

The Distribution of Carbon-14 in Nature

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Abstract

The carbon-14 activity of oceanic materials indicates that the mixing half-time for carbon between the atmosphere and ocean surface waters is one or two decades, while the turnover time for the ocean as a whole is several hundred years. This conclusion is consistent with estimates based on the measured decrease in carbon-14 specific activity of wood grown in recent years compared with 19th century wood.

1. Introduction

Early studies on the distribution of carbon-14 in diverse samples of living matter (ANDERSON and LIBBY, 1951) indicated the essential constancy of the activity (or concentration) of carbon-14 in the carbon of these materials. It was postulated that the specific activity is constant except for the effect of isotopic fractionation throughout what is now called the "exchange reservoir", consisting of the atmosphere, living matter (biosphere), and the seas. (The C-13/C-12 ratio permits accurate correction for the fractionation effect which can amount to as much as 6 % between materials such as wood and carbonate ion.)

Two small deviations from this state of affairs are now known to occur:

1) Age of the oceans. Measurements seem to show that the specific activity of surface ocean water is lower by perhaps 4 to 8 % than its equilibrium value if mixing with the atmosphere were rapid. The deeper water seems to be even older.

2) The Suess effect (SUESS, 1955). Twentieth century wood shows a lower specific activity than expected from earlier samples. This is ascribed to the rapidly increasing rate of

combustion of fossil fuels. The resulting inert carbon dioxide dilutes the radioactivity of the carbon with which it mixes.

We propose to use these two effects, which are to be regarded as minor nuisances in radiocarbon dating work, as indicators of the rates of mixing of various parts of the exchange reservoir. In addition, we will employ our knowledge of the rate of production Q and of the absolute specific activity of carbon-14 to set certain important limits.

We shall be forced to simplify the complex situation in order to make practical calculations. As a result of this and the uncertainties in the data the computed mixing times must be regarded as rough approximations.

The data we shall employ are given in Table I. The quantities of carbon in various parts of the reservoir shown in column two are taken from LIBBY (1955), with the addition of 0.2 g/cm² for humus, and a partially compensating lowering of the "biosphere" component. In column three are given the values increased by a factor of 1.05 for the atmosphere and 1.06 for ocean "carbonate", an artificial device which takes into account isotopic fractionation for purposes of our model calculations. The

Table I. Assumed size and specific activity of the components of the exchange reservoir

	Carbon content g/cm ⁻²	Carbon content (corr. for frac- tionation)	Relative specific activity (corr. for frac- tionation)
Atmosphere.....	0.12	0.13	1.00
Biosphere.....	0.21	0.21	
Land.....	0.05	0.05	1.00
Ocean.....	0.16	0.16	0.960
Ocean, dissolved organic.....	0.6	0.6	0.928
In top 100 metres	0.02	0.02	0.960
Humus.....	0.2	0.2	1.00
Ocean carbonate.	7.25	7.7	0.928
In top 100 meters	0.2	0.2	0.960

relative specific activities for average oceanic materials are estimates from the data of RUBIN (1956). Other measurements are available. It is assumed that humus and dissolved organic matter are in fairly rapid equilibrium with the local life.

It should be stressed that these numbers are all more or less inaccurate, and may not even represent the best values available currently. The conclusions we shall draw from our model calculations will not depend at all strongly on the numbers used.

2. Models

The simplest useful model which we can make of the mixing process divides the exchange reservoir into two parts whose boundary is the ocean surface. The upper reservoir A is taken to include the atmosphere, land-life and humus, or a total of 0.38 g/cm². Reservoir C contains ocean "carbonate", the remainder of the living matter and dissolved organic carbon, a total of 8.5 g/cm².

Consider the transfer of ordinary carbon and of carbon-14 from one reservoir to the other.

We have for the equilibrium $A \xrightleftharpoons[k_{-1}]{k_1} C$, a pair of first order rate constants related to the half-times for mixing by the definition $t_{1/2} = 0.693/k$. Exchange of normal carbon between the two reservoirs, in steady state, leads to two equations:

$$\left. \begin{aligned} \frac{dn_A}{dt} = 0 &= -k_1 n_A + k_{-1} n_c \\ \frac{dn_c}{dt} = 0 &= k_1 n_A - k_{-1} n_c \end{aligned} \right\} \quad (1)$$

The second equation is redundant. For the C-14 distribution there is again a pair of equations, one of which is redundant. For reservoir A:

$$\frac{df_A}{dt} = 0 = \lambda(f_A + f_c) - \lambda f_A - k_1 f_A + k_{-1} f_c \quad (2)$$

In these equations n_A is the quantity of normal carbon in gm per cm² in reservoir A, and f_A the quantity of C-14, the latter in arbitrary units. λ is the decay constant of C-14, $1.25 \times 10^{-4} \text{yr}^{-1}$. Equation 1 serves to define the ratio k_{-1}/k_1 ; equation 2 gives us the individual values if the quantities n, f, λ are given. Calculations for more complex models follow the same form.

In the ocean there is a rather striking difference between a surface layer which is well mixed both vertically and horizontally by thermal convection and wind action, and middle and deep waters of nearly uniform temperature and slow circulation. To approximate the effect of such a division a second model has been constructed in which a surface sea layer B appears.

In this model, $A \xrightleftharpoons[k_{-1}]{k_1} B \xrightleftharpoons[k_{-2}]{k_2} C$. Reservoir A

remains as before and reservoir B is taken to represent the ocean to a depth of 100 meters, approximately the level of the thermocline. It is assumed that reservoir B contains all the ocean life and that dissolved organic matter is uniformly mixed through the sea.

The results, shown in Table II, indicate that the mixing times depend on reservoir size, on the model used, and on the choice of C¹⁴ data. At the same time the orders of magnitude are fixed within rather narrow limits. In the second model, the reverse mixing times of 12 and 250 years may seem too short to account for the 600-yr age of C corresponding to a specific activity of 0.926. It must be remembered that the 10-yr half-time for B to A is the time to cycle half of the 0.38 g/cm⁻² reservoir B through A. Since C is 20 times as large as B, the half-time of cycling the mass of C from B to A is 20 x 10 or 200 yr. This combined

Table II. Mixing times for several reservoir models

System	Reservoir	Carbon Content ¹ g cm ⁻²	Specific Activity ²	Total C ¹⁴ Content	Mixing half-time, years	
					Forward	Reverse
AC	A	0.38	1	0.38	20	440
	C	8.46	0.928	7.85		
ABC	A	0.38	1	0.38	10	10
	B	0.38	0.965	0.367	12	250
	C	8.08	0.926	7.48		
ACD	A	0.38	1	0.38	13	290
	C	8.46	0.928	7.85		
	D	large	small	3.0		

¹ corrected for isotopic fractionation.

² relative to reservoir A.

with the 250-yr $t_{1/2}$ for C-B is sufficient to give the required 600-yr average life (=416 yr $t_{1/2}$).

Several other models, breaking up reservoirs A and C into sub-reservoirs in different ways, have been used to calculate mixing times. The results are essentially similar to those given above.

The "age" of the sea might be explained by another hypothesis, namely, that carbon of low or zero activity in the underlying sediments might be redissolving at an appreciable rate and diluting this reservoir. The preservation of the isotopic gradients in ocean bottom cores excludes the possibility of large-scale chemical exchange between sediments and sea, but gross solution and redeposition in different regions are still possible. To demonstrate the consequences of such an effect, we have set

up a model in which $A \xrightleftharpoons[k_{-1}]{k_1} C \xrightleftharpoons[k_{-2}]{k_2} D(\text{sediments})$.

Here reservoirs A and C are as in the first model. The size of reservoir D is indeterminate, since we cannot estimate the quantity of sediments available for solution. If this is large compared with the size of reservoir C, however, so that the specific activity of sediment carbon remains low, only the total amount of C¹⁴ in reservoir D is important.

An upper limit to this quantity can be given based on our knowledge of the C¹⁴ production

rate Q, as compared with the known specific activity of carbon in reservoir A. In steady state the production rate of C¹⁴ is equal to its disintegration rate, and the existence of a steady state is implied by the success of the C¹⁴ dating method. The decay rate is about 15 min⁻¹ g⁻¹ in reservoir A (Suess, 1955). The disintegration rate Q is then 2.0 sec⁻¹ cm⁻² if all the C¹⁴ is in A and C. A rough upper limit for Q from the cosmic ray neutron flux is 2.6 sec⁻¹ cm⁻². If recent measurements of SOBERMAN (1955) are correct, the value is much lower. Thus, at most 0.6 sec⁻¹ cm⁻² or about 30 % of the C¹⁴ inventory might be in D. Using this number we compute the ACD mixing times shown in Table II. It is clear that the mixing times between A and C are not much affected by the existence of reservoir D. In fact, in order to decrease these mixing times by an order of magnitude, an order of magnitude increase in Q would be necessary. This is, of course, entirely excluded by the cosmic ray data.

3. Fossil fuel

The effect of fossil fuel consumption on the CO₂ content of the atmosphere has been considered by a number of writers (CALLENDAR, 1940; BUCH, 1942, 1948; STEPANOVA, 1952; SUESS, 1953). Production of CO₂ by this process has reached truly geochemical proportions and the rate of introduction of "new" (i.e., "old") carbon into the exchange reservoir by fuel consumption seems to exceed the natural production rate of juvenile carbon by two orders of magnitude. As long ago as 1919 KROGH (1919) was able to show that local increases in the CO₂ of the air of Copenhagen were due to combustion processes by measuring the concomitant decrease of O₂ and the respiratory quotient. The quantitative effect of this fossil CO₂ on the C¹⁴ assay depends strongly on the rates of mixing of the several components of the exchange reservoir. The total amount of dead C added to the atmosphere since 1900 amounts to 0.016 g cm⁻². The rate of production of fossil CO₂ has been exponential with a half-time of 17 yr up to 1910 and about 40 yr since then. If all this were to remain in the atmosphere, it would lead to a world-wide depression of the C¹⁴ assay of atmospheric CO₂ of about 12 %. If it mixed with the atmosphere, land-life and humus,

the depression would be 4 %. If diluted with the entire exchange reservoir, the effect would be only 0.2 %.

Because the CO_2 of the atmosphere appears to have increased by some 10 % since 1900, it has been postulated by CALLENDAR (1940) that the fossil fuel CO_2 has indeed remained in the atmosphere so that the atmosphere-sea and atmosphere-biosphere mixing times must be long compared with 50 yr. The observed level of the SUESS effect is very difficult to reconcile with CALLENDAR's hypothesis. While local depressions of the assay of up to 4 % are observed, the world-wide depression must be of the order of 1 %. In order for 0.016 g/cm^{-2} of inert carbon to produce this small reduction in the assay, it must be exchanged with at least reservoirs *A* and *B*. On the basis of the detailed analysis of the sea-water-air equilibrium by BUCH *et al.* (1932), one can compute that a given per cent increase in the CO_2 partial pressure in the air results in a 10-fold smaller per cent increase in total CO_2 concentration of the sea (this was called to our attention by R. REVELLE). The entire reservoir *B* is, therefore, available for specific activity reduction by exchange while in terms of actual removal of CO_2 from the air, it is only $1/10$ as effective. Putting in these numbers one finds that a specific activity reduction of $0.016/0.76 = 2.1$ % is predicted, which is not much too high, along with an increase in partial pressure of $0.016/0.42 = 3.8$ %. This is a factor of three too small to account for the observed increase in atmospheric CO_2 .

One can make the numbers fit by assuming the land biosphere to be very small or to mix very slowly. In this case the predicted SUESS effect for *A* and *B* is $0.016/0.50 = 3.2$ % and the atmosphere concentration increase is 9 % in good agreement with some of the local results in the northern hemisphere. However, the southern hemisphere numbers seem to show no SUESS effect as large as 1 % and since inter-hemisphere atmospheric mixing is probably rapid, this indicates the large SUESS effects to be purely local phenomena. One is, therefore, compelled to return to something like the first formulation, in which case CALLENDAR's explanation of atmospheric CO_2 increase cannot be maintained.

The reason for the increase in atmospheric CO_2 remains obscure. HUTCHINSON (1954) has

suggested an agricultural origin for the excess. Another possibility is the effect of the increase in temperature of the oceans during the past 50 yr which may have displaced the complex dynamic equilibrium between CO_2 in the sea and the air.

The data used in the calculation of the SUESS effect are those previously reported by SUESS (1955) and ARNOLD (HAYES, ANDERSON, and ARNOLD, 1955). Samples were tree-ring sections from selected localities. The C^{14} activity and the C^{13} content were determined and the C^{14} values corrected for age and for isotopic fractionation. The results are sum-

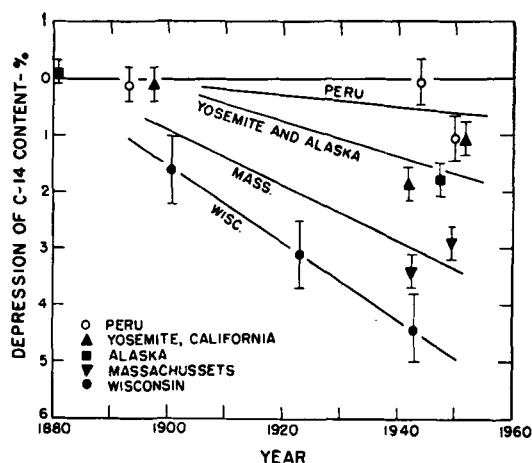


Fig. 1. Decrease in C^{14} assay of wood in the twentieth century. Activity corrected for radioactive decay. Data from SUESS (1955) and HAYES, ANDERSON and ARNOLD (1955).

marized in Figure I. The Wisconsin and Massachusetts trees are assumed to represent local conditions near industrial centers; the Yosemite and Alaska trees perhaps represent a non-industrial northern hemisphere average; and the Peruvian tree (analyzed by both investigators) the southern hemisphere.

Because the effect is so small and the number of samples so limited, no quantitative estimate of mixing times can be derived from these results, but comparison of orders of magnitude with the model is possible. The 4 % depression near industrial centers is reasonable in terms of known total fossil fuel consumption. If Yosemite and Alaska are indeed representative of the general northern hemisphere effect, then dilution with a reservoir 2 to 3 times the size of *A* is indicated, requiring mixing with a total

of 1.0—1.5 g/cm² C on a time-scale of the order of 20 yr. It is gratifying to note that these quantities are close to those obtained in the ABC model based on the ocean "age". A and B together contain about 0.8 g/cm² with a mixing time of 10 yr and the short turnover of B through C (12 yr) in effect enlarges the "dilution capacity" of B.

The interpretation of the southern hemisphere SUESS effect is less clear. If the time for ocean mixing is indeed years and if inter-hemisphere atmospheric mixing time is short compared to inter-reservoir mixing times, then the average SUESS effect in the southern hemisphere should be comparable to that in the northern hemisphere. The limited data so far available seem to indicate that this is not so. The southern SUESS effect appears to be less than 0.5 % if indeed it is not zero. More data are needed to clarify this situation.

4. Conclusions

The discussion based on the carbon-14 activity of marine samples has indicated that

the mixing half-time for carbon between the atmosphere and ocean surface water is perhaps one or two decades, while the turnover time for the ocean as a whole is several hundred years. This conclusion is consistent with the data on the SUESS effect, which would tend if anything to favor the lower values. As more reliable data are accumulated, and as the analysis are made more detailed, these figures will doubtless change. However, their order of magnitude seems reasonably well defined at the present time.

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