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On the Radiocarbon Record in Banded Corals: Exchange Parameters and Net Transport of ^{14}C Between Atmosphere and Surface Ocean

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We have made radiocarbon measurements of banded hermatypic corals from Florida, Belize, and the Galapagos Islands. Interpretation is presented here of these previously reported results. These measurements represent the $^{14}\text{C}/^{12}\text{C}$ ratios in dissolved inorganic carbon (DIOC) in the surface ocean waters of the Gulf Stream and the Peru Current at the time of coral ring formation. A depletion in radiocarbon concentration was observed in coral rings that grew from A.D. 1900–1952. It was caused by dilution of existing ^{14}C levels with dead CO_2 from fossil fuel burning (the Suess effect, or S_e). The observed depletion of radiocarbon was greater in corals from the Gulf Stream (-11%) than in corals from the Peru Current (-6%). A similar trend was observed in the distribution of bomb-produced ^{14}C in corals that had grown during the years following A.D. 1952. The concentration of bomb-produced radiocarbon was much higher in corals from temperate regions (Florida, Belize, Hawaiian Islands) than in corals from tropical regions (Galapagos Islands and Canton Island). A linear relationship appears to exist between the preanthropogenic $\Delta^{14}\text{C}$ values and the S_e values measured in the individual corals, because the ^{14}C in corals is derived from two different carbon reservoirs: (1) the atmosphere and (2) the subsurface ocean. A linear relationship is also observed between the preanthropogenic $\Delta^{14}\text{C}$ values and the concentration of bomb-produced ^{14}C in the individual corals during A.D. 1973. The apparent radiocarbon ages of the surface waters in temperate and tropical oceans during the preanthropogenic period range from about 280 to 520 years B.P. (-40 to -69%). At all investigated locations, it is likely that waters at subsurface depths have the same apparent radiocarbon age of about 670 years B.P. From the change of oceanic $\Delta^{14}\text{C}$ in the surface ocean during post-bomb times, the approximate annual rate of net input of $^{14}\text{CO}_2$ to the ocean waters is calculated to be about 8% of the prevailing ^{14}C difference between atmosphere and ocean. From this input and from preanthropogenic $\Delta^{14}\text{C}$ values found at each location, it can be seen that vertical mixing of water in the Peru Current is about 3 times greater than that in the Gulf Stream.

INTRODUCTION

Cosmogenic ^{14}C is produced in the earth's upper atmosphere by an (n, p) reaction with atmospheric ^{14}N , oxidized to $^{14}\text{CO}_2$ and is subsequently distributed into the world's oceans and other exchangeable carbon reservoirs. The steady state concentration of ^{14}C in atmospheric CO_2 and in the dissolved inorganic carbon (DIOC) in surface ocean waters is at present perturbed by human activities. Since A.D. 1850, the burning of fossil fuels has produced ^{14}C -free CO_2 that caused atmospheric ^{14}C levels to decrease 2.5% by 1950 [Suess, 1953; Houtermans *et al.*, 1973; Cain and Suess, 1976; Tans, 1978]. Also the testing and use of nuclear devices in the late 1950's and early 1960's produced enough ^{14}C to cause the atmospheric concentrations of $^{14}\text{CO}_2$ in the northern hemisphere to almost double by 1963 (Figure 1).

Whereas records of atmospheric $^{14}\text{CO}_2$ concentrations have been obtained for many centuries from tree rings [Suess, 1980; Stuiver and Quay, 1980], there existed no analogous records for ^{14}C in the oceans. It was not until recently that oceanographic ^{14}C records were obtained using annually banded hermatypic coral rings [Druffel and Linick, 1978; Nozaki *et al.*, 1978; Druffel, 1980a, b, 1981a, b]. These corals accrete annual density bands with radiocarbon activities equal to those in the DIOC in the surface waters of the

ocean. The accreted skeleton is aragonite, a crystalline form of calcium carbonate that does not exchange its carbonate with carbon from any other source. Therefore coralline aragonite retains a permanent, unaltered record of the radiocarbon activity of the DIOC in the sea water at the time of ring formation. Continuous coral records, frequently older than 100 years, are commonly found in temperate regions of the world ocean. Thus records of radiocarbon activities can be determined for the past 100 years or more in surface waters that harbor healthy coral growth.

The numerical data evaluated here were reported previously [Druffel and Linick, 1978; Druffel, 1980a, 1981a]. They were obtained using gas proportional counting techniques. Data obtained by Nozaki *et al.* [1978] using liquid scintillation counting were included for comparison. All the measured ^{14}C values are reported here as $\Delta^{14}\text{C}$, defined as the per mil (‰) deviation from the activity of 19th century wood, taken as 95% of the activity of an NBS oxalic acid standard. Each measurement was corrected for decay from the time of formation until A.D. 1950 and for isotope fractionation by normalizing to a $\delta^{13}\text{C}_{\text{PDB}} = -25.0\%$ [Broecker and Olson, 1961]:

$$\Delta^{14}\text{C}(\text{‰}) = \delta^{14}\text{C} - 2(\delta^{13}\text{C} + 25)(1 + \delta^{14}\text{C}/1000) \quad (1)$$

FOSSIL FUEL CO_2

Radiocarbon values of corals from two locations in the Gulf Stream (Florida and Belize) [Druffel and Linick, 1978;

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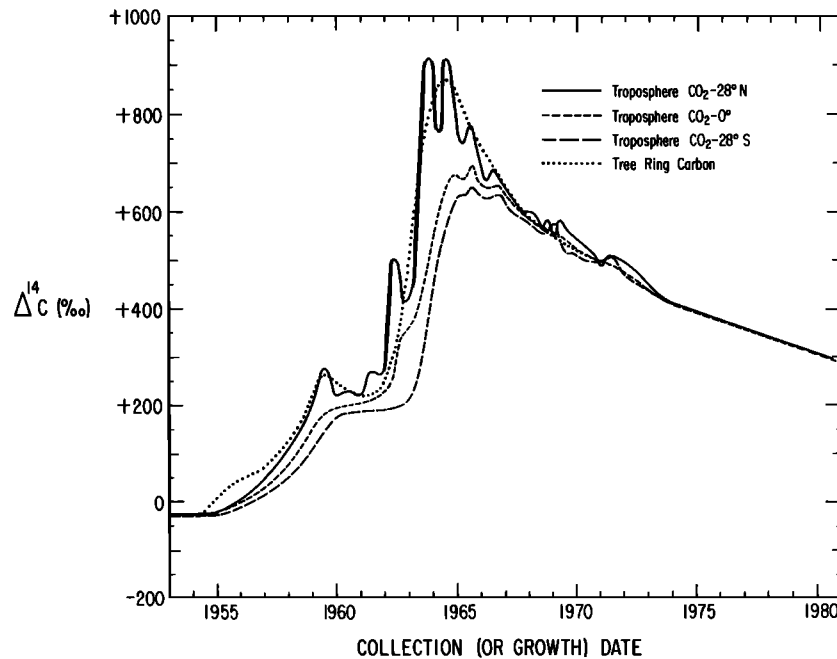


Fig. 1. Radiocarbon levels in tropospheric carbon dioxide and tree ring carbon from 1953 to 1980. These levels are expressed as parts per thousand deviation from natural (preindustrial, prebomb) concentrations. Tropospheric $\Delta^{14}\text{C}$ results are based on data from Rafter and Fergusson [1965], Rafter and O'Brien [1970], Nydal et al. [1979], and Druffel (manuscript in preparation). Tree ring $\Delta^{14}\text{C}$ results are from a Bear Mountain Oak from rural New York State [Cain and Suess, 1976].

Druffel, 1980a] and corals in the Peru Current located in the eastern tropical Pacific (Galapagos) [Druffel, 1981a] were considered. The respective data are shown in Figures 2–5. The discussion below is restricted to those results from corals that grew after A.D. 1800, although there are $\Delta^{14}\text{C}$

results available for Florida corals that grew in the 1600's [Druffel, 1982].

During the nineteenth century, the mean $\Delta^{14}\text{C}$ value in the Florida coral was $-49 \pm 3\text{‰}$ (Figure 2). A significant deviation from this average value occurred only from A.D.

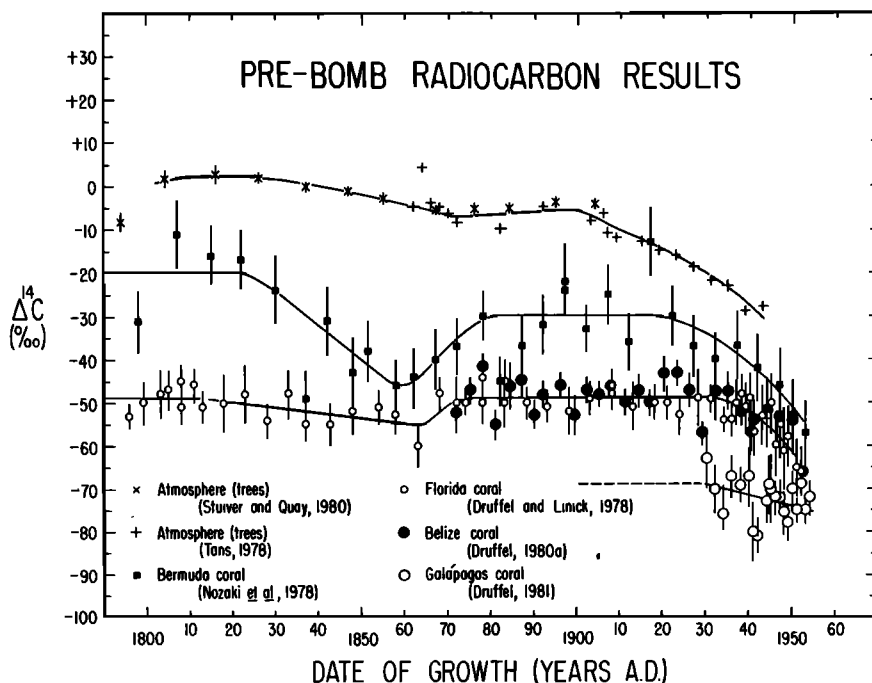


Fig. 2. Radiocarbon measurements for corals and tree rings that grew during the period A.D. 1800–1952. The trees were collected from the Pacific Northwest in the United States [Stuiver and Quay, 1980] and from the Netherlands [Tans, 1978]. The corals were *Montastrea annularis* collected from Florida and Belize [Druffel and Linick, 1978; Druffel, 1980a], *Pavona clavus* from the Galapagos [Druffel, 1981a] and *Diploria labyrinthiformis* from Bermuda [Nozaki et al., 1978]. See text for detail.

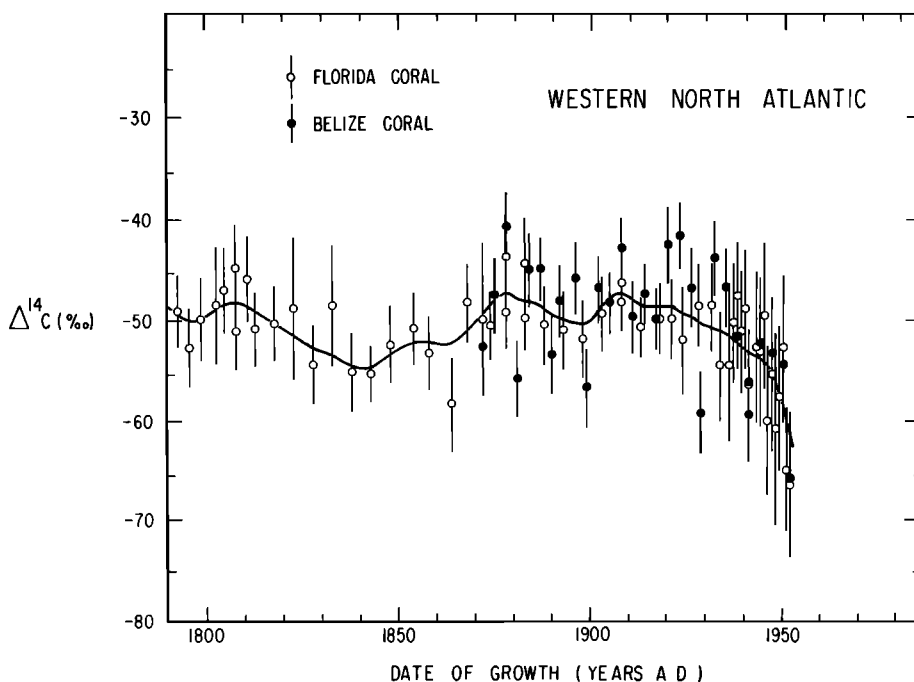


Fig. 3. Spline curve fit of the $\Delta^{14}\text{C}$ measurements from Florida and Belize corals (1790–1952). These trends are apparent: (1) 1820–1870: 5‰ decrease in $\Delta^{14}\text{C}$, which may have been the result of decreased ^{14}C levels in the atmosphere during the nineteenth century (Figure 2); (2) 1900–1952: S_e (Suess effect) is about -12% in the Gulf Stream surface ocean waters. The S_e in the atmosphere was about -25% . This decrease is the result of dilution of atmospheric ^{14}C levels due to input of fossil fuel CO_2 .

1820 to 1865, when the $\Delta^{14}\text{C}$ values decreased to about -54% . All but one of the eight $\Delta^{14}\text{C}$ values measured for this time period (1820–1865) were less than the mean value for the rest of the nineteenth century. A spline function (third-order polynomial) fitted to the Florida results is plotted in Figure 3. This plot clearly illustrates a decrease of 5‰ in the ^{14}C activity during the mid-1800's.

The $\Delta^{14}\text{C}$ measurements reported by Nozaki *et al.* [1978] for a Bermuda coral (Figure 2) indicate a similar though much larger minimum in the mid-1800's. The $\Delta^{14}\text{C}$ results averaged -20% from 1800 to 1820 and -30% from 1870 to 1900. For the time period 1820–1870, the values appear to have dropped continuously from -20 to -40% .

The decrease of ^{14}C activity in the mid-1800's in the Atlantic corals may well have been the result of declining ^{14}C levels in the atmosphere. Stuiver and Quay [1980] measured a 9‰ decrease of $\Delta^{14}\text{C}$ from $+3$ to -6% in tree rings from 1820 to 1870 (Figure 2). However, one would expect the corresponding decrease in oceanic ^{14}C to be less than that observed in the atmosphere [Oeschger *et al.*, 1975]. This is the case for the Florida coral record where $\Delta^{14}\text{C}$ values dropped 5‰ and atmospheric levels dropped 9‰. The Bermuda record, however, shows a much larger decrease in ^{14}C activity (-20%) which suggests temporary enhancement of vertical exchange between the mixed layer and subsurface water masses [Nozaki *et al.*, 1978].

Results obtained for *Montastrea annularis* that grew in Glover Reef, Belize from 1870 to 1900 average $-48 \pm 4\%$ and show no significant variations (Figure 2). A least-squares analysis of these data yields no significant slope. This value is the same as that obtained for Florida coral ($-49 \pm 3\%$) that grew during the same period, 1870–1900. Hence during the preanthropogenic period, surface waters in the Gulf Stream contained the same $^{14}\text{C}/^{12}\text{C}$ ratio at different

locations. It appears that the $\Delta^{14}\text{C}$ value of -49% represents the general preanthropogenic radiocarbon level in the surface waters of the Gulf Stream System. The atmospheric level had remained constant at -6% during this period (Figure 2). Thus under steady state conditions (excluding the possibility of nuclear spin effect on chemical constants), there appears to be a 43‰ deficiency of radiocarbon in the surface ocean compared to what is to be expected from equilibrium considerations. This deficiency value seems to have a general significance for surface ocean water. It is absolutely essential for estimating the exchange rate of $^{14}\text{CO}_2$ between atmosphere and ocean.

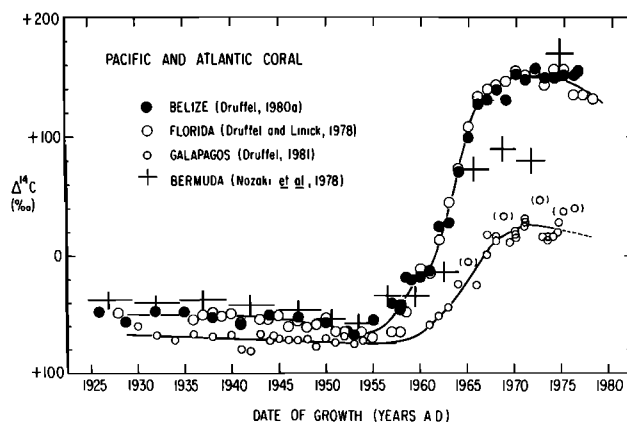


Fig. 4. Radiocarbon measurements for coral that grew in the Galapagos Islands [Druffel, 1981a], Florida [Druffel and Linick, 1978], Belize [Druffel, 1980a], and Bermuda [Nozaki *et al.*, 1978] from 1925 to 1978. The Galapagos points surrounded by parentheses represent the coral growth during El Niño years (see text for detail). A considerable difference is noticed among the coral locations. This is attributed to the source of surface waters for each location.

The $\Delta^{14}\text{C}$ results for *Pavona clavus* from the Galapagos Islands [Druffel, 1981a] are presented in Figure 2. The earliest $\Delta^{14}\text{C}$ results in this series represent values close to or equal to that which existed during preanthropogenic times. The average of the four data points for the period 1929–1937 is -69% . This preanthropogenic $\Delta^{14}\text{C}$ value is substantially lower than the values for corals from the North Atlantic (Figure 2). The difference is certainly due to upwelling into the surface waters surrounding the Galapagos Islands. The waters are undersaturated in oxygen and enriched in nutrients such as phosphate and nitrate [Love, 1971, 1972, 1975]. Isopycnals (lines of constant density) outcropping in waters surrounding the Galapagos Islands slope upward toward the equator. These isopycnals submerge to depths of 60–180 m below the surface in areas both north and south of the equator. As mixing occurs most readily along isopycnals, the waters that come to the surface at the Galapagos have originated from depths of 60–180 m below the surface. It has been shown by many investigators [Broecker et al., 1960; Bien et al., 1965; Rafter, 1968] that during prebomb times, $\Delta^{14}\text{C}$ values in waters below the thermocline (100–200 m) were significantly lower (by 15–25%) than those at the surface. Subsurface waters have been isolated from the atmosphere for a long enough period of time to allow for significant decay of radiocarbon. This substantial subsurface water component is responsible for the 20% depletion of radiocarbon levels in the Galapagos as compared to those in the Gulf Stream waters (Figure 2).

Figure 2 also shows the $\Delta^{14}\text{C}$ measurements for corals that grew during the period 1900–1952. During this time period, the data show a decrease in the $\Delta^{14}\text{C}$ values. This decrease is the result of dilution of existing levels of ^{14}C in the surface ocean by ^{14}C -free CO_2 , which has been released into the atmosphere by the burning of fossil fuels. Since the late 1800's, the release of industrial CO_2 to the atmosphere has increased at nearly an exponential rate. During this same

period the carbon in tree rings recorded a decline in atmospheric radiocarbon concentration [Suess, 1953]. From the late nineteenth century until 1950, the decrease of $\Delta^{14}\text{C}$ for trees grown in the northern hemisphere was about -20 to -25% [Tans, 1978; Stuiver and Quay, 1981]. This decrease is denoted here as S_e .

The values for S_e recorded by corals vary from location to location (Figure 2). Florida coral recorded an S_e of -11% from 1900 to 1952. Belize coral decreased by 12% during this period. Galapagos coral showed the smallest S_e , -6% . Fossil fuel CO_2 admitted to the ocean's surface dilutes the existing (preanthropogenic) radiocarbon concentration. Since the S_e is a measure of the fraction of anthropogenic CO_2 in a given area of the surface ocean, it is possible to calculate the relative amounts of fossil fuel CO_2 in the various water bodies for which S_e has been measured. Of these four sites, Bermuda surface waters contain the highest concentration of fossil fuel CO_2 ($S_e = -25\%$). The value for S_e in Gulf Stream waters (-11.5%) is twice that found in Peru Current waters (-6%). Hence for a given amount of DIOC there is approximately twice as much industrial CO_2 present in the Gulf Stream surface waters than in the surface waters of the Peru Current.

BOMB-PRODUCED RADIOCARBON

The testing of thermonuclear devices in the stratosphere during the late 1950's and early 1960's released large amounts of neutrons, which reacted with ^{14}N to produce ^{14}C . Rapid oxidation converted atomic ^{14}C to $^{14}\text{CO}_2$, and the $^{14}\text{CO}_2$ was subsequently distributed to the troposphere, biosphere, and surface ocean. After 1965, the ^{14}C concentration in the atmosphere decreased (Figure 1), primarily as a consequence of isotope exchange with the DIOC in the surface oceans and with exchangeable carbon in other reservoirs.

All post-1925 $\Delta^{14}\text{C}$ results for corals are displayed graphi-

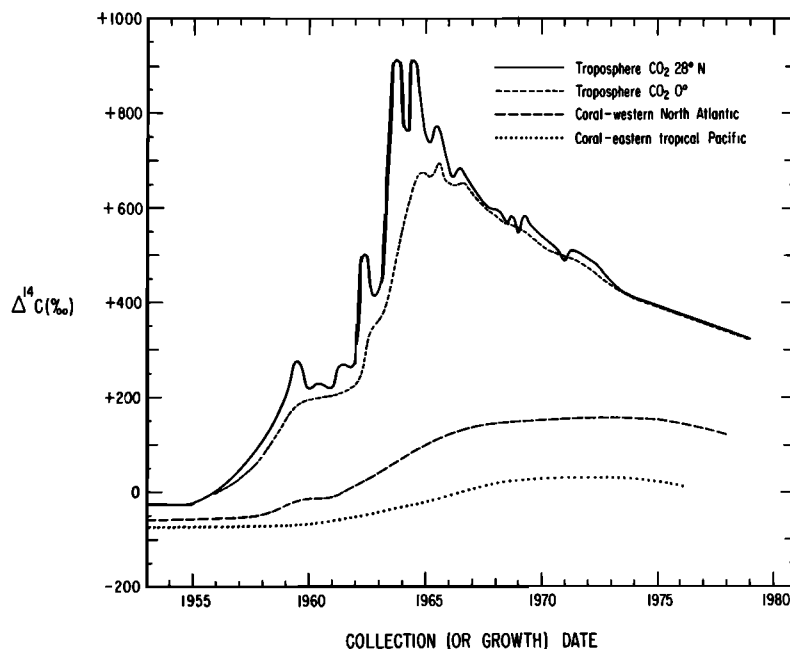


Fig. 5. Carbon 14 levels of tropospheric carbon dioxide and of annual coral rings from 1953 to 1980. Tropospheric $\Delta^{14}\text{C}$ results are identical to those in Figure 1. Coral $\Delta^{14}\text{C}$ results are based on data from the western North Atlantic (Florida and Belize) and from the eastern tropical Pacific (Galapagos Islands).

cally in Figure 4. Each set of data shows a large rise of ¹⁴C concentration from about 1954 to the present. This rise is caused by the net input of bomb-produced ¹⁴C from the atmosphere to the surface ocean. Radiocarbon in both Florida and Belize corals increased from -61‰ in 1953 to a maximum value of 153‰ in the early 1970's. This reflects an overall increase of 214‰ due to the input of bomb ¹⁴C to the surface waters of the Gulf Stream System (Figure 4). From 1958 to 1961, the increase of Δ¹⁴C from 1958 to 1961 in these corals was only 45‰. However, the input of bomb ¹⁴C to the surface ocean increased markedly after the major high-altitude weapons testing of 1962 (Figure 1). As a result, Δ¹⁴C values increased by 145‰ from 1961 to 1966. The time delay between the atmospheric and oceanic maxima of bomb-produced ¹⁴C (Figure 5) illustrates that several years are required for the atmosphere and surface ocean to approach a steady state with respect to ¹⁴CO₂ exchange.

The Δ¹⁴C values obtained for Florida and Belize corals agree remarkably well with those obtained for surface sea water in the Atlantic. Temperature and salinity measurements of surface waters entering the Yucatan Channel [Iselin, 1936] show that about three-fourths of this water originates in the western Sargasso Sea. The remaining one-fourth comes from the South Atlantic. This composition of Gulf Stream waters agrees with Δ¹⁴C measurements made of DIOC in Atlantic surface waters during the GEOSECS project of the early 1970's. Radiocarbon values of the GEOSECS samples collected in 1972-1973 ranged from 140 to 180‰ in North Atlantic and from 130 to 150‰ in South Atlantic surface waters [Östlund *et al.*, 1974, 1976; Broecker *et al.*, 1978]. Hence with three-fourths of the Gulf Stream water from the North Atlantic (0.75 × 160) and one-fourth from the South Atlantic (0.25 × 140), the expected Δ¹⁴C for 1972-1973 is 155‰. This value agrees with the Florida and Belize corals (153‰) in the early 1970's; hence Δ¹⁴C values of corals from Belize and Florida reflect mainly the values in the western Sargasso Sea.

Radiocarbon results obtained from four coral heads collected at the Galapagos Islands are shown graphically in Figure 4. Due to El Niño events, values for the years 1965, 1969, 1972, 1975, and 1976 are significantly higher than for the other years [Druffel, 1981a]. The appearance of warm, low-salinity surface waters in the eastern tropical Pacific is known as El Niño [Wyrski *et al.*, 1976]. These waters come from north of the equator and contain higher levels of ¹⁴C than the upwelled surface waters normally present in the Galapagos area. During the period 1961-1972, values for non-El Niño years steadily rose from -59‰ to +25‰. If -75‰ is considered the prebomb Δ¹⁴C value (Figure 2), an overall rise of 100‰ due to bomb ¹⁴C is observed for the surface waters of the eastern equatorial Pacific. This increase is much smaller than that observed in North Atlantic corals (Figure 4), due to increased mixing with subsurface waters in the Peru Current that have lower Δ¹⁴C values.

The time at which a steady state was reached in the mixed layer can be recognized from the beginning of the decrease of the Δ¹⁴C values in the corals. It is the time at which the rate of net uptake of atmospheric ¹⁴CO₂ by the mixed layer is equal to the rate of loss of ¹⁴C either to the deeper layers of the ocean or to higher latitudes via lateral transport. Figures 4 and 5 show that this time was reached in the northwestern Atlantic by about 1975. This time will not be the same for all locations. In fact, as late as 1979 [Druffel, 1981b;

Toggweiler, 1982] there is no evidence of a decline in radiocarbon concentrations at tropical locations in the Pacific. This is likely due to horizontal transport of bomb ¹⁴C-laden subsurface water from temperate locations to the surface at equatorial regions.

RATE PROCESSES INVOLVING ¹⁴CO₂ TRANSFER

The exchange of CO₂ between the atmosphere and the surface ocean is of utmost importance in connection with the fate of fossil fuel CO₂ on earth. Using the data obtained from post-bomb coral growth, the net input of bomb-produced ¹⁴C into the surface ocean, *I*₁₄, can be calculated by taking the first derivative of the Δ¹⁴C trends observed in the oceans since 1950 (Figure 4). The input of ¹⁴CO₂ to the ocean is also directly proportional to the ¹⁴CO₂ concentration gradient between atmosphere and surface ocean. In Figure 6, the change of Δ¹⁴C per year as seen in corals, denoted Δ_{*m*} (first derivative of curves in Figure 4), is plotted versus the difference Δ_{*am*} between Δ¹⁴C in the atmosphere and in the surface ocean during individual years (Figure 5). The points of interest are those that represent post-1964 values (post-1966 for the Galapagos data), after which there was no further increase of ¹⁴C in the atmosphere (Figure 1), and bomb ¹⁴C can be considered simply a spike of tracer into the atmosphere. Both the North Atlantic and Equatorial Pacific data show a nearly linear time dependence in Figure 6, although offset from each other. Only in the Gulf Stream data does there appear to be a deviation from linearity from 1967 to 1974. The slope (*I*₁₄⁻¹) for this period is about twice the average value and may represent a period when climatic variations reduced the net input of ¹⁴CO₂ to the surface waters of the Gulf Stream. Jenkins [1982] observed a reduction in water mass renewal in the Sargasso Sea during the late 1960's and early 1970's using rates of apparent oxygen utilization along isopycnals.

Regardless of this variation least-squares analyses of the two sets of data in Figure 6 reveal the following numerical relationships:

Gulf Stream system (northwestern Atlantic)

$$\Delta_m = (0.079)\Delta_{am} + 345 \quad (2)$$

Peru Current (eastern tropical Pacific)

$$\Delta_m = (0.080)\Delta_{am} + 440 \quad (3)$$

Equations (2) and (3) represent the inverse of the functions in Figure 6. The slope of these lines (0.079 and 0.080‰ per year per ‰) are the same. The agreement of the two values indicates that the net input of ¹⁴CO₂ into the oceans is proportional only to the ¹⁴C difference between atmosphere and ocean. The average value for *I*₁₄ is 0.080 ± 0.015‰ per year per ‰, which means that the annual rate of net input of bomb ¹⁴CO₂ to the surface ocean is 8 ± 2% of the prevailing ¹⁴C difference between atmosphere and ocean. This represents an upper limit for the net input rate of ¹⁴CO₂ to the surface waters of the ocean, as part of the atmospheric ¹⁴CO₂ can be taken up by other reservoirs, in particular by the biosphere. However, although the fraction of atmospheric CO₂ taken up by photosynthesis every year is not negligibly small, most of it is returned to the atmosphere within a year or two so that its effect upon the total rate by which ¹⁴CO₂ disappears from the atmosphere is small. The slope of the lines through the points in Figure 6 can therefore

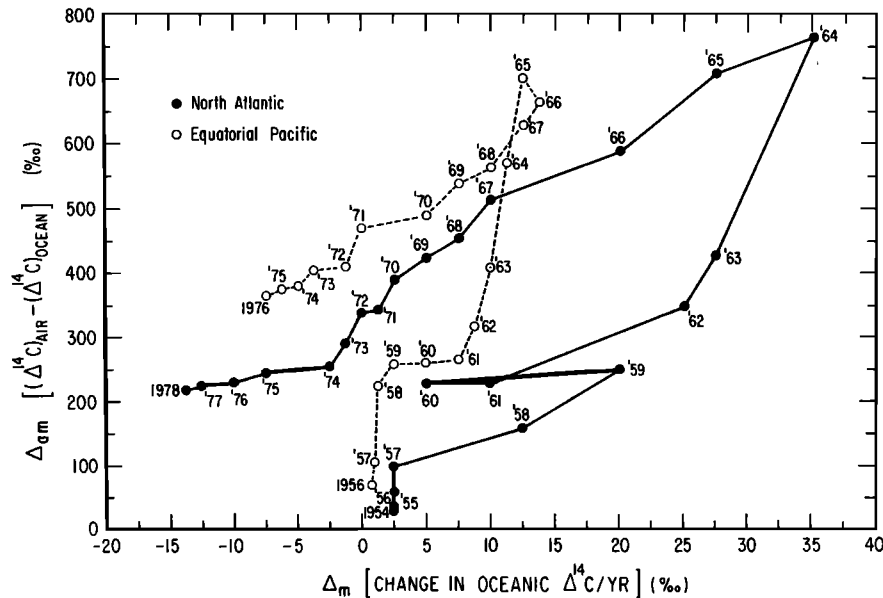


Fig. 6. Annual changes of $\Delta^{14}\text{C}$ noticed in post-bomb corals (Δ_m) versus the difference between $\Delta^{14}\text{C}$ in the atmosphere and those in corals (Δ_{am}). North Atlantic results were reported by Druffel and Linick [1978] and Druffel [1980a] and equatorial Pacific results by Druffel [1981a]. Each point is labelled with the corresponding year to which the data apply, and a line connects data points representative of consecutive years. The slope of the two lines is virtually always positive; this indicates that the uptake of bomb ^{14}C by the surface waters was indeed directly proportional to the ^{14}C gradient between the atmosphere and the surface ocean. The net input of $^{14}\text{CO}_2$ to the surface ocean is calculated from the inverse slopes of these lines (post-1966) and is $I_{14} = 0.08\text{‰}$ per year per ‰ difference between atmosphere and ocean.

be used to calculate in good approximation the value of I_{14} . As the biospheric carbon reservoir fills up, the value will decrease and the apparent residence time of $^{14}\text{CO}_2$ in the atmosphere will increase. This, however, will not significantly affect our conclusions.

From the nearly constant $\Delta^{14}\text{C}$ values displayed during preanthropogenic times (Figure 2), it can be concluded that the loss of atmospheric $^{14}\text{CO}_2$ to the surface ocean was balanced by its cosmic ray production (2.5 ^{14}C atoms/cm²/s or 7.9×10^7 atoms/cm²/year). If we assume that nearly all of the ^{14}C produced goes into the oceans (>90%) and that the ocean mixed layer is 100 m deep, an average value for Δ_{am} of 90‰ would be required to balance the loss of ^{14}C to the ocean with its production by cosmic rays.

A net flux of $^{14}\text{CO}_2$ to the surface ocean can be calculated using I_{14} . If the average value for Δ_{am} was 90‰ during the pre-industrial period, then the net flux of atmospheric $^{14}\text{CO}_2$ to the world's surface ocean was 630 moles/year.

From the coral data presented in Figure 2, it is possible for the first time to determine accurately the depletion of ^{14}C in the surface ocean relative to the preanthropogenic atmosphere. Values for Δ_{am} ranged from 43‰ for corals in the Gulf Stream to 63‰ for corals in the Peru Current. These values represent apparent radiocarbon ages for the surface ocean of 350 and 520 years B.P., respectively. In polar regions, the apparent radiocarbon ages are much higher [Linick and Suess, 1972]. The apparent age of the surface ocean carbonate is maintained by mixing with subsurface waters whose ^{14}C activity has been depleted by radioactive decay.

In Figure 7, there is plotted the difference between the $\Delta^{14}\text{C}$ in the atmosphere and in the surface sea water versus time. This difference, Δ_{am} , decreases by about 10% per year after 1965. This indicates that the turnover time of $^{14}\text{CO}_2$ in

the atmosphere with respect to transfer to the surface ocean (τ_{am}), is of the order of 10 years.

An independent check of the τ_{am} value approximated above can be achieved by applying a simple three-box model, where one box is the troposphere, the second the surface ocean (100 m depth), and the third the deep ocean [Houtermans et al., 1973]. Using known atmospheric values in the northern hemisphere and at the equator (Figure 5), a close fit of the post-bomb $\Delta^{14}\text{C}$ measurements of corals from the Gulf Stream and the Peru Current from 1959 to 1978 requires apparent turnover times for $^{14}\text{CO}_2$ in the atmosphere (τ_{am}) of 16 ± 3 and 31 ± 10 years and for the mixed layer (τ_{md}) of 12 ± 3 and 8 ± 3 years, respectively. The estimates using $\Delta^{14}\text{C}$ measurements of corals from the Peru Current are biased because of the increased communication

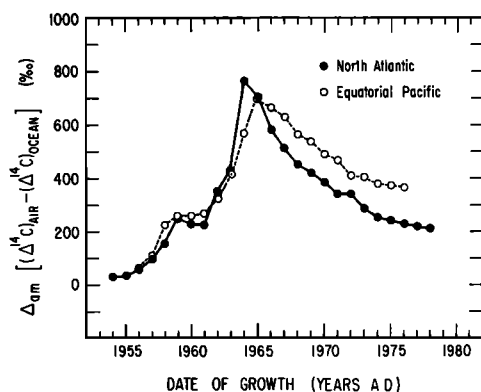


Fig. 7. Difference between the $\Delta^{14}\text{C}$ values in the atmosphere and those in the surface water (corals), Δ_{am} , during post-bomb years. Bomb ^{14}C was considered a spike in the troposphere only after 1964 (after 1966 near the equator and in the southern hemisphere).

between the deep reservoir and the mixed layer through upwelling.

Assuming that atmospheric CO₂ will continue to increase [Keeling, 1973] at its present exponential rate, the S_e calculated using these τ_{am} and τ_{md} values will be -14‰ in the Peru Current and -27‰ in the Gulf Stream system by the year A.D. 2000 (where S_e in the atmosphere is expected to be -60‰). Therefore the decrease in $\Delta^{14}\text{C}$ (S_e) from 1950 to 2000 would be an additional 8‰ in the Peru Current and an additional 16‰ in the Gulf Stream system.

APPARENT RADIOCARBON AGE OF THE SURFACE OCEAN AND IMPLICATIONS FOR VERTICAL MIXING

The apparent radiocarbon age of the surface ocean is maintained by mixing with subsurface waters whose radiocarbon activity has been depleted due to radioactive decay. An estimate of the maximum rate of mixing between subsurface and surface waters can be obtained if $\Delta^{14}\text{C}$ in these subsurface waters is known. In Figure 8, it is shown that at any given time an approximately linear relationship exists between the preanthropogenic $\Delta^{14}\text{C}$ values present in the early 1900's and the S_e values in corals and in atmospheric CO₂ (Figure 2). The S_e values by 1930, 1940, and 1952 in corals and in the atmosphere are plotted in Figure 8. The least-squares fit of each set of measured data intersects the y axis at similar points (Figure 8). Their values correspond to an average $\Delta^{14}\text{C}$ of $-87 \pm 10\text{‰}$. This linear relationship can be viewed as a mixing line for two water masses that contain CO₂ of two different origins which mix in varying proportions to produce surface waters with intermediate preanthropogenic $\Delta^{14}\text{C}$ values. One end member is atmospheric CO₂ ($\Delta^{14}\text{C} = -6\text{‰}$, pre-1900) and the other is CO₂ with a preanthropogenic $\Delta^{14}\text{C}$ value of -87‰ . It appears that as a rule, waters in temperate and tropical regions with $\Delta^{14}\text{C}$ values of -87‰ have not been in contact and exchanged to a noticeable extent with the atmosphere since the onset of the industrial revolution. The higher the preanthropogenic $\Delta^{14}\text{C}$ value in surface water masses, the larger is the percentage of water that has equilibrated with the atmosphere. These waters contain relatively more fossil fuel CO₂ (S_e is more negative) than surface waters whose preanthropogenic $\Delta^{14}\text{C}$ values were lower (S_e is less negative).

Figure 9 illustrates the linear relationship between the maximum rise (by 1973) of $\Delta^{14}\text{C}$ in corals due to bomb-produced ¹⁴C and the preanthropogenic $\Delta^{14}\text{C}$ value. Two data points have been included in Figure 9 for corals whose radiocarbon record is not yet completed. Both are *Porites*, one of which was collected at Canton Island in the mid-equatorial Pacific and the other at Oahu in the Hawaiian Islands [Druffel, 1981b, and manuscript in preparation]. The increase by 1973 of $\Delta^{14}\text{C}$ in the atmosphere was $+470\text{‰}$ (which includes compensation for an S_e of -40‰ by 1973). The year 1973 was chosen because it was during this time that maximum $\Delta^{14}\text{C}$ values were observed in the temperate ocean and a quasi-steady state appeared to have been established for the exchange of ¹⁴CO₂ between atmosphere and ocean (Figure 5). Those values corresponding to the rise in $\Delta^{14}\text{C}$ by 1968 (see Figure 5) are also included in Figure 9.

The x intercept ($\Delta^{14}\text{C} = -84 \pm 3\text{‰}$) is the same, within limits of error, as the y intercept in Figure 8 ($-87 \pm 10\text{‰}$). In the same manner as Figure 8, the linear relationship in Figure 9 can correspond to a mixing line for two water masses that mix in varying proportions to produce surface

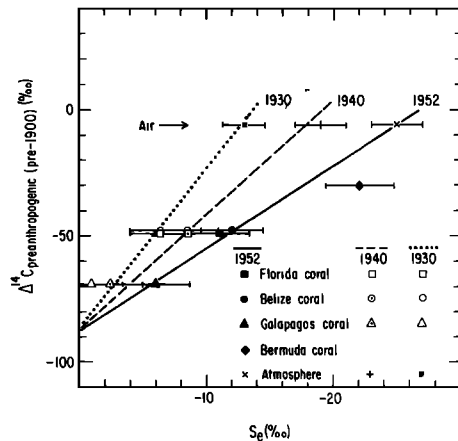


Fig. 8. The depletion of radiocarbon levels (S_e) due to dilution by fossil fuel CO₂ by 1952, 1940, and 1930 versus preanthropogenic $\Delta^{14}\text{C}$ in corals and in the atmosphere. These values were previously reported for coral from Florida [Druffel and Linick, 1978], Belize [Druffel, 1980a], the Galapagos Islands [Druffel, 1981a], Bermuda [Nozaki et al., 1978], and for atmospheric CO₂ [Tans, 1978; Stuiver and Quay, 1980]. S_e in the Bermuda coral (-22‰) is unusually large and is probably the result of local upwelling that occurred during the twentieth century [Nozaki et al., 1978]. Despite the large error bars, the linear relationship can be viewed as a mixing line for two water masses that mix in varying proportions to produce surface waters with intermediate preanthropogenic $\Delta^{14}\text{C}$ values. One end member is atmospheric CO₂ ($\Delta^{14}\text{C} = -6\text{‰}$, pre-1900) and the other is CO₂ at underlying depths with a $\Delta^{14}\text{C}$ value of $-87 \pm 10\text{‰}$.

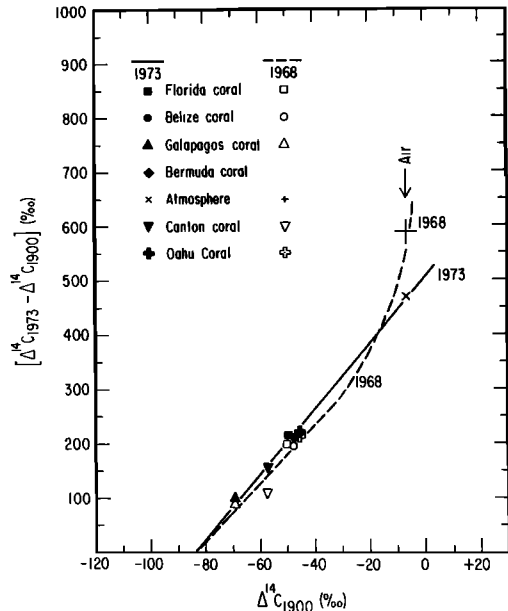


Fig. 9. The maximum rise of $\Delta^{14}\text{C}$ by 1973 due to bomb-produced ¹⁴C versus preanthropogenic $\Delta^{14}\text{C}$ in corals and in atmospheric CO₂. These values were previously reported for coral from Florida [Druffel and Linick, 1978], Belize [Druffel, 1980a], Galapagos Islands [Druffel, 1981a], and Bermuda [Nozaki et al., 1978]. Two data points, representing coral from Canton Island in the mid-equatorial Pacific and Oahu Island in the North Pacific [Druffel, 1981b], have been included whose radiocarbon records are not yet completed. Those values corresponding to the rise in $\Delta^{14}\text{C}$ by 1968 are also included. In the same manner as Figure 8, the linear relationship of the 1973 data corresponds to a mixing line for two water masses that mix in varying proportions to produce surface waters with intermediate $\Delta^{14}\text{C}$ values. Note that the intercept ($-84 \pm 3\text{‰}$) is essentially the same as in Figure 8. This value represents the preanthropogenic $\Delta^{14}\text{C}$ value of waters from subsurface depths.

waters with intermediate $\Delta^{14}\text{C}$ values. One end member is in complete equilibrium with the atmosphere ($\Delta^{14}\text{C}_{\text{pre-1900}} = -6\text{‰}$) and the other represents subsurface water with a $\Delta^{14}\text{C} = -86 \pm 4\text{‰}$ (average of intercepts in Figures 8 and 9).

The existence of linear relationships between S_e and $\Delta^{14}\text{C}_{1900}$, as shown in Figure 8, is not surprising. All it means is that at the time of growth of the corals steady state conditions prevailed with respect to water mixing at each location of the surface ocean during the postindustrial period (1900–1952). This had not been the case during the first 6–8 years following the major bomb tests (1962–1970) but had after 10 years and later. What might be somewhat surprising is the fact that the $\Delta^{14}\text{C}$ values (viz., the ^{14}C ages) of the $S_e = 0$ components are so very similar at greatly different areas and oceanographic conditions. This may be a coincidence, or it may indicate a general feature of fundamental importance in ocean mixing patterns.

One major conclusion can be drawn from Figure 9 regarding the age of the surface ocean. Numerous authors have reported that the largest increase of $\Delta^{14}\text{C}$ in the DIOC in any area in the surface ocean due to bomb ^{14}C input was about +260‰. This rise was observed in the mid-North Atlantic gyre and in the mid-North Pacific gyre during the early 1970's [Linick and Suess, 1972; Östlund *et al.*, 1974, 1976; Stuiver and Östlund, 1980]. From the linear relationship in Figure 9, a value of +260‰ for the maximum bomb ^{14}C increase corresponds to a $\Delta^{14}\text{C}_{\text{pre-1900}} = -40 \pm 2\text{‰}$. This implies that the highest preanthropogenic $\Delta^{14}\text{C}$ value in the surface ocean was -40‰ and was present only in the mid-gyre regions of the North Atlantic and North Pacific oceans. This value corresponds to a radiocarbon age of 280 ± 20 years B.P., with respect to the atmosphere (-6‰ , 0 years B.P.), and is the youngest age of any surface waters present in the preanthropogenic ocean. As the Galapagos coral lie in an area (Peru Current) where the upwelling intensity is as great or greater than at any other temperate or tropical location, the preanthropogenic $\Delta^{14}\text{C}$ value for these corals ($-69 \pm 2\text{‰}$) represents the oldest radiocarbon age present in the surface ocean (520 ± 20 years B.P.) between 40°N and 40°S .

The age of the surface ocean provides some important constraints on the rate of vertical exchange between surface and subsurface water masses [Oeschger *et al.*, 1975]. With the following three assumptions, vertical mixing rates that prevailed during preindustrial times can be calculated if one uses a one-dimensional model for each of the surface locations studied: (1) $\Delta^{14}\text{C}$ of the underlying waters (200–300 m depth) is $-86 \pm 4\text{‰}$ (this agrees (within $\pm 15\text{‰}$) with early measurements made by several investigators [Broecker *et al.*, 1960; Bien *et al.*, 1965; Raftar, 1968] of subsurface water masses in the southwestern and tropical Pacific and the North Atlantic Oceans), (2) net input rate I_{14} during preindustrial times was 0.08‰ per year per ‰, and (3) there is no appreciable horizontal transport of water. However, as horizontal advection is indeed an important mixing parameter in the oceans [Michel and Suess, 1975; Jenkins, 1980] and since 0.08 is a maximum estimate of the true value for I_{14} , the vertical exchange rates obtained in this manner are relatively crude estimates of their maximum values. To offset this trend is the consideration that the $\Delta^{14}\text{C}$ of the underlying waters may be higher than -86‰ , due to the possibility that S_e (by 1950) in these waters was greater than zero (see Figure 8). This assumption will cause estimates of

the vertical mixing rates to appear as minimums. It is estimated that S_e by 1950 in waters underlying the Peru Current was $<2\text{‰}$ and for the Gulf Stream was $<3\text{‰}$.

Gulf Stream waters are highly stratified with regard to density and consist mainly of recycled water from the Sargasso Sea. As downwelling (or 'Ekman pumping') is the major mixing mechanism here [Stommel, 1979], it would be incorrect to assume that subsurface waters rose to the surface in the subtropical gyre. In reality, equatorial water which is itself influenced by upwelling is transported laterally via the Gulf Stream and is mixed into Sargasso Sea water. In view of the isopycnal structure of waters in the Peru Current, however, direct upwelling of water from subsurface levels is a reasonable view of the actual mixing processes in this region.

As the preanthropogenic $\Delta^{14}\text{C}$ value in the atmosphere (in 1900) was -6‰ (Figure 2) and preanthropogenic $\Delta^{14}\text{C}$ values for the surface ocean were -49‰ in the Gulf Stream and -69‰ in the Peru Current (Figure 2), Δ_{am} values in these regions were 43 and 63‰, respectively. Thus the net input of $^{14}\text{CO}_2$ to Gulf Stream waters at the turn of the twentieth century could have caused a 3.4‰ increase (0.080×43) per year of the ^{14}C activity in these waters. Instead, a 43‰ depletion, which corresponds to a 350-year age with respect to the atmosphere, is maintained by mixing with subsurface waters whose radiocarbon activity has been depleted by radioactive decay. In order to retain a steady state, the vertical ascension of subsurface waters required to maintain a 350-year age of the surface waters in the Gulf Stream must compensate the net input of $^{14}\text{CO}_2$ from the atmosphere to the mixed layer. Thus there is a net input of -3.4‰ per year of $^{14}\text{CO}_2$ from the subsurface ocean to the mixed layer. An estimate of the upper limit of the vertical mixing rate, w , for waters in the Gulf Stream can be determined by using a simple dilution equation to find the amount of subsurface water, f , that would be required to dilute the ^{14}C in the mixed layer by 3.4‰, to -52.4‰ :

$$86f + 49g = 52.4 \quad (4)$$

where $f + g = 1$. Using these equations, $f = 0.092$. As 75 m is taken as the depth of the mixed layer, the maximum vertical exchange rate in the Gulf Stream waters is about 0.092 per year \times 75 m, or 7 ± 2 m/year. This value implies that the mean life of $^{14}\text{CO}_2$ in the mixed layer is a minimum of about 11 years ($75 \text{ m} \div 7 \text{ m/year}$). This is in agreement with the value of 12 years calculated for τ_{md} in the Gulf Stream waters.

The upwelling rate required to reduce the $\Delta^{14}\text{C}$ in Peru Current surface waters from -69 to -74‰ ($63 \times 0.08 = 5.0$) can be calculated in this manner:

$$86f + 69g = 74 \quad (5)$$

Here, the value for f is 0.29, and an upwelling rate of 22 ± 10 m/year follows. As upwelling is most intense in eastern boundary currents, the value for w found in the Peru Current likely represents the largest value for any surface area in the temperate or tropical world ocean. Very few locations (with the exception of polar oceans) experience such an intense vertical mixing component as that which exists in the Galapagos region. These data appear to set maximum limits on vertical mixing in the oceans, from less than 7 ± 2 m/year in temperate regions to as high as 22 ± 10 m/year in eastern boundary currents.

These estimates are lower than the value of 27 m/year made by Broecker *et al.* [1978], who used a one-dimensional model to explain the anomalous depletion of radiocarbon in the equatorial Atlantic. As upwelling in the Peru Current is much more intense than that in the broad equatorial band between 15°N and 15°S in the Atlantic Ocean, a lower estimate would be expected for the upwelling rate in the equatorial Atlantic. The discrepancy demonstrates that one-dimensional models are inadequate, a fact that has been lucidly shown by tritium [Rooth and Östlund, 1972; Michel and Suess, 1975; Fine *et al.*, 1981] and tritium/helium profiles [Jenkins, 1980].

The importance of the vertical exchange rates calculated above is actually not with the numerical values themselves, as they were obtained using grossly oversimplified assumptions (no horizontal mixing). But a comparison of the two estimates is of some value. If we divide w found for the Peru Current (22 m/year) by that for the Gulf Stream (7 m/year), we obtain a factor of about 3. This signifies that the exchange between surface and subsurface waters in the Peru Current is approximately 3 times greater than that in the Gulf Stream system. This difference in vertical exchange rates has important implications for the determination of rates of distribution of anthropogenic contaminants in the oceans and for projecting the present and future input of anthropogenic carbon dioxide to the oceans of the world.

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