or old carbon into the oak and gum trees, and of a greater amount of old or dead carbon into the cypress tree.

A second feature of interest revealed by the assays of the four woods is that, in every case, the radiocarbon content of the very recent wood was noticeably lower than the radiocarbon content computed by extrapolation to the present of old wood from the same tree. Dilution of atmospheric radiocarbon by ancient carbon introduced by combustion of fossil fuels is thus quite evident.

The extent of dilution exhibited by the Douglas fir, 3.6 pct, is in excellent agreement with the value of 3.5 pct predicted by Harrison Brown (private communication) on the basis of detailed studies of the $C^{12} - C^{13}$ ratio made by Brown's co-workers on rings from the same tree (Table 3).

Quite evident in the foregoing tabulation is a trend of decreasing degree of dilution with decrease in the extrapolated contemporary assay. In spite of the relatively large uncertainties which exist in the estimated percentages of dilution, and in spite of the fact that the number of woods considered is small, the indication that such a trend exists cannot be ignored.

If, as postulated, the difference in the extrapolated contemporary assays are attributable to the incorporation in some of the trees of old carbon, then, by extension, the same posulate may be utilized to furnish a qualitative explanation of the trend of degree of dilution with extrapolated assay. For example, if the cypress utilized a large percentage of carbon older than about 50 years in the synthesis of its woody material, this carbon would not be affected by dilution accompanying the industrial revolution, and the apparent over-all effect due to combustion of fossil fuels would be diminished correspondingly. Although such an explanation may not be adequate to account quantitatively for the results obtained, there apparently exists a connection between the ecology of a tree and the degree of dilution due to the industrial revolution which it exhibits.

As a corollary, it is likely that the most reliable record of the true extent of dilution of atmospheric radiocarbon by carbon from fossil fuels is that furnished by the Douglas fir, the tree which apparently was least affected by assimilation of old carbon. The extent of dilution shown by the Douglas fir is in close accord with the dilution which may be calculated from results reported by *Suess* [1954], but is appreciably higher than his later interpretation [*Suess*, 1955] of less than one per cent.

Evidence on dilution of oceanic carbon—To investigate the possibility that the radiocarbon concentration in shallow oceanic carbonates may have been decreased perceptibly by dilution from dead carbon derived from the burning of fossil fuels, assays were made of the radiocarbon contents of calcareous shells of marine organisms collected in the nineteenth century, and, for comparison, of the radiocarbon contents of their modern counterparts.

Past experience in Humble's laboratories has indicated that modern shells of organisms which grow in restricted bays or estuaries may often have abnormally low radiocarbon concentrations. For this reason, only those historically-dated old marine shells were used which came from open coastal waters. All of the shells were from Atlantic or Caribbean waters.

Through the courtesy of William J. Clench of the Museum of Comparative Zoology, Harvard University, it was possible to obtain an ark shell, collected in South Carolina in 1850 by Louis Agassiz, and an ark shell collected in Jamaica in 1845 by Governor Adams of Jamaica. The Charles-

ton Museum generously contributed a Venus clam collected in 1859 at Sullivan's Island, Georgia, by Edmund Ravenal, and Harry S. Ladd of the U. S. National Museum in Washington graciously gave a *Buccinum* collected in 1873 at Casco Bay, Maine. Table 4 lists the actual radiocarbon contents of the old, historically-dated shells and the corresponding contents after extrapolation to zero age.

For comparison with the Venus clam collected by Ravenal, good values of the radiocarbon assay of the modern counterpart were available. Robert A. Moody, then of Humble's Production Research Division, with the generous cooperation of his father, Clarence L. Moody, had collected a number of genera of living organisms from a variety of environments on the Atlantic coast. Three Venus clams from different environments, collected near Sullivan's Island, the location from which the Ravenal shell came, gave assays of 20.33, 20.39, and 20.24 cmp, each with a statistical uncertainty of ±0.17 cpm. If the average of these, 20.34 ± 0.17 cpm, be used as the representative assay of the modern counterpart, the extent of dilution indicated by the Venus clam is 2.1 ± 1.6 pct.

In the computation of dilution by use of data from the Agassiz and from the Jamaica samples, there is some uncertainty in assigning assays to the respective modern counterparts. No sample of living ark could be obtained from the South Carolina coast, whence the Agassiz sample came, since the Incongruous Ark is now relatively rare on this coast. No modern sample of Cut Ribbed Ark from Jamaica was readily available. Consequently, for comparison with the Agassiz sample, use was made of a sample of *Anadara brasiliana Lamarck* collected at Coronado Beach, Florida, in 1938, and for comparison with the Jamaica sample a shell of *Barbatia candida Helbling* was employed which had been collected at Fort Myers, Florida, in 1921. Both of the latter shells were obtained through the courtesy of William J. Clench.

The assay of the 1938 Coronado Beach ark was 19.52 ± 0.17 cpm, which extrapolates to 19.56 ± 0.17 cpm for zero age before the present. If this value be used as representative of the modern counterpart of the Agassiz sample, the amount of dilution which had taken place to 1938 is indicated to be 3.2 ± 1.6 pct.

The assay of the 1921 *Barbatia candida* from Fort Myers, Florida, was 20.31 ± 0.17 cpm, equivalent to 20.39 ± 0.17 cpm extrapolated to the present. Use of this value for comparison with the Jamaica sample yields an estimated dilution, as of 1921, of negligible percentage.

TABLE 4 – *Radiocarbon contents of historically dated marine shells*

Shell	Actual assay	Assay extrapolated to zero age
	cpm	cpm
Venus clam (*Veneridae Mercenaria*), collected by Ravenal, Sullivan's Island, S. C., 1859	20.54 ± 0.16 20.42 ± 0.16 20.60 ± 0.16	
Av.	20.52 ± 0.16	20.77 ± 0.16
Incongruous Ark (*Anadara brasiliana Lamarck*) collected by Louis Agassiz, South Carolina, 1850	19.95 ± 0.17	20.21 ± 0.17
Cut Ribbed Ark (*Barbatia candida Helbling*) collected by Gov. Adams, Jamaica, 1845	20.18 ± 0.17	20.44 ± 0.17
Buccinum undatum (*L*) collected by U.S. Fish & Wildlife, Casco Bay, Maine, 1873	19.98 ± 0.17	20.11 ± 0.17

Unfortunately, no assay has yet been made of modern *Buccinum* from Casco Bay for comparison with that of the 1873 specimen. A modern sample from Digby Neck, Nova Scotia, has been examined, however, and has given 20.41 ± 0.17 cpm, which is higher than the extrapolated counting rate of the 1873 Casco Bay sample.

In an appraisal of the evidence bearing on dilution of the radiocarbon in these marine shells, most weight should be given to that furnished by the comparison of the results obtained from the Ravenal shell with those obtained from modern Venus clam shells. Slightly less weight should probably be given to the evidence supplied by the Agassiz sample and its Coronado Beach modern counterpart, and, because of the probability of environmental differences, less reliance can be placed on the comparison between the Jamaica and the Fort Myers samples and on the comparison between the Casco Bay and the Digby Neck samples. Such an appraisal leads to the conclusion that marine shells, and hence the dissolved carbonates of shallow oceanic waters, appear to show a perceptible dilution effect. Although the evidence at hand is extremely limited, it indicates that the extent of the dilution may be in the neighborhood of one to two per cent.

Implications of the radiocarbon evidence—From

the radiocarbon evidence on the dilution of atmospheric and oceanic carbon by carbon dioxide from fossil fuels it is possible to estimate the rate at which carbon dioxide enters the oceans, and to deduce some information on the mixing times of the oceans. These topics are considered in the following sections.

Rate of entrance of atmospheric carbon dioxide into the oceans—It has been deduced in a preceding section that the dilution of atmospheric carbon dioxide by fossil carbon dioxide is, at present, likely in the neighborhood of about $3\frac{1}{2}$ pct. If it be assumed that the carbon dioxide introduced into the atmosphere as a result of the industrial revolution is predominately that from fossil fuels (tantamount to the assumption that the amount of 'recent' carbon dioxide resulting from agricultural activity is small in comparison), then the increase in mass of atmospheric carbon dioxide is correspondingly about $3\frac{1}{2}$ pct.

In order that the rate of exchange of carbon dioxide between atmosphere and ocean may be estimated, it is desirable to postulate that (1) the entrance rate of carbon dioxide into the ocean is proportional to the mass of carbon dioxide in the atmosphere, and (2) the exit rate of carbon dioxide from the ocean to the atmosphere is constant, since it may be assumed that no appreciable change in carbon dioxide concentration in the upper part of the ocean results from the addition of the fossil carbon.

By utilization of an approximate expression for the rate of production of carbon dioxide shown in Figure 1, the rate of change of carbon dioxide in the atmosphere is given by

$$\frac{dM_a}{dt} = Bke^{kt} - \alpha M_a + \beta \qquad (1)$$

where

M_a = mass of carbon dioxide in the atmosphere
t = time
Bke^{kt} = rate of production of carbon dioxide by combustion of fossil fuel, as derived from the curve $B(e^{kt} - 1)$ fitted to Fig. 1
α = entrance coefficient
β = exit rate

The solution, on integration of (1), is

$$M_a = M_a|_{t=0} + \frac{Bk}{k + \alpha}\left[e^{kt} - e^{-\alpha t}\right] \qquad (2)$$

In this solution, $t = 0$ at the year 1860.

Solution of (2), utilizing the estimated increase of $3\frac{1}{2}$ pct for the mass of carbon dioxide in the atmosphere, yields a value for a of 0.062 per year. This is the fractional part of the atmospheric carbon dioxide which enters into the ocean each year.

In comparison, *Suess* [1953] has given a value, which may be considered as comparable, of from 0.02 to 0.05. Expression of an entrance coefficient given by *Dorsey* [1940, pp. 552–553], determined in the laboratory for carbon dioxide and pure water, in terms similar to those above yields a value of 0.044.

Mixing times of the oceans—From the evidence on dilution of oceanic carbonates, the information on rate of exchange of carbon dioxide between atmosphere and ocean, and an estimation of the ratio of radiocarbon concentration in the ocean to that in the atmosphere, it is possible to draw rough conclusions as to the rate of mixing in the oceans. For this purpose, it is necessary to formulate a simplified model representative of the atmosphere-ocean system which embodies, in a broad sense, the major physical factors involved, yet which is amenable to analytical treatment.

A convenient model embodying the atmosphere, an upper ocean, and a deep ocean, is illustrated schematically in Figure 2. In this model, it may be assumed that (1) the mixing of carbon dioxide in the atmosphere is rapid, and the concentration of radiocarbon is uniform, and (2) the mixing of carbon dioxide (and carbonates) in the upper ocean is rapid, and the concentration of radiocarbon is uniform.

With these assumptions, the radiocarbon distribution in the model can be described by

$$\alpha M_a q_a + \eta q_d - \alpha M_a q_o - \eta q_o - \lambda q_o M_o = 0 \qquad (3)$$

$$\eta q_o - \eta q_d - \lambda q_d' M_d = 0 \qquad (4)$$

where

α = entrance coefficient of carbon dioxide into the ocean
M_a = mass of carbon dioxide in the atmosphere
q_a = concentration of radiocarbon in atmospheric carbon dioxide
η = rate at which carbon dioxide components are transferred out of the upper ocean into the deep ocean
q_d = average concentration of radiocarbon in carbon dioxide components returned from the deep ocean to the upper ocean
q_o = concentration of radiocarbon in the carbon dioxide components of the upper ocean
M_o = mass of the carbon dioxide components of the upper ocean
λ = decay constant of radiocarbon
q_d' = average concentration of radiocarbon in the carbon dioxide components of the deep ocean
M_d = mass of the carbon dioxide components of the deep ocean.

Simultaneous solution of (3) and (4) yields

$$\frac{q_d'}{q_o} = \left[\left(\frac{q_a}{q_o} - 1\right) - \frac{\lambda M_o}{\alpha M_a}\right]\frac{\alpha M_a}{\lambda M_d} \tag{5}$$

Introduction of

$$a = \frac{q_a}{q_o} - 1 \tag{6}$$

gives

$$\frac{q_d'}{q_o} = a\frac{\alpha M_a}{\lambda M_d} - \frac{M_o}{M_d} \tag{7}$$

To evaluate the transit time of the carbon dioxide components through the deep ocean in terms of the average concentration of radiocarbon as given in (7), it is necessary to postulate a mechanism for the transfer. If it be assumed that the transfer is as that through a uniform pipe, then it is easily shown that

$$\frac{q_d'}{q_o} = \frac{1 - e^{-\lambda T}}{\lambda T} \tag{8}$$

where T = transit time through the pipe.

Combining (7) and (8) permits calculation of the transit time if values can be assigned to the quantities a, M_o, M_a, and α.

A value for a may be obtained by assuming that a radiocarbon fractionation of five per cent occurs in photosynthesis, and by use of extrapolated values of radiocarbon assays of historically-dated shell and wood samples. Values of M_o may be obtained by use of estimates of the dilution of radiocarbon in near-surface oceanic carbonates and in atmospheric carbon dioxide, and by consideration of the total masses of carbon dioxide in the atmosphere and in the ocean. In the estimation of the masses of carbon dioxide in the atmosphere and in the ocean, several sources of data were considered. The values chosen for carbon dioxide contents were

$$M_a = 2.4 \times 10^{18} \text{ gms.}$$

$$M_o + M_d = 1.4 \times 10^{20} \text{ gms.}$$

The value of α has been estimated in a preceding section. Use of these quantities in (7) and (8) yields the results shown in Table 5.

In this tabulation, the thickness of the upper ocean was computed from $\dfrac{M_o}{M_o + M_d}$ and from data on depth and volume of the oceans given by *Sverdrup* and others [1942].

In the particular model used, the value of the transit time, or turnover time, is strongly dependent on the values chosen for α and for a. These, in turn, depend strongly on the values used for the extent of dilution, for the extrapolated contemporary assays of woods and of shells, and for the isotopic fractionation of radiocarbon. An increase either in α or in a leads to a smaller transit time.

The transit times listed in the above table have been criticized by Roger Revelle (private communication) as being too great, on the ground that they are not consistent with estimates of turnover time made by use of data on heat flux through the ocean floor. In view of the crudeness of the model utilized, the assumptions employed, and the uncertainties in various of the values which were used, the results, quantitatively, are certainly open to question.

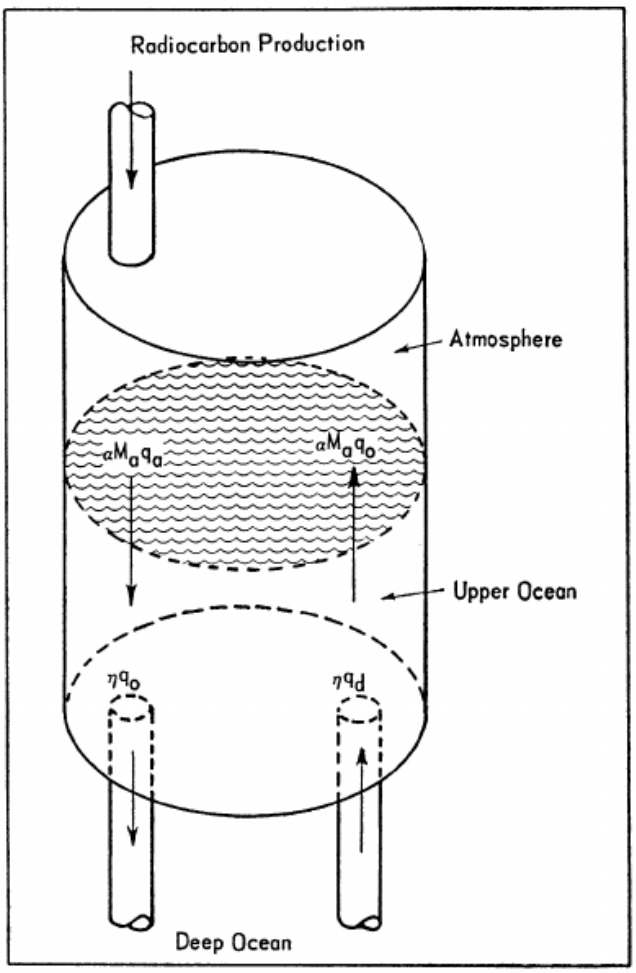

FIG. 2 — Model used for distribution of radiocarbon

TABLE 5 – *Results of computations*

Dilution of upper oceanic carbonates by carbon from fossil fuels	T	$\frac{M_o}{M_o + M_d}$	Thickness of upper ocean	Apparent age of carbon in upper ocean
pct	years		m	years
1	*3200*	*0.22*	*800*	*620*
1½	5100	0.16	600	580
2	7200	0.11	400	540

The simplified model employed in this treatment is by no means the only model that might be used to portray radiocarbon in the atmosphere-ocean system, and the choice of the particular model was influenced by its being amenable to a relatively simple analytical treatment. Models somewhat similar have been employed in unpublished works by Harmon Craig (private communication) and by J. R. Arnold and E. C. Anderson (private communication).

Summary and conclusions—The radiocarbon evidence indicates that, although there are variations in the degree of dilution with fossil carbon exhibited by different trees, these variations are probably a consequence of differences in ecologies of the trees. If allowance be made for this, it follows that atmospheric carbon dioxide has probably been diluted to the extent of about $3\frac{1}{2}$ pct with carbon dioxide from the combustion of fossil fuels.

The radiocarbon evidence indicates, on the basis of a comparison of the radiocarbon assays of old, historically dated marine shells from the Atlantic coast with the assays of their modern counterparts, that there has been a perceptible dilution of shallow oceanic carbonates with dead carbon from fossil fuels. The limited data available suggest that the extent of dilution is possibly one to two per cent.

Of interest in connection with the distribution of radiocarbon in the carbon cycle are (1) the rate of exchange of carbon dioxide between the atmosphere and the ocean, and (2) the rate of turnover of carbonates in the ocean. The use of simplified mathematical models and of assays of historically dated shell and wood samples allows an estimate to be made of the rate of exchange and turnover time. The limited experimental data available suggest a turnover time of a few thousand years and an exchange rate of about $\frac{1}{16}$ of the atmosphere per year. It may further be deduced that the thickness of the upper ocean, assumed to be thoroughly mixed, is a few hundred meters and that the apparent age of the carbon in the upper ocean is about 600 years.

The apparent age of about 600 years for the upper ocean is a consequence of return of old carbon from the deep ocean; in some shallow seas, where the rate of exchange with the atmosphere may be the governing factor, it may be expected that the apparent age will be much less. As a corollary, it is likely that significant variations will be found in the radiocarbon contents of marine shells from areas which participate to varying extents in the interchange of waters with the deep oceans.

Most of the conclusions reached in this work must necessarily be considered as tentative, and more data are required to substantiate, modify, or refute them. Many points remain obscure, and they can be elucidated only by bringing to bear on them new evidence from additional data.

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