

The Natural Distribution of Radiocarbon and the Exchange Time of Carbon Dioxide Between Atmosphere and Sea

By HARMON CRAIG, Scripps Institution of Oceanography, University of California, La Jolla, California

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Abstract

Steady-state equations governing the transfer and distribution of a radioactive isotope between its various exchange reservoirs are applied to the natural distribution of carbon 14. The radiocarbon enrichment or depletion in each reservoir, relative to the hypothetical state in which mixing is infinitely faster than the decay rate, is evaluated as a quantitative function of the exchange rates between the reservoirs. From the observed distribution of C^{12} , C^{13} , and C^{14} in the atmosphere, biosphere, and sea, and from the estimated production rate of C^{14} by cosmic rays, the residence time of a carbon dioxide molecule in the atmosphere, before entering the sea, is found to be between four and ten years.

The atmospheric residence time may also be evaluated, independently of the estimated C^{14} production rate, by considering the functional dependence of the C^{14} concentration in the oceanic mixed layer on the residence times in the atmosphere and the deep sea. This second method of evaluation also leads to an atmospheric residence time of about seven years. The average annual exchange flux of carbon dioxide into the sea is thus about 2×10^{-8} moles per square centimeter of sea surface. The average residence time of carbon dioxide in the deep sea is estimated as probably not more than about 500 years.

Introduction

Some years ago, the writer made a study of the expected and observed relationships between C^{13} and C^{14} variations in natural materials (CRAIG, 1954). The ratio C^{13}/C^{12} varies by some 5 % in natural sources of carbon (NIER and GULBRANSEN, 1939; CRAIG, 1953), and it was shown that for isotopic fractionation processes, the C^{14} fractionation factors should be the square of the equivalent C^{13} fractionation factors. Since the fractionation factors are close to 1, then barring effects due only to the radio-

activity of C^{14} , the percentage enrichment of C^{14} in any compound should be approximately twice the C^{13} enrichment relative to the same source material. Thus, since the carbonate shells of marine mollusks are enriched some 2.5 % in C^{13} relative to terrestrial wood, such shells should show a C^{14} enrichment, relative to wood, of about 5 %. The analytical data then available indicated, however, that wood and shell have about the same radiocarbon concentration, and it was concluded therefore, that the exchange rate of CO_2 between atmosphere and sea was slow enough to produce an apparent radiocarbon age of 400 years for the surface ocean bicarbonate, corresponding to 5 % of the radiocarbon mean life of 8,033 years. It was further pointed out that only slow

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transfer of carbon across the ocean-atmosphere interface could account for this isotopic discrepancy between the concentrations of the stable and radioactive isotopes.

Recently, more detailed studies of the natural distribution of radiocarbon have established unequivocally the reality of this effect, and it appears that the apparent age of the surface ocean bicarbonate may be taken as 400 ± 100 years for the sake of general calculations (Suess, 1954, 1955; RAFTER, 1955). It is therefore possible to present a more detailed discussion of the factors affecting the concentration of radiocarbon in its natural reservoirs, and to derive some quantitative values for the exchange rate of carbon dioxide between the atmosphere and the sea.

Recent estimates of the residence time of a molecule of carbon dioxide in the atmosphere, before entering the sea, range from 16 hours (DINGLE, 1954) to the order of 1,000 years (PLASS, 1956). It is, therefore, of considerable interest to determine how precisely this figure may be evaluated from the known distribution and properties of the carbon isotopes. In the following study, we evaluate the characteristics of the radiocarbon distribution in a model of the atmosphere—sea system which is constructed in accord with the known layered structure of the sea, and deduce the atmospheric exchange time by two different methods which are quasi-independent. Both of these methods are based on considerations of the steady state transfer phenomena; a third method of evaluating the CO_2 exchange time, based on the dilution of the atmospheric radiocarbon concentration by the combustion of coal, has been given by SUSS (1953), and recently in a more detailed treatment by REVELLE and SUSS (1957). As we shall see, all these methods lead to the same atmospheric exchange rate but yield essentially no new information on the rate of internal mixing in the sea. However, we shall derive an estimated upper limit for the internal mixing time of the sea, by consideration of the possible dilution of radiocarbon activity in the mixed layer of the sea by production of dead CO_2 . (The steady-state radiocarbon balance and the Suess effect have both been treated in a recent study by Arnold and Anderson, in which the internal mixing time of the sea is taken as fixed from recent measurements of M. Rubin; their

calculations differ considerably from those given here and are commented on under Acknowledgements.)

Distribution of the carbon isotopes within the exchangeable system

We shall denote the total carbon in the active reservoirs of the atmosphere, biosphere, and sea, as the *exchangeable system*, containing about 7.9 grams of carbon per square centimeter of earth surface (cm^2). Table 1 shows the amounts of carbon assumed for the various components of the exchangeable system, the characteristic carbon 13 concentration in each of the components (given as per mil enrichments relative to the Chicago isotopic standard), and the carbon 14 fractionation factor relative to modern wood, computed as the square of the equivalent factor for carbon 13. The values of α_{14} are the C^{14} concentration factors relative to modern wood which would be observed if carbon 14 were stable, i.e. if the relative concentrations were unaffected by radioactive decay.

Figure 1 shows the model used for calculation; the exchangeable system is divided into five reservoirs containing amounts of carbon relative to N_a , the amount in the atmosphere, as shown in the various boxes. For convenience the term *biosphere* is restricted to denote the living terrestrial plants. The transfer between units is assumed to be determined by first order rate constants, denoted as shown, except in the case of biosphere assimilation, where the uptake is probably proportional to $N_a^e N_b$, ϵ being a number between 0 and 1.

The amounts of carbon in the atmosphere, biosphere, humus, and in the entire ocean, are taken directly from Table 1. However, in accord with observation, the ocean has been taken as consisting of two reservoirs, a mixed layer and the deep sea, separated by the thermocline. The average depth of the thermocline is a question of considerable geochemical significance with respect to problems where rates of uptake or mixing are concerned. We are here interested in the average depth as defining the volumes of material in the two more or less permanent layers of the sea, relative to the total volume of material in the sea. Dr. Warren Wooster of the Scripps Institution has kindly made a study of this important relationship, using most of the

Table 1. Amounts of carbon, characteristic C¹³ concentration, and C¹⁴ fractionation factor relative to terrestrial wood, of the various components of the exchangeable system of natural carbon

	δC^{13} (‰) (1)	α_{14} (2)	Carbon content grams/cm ² (3)
Atmospheric CO ₂ .	— 7	1.037	0.126 (3)
Terrestrial biosphere (living) . .	— 25	1	0.06 (4)
Terrestrial humus . . .	— 25	1	0.215 (5)
Marine biosphere.	— 13.5	1.024	0.002 (6)
Dissolved organic carbon in sea . .	— 13.5	1.024	0.533 (7)
Total inorganic carbon in sea . .	— 1.5	1.049	6.94 (7)
Total exchangeable system . . .			7.88

- (1) Data from H. CRAIG (1953, 1954). $\delta = [(R \text{ sample}/R \text{ standard}) - 1] \times 1,000$, where $R = C^{13}/C^{12}$ and the standard is the Chicago isotopic standard. Data on the various isotopic reference standards in use are given by CRAIG (1957).
- (2) Fractionation factor for C¹⁴ relative to terrestrial wood; i.e. the expected C¹⁴/C¹² ratio in the component material, divided by the C¹⁴/C¹² ratio of modern wood. From column 1, the C¹³ fractionation factors relative to modern wood (— 25 ‰) were computed for each component; these values squared give the values in column 2 (see text). α is the chemical fractionation factor which would give the observed C¹⁴ concentration relative to wood if the mixing between components were infinitely fast.
- (3) Data from HUTCHINSON (1954).
- (4) Data from SCHROEDER and NODDACK, as given by GOLDSCHMIDT (1954, p. 355). HUTCHINSON (1954) roughly estimates this figure as one order of magnitude lower; however he uses the estimates of Schroeder and Noddack for the rate of photosynthesis by terrestrial plants. Their calculated rate is based on their estimate of the size of the biosphere, and thus calculations of the atmosphere-biosphere flux cannot be consistent unless both (or neither) of their estimates are adopted.
- (5) Mean of estimated values 0.29 by GOLDSCHMIDT (1954), and 0.14 by RUBEY (1951).
- (6) Estimated upper limit from data of RILEY, STOMMEL, and BUMPUS (1949). Using their data for the Sargasso sea only, one obtains an order of magnitude less, and according to them the Sargasso crop is about the same as the mean temperate ocean water crop, exclusive of the spring flowering period. In our units, their highest recorded value is 0.007 in Long Island Sound; the bulk of their data indicate the average ocean crop is an order of magnitude less.
- (7) Data from REVELLE and SUSS (1957).

available records of observation of the variations in temperature and density in the various seas. He concludes that the mean thermocline depth, averaged over an entire year and over all oceans, is certainly between 50 and 100 meters. We have thus adopted the figure 75 ± 25 meters for the mean thermocline depth, for all calculations. The average depth of the ocean and all seas is taken as 3,800 meters (SVERDRUP *et al.*, 1942), and thus the mixed layer and the deep sea are taken as containing respectively 2 % and 98 % of the total carbon in the sea. (The marine biosphere was assumed to be entirely in the mixed layer.) The amounts of carbon relative to the amount in the atmosphere are then $N_m = 1.2 N_a$ and $N_d = 58.3 N_a$.

Figure 1 also shows the values used for the observed radiocarbon concentrations in the various reservoirs, relative to R_w , the ratio C¹⁴/C¹² in terrestrial wood. RAFTER (1955) has shown that the atmospheric ratio is about that expected on the basis of the C¹³ data, namely $1.037 R_w$. The average radiocarbon activity in humus is not known, but must lie within limits of $0-1 R_w$; the effect of this uncertainty on the following calculations is negligible. As discussed above, the activity in the mixed layer may be taken as equal to R_w ; however the average activity in the deep sea is not known and we take this as a variable parameter. The absolute value of R_w is taken as 1.24×10^{-12} from the measurements of SUSS (1955) on 19th century wood normalized for time and isotopic fractionation.

Notation and symbols:

- N_i = amount of (C¹² + C¹³) in reservoir *i*.
- N_i^* = amount of C¹⁴ in reservoir *i*.
- k_{i-j} = rate constant for transfer of carbon from reservoir *i* to reservoir *j*, (first order process assumed, i.e. flux from *i* to *j* = $k_{i-j} N_i$, except for transfer from atmosphere to biosphere), years⁻¹.
- k_{i-j}^* = rate constant for transfer of C¹⁴, used when $k^* \neq k$.
- τ_{i-j} = $1/k_{i-j}$ = residence time (years) of a stable carbon atom in reservoir *i* before transfer to reservoir *j*.
- τ_{i-j}^* = $1/k_{i-j}^*$ = residence time of a C¹⁴ atom in reservoir *i* before transfer to reservoir *j*.

CARBON RESERVOIRS

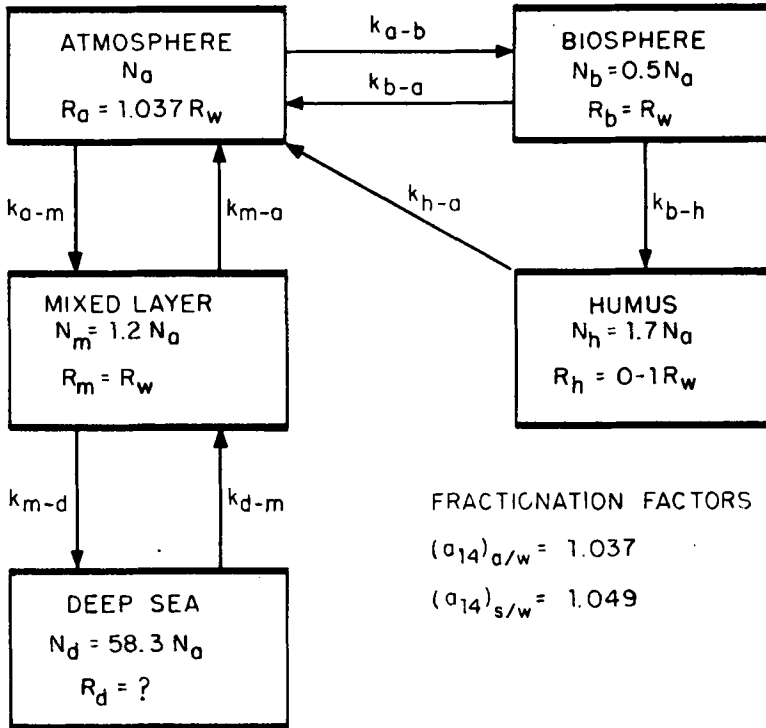


Figure 1. Carbon reservoirs in the exchangeable system. N_a = atmospheric carbon = 0.126 grams C/cm². R_w = C^{14}/C^{12} ratio in standard wood = 1.14×10^{-12} .

- τ_r = $1/\lambda$ ($\lambda = C^{14}$ decay constant) = radioactive mean life of C^{14} = 8,033 years.
- R_i = $N_i^*/N_i = C^{14}/C^{12}$ ratio in carbon in reservoir i .
- \bar{Q} = mean production rate of C^{14} from cosmic ray flux, atoms/cm² sec.

The meaning of τ :

We shall define τ rigorously and identify its particular meanings with specific subscripts; in order to avoid possible confusion with respect to the many usages of this symbol. Assume a reservoir with a steady-state fixed content of N molecules of a substance, and a continuous flux into and out of the reservoir of ϕ molecules/year. At a particular time, $t=0$, we have N_0 particular molecules in the reser-

voir, and at some later time t , we have N' of these original N_0 molecules still present. Then we define the average life of a molecule in the reservoir in the usual way, as

$$\tau = \frac{\sum_i t_i n_i}{\sum_i n_i} \approx -\frac{1}{N_0} \int_{N'=N_0}^{N'=0} t dN'$$

where n_i is the number of molecules of the original N_0 which remain in the reservoir for each time t_i , and dN' is the number of molecules removed in the interval t and $t+dt$, i.e. the number of molecules with a reservoir life-time equal to t .

The number of molecules of the original particular set of N_0 which are removed in any

interval dt is simply given by the concentration of such molecules in the reservoir, multiplied by the total flux from the reservoir, i.e.:

$$dN' = -\frac{N'}{N} \phi dt$$

which yields on integration $N' = N_0 \exp(-\phi t/N)$.

Substituting for dN' and then for N' in the integral expression for τ , and integrating between $t=0$ and infinity, we obtain:

$$\tau = \frac{N}{\phi}$$

and from the expression for N' one sees that τ , the average life, is also the time required for the original number of N_0 particular molecules to be reduced to $1/e$ times the initial number. τ is thus formally equivalent to a radioactive mean life.

In many cases, the rate of removal is dependent only on the total amount of substance, N , in the reservoir, and we can write the outgoing flux as the product of N and a first order rate constant, i.e. $\phi = kN$. In such cases we see that $\tau = 1/k$, just as the radioactive mean life is equal to $1/\lambda$.

We shall call τ , as rigorously defined above, the residence time or average reservoir life. In particular, we denote by subscripts i and j , as shown above under *Notation*, a particular residence time in reservoir i before removal to a specific reservoir j . When a reservoir exchanges with n different reservoirs, then we denote the *total* residence time in reservoir i , relative to removal by all routes, as τ_{i-T} where:

$$\frac{1}{\tau_{i-T}} = \sum_{j=1}^{j=n} \frac{1}{\tau_{i-j}}$$

For a radioactive isotope, the average reservoir life will not be the same as for the corresponding stable isotope, because of the following effects. (1) There may be isotopic fractionation in the removal process. This effect is of course independent of the radioactivity and dependent only on the isotopic mass difference; when it occurs it will cause the residence times of the isotopic species, relative to that specific removal process, to be slightly different. (2) Because of the radioactivity, the total removal rate of a radioactive species will be the sum

of the physical removal rates plus λN_i , the decay rate. (3) In the steady state, after normalizing for effects (1) and (2), the residence times of the isotopic species will always be the same. However, it should be noted that in a *transient* state, the concept of residence time, as given above, may break down, and a somewhat different rigorous definition may be required. In particular, it is well known that, for transfer from a reservoir i to a reservoir j , the transfer process for an isotope in low concentration will always be a first order process (the exponential exchange law, based on the low probability of interaction) as long as the rate of mixing in reservoir j is fast relative to the transfer process, so that the isotope does not pile up at the boundary. (Humus, and the deep-sea carbon, represent reservoirs where such a pile-up might occur in the transient state.) On the other hand, the transfer process for the abundant isotopic species may or may not be first order, depending on the specific chemical and physical processes involved. Conversely, the more abundant isotope may pile up at the surface of reservoir j and mix backwards more rapidly than forward, if this is the isotope involved in the transient process. (An example of this might be the $C^{12}O_2$ produced by the combustion of fossil fuel, which might pile up in the surface layers of the deep sea or the humus.)

We shall not be concerned with the transient state in this study and thus the effects given under (3) above may be disregarded in this paper. Moreover, we shall consider only those processes in the carbon cycle which happen to be so fast, relative to the decay rate of C^{14} , that the effect of its radioactivity on the residence times is negligible. However, considering isotopic fractionation, as discussed under (1) above, we shall denote the residence times and rate constants for C^{14} as τ_{i-j}^* and k_{i-j}^* for processes in which isotopic separation may be involved (specifically for absorption and release of CO_2 by the sea).

Calculation of the CO_2 exchange time from the radiocarbon production rate

We consider the radiocarbon material balance, relative to cosmic-ray production, physical removal, and decay, in the atmosphere. Equating the flux of C^{14} entering the atmosphere, from production and from the sea and biosphere, to that leaving by physical means

and decay, we write for the assumed steady state:

$$k_{a-m}^* N_a^* - k_{m-a}^* N_m^* = \bar{Q} - \lambda(N_a^* + N_b^* + N_h^*) \quad (1)$$

in terms of the isotopic rate constants for C^{14} . The steady state difference in the C^{14} flux between the atmosphere, and biosphere + humus, is simply $\lambda N_b^* + \lambda N_h^*$.

For $C^{12}O_2$ the steady state interaction of atmosphere and sea is:

$$k_{a-m} N_a = k_{m-a} N_m \quad (2)$$

and we then write the relation between the two sets of isotopic rate constants as:

$$\frac{k_{a-m}^*}{k_{m-a}^*} = \alpha_{s/a} \frac{k_{a-m}}{k_{m-a}} = \alpha_{s/a} \frac{N_m}{N_a} \quad (3)$$

where $\alpha_{s/a}$ is the ratio of the fractionation factor for C^{14} in the ocean bicarbonate, relative to wood, to the C^{14} factor in atmospheric CO_2 relative to wood; i.e. from table I, $\alpha_{s/a} = 1.049/1.037 = 1.012$. (In these and the following derivations, we take all the factors relative to wood, which is the general radiocarbon standard.)

Substituting in (1) to eliminate k_{m-a}^* , and substituting $N_i^* = R_i N_i$, we obtain the expression for k_{a-m}^* in terms of the various R and N parameters, which may be written explicitly for the residence time of a $C^{14}O_2$ molecule in the atmosphere, before entering the sea, as:

$$\tau_{a-m}^* = \frac{\tau_r \left[\alpha_{s/a} - \frac{R_m}{R_a} \right]}{\frac{\bar{Q}}{\lambda N_a^*} - \frac{R_b}{R_a} \frac{N_b}{N_a} - \frac{R_h}{R_a} \frac{N_h}{N_a} - 1} \quad (4)$$

wherein we note that the numerator of the expression is the fractional isotopic effect times the radiocarbon mean life. The denominator is the ratio of the total amount of radiocarbon in the sea to the amount in the atmosphere, \bar{Q}/λ being equal to the total amount of radiocarbon in the world.

Using \bar{Q} as 2 atoms/cm² sec and $R_h/R_a = 0.5/1.037$ (see below for discussion of these values), setting $N_a^* = R_a N_a$, and using the various R and N values shown in Figure 1 and the other numerical values needed as given in the text, we find τ_{a-m}^* to be 6.2 years. The rate constant for absorption of $C^{12}O_2$ into the sea

will be slightly greater than the rate constant for $C^{14}O_2$ because of an isotopic effect. For the case of absorption of $C^{12}O_2$ and $C^{13}O_2$ by barium hydroxide, the difference in rate is 1.5 % (CRAIG, 1953), and no significant error can be made by assuming a 3 % effect for the $C^{12} - C^{14}$ absorption by the sea. We thus find $\tau_{a-m} = .97 \tau_{a-m}^* = 6$ years.

The range of possible error in the numerical values may be defined as follows. At present the most uncertain value is probably the cosmic ray production of C^{14} . Recent calculations of \bar{Q} have yielded values of 2.6 (ANDERSON, 1953; LIBBY, 1955), and 2.4 (LADENBURG, 1952; KOUTS and YUAN, 1952). Anderson suggests these values may be systematically too high because of uncertainty in the calculation of the capture rate of cosmic ray neutrons in the energy range just above the sharp increase in the cadmium cross section at 0.4 ev. More recently, SOBERMAN (1956) has made a general study of the neutron intensity variations at high altitudes. With essentially the same experimental data, he calculates \bar{Q} to be 1.1, neglecting the resonance capture, by nitrogen, of neutrons with energies greater than 0.5 Mev. KOUTS and YUAN (1952) found that the local production rate at Princeton was increased from $Q = 3.50$ to 4.13 by inclusion of the resonance capture rate. They also pointed out that the counters used in the slow neutron measurements are calibrated to no greater accuracy than 20 %, reflecting the uncertainty in the flux values of the Argonne standard reactor. All things considered, it appears that \bar{Q} should be assigned an uncertainty of 25 %, and we shall assume the value $2 \pm .5$, though as noted below, it seems unlikely that the correct value can be greater than 2.

The apparent age of carbon in the mixed layer of the sea may be taken as 400 ± 100 years¹ (Suess, 1954, 1955; RAFTER, 1955). The

¹ Suess' measurements on Atlantic shells and organic carbon average 430 years relative to his standard. Rafter's measurements on Pacific shells, organic carbon, and surface sea water, average 290 years relative to a modern wood standard (Rafter, 1955). Correction of his wood standard for the Suess effect adds 110 years to all the Pacific measurements (FERGUSON and RAFTER, New Zealand C^{14} Age Measurements III, in press); thus the average age for Pacific samples, relative to age corrected 19th century wood, becomes 400 years, in exact agreement with the data of Suess. This age is obtained from the 5 % isotopic fractionation factor between wood and

data by Suess represent the apparent age relative to a composite 19th century wood standard, corrected for isotopic fractionation and age, and thus the Suess effect, i.e. the slight dilution of the activity of modern wood and the atmosphere by combustion of coal during the past decades, does not affect this figure. However, there may be a slight dilution of the activity of the oceanic mixed layer samples. The average Suess effect over the world is probably of the order of 1 %, since the highest values found are near areas subject to local industrial contamination and are thus not representative. As pointed out below, the residence time of carbon in the mixed layer, before entering the deep sea, is probably about the same as the atmospheric residence time, and thus the dilution effect on the mixed layer is probably not more than 1 %.

This effect is well within the over-all uncertainty, and we shall use the 400 year figure, taking the activity ratio R_m/R_a as $(1 \pm 0.01)/1.037$, introducing an error of $\pm 20\%$ in equation (4).

The counting error in the absolute value of R_w is 2 % (Suess, 1955) and the value itself is based on a mass spectrometrically calibrated C^{14} standard for which the calibration data showed a range of 3 %. The error in the C^{14} decay constant can scarcely exceed 2 % (Libby, 1955, p. 42). Finally, one sees that the term $\bar{Q}/\lambda N_a^*$ in the denominator of equation (4) is about 60, while the remaining terms are of the order of 1. In particular, with the amount of humus assumed as $N_h = 1.7 N_a$, a possible range in R_h of 0 to R_w produces a range of only 3 % in τ_{a-m}^* . Thus we take $R_h = 0.5 R_w$ for calculation, introducing an error of only $\pm 1.3\%$. Even assuming that the humus value of $1.7 N_a$ is underestimated by a factor of 10, and that all humus has modern activity, would cause an error of only 1.6 years in τ_{a-m} .

A reasonable estimate of the maximum error possible is a range of $\pm 50\%$. The value obtained from (4) is then: $\tau_{a-m} = 6 \pm 3$ years; the maximum value representing assumed values of 1.5 for \bar{Q} and 500 years for surface ocean carbon, and the minimum value representing assumed values of 2.5 and 300 years.

shell; the observed radiocarbon activities of wood and shell are about the same, but apparent ages are usually tabulated instead of relative activities.

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(The actual errors are not symmetrical because one enters in the numerator and one in the denominator.)

Distribution of carbon 14 in the atmosphere and sea

We now proceed to derive equations expressing the functional dependence of the amounts and specific activities of radiocarbon in the atmosphere, mixed layer, and deep sea, on the various rate constants or residence times involved. We assume that the residence time of C^{14} in the deep sea, relative to physical removal, is the same as that for C^{12} , i.e. that no isotopic fractionation is involved in the internal mixing in the sea. We shall then show how τ_{a-m}^* can also be calculated as an explicit function of the rate of mixing within the sea.

Writing out the expressions for steady state material balance of the radiocarbon flux in the mixed layer and in the deep sea, we have:

$$k_{a-m}^* N_a^* + k_{d-m} N_d^* = N_m^* (k_{m-a}^* + k_{m-d} + \lambda) \quad (5)$$

$$k_{m-d} N_m^* = N_d^* (k_{d-m} + \lambda) \quad (6)$$

where we have assumed, as stated above, that the isotopic rate constants for mixing within the sea are identical. The steady state C^{12} balance between the mixed layer and deep sea is given by:

$$k_{m-d} N_m = k_{d-m} N_d \quad (7)$$

For simplification, we shall now omit from the model the terrestrial biosphere and humus, i.e. we take the total radiocarbon balance as:

$$\bar{Q} = \lambda (N_a^* + N_m^* + N_d^*) \quad (8)$$

The effect of the biosphere could be included by substituting for \bar{Q} in all equations in this section, the expression: $[\bar{Q} - \lambda(N_b^* + N_h^*)]$. This would change the calculated percentage changes in activity of the various reservoirs for a given change in mixing rates (δ values) by only 1 % of their numerical values, and thus the error introduced by this simplification is negligible. (The percentage error is actually variable and roughly equal to δ_a in percent divided by 30.)

From the above expressions and equation (3), one may derive the explicit relationships for the amounts of C^{14} in the three reservoirs as functions of the C^{14} decay constant, the rate

constants k_{a-m}^* and k_{d-m} ($=1/\tau_{d-m}$), the production rate, and the known distribution of C^{12} , which are as follows:

$$N_a^* = \frac{\bar{Q}}{\lambda} \left[1 + \frac{1}{\frac{\lambda}{k_{a-m}^*} + \frac{1}{\alpha_{s/a} F}} \right]^{-1} \quad (9)$$

$$N_m^* = \frac{\bar{Q}}{\lambda} \frac{N_m}{N_a} \left[\frac{1}{F \left(1 + \frac{\lambda}{k_{a-m}^*} + \frac{1}{\alpha_{s/a} F} \right)} \right] \quad (10)$$

$$N_d^* = N_m^* \left[\frac{N_a}{N_m} F - 1 \right] \quad (11)$$

$$F = \frac{N_m}{N_a} + \frac{N_d}{N_a} \left[\frac{1}{1 + \frac{\lambda}{k_{d-m}}} \right] \quad (12)$$

From these expressions one sees that N_a^* varies inversely with both rate constants, i.e. slow exchange between atmosphere and sea and slow internal mixing in the sea will both increase the radiocarbon concentration in the atmosphere. The reason of course is that the rate of decay is constant and proportional to the concentration, so that if the rate of physical removal is decreased more C^{14} is removed by decay with a consequent increase in the concentration. In the same way, N_m^* is seen to vary directly with k_{a-m}^* but inversely with k_{d-m} , while N_d^* varies directly with both rate constants. Setting k_{d-m}/λ equal to infinity in the above expressions gives the equations governing the simple model of an atmosphere and a uniform ocean, and if k_{a-m}^*/λ is then also set equal to infinity, one obtains the simple statistical partitioning of C^{14} corrected by the isotopic fractionation factor.

The function F is seen to be the "effective volume" or "effective carbon reservoir" of the sea, relative to the amount of carbon in the atmosphere. As k_{d-m}/λ varies from infinity to 0, F varies from $(N_m + N_d)/N_a$, i.e. the total amount of carbon in the sea relative to the atmosphere, to N_m/N_a , i.e. the carbon in the mixed layer only. In the derivation of the above equations, F falls out quite naturally as an algebraic entity; the physical significance of this function is discussed in the next section. Values of F as a function of the residence time of carbon in the deep sea are tabulated in the

next section, and we shall use these values here to demonstrate the magnitude of the concentration changes in the various reservoirs as functions of the mixing rates.

Noting that for each reservoir, $R_i = N_i^*/N_i$, we denote by δ_i the percentage difference in radiocarbon activity (C^{14}/C^{12}), for any pair of rate constants k_{a-m}^* and k_{d-m} , from the state in which these rate constants are both infinitely greater than the decay constant, i.e. when the radioactivity of C^{14} has no effect on its natural distribution. Thus we define:

$$\delta_i (\%) = \left[\frac{R_i}{R_i(\tau_{i-j}=0)} - 1 \right] \times 100 \quad (13)$$

where the notation $(\tau_{i-j}=0)$ signifies the hypothetical state in which the residence time in each reservoir before physical removal is essentially 0 relative to the residence time before radioactive decay (i.e. $k_{i-j}/\lambda = \text{infinity}$). The following equations give δ for the atmosphere, mixed layer, and deep sea, as explicit functions of the residence time in the atmosphere before entering the sea, the residence time in the deep sea before entering the mixed layer, the radioactive mean life τ_r , and the fixed amounts of carbon 12 in the various reservoirs.

$$\delta_a = \frac{\alpha_{s/a} \frac{N_s}{N_a} \frac{\tau_{a-m}}{\tau_r} + \frac{N_s}{N_a} \frac{1}{F} - 1}{\frac{\tau_{a-m}}{\tau_r} + \frac{1}{\alpha_{s/a} F} + 1} \quad (14)$$

$$\delta_m = - \frac{\frac{\tau_{a-m}}{\tau_r} - \frac{N_s}{N_a} \frac{1}{F} + 1}{\frac{\tau_{a-m}}{\tau_r} + \frac{1}{\alpha_{s/a} F} + 1} \quad (15)$$

$$\delta_d = \frac{\tau_r \delta_m - \tau_{d-m}}{\tau_r + \tau_{d-m}} \quad (16)$$

In these expressions we have used N_s , the total stable carbon in the sea, $= N_m + N_d$. For the simpler model in which the ocean is taken as a single reservoir, uniformly mixed at a rate infinitely greater than the C^{14} decay rate, the function F is equal to N_s/N_a . The numerators of equations (14) and (15) are then reduced to containing the first term only, and one sees that, for a given atmospheric residence time, the percentage decrease in C^{14} activity in the

mixed layer is approximately N_a/N_s or $1/60$ of the increase in the atmospheric activity, as of course it must be. In this case, of course, δ_a and δ_m are identical, as shown by (16).

In table 2 we tabulate the calculated δ_i values for atmospheric residence times, relative

Table 2. Effect of the residence times of CO₂ in the atmosphere and deep sea, both relative to exchange into the mixed layer, on the specific activity of radiocarbon in the atmosphere, mixed layer, and deep sea. δ = per cent difference in activity (C¹⁴/C¹² ratio) from the condition of infinitely fast mixing relative to the radioactive decay rate

	$\tau_{a-m}^* = 5 \text{ y.}$	$\tau_{a-m}^* = 10 \text{ y.}$	$\tau_{a-m}^* = 20 \text{ y.}$
$\tau_{d-m} = 0$			
δ_a	+ 3.7	+ 7.4	+ 14.7
δ_m, δ_d	— 0.06	— 0.12	— 0.24
$\tau_{d-m} = 500 \text{ y.}$			
δ_a	+ 9.7	+ 13.4	+ 20.7
δ_m	+ 5.93	+ 5.86	+ 5.73
δ_d	— 0.28	— 0.34	— 0.46
$\tau_{d-m} = 1,000 \text{ y.}$			
δ_a	+ 15.6	+ 19.3	+ 26.6
δ_m	+ 11.88	+ 11.81	+ 11.67
δ_d	— 0.51	— 0.57	— 0.69

to the mixed layer, of 5, 10, and 20 years, and deep sea residence times, relative to the mixed layer, of 0 (rapidly mixed sea), 500, and 1,000 years. For the case of rapid mixing of the sea, the C¹⁴ activity in the atmosphere is increased by about 0.74 % for each year of atmospheric residence time, relative to the condition of rapid atmospheric exchange with the sea, while the activity in the sea is reduced by $1/60$ of the atmospheric increase. If the internal mixing within the sea is slow, corresponding to a deep-sea residence time of 500 years relative to the mixed layer, the effect is to increase the activity in both the atmosphere and the mixed layer by 6 %, while reducing the deep-sea activity by 0.28 %; thus the difference in the observed activities in the atmosphere and mixed layer remains about the same. As the table shows, the atmospheric and mixed-layer activities are each increased by about 1.2 %, relative to the condition of a rapidly mixed sea, for each 100 years of residence time in the deep sea, or “age” of the deep sea water.

It is clear that the “apparent age” of the

surface ocean bicarbonate does not reflect a simple decrease of activity due to slow transfer of radiocarbon into the sea, as is sometimes stated. The actual effect is a piling up of the radiocarbon in the atmosphere by the mixing barrier, amounting to several percent of the activity which would be observed in the case of very rapid exchange with the sea. The actual decrease in specific activity of the sea is seen to be an insignificant contribution to the observed difference of activity between the atmosphere and the sea. The “piling up” effect in the atmosphere and mixed layer, by slow internal mixing in the sea, is about the same for each of these reservoirs, because they contain about the same amounts of carbon (fixed by the chemical equilibrium between atmosphere and sea and the average depth of the thermocline); thus observations of the activity difference between the atmosphere and the mixed layer cannot yield much information about the rate of internal mixing in the sea.

Calculation of the CO₂ exchange time from the distribution of carbon 14

Table 2 shows that over the range of deep-sea residence time considered, the difference in activity between the atmosphere and mixed layer is practically unaffected by the internal mixing rate within the sea, and is essentially a function of the atmospheric residence time of CO₂ only. Thus we can estimate the atmospheric residence time rather closely by considering the atmosphere-mixed layer activity difference, if we have some idea of the order of magnitude of the mixing rate within the sea.

From equations (3), (5), (6), and (7), we derive the expression for the ratio of the radiocarbon activity in the atmosphere to the activity in the mixed layer, in terms of the mixing rate constants, as:

$$\frac{R_a}{R_m} = \frac{1}{\alpha_{s/a}} + \frac{\lambda F}{k_{a-m}^*} \tag{17}$$

where the function F was given by (12). For an infinite deep-sea residence time, i.e. no mixing between the layers of the sea, F reduces to N_m/N_a and the activity ratio is seen to become dependent on the size of the mixed layer reservoir only. It should be noted that (17) is derived from considerations of the steady state balance in the mixed layer and in the deep

sea, and is independent of any assumptions about the terrestrial biosphere and humus.

Equation (17) may be rewritten as:

$$\tau_{a-m}^* = \frac{\tau_r}{F} \left[\frac{R_a}{R_m} - \frac{1}{\alpha_{s/a}} \right] \quad (18)$$

and using R_a and R_m as given in figure 1, we now tabulate τ_{a-m}^* vs. τ_{d-m} , together with the function F and the ratio F/F_0 in percent, where $F_0 = N_s/N_a$ = the value of F for infinitely rapid mixing in the sea on the radiocarbon time scale.

$\tau_{d-m}(y)$	F	F/F_0 (%)	$\tau_{a-m}^*(y)$
0	59.5	100	6.54
100	58.8	98.8	6.62
300	57.4	96.5	6.78
500	56.1	94.3	6.93
1,000	53.0	89.1	7.34
5,000	37.1	62.4	10.5
10,000	27.2	45.7	14.3
20,000	18.9	31.8	20.6
50,000	9.3	15.6	41.8

By equating (18) with (4) we see that:

$$\frac{N_s^*}{N_a^*} = \frac{R_m}{R_a} F \quad (19)$$

since, as noted in the discussion of (4), the denominator of (4) is equal to N_s^*/N_a^* . It is then easy to show rigorously the physical meaning which may be attached to F . For any given internal mixing rate in the sea, we may suppose the sea to be divided into two portions, the uppermost of which contains all the radiocarbon of the sea at a uniform concentration equal to that presently observed in the surface of the sea; i.e. the internal mixing in this portion is infinitely rapid on the radiocarbon time scale and the C^{14}/C^{12} ratio in this portion is $R_m (= R_w)$. The lowermost portion contains no radiocarbon. Then if X is the amount of C^{12} in the uppermost portion containing the radiocarbon, $X = FN_a$, and F is simply the ratio of the amount of stable carbon in the upper portion to the amount in the atmosphere. Moreover, $F/F_0 = X/N_s$, so that the ratio F/F_0 is simply the fraction of the total sea contained in the rapidly mixed upper portion.¹ Thus from the numerical values

¹ Alternatively one could assume a model in which the uppermost portion of the sea, containing all the radiocarbon, grades from a C^{14}/C^{12} ratio of R_m at the

tabulated above, one sees that a deep-sea residence time of 5,000 years in the actual two-layer model assumed in this study, is equivalent to having 62 % of the sea, at C^{14} concentration R_m , rapidly mixed and functioning as an effective component of the exchangeable system, and 38 % of the sea completely isolated and containing no radiocarbon. This would correspond to complete mixing in the upper 2,400 meters of the sea and no communication with the bottom 1,400 meters.

The dependence of τ_{a-m}^* on τ_{d-m} is seen to be of such low order that a 5,000 year mixing time in the sea adds only 4 years to the atmospheric residence time calculated for a homogeneous sea with infinitely rapid internal mixing. This is simply the consequence of the long C^{14} half-life, coupled with the fact that one is dealing with a steady-state mixed system, rather than a case of simple exponential decay from an initial concentration.

Only one set of precise radiocarbon measurements on deep-sea water appears to exist at present. M. Rubin of the U.S. Geological Survey has found that in the area east of the Lesser Antilles, the water at 1,750 meters is only 200 years "older" than the surface water (personal communication). However, it appears to be well established that, in general, the internal mixing time of the sea is less than 1,000 years. WOOSTER and KETCHUM (1956) have calculated the mean displacement time of the deep water of the North Atlantic as 250 years, from oceanographic data. WORTHINGTON (1954) has studied the secular decrease of dissolved oxygen in these waters and estimates the age, relative to the surface water, as 140 years. His data indicate that the North Atlantic deep water may be formed sporadically, rather than replenished by a continuous mixing process. The deep Pacific water is probably older than the deep waters of the Atlantic. However, REVELLE and MAXWELL (1952) found that the heat flux through the floor of the Pacific is such that the deep Pacific water must be replenished in less than a thousand years.

From the figures tabulated above, one sees that a range in the deep sea residence time of

surface to 0 at the lower boundary. In this case $X = (R_m/R_x)FN_a$ and $X/N_s = (R_m/R_x) (F/F_0)$, where $R_x = N_s^*/X$ = the average C^{14}/C^{12} ratio in the upper layer. The correspondence with our actual model would then depend on the type of activity gradient assumed.

0—1,000 years corresponds to a range in τ_{a-m}^* of only 0.8 years, an insignificant error. Thus we take τ_{a-m}^* as 6.8 years, corresponding to $\tau_{a-m}=6.6$ years, with an estimated uncertainty of about 40 %, reflecting uncertainties of 5 % due to the internal mixing rate in the sea, 20 % in the measured percentage activity difference between the atmosphere and mixed layer, perhaps 10 % in the absolute amount of carbon in the sea, and 2 % in the decay constant. The error in F due to the uncertainty in the average depth of the thermocline is only 1 %, as the absolute amount of carbon in the mixed layer alone does not enter into the calculation. (Thus the possible error in estimating the size of the marine biosphere is seen to be entirely negligible.)

The value 6.6 years is in excellent agreement with the previous figure of 6 years, calculated by (4) from the radiocarbon production rate with a very minor dependence on the size of the biosphere and humus. Both calculations, however, require the measured “apparent age” of the mixed layer carbon, and thus they are not completely independent. The errors in each of these results are probably such as to make the values slightly higher, and \bar{Q} is more probably less than, rather than greater than, 2.0. Weighting the errors, and using (2) we adopt the values:

$$\begin{aligned} \tau_{a-m} &= 7 \pm 3 \text{ years} & \tau_{m-a} &= 8.4 \text{ years} \\ k_{a-m} &= 0.14 & k_{m-a} &= 0.12 \end{aligned}$$

and the mixing rate constants are thus a thousand times larger than the radioactive decay constant.

Taking the amount of CO_2 in the atmosphere as 2.35×10^{18} grams, (HUTCHINSON, 1954) and k_{a-m} as 0.14, we find the exchange rate of CO_2 between atmosphere and sea to be 2×10^{-3} moles of CO_2 per square centimeter of sea surface, per year, or about 45 cc (STP) of CO_2 .

\bar{Q} and the radiocarbon content of the deep sea

Using Suess’ value for R_w and the data given in table I and figure I, we can calculate the maximum amount of radiocarbon on the earth by assuming the average “age” of the ocean water to be 600 years and all the humus to have modern activity. In this way we can

account for 57 metric tons of C^{14} on the earth, corresponding to 260 megacuries of activity. Using the \bar{Q} value of 2.4 (LADENBURG, 1952), the predicted amount of C^{14} , corresponding to secular equilibrium with the production rate, is 72 metric tons. The discrepancy is thus about equivalent to the 20 % uncertainty assigned to the production rate by KOUTS and YUAN (1952).

We may write the relationship between τ_{d-m} and \bar{Q} as:

$$\frac{\tau_{d-m}}{\tau_r} = \frac{N_d R_m}{\bar{Q} - N_{a+b+h+m}^*} - 1 \quad (20)$$

and we calculate the following values of τ_{d-m} for the previously assumed mean and limits for \bar{Q} :

\bar{Q}	τ_{d-m} (y)
1.5	+ 2,580
2.0	- 265
2.5	- 1,910

Thus from the uncertainty in \bar{Q} , the steady state conditions are consistent with any oceanic mixing time up to 2,500 years; however, the radiocarbon distribution data suggest that \bar{Q} is actually about 1.8 and not greater than 2. In this calculation we have assumed all the humus to have modern activity; it seems unlikely that limestone can have acquired enough C^{14} by exchange to make up the balance required by the high value of \bar{Q} .

The relation between τ_{d-m} as defined for steady state mixing conditions, and t_c , the “age” of deep-sea water, relative to surface water, as calculated by the simple exponential decay relationship, is given by:

$$\frac{\tau_{d-m}}{t_c} = \frac{e^{\lambda t_c} - 1}{\lambda t_c} = 1 + \frac{1}{2} \frac{t_c}{\tau_r} + \frac{1}{6} \left[\frac{t_c}{\tau_r} \right]^2 \quad (21)$$

and thus τ_{d-m} will be greater than t_c , the “measured age”, by about 0.6 % for each 100 years of t_c .

Summation and discussion

Using the empirical data on the relative distribution of C^{12} , C^{13} , and C^{14} in the exchangeable system of carbon, and a model for the sea consisting of a rapidly-mixed surface

layer, coupled with the deep sea, a quantitative evaluation of the effects of the carbon transfer rates on the radiocarbon concentration in the various reservoirs has been made. Relative to the hypothetical state in which the various mixing rates are infinitely faster than the radiocarbon decay rate, we find that the specific activity of C^{14} in the atmosphere is increased about 5 %, while the activity in the mixed layer is decreased by about 0.08 %, by an atmospheric residence time, relative to the sea, of 7 years. However, slow mixing between the mixed layer and the deep sea increases the activity in both the atmosphere and the mixed layer, relative to the rapidly mixed state, by 1.2 % for each 100 years of deep-sea residence time of carbon. Thus, if the residence time in the deep sea is assumed to be about 250 years, as several lines of evidence indicate, the total effects of the mixing rates on the reservoir concentrations are: an 8 % increase in the atmospheric activity, a 2.9 % increase in the mixed-layer activity, and a 0.2 % decrease in the activity in the deep sea, all relative to the activities which would be observed if the transfer of carbon were so rapid that there were no effects from the radioactivity.

The exchange time of CO_2 between atmosphere and sea was found by two methods which are quasi-independent. The first method depends on the cosmic-ray production rate of radiocarbon, as calculated by various workers, on the C^{14} concentration in the mixed layer of the sea, and on the steady-state material balance in the atmosphere. The second method considers the steady-state material balance in the mixed layer, and the mixed-layer C^{14} concentration as a function of the exchange time between the mixed layer and the deep sea. Both these methods yield an atmospheric residence time of CO_2 , relative to entrance into the sea, of 7 ± 3 years, corresponding to a rate constant $k_{a-m} = 0.14$.

According to HUTCHINSON (1954) the flux of atmospheric CO_2 into the biosphere corresponds to about 3 % of the amount in the atmosphere per year. In our notation, with $\tau_{a-m} = 7$ years, and $\tau_{a-b} = 33$ years, the total residence time of a CO_2 molecule in the atmosphere is $\tau_{a-T} = 6$ years, after which it goes either into the sea (9 chances out of 11) or into the terrestrial biosphere (2 chances out

of 11). Thus the carbon dioxide flux into the sea is about 4.5 times larger than the flux into the biosphere, and about 82 % of the CO_2 leaving the atmosphere goes into the sea, while only 18 % goes into the terrestrial plants. This ratio represents a considerable departure from previous estimates, and indicates that the spatial distribution of plants and soils is probably not the dominant factor in determining the steady-state CO_2 concentration in the atmosphere, contrary to what has been supposed (HUTCHINSON, 1954, p. 391). In fact it appears more likely that the spatial pattern of absorption and release of CO_2 by the sea, and the seasonal variations in this pattern, are the dominant factors.

If the residence time of CO_2 in the Northern hemisphere atmosphere is even a few years, then the rapid rate of transfer into the sea should produce an appreciable difference in the observed Suess effects in the Northern and Southern hemispheres, because of the much greater industrial concentration in the Northern hemisphere. Thus, if the Northern hemisphere residence time, relative to cross-hemisphere mixing, is from 2 to 5 years, the Southern hemisphere Suess effect should be from 75 to 50 %, respectively, of the effect observed in the Northern hemisphere. There is some indication that the Southern effect may in fact be only about half the Northern effect (SUESS, 1955), but a great many precise measurements will be needed to establish the exact nature of the effect. Nevertheless, it is clear that the rapid exchange of CO_2 with the sea will allow one to make rather close estimates of the cross-hemispheric exchanges; the precision with which this can be done is of course a direct function of the exchange rate with the sea.

Turning to the mixed layer in the sea, we see that τ_{m-a} , the residence time of CO_2 relative to entrance into the atmosphere, is equal to N_m/N_a times τ_{a-m} , and is thus 8.4 years, corresponding to $k_{m-a} = 0.12$. If the residence time in the deep sea, τ_{d-m} , is about 200 years, the residence time in the mixed layer, before transfer into the deep sea, is $\tau_{m-d} =$ about 4 years, corresponding to k_{m-d} about 0.25. The total residence time is then $\tau_{m-T} = 2.7$ years, after which a CO_2 molecule can go into the deep sea (2 chances out of 3), or into the atmosphere (1 chance out of 3). Thus with τ_{d-m} about 200 years, about $\frac{2}{3}$ of

the carbon cycled into and out of the mixed layer would exchange with the deep sea, and about $\frac{1}{3}$ with the atmosphere. The precise ratio depends of course on the actual residence time in the deep sea, but it is clear that for any reasonable mixing time of the deep sea, the exchange of the mixed layer is about equally proportioned between the atmosphere and the deep sea.

It should be emphasized that the indicated uncertainty in the atmospheric exchange time refers only to the rigorous model calculation; there is, of course, an additional uncertainty concerning the relationship of the model to the real physical situation. Our model does not exclude the existence of large horizontal gradients across the surfaces of the reservoirs, since we are dealing with steady-state average fluxes. However, the basic construction of the model assumes that the two reservoirs in the sea are each internally mixed over times comparable with their residence times, so that the material removed from each of these reservoirs has the average radiocarbon concentration of the reservoir as a whole.

Fortunately, the two methods of calculating τ_{a-m} depend on different assumptions. The calculation based on \bar{Q} considers the material balance in the atmosphere only, and requires only that the CO_2 entering the atmosphere from the sea have the radiocarbon concentration corresponding to the measured activity of the mixed layer carbon; i.e. only a negligible amount of the CO_2 should be contributed directly from the deep sea to the atmosphere, without passing through the mixed layer first. Since the exchange of water between near-surface and deep waters takes place predominantly in high latitudes where the thermocline ceases to exist, there may well be some direct exchange of CO_2 between deep water and the atmosphere. On the other hand, inspection of equation (4) shows that decreasing R_m/R_a to correspond with all the CO_2 furnished to the atmosphere from a carbon source with an apparent age of 650 years relative to the atmosphere (i.e. $\tau_{d-m}=250$ years), increases the calculated value of τ_{a-m} to only 10 years. Since it is hardly likely that all the CO_2 released from the sea comes directly from the deep sea to the atmosphere, we conclude that the calculation of τ_{a-m} from

\bar{Q} cannot be significantly in error from the model assumption.

Our second calculation of τ_{a-m} , by equation (18) is more dependent on the actual model of oceanic mixing constructed; it assumes that the mixed layer is well mixed over times of the order of a few years, so that the bulk of the mixed layer has the same C^{14} concentration as the portions exchanging with the atmosphere and the deep sea, and that the deep sea is internally mixed over times of the order of the average reservoir life in the deep sea. The first assumption is fulfilled, for the mixed layer is known to mix by convection and wind action over times of the order of days. If the second assumption were not valid, the function F would be slightly changed because the C^{14} concentration in the carbon exchanged with the mixed layer would not represent the average reservoir concentration (as assumed in equation (6)). However, the very minor dependence of the value of τ_{a-m} on F was shown, and moreover, it seems not unlikely that in the mixing process by which exchange with the mixed layer is effected, the deep sea is itself mixed at least partially in a time equivalent to the residence time.

The close agreement of the two values of τ_{a-m} , based on the assumption that the deep-sea residence time is not more than several thousand years, indicates that the model approximates well enough the actual mixing conditions in the sea. The additional assumption of the steady state has of course also been made; from the close agreement between the historical ages and the radiocarbon dates on samples of known age, this assumption is clearly valid enough for our purposes. (For the most recent data on comparison of measured and historical ages, see LIBBY, 1955, p. 10.)

Suess (1953) has attacked the problem of the atmosphere-sea exchange rate from an entirely different viewpoint, namely the dilution of the atmospheric radiocarbon activity by the dead CO_2 from the combustion of fossil fuels, as recorded in the tree rings of the last 100 years. His measurements indicated a "Suess effect", as we shall indicate it for convenience, of about 3%, from which he deduced an atmospheric CO_2 residence time, relative to the sea, of 20–50 years. The integrated amount of "dead" CO_2 which has been produced by

human activity is equivalent to a constant production rate of 0.25 % of N_a for the past 40 years (REVELLE and SUESS, 1957), which is long enough for the atmosphere to have reached secular equilibrium (to a close enough approximation) with the production rate. Thus from our present figure of $\tau_{a-m} = 7$ years, the predicted Suess effect is 7×0.25 or 1.75 % dilution of the atmospheric radiocarbon activity.

More recent and extensive measurements by SUESS (1955) have shown that the observed effect is actually less than 3 %, and that effects of about 3 %, as previously observed, represent local effects in areas near industrial concentrations. As Revelle and Suess point out, the average figure obtained from the recent data of Suess turns out, by coincidence, to be 1.73 %. They reverse the present procedure, evaluating the atmospheric residence time from the Suess effect with a more detailed treatment than made previously by Suess, and conclude that, all things considered, the atmospheric CO_2 residence time is of the order of magnitude of 10 years relative to the sea. The close agreement of their value, obtained from considerations of the transient state and the measured changes in atmospheric radiocarbon activity over past decades, and the value found in this study of the steady-state distribution of C^{14} , is gratifying, and indicates that the factors governing the natural distribution of radiocarbon are now fairly well understood.

Some comment should be made on the differences between the treatment by REVELLE and SUESS (1957) and by the present writer. Their conclusions are based on a generalized evaluation of the interaction of all the following parameters: τ_{a-m} , the "apparent age" of surface ocean carbonate, and an "effective" sea reservoir, essentially as related by equation (18), an "effective" atmospheric reservoir (as a function of interaction with the biosphere and humus), and the Suess effect. The reason for the much larger uncertainty assigned to their estimate of τ_{a-m} , compared to the estimate of ± 3 years for the figure deduced in this paper, is two-fold. First, their treatment involves the Suess effect, which, being very small, is not amenable to precise measurement, and moreover, is directly related to the interaction between atmosphere and biosphere. Thus given the exact magnitude of the Suess effect and the

"apparent age" of surface sea carbon as fixed values, then e.g., if the CO_2 in the atmosphere is in rapid exchange with an equivalent amount of carbon in the biosphere, the value of τ_{a-m} deduced for no interaction is doubled. The amounts of carbon tied up in the biosphere and humus, and the rate and extent of their interaction with the atmosphere, are subject to order of magnitude uncertainty.

Secondly, they take the ocean as a single reservoir and deliberately refrain from attempting to construct a model of the sea to which physical significance must be attached. On the other hand, the model constructed for the present study is based on breaking the sea into two reservoirs, which correspond, more or less, to those actually observed in the sea. As was shown in the second calculation of the atmospheric residence time, the interaction of the deep sea with the atmosphere in the present model is so weak that a precise estimate of the atmospheric exchange time can be made, even though the internal mixing rate of the sea is not known to within several thousand years. In fact, the mixed layer of the sea functions as a buffer, both in nature and in the present model, serving to damp out almost completely the interaction between the atmosphere and the deep sea.

We turn, finally, to the question of the internal mixing rate in the sea, and to what one can say about this rate from the present knowledge of the distribution of radiocarbon. As pointed out in the previous section of this paper, the uncertainty in the production rate of C^{14} is consistent with deep-sea residence times up to about 2,500 years. Unfortunately, the Revelle-Suess analysis provides no closer estimate.

Revelle and Suess define an "effective sea reservoir", smaller than the actual amount of carbon in the sea because of incomplete mixing, but as noted above, do not attach a physical meaning to their definition. The reason for our discussion of the physical significance of the function F , in a previous section, is now apparent; this function is their "effective sea reservoir", and their ratio S^*/S , where S in our notation is N_s , the total amount of stable carbon in the sea, is simply the ratio F/F_0 . Values of F and F/F_0 were tabulated as functions of the deep-sea residence time, τ_{d-m} , at the point where equations (18) and (19) were

introduced. Revelle and Suess find that the interaction of their various parameters is such that ratios of S^*/S as low as 70 % are acceptable, and from the tabulated values of F/F_0 given with (18), we see that τ_{d-m} could then be as long as about 3,000 years and still be consistent with their requirements. Even if the effective sea reservoir can be restricted to 90 % of N_s , the deep-sea residence time can still be 1,000 years.

There is, however, one way in which the mixing rate of the sea can be defined more closely, from the radiocarbon data, than the 0—3,000 range obtained by the two methods discussed above. As mentioned above, the atmosphere can be considered to be essentially in secular equilibrium with a flux of dead CO_2 amounting to a constant input of 0.25 % of N_a over the past 40 years. From the discussion of τ_{a-T} given above, it appears that about 80 % of the CO_2 leaving the atmosphere goes into the sea, and thus we can assume a flux of about 0.2 % of N_a into the sea of dead CO_2 . We may then ask what the maximum dilution of the radiocarbon activity in the mixed layer can have been.

The difference between the expected and observed radiocarbon activity of the mixed layer, relative to 19th century wood corrected for age, appears to be about 5 % and probably cannot be more than 6 % (Suess, 1955). From the calculation based on \bar{Q} , equation (4), we found that τ_{a-m} is probably not less than 4 years; it is almost certainly not less than 3 years. These minimum figures for τ_{a-m} would account for 3 % and 2 %, respectively, of the observed 5 %, or maximum 6 %, mixed-layer effect, by virtue of the effect of the mixing rates on the atmospheric concentration, which was discussed in a previous section. Thus it appears that the maximum dilution of C^{14} activity the mixed layer can have suffered is most probably 2 %, and almost certainly not more than 4 %.

The forward mixing residence time in the mixed layer, τ_{m-d} , is found by dividing the percentage dilution by the percentage flux, assuming secular equilibrium (which is shown by the result to be valid enough). If τ_{a-m} is as low as 4 years, then actually 90 % of the atmospheric CO_2 goes into the sea, and the mixed layer carbon, N_m , is 1.2 times N_a , thus the dead CO_2 from industrial combustion has

a flux rate through the mixed layer of approximately 0.2 % of N_m . Dividing the percentages given above, we find that τ_{m-d} is most probably not more than 10 years, and almost certainly not more than 20 years.

The residence time of a CO_2 molecule in the deep sea, τ_{d-m} , as given by (7) is about 50 times the residence time in the mixed layer before transfer to the deep sea. We thus find that τ_{d-m} is most probably not more than 500 years, and almost certainly not greater than 1,000 years.

The above statement on the mixing rate in the sea is the most precise limitation which can be put on the average mixing time in the sea by the present radiocarbon data. Direct measurements on deep waters should, of course, delineate the situation much more precisely. Nevertheless, it should be pointed out that measurements on 50 or 100 year old shells and seaweed to determine the Suess effect in the sea will give an independent check on the average mixing rates in the sea.

The detailed analysis of the steady-state distribution of a radioactive isotope is seen to be a powerful tool for the evaluation of rates of mixing in natural reservoirs. An analysis, similar to the present study of radiocarbon, has been made of the distribution of natural tritium in the atmosphere and the sea. The results indicate that the production rate of tritium from cosmic rays is probably five to seven times higher than the rates currently estimated by consideration of the cosmic-ray flux. Because of the short mean life of tritium (18 years), as contrasted with radiocarbon, a closer estimate of the internal mixing rate in the sea can be made from the steady-state distribution observed in the atmosphere and the mixed layer. The tritium distribution was found to indicate a deep-sea residence time of about 200—300 years, as a world average. Details of the tritium study will be published shortly.

Acknowledgements

This paper represents in part the results of a general study of the use of natural isotopic effects in the analysis of mixing rates in the atmosphere and the sea, begun while the writer was a member of a National Academy of Sciences Study Group on applications of

nuclear phenomena to oceanography; some of the material presented here is included in the final report of that group. It will be obvious from the text that I am greatly indebted to Drs. Hans Suess and Roger Revelle for discussion of many aspects of the subject, and that this paper has benefited in many ways from their own contribution (1957) and from the extensive radiocarbon studies of Suess. The present work was not aimed at duplication of their study, which is mainly concerned with the problem of the possible increase in the atmospheric carbon dioxide, and the limits which can be placed on this effect by knowledge of the CO_2 exchange rate between atmosphere and sea. Rather, the purposes of the writer's investigation were, first, to evaluate, on as quantitative a level as possible, the general factors affecting the distribution of natural radiocarbon in its various reservoirs, and second, to determine precisely what could be said, from the radiocarbon distribution, about the mixing of this isotope into the deep sea, because of the importance of this aspect relative to the study of the distribution of natural tritium.

Drs. James Arnold and Ernest Anderson had made calculations similar to some of the ones presented here, and I thank them for a preprint of their paper received during the early stages of this study. The present considerations were carried out independently of their work and we have not discussed our differences. Their estimate of the atmospheric residence time, as here defined, of about 14 years is

obtained by a material balance calculation, independent of \bar{Q} , but they do not give their method of calculation and it is difficult to determine how their calculation differs from the method given by equation (18) above. They assume the flux of CO_2 into the sea to be proportional to the sum of $N_a + N_b + N_h$ as used in this paper, treating these three units as one large reservoir, and they assume the radiocarbon concentration in the deep sea to be given by Rubin's measurement, thus adopting a figure of 250 years for τ_{d-m} . Moreover, they use a figure for the amount of carbon in the marine biosphere 80 times higher than the maximum possible value estimated as an upper limit in the present study (see table 1); this essentially doubles the amount of carbon assumed to be in the mixed layer. (In the present study, the material balance for the mixed layer was derived in such a way that, as shown by (18), the calculated value of τ_{d-m} is decreased by only 2 % if the amount of carbon in the mixed layer is doubled.) It seems likely that our different results for τ_{d-m} are due to the interaction of these factors, and it is, in fact, gratifying, that with such serious differences in initial assumptions, the figures differ by no more than a factor of two.

Finally, I wish to thank Dr. Warren Wooster for extensive discussion of mixing phenomena in the sea, and for his efforts in examining the question of the average thermocline depth; and Dr. Meyer Rubin for the information on his radiocarbon measurements on deep-sea samples.

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