26 October 1979, Volume 206, Number 4417 **SCIENCE**

Fate of Fossil Fuel Carbon Dioxide and the Global Carbon Budget

W. S. Broecker, T. Takahashi, H. J. Simpson, T.-H. Peng

Claims have recently been made that the cutting and burning of forests is currently a major source of carbon dioxide (CO_2) (*1–4*). These claims come as a shock to those of us engaged in global carbon budgeting, as we have been calling for a modest increase in the size of the terrestrial biosphere (*5–8*) in order to achieve a balance in the carbon budget. In this article we review the elements of the carbon budget and attempt to reconcile these seemingly conflicting views.

Summary. The fate of fossil fuel carbon dioxide released into the atmosphere depends on the exchange rates of carbon between the atmosphere and three major carbon reservoirs, namely, the oceans, shallow-water sediments, and the terrestrial biosphere. Various assumptions and models used to estimate the global carbon budget for the last 20 years are reviewed and evaluated. Several versions of recent atmosphere-ocean models appear to give reliable and mutually consistent estimates for carbon dioxide uptake by the oceans. On the other hand, there is no compelling evidence which establishes that the terrestrial biomass has decreased at a rate comparable to that of fossil fuel combustion over the last two decades, as has been recently claimed.

The carbon budgeting strategy is as follows. Since 1958, it has been possible to measure the secular trends in the atmospheric CO_2 concentration with sufficient accuracy to permit a quantitative assessment of the buildup of CO_2 in this reservoir (see Fig. 1) (*9, 10*). We have good records over this time period of the amount of CO_2 released through the combustion of fossil fuels, that is, coal, oil, and gas (see Fig. 2) (*11, 12*). These inventories show that the CO_2 content of the atmosphere has risen by about one-half as much as would be the case if all the CO_2 released from fossil fuel combustion had remained in the air (assuming no significant change in the terrestrial biomass). In view of the uncertainties in estimates of both the fuel consumed and the atmospheric CO_2 increase, the actual value for the airborne fraction of CO_2 could lie anywhere in the range from 0.48 to 0.56. We will use the value of 0.52 ± 0.04 adopted by Oeschger *et al.* (*8*).

The problem is then to account for the missing CO_2. Three possibilities exist. This CO_2 could be stored in the terrestrial biosphere (mainly as wood and soil humus), in the sea (mainly as dissolved inorganic carbon), or in shallow-water sediments (mainly as organic residues). Of these, seawater storage must dominate. The results of ocean uptake modeling (to be described below) indicate that 0.37 ± 0.04 of the fossil fuel CO_2 generated between 1958 and the present has been taken up by the sea. Adding this value to the airborne fraction (0.52 ± 0.04), we obtain a total of 0.89 ± 0.06. As we explain below, the reaction of carbon atoms with anthropogenic phosphorus atoms to form organic residues accounts for about 0.02 of the amount of fossil fuel CO_2 released since 1958. Adding this contribution to the ocean and atmosphere inventories, we achieve a total of 0.91 ± 0.07.

Estimates of forest cutting and burning suggest that the amount of CO_2 released by these processes since 1958 ranges from 20 to 100 percent of that released by the burning of fossil fuels (*1–4*). If true, the unaccounted for residual [that is, (fossil fuel CO_2) + (forest cutback CO_2) − (CO_2 taken up by the ocean) − (CO_2 taken up in organic residues)] then lies in the range from one-quarter to the total amount of fossil fuel CO_2 released (see Table 1). Thus, if the forests are decreasing in biomass at anywhere near the rates claimed, there must be a major error in our budgeting.

We examine below the assumptions associated with estimates of the transfer of excess CO_2 from the atmosphere to other reservoirs. We do not review the fuel consumption or atmospheric increase estimates, as they have been discussed and reevaluated by several investigators (*9–12*). Rather, we will start with a discussion of uptake of CO_2 by the ocean. Our conclusion will be that current estimates of ocean uptake are sufficiently firm to exclude the possibility that appreciably more excess CO_2 is dissolved in the sea than has been estimated through the use of existing models (*5–8*). This being the case, we will look to the biosphere (living and dead) for resolution of the budgetary contradiction. We conclude that the regrowth of previously cut forests and the enhancement of forest growth resulting from the excess CO_2 in the atmosphere have probably roughly balanced the rate of forest destruction during the past few decades.

Seawater Uptake of Carbon Dioxide

Existing estimates of the amount of fossil fuel CO_2 that has thus far been taken up by the ocean are based entirely on modeling. The secular increase in the dissolved inorganic carbon content of seawater is as yet too small to be mea-

---

The authors are members of the Lamont-Doherty Geological Observatory and the Department of Geological Sciences, Columbia University, Palisades, New York 10964.

0036-8075/79/1026-0409$02.00/0

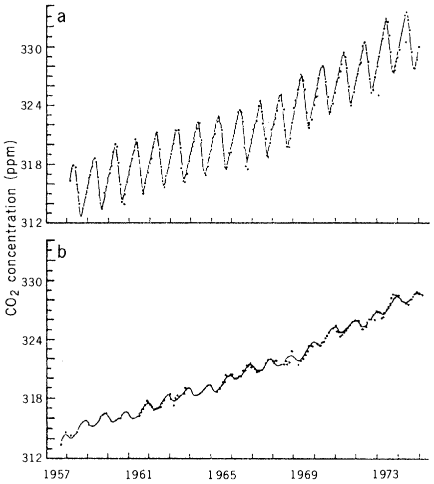

Fig. 1. The records of the atmospheric CO_2 concentrations (by volume in dry air) (a) at the Mauna Loa Observatory, Hawaii, and (b) at the South Pole over the period from 1958 through 1975. These measurements were made by Keeling and his coworkers (*9, 10*).

sured. The models suggest that since the onset of the industrial revolution the increase in the dissolved inorganic carbon content of surface water has been about 1.3 percent (*13*) and that at present the rate of increase is about 0.35 percent per decade. Historical oceanic data on dissolved CO_2 are accurate to only a few percent; the accuracy of recent measurements is about 0.3 percent. Thus, unless measurements that are more accurate by an order of magnitude can be made, at least a decade will pass before a direct confirmation of the model-based estimates will be obtained. Fortunately, as outlined below, the basic assumptions needed for modeling are reasonably well grounded.

Three basic components are needed in the oceanic model. The first is the static capacity of seawater to take up excess CO_2. For any given increase in the atmospheric CO_2 content, by how much will the CO_2 content of a cubic meter of seawater maintained at chemical equilibrium with the atmosphere increase? The second component is the rate of CO_2 transport across the air-sea interface. This rate determines how rapidly the dissolved inorganic carbon content of surface seawater responds to changes in the atmospheric CO_2 content. Finally, the rate of vertical mixing within the sea must be known. The amount of CO_2 taken up by the sea depends on the rapidity with which the CO_2 taken up is stirred into the body of the sea. As all three of these factors show geographic and seasonal variations, the model must either average these variations or treat various oceanic regions and seasons of the year separately. Thus far, only the former approach has been taken.

The static capacity of seawater for the uptake of excess atmospheric CO_2 is a thermodynamic property subject to precise measurement in the laboratory. Since the major mechanism of CO_2 uptake by the ocean is its reaction with carbonate ions (CO_3^{2-}) to form bicarbonate ions (HCO_3^-), the static capacity depends on the chemical composition of the sea, the solubility of CO_2 gas in seawater, the first and second dissociation constants for carbonic acid in seawater, and the first dissociation constant of boric acid in seawater. The boric acid dissociation constant is important because borate ion competes with CO_3^{2-} for the hydrogen ions present in seawater; the excess CO_2 entering the sea will perturb the boric acid speciation as well as the carbonic acid speciation. Although there is some uncertainty about the values of these constants, the error in the static capacity estimate due to the residual uncertainties in the equilibrium constants is no more than ± 5 percent (*14*).

The static capacity for any given sample of seawater can be expressed in terms of the Revelle factor, R, which is defined as follows:

$$R = \frac{\Delta pCO_2/pCO_2}{\Delta[\Sigma CO_2]/[\Sigma CO_2]}$$

where pCO_2 is the partial pressure of CO_2 in seawater and $[\Sigma CO_2]$ is the concentration of dissolved inorganic carbon (that is, $[CO_2] + [HCO_3^-] + [CO_3^{2-}]$) in seawater. This definition of R assumes that the temperature, salinity, and alkalinity of the seawater remain constant and that $\Delta[\Sigma CO_2]$ is much less than $[\Sigma CO_2]$. Figure 3 shows R values at various points on the sea surface as part of the Geochemical Ocean Section Study (GEOSECS) program (*14*); the Revelle factor is a function of the ratio of $[\Sigma CO_2]$ to the alkalinity and of temperature. Since the geographic variations in the chemical composition of surface seawater correlate with water temperature, the R for surface ocean water correlates well with temperature. The range is from 8 for the warmest surface waters to 15 for the coldest surface waters. The best choice of a value to be used in an average ocean model is 10. This is the value chosen by Oeschger *et al.* (*8*) in their oceanic model for CO_2 uptake as a result of fossil fuel combustion. Because of the uncertainty with regard to the appropriate average temperature of the seawater which has partially equilibrated with the atmosphere during the industrial revolution, the choice for R could be anywhere in the range from 9 to 11. Thus, in order to produce an increase of 1 percent in the equilibrium total content of dissolved inorganic carbon of average surface seawater, the partial pressure of CO_2 in the atmosphere must rise between 9 and 11 percent.

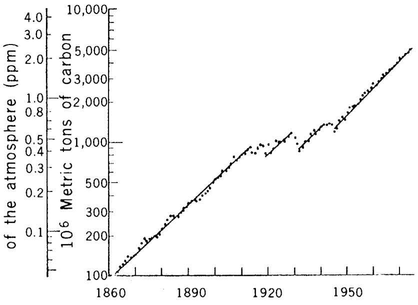

Fig. 2. Production rate of CO_2 from fossil fuels between 1860 and 1974 as reconstructed from the production of coal, oil, natural gas, and cement (*11, 12*). The estimate for the period from 1860 to 1941 was made by Keeling (*11*); that for the period from 1950 to 1974 was made by Baes *et al.* (*12*).

Table 1. Summary of the carbon budget (in units of 10^{15} moles) for the period 1958 to 1975.

Component	Carbon
Model 1 (excludes forests)	
Atmosphere	2.7 ± 0.2
Ocean	1.9 ± 0.4
Phosphorus matching	~0.1
Total	4.7 ± 0.5
Fossil fuel	5.2 ± 0.6
Unaccounted for residual	0.5 ± 0.8
Model 2 (includes forests, with other entries the same as for model 1)	
Terrestrial biomass decrease	
Bolin (*1*)	2 ± 1
Woodwell and Houghton (*2*)	~5
Stuiver (*31*)	~0
Unaccounted for residual	
Bolin (*1*)	2 ± 1
Woodwell and Houghton (*2*)	~5
Stuiver (*31*)	~0

From this result an upper limit can be set on the fraction of the fossil fuel CO_2 produced to date that has entered the sea. Per square meter of ocean surface, the preindustrial atmosphere contained about 145 moles of CO_2 and the ocean about 8740 moles (*15*). Taking the average R to be 10, the fraction f_0 of CO_2 taken up by the sea after equilibration with the atmosphere is

$$f_0 = \frac{8740/10}{(8740/10) + 145} = 0.86$$

As we shall see, the actual fraction taken up is much smaller.

There are two methods by which the transfer rate of CO_2 between the atmosphere and the surface ocean has been estimated. The first method is based on the requirement that the net invasion of naturally produced $^{14}CO_2$ into the ocean be just fast enough to balance the rate of decay of ^{14}C residing in the sea (*5*). The decay rate of ^{14}C within the sea can be estimated from ΣCO_2 contents and $^{14}C/C$ ratios measured in the major oceanic water masses. The net influx of $^{14}CO_2$ depends on the fractionation-corrected difference between the $^{14}C/C$ of atmospheric CO_2 and the mean $^{14}C/C$ ratio in surface waters and on the gas exchange rate. Thus, from a knowledge of the whole ocean ^{14}C inventory and of the difference between the $^{14}C/C$ ratio of atmospheric CO_2 and of the surface ocean water, the gas exchange rate can be calculated. The result is 19 ± 6 moles of CO_2 per square meter per year. The major source of error in the estimate is the uncertainty in the fractionation-corrected difference in the $^{14}C/C$ ratio of atmospheric CO_2 and of the surface waters for the time prior to the industrial revolution (−45 ± 15 per mil) (*16*).

The second approach is based on the deficiency of radon gas observed in the surface ocean mixed layer (*17*). This method takes advantage of the fact that radon gas (half-life, 3.9 days) is being generated within the sea by the decay of its parent, ^{226}Ra, that the atmosphere over the sea is sufficiently free of radon to be considered an infinite sink, and that the rate of interchange between surface mixed-layer water and the stratified water beneath the mixed layer is so slow that the transfer of radon from the upper thermocline to the depleted mixed layer can be neglected. The amount of radon found within the mixed layer averages about 70 percent of that expected at equilibrium with the ^{226}Ra dissolved in the mixed layer water. Thus, during their mean lifetime of 6 days, about 30 percent of the radon atoms generated within the mixed layer escape to the air. For the 100 stations measured in the GEOSECS program in the Atlantic and Pacific, the average stagnant film thickness obtained by the radon method is 35 micrometers (*18*). The application of this radon result to CO_2 requires a knowledge of the ratio of the molecular diffusivities of the two gases, of the dependence of the transfer coefficient on diffusivity, and on the assumption that an increase in the CO_2 flux caused by the reaction between CO_2 and water is negligible. The transfer coefficient is linearly related to the diffusivity if the stagnant film model is used to describe the gas-water interface (*19*), whereas it is related to the square root of diffusivity if the surface renewal model is considered (*19*). The best radon-based estimate for the CO_2 exchange rate is 16 moles per square meter per year (*18*). This result is close to that obtained with the natural radiocarbon model. In making this comparison, we must point out several reasons why these estimates might not agree.

Table 2. Distribution of fossil fuel CO_2 between the atmosphere and the ocean as a function of mixing depth and the gas exchange rate, E. In the calculations we assumed infinitely rapid mixing within the upper mixed layer and no fossil fuel uptake by the lower layer; R = the Revelle factor.

Depth of the upper layer (m)	Fraction of the ocean volume in the upper layer	Fraction of the total fossil fuel CO_2 taken up by the oceans	
		$E = \infty$, $R = 10$	$E = 16$ (mole m^{-2} $year^{-1}$), $R = 10$
76	0.2	0.136	0.132
380	0.10	0.441	0.406
950	0.25	0.663	0.591
1900	0.50	0.798	0.695
3800	1.00	0.886	0.761

1) The exchange of CO_2 may be enhanced by chemical reactions within the stagnant film. Although kinetic studies in the laboratory suggest that these reactions are normally too slow to be significant (*20*), they may be catalyzed in the sea as suggested by Berger and Libby (*21*).

2) The radon measurements in temperate and high latitudes were made mainly under summer conditions (that is, during periods of lower than average wind velocity). In view of the fact that laboratory studies indicate that the gas exchange rate increases with wind velocity, the GEOSECS radon measurements may underestimate the global average exchange rate.

3) The CO_2 exchange rate based on the distribution of natural radiocarbon is based on the assumption that the decay of ^{14}C in the deep sea is balanced entirely by the input of ^{14}C through the warm surface ocean. If, on the other hand, a substantial portion of this input is through the high latitude outcrops of deepwater masses, then the CO_2 exchange rate needed for maintaining the ^{14}C in the ocean at steady state would be lower than the 19 mole m^{-2} $year^{-1}$ given above (*22*).

In the calculations we will carry out below, we adopt a CO_2 exchange rate of 16 mole m^{-2} $year^{-1}$, the value chosen by Oeschger *et al.* (*8*) in their model calculations. A feeling for the importance of this exchange rate can be obtained from the calculations summarized in Table 2. In each calculation the ocean is divided into two reservoirs; the upper reservoir is stirred with infinite rapidity, and the lower reservoir is isolated from the at-

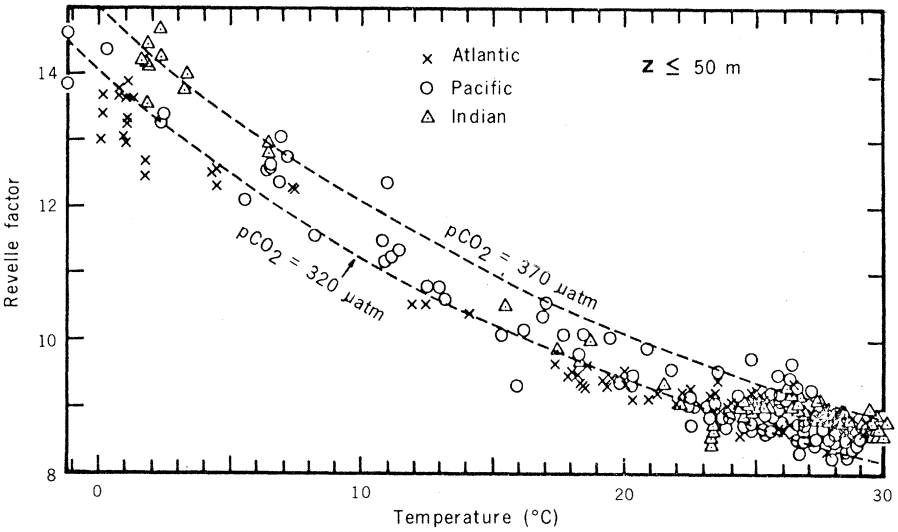

Fig. 3. Revelle factor for the surface waters of the Atlantic, Pacific, and Indian oceans. The values presented here have been calculated on the basis of the alkalinity and total CO_2 data obtained by the GEOSECS program. The first and second apparent dissociation constants of carbonic acid in seawater of Mehrbach *et al.* (*54*), the apparent dissociation constant of boric acid in seawater of Lyman (*55*), and the solubility of CO_2 in seawater as determined by Weiss (*56*) have been used for the calculation. The dashed curves represent the effect of temperature on the Revelle factor for a typical surface water (salinity = 35.00 per mil and alkalinity = 2.320 milliequivalents per kilogram) at constant pCO_2 values of 320 and 370 × 10^{-6} atm, respectively. The total CO_2 varies from 1.95 millimoles per kilogram at 26°C to 2.19 millimoles per kilogram at 0°C.

mosphere. For each such case the ocean uptake of fossil fuel CO_2 to date is calculated, based on the use of an infinite gas exchange rate and the CO_2 exchange rate of 16 mole m^{-2} $year^{-1}$. As will be shown below, the case with an upper mixed-layer thickness of 380 m lies closest to the true situation. For this case the finite rate of gas exchange reduces the amount of CO_2 taken up by the ocean by 10 percent. Had the value based on natural radiocarbon (19 mole m^{-2} $year^{-1}$) been chosen, the reduction would have been about 8 percent. Thus, although a sizable uncertainty does exist in the mean oceanic CO_2 exchange rate, its influence on the results of calculations of the ocean uptake of CO_2 is no larger than 5 percent.

The rate of vertical mixing within the sea can best be understood in the context of the large-scale density structure. For our purpose, a three-layer subdivision of the ocean is adequate. Capping the ocean is a layer averaging about 75 m thick, which is completely stirred on a time scale of hours to days. This layer is underlain by the thermocline, which averages about 1000 m thick. Ventilation of this layer occurs on a time scale of years to decades. Beneath the thermocline is the deep sea, which averages about 2700 m thick. Radiocarbon data on deep seawater indicate that it is ventilated on time scales ranging from a few hundred years for the Atlantic (*23*) to more than 1000 years for the North Pacific (*24*). The average is about 1000 years (*16*). On the other hand, the mean age of fossil fuel CO_2 is 28 years (*25*). During the 28 years, the average fossil fuel CO_2 molecule has penetrated only about 28/1000 of the ocean system, or 2.8 percent of the deep sea has been ventilated. This corresponds to a characteristic depth of 75 m. Thus, the surface mixed layer (75 m thick) and the deep sea together contribute a total of 150 m to the characteristic mixing depth for CO_2 in the uppermost and deep-sea layers. To this must be added that fraction of the thermocline ventilated on a time scale of several decades. In view of the thickness of the thermocline, the potential range in the overall characteristic depth is quite large (150 to 1150 m). The corresponding static oceanic uptake fractions range from 0.18 to 0.63.

The best current means of calibrating models for thermocline ventilation is through the distribution of bomb-produced tritium (^3H). The injection of this radioactivity to the sea surface occurred primarily during the years 1962 through 1964, with lesser inputs prior to and subsequent to this period (*26*). As part of the GEOSECS program, the depth distribution of tritium was determined throughout the Atlantic and Pacific oceans (*27*). As this program was carried out during the period July 1972 to June 1974, it provides an estimate of the extent of mixing during roughly a 10-year period. As summarized in Table 3, the mean depth of penetration of tritium was 360 m.

Table 3. Tritium penetration as of the time of the GEOSECS survey (July 1972 to June 1974) (*27*).

Latitude range	Fraction of the oceanic area	Mean mixing depth (m)	Depth if spread over the entire ocean (m)
0°–15°	0.28	130	36
15°–45°	0.45	500	225
Arctic	0.04	200	8
North Atlantic > 45°	0.03	1000	30
North Pacific > 45°	0.03	300	9
Antarctic > 45°	0.17	300	51
Total	1.00	360*	360*

*Area-weighted mean; Σ (fraction of the oceanic area) × (mean mixing depth) = 360 m.

In order to apply this result to fossil fuel CO_2, two differences between the inputs of these substances must be considered. First, the mean age of the tritium at the time of the GEOSECS survey was 10 years, whereas that of fossil fuel CO_2 is currently 28 years. Second, the tritium was delivered to the sea within a year or two after its production (actually the age of 10 years is measured from its arrival at the sea surface). On the other hand, much of the fossil fuel CO_2 still resides in the air. To see the influences of this effect, let us approximate the tritium input as a delta-function (in 1963) and that of CO_2 as diffusion into the sea from a reservoir (the atmosphere) held at a constant concentration. In this case, the ratio of the mean penetration depths $h_{^3H}$ and h_{CO_2} of these two tracers would be

$$\frac{h_{CO_2}}{h_{^3H}} = \frac{2}{\pi}\sqrt{\frac{\text{mean age of fossil fuel } CO_2}{\text{mean age of tritium}}}$$

$$= \frac{2}{\pi}\sqrt{\frac{28}{10}} \cong 1$$

where the mean penetration depth is defined as follows:

$$h = \int_0^\infty \frac{C dz}{C_{surf}}$$

where C is the concentration at a depth z and C_{surf} is the concentration at the ocean surface. Thus, as a rough approximation, the mean depth of penetration of fossil fuel CO_2 into the thermocline can be taken to be the same as that for tritium. This result strengthens the argument for using tritium to calibrate CO_2 mixing models.

In order to obtain more precise estimates of the amount of CO_2 that has entered the sea, a model combining vertical mixing and gas exchange must be used. Oeschger *et al.* (*8*) developed such a model. It is one-dimensional and is based on vertical diffusion into the body of the sea from a well-mixed reservoir 75 m thick. They selected the vertical diffusivity of 1.25 square centimeters per second used in their model to provide a best mutual fit for the distribution of natural and bomb-produced radiocarbon. The tritium data referred to here were not available at the time the paper of Oeschger *et al.* was published. Were the tritium data used to obtain the diffusivity, a value of 0.90 cm^2 sec^{-1} would be obtained (in order to explain the mean depth of penetration 285 m beneath the surface mixed layer 75 m thick). Were 0.90 cm^2 sec^{-1} used for the diffusivity instead of 1.25 cm^2 sec^{-1} the mean depth of penetration of CO_2 into the ocean below the mixed layer would have been reduced by about the factor $(0.90/1.25)^{1/2}$ or 0.85. This would reduce the mean penetration depth (beneath the mixed layer) from 325 to 275 m.

However, Oeschger *et al.* (*8*) did not consider the direct ventilation of the deep sea by way of its high latitude source regions. This ventilation is equivalent to an oceanwide layer about 75 m thick. Hence the extra CO_2 invasion obtained by including deep ventilation would more or less balance the reduction in thermocline uptake that would have been obtained had Oeschger *et al.* (*8*) been able to use the tritium results. Thus their value for the ocean uptake of CO_2 is probably as good a value as can be obtained with our present state of knowledge. They obtained a 60-40 atmosphere-ocean distribution of the fossil fuel CO_2 for the present (that is, if 52 percent of the CO_2 has remained in the air, 35 percent has gone into the sea).

Cross-Checks on the Ocean Uptake Models

Two cross-checks on the parameters selected for the ocean mixing model are available. Both involve perturbations in the ^{14}C cycle. The first, often referred to as the Suess effect, concerns the dilution of atmospheric CO_2 with ^{14}C-free CO_2 from fossil fuel burning. The change in

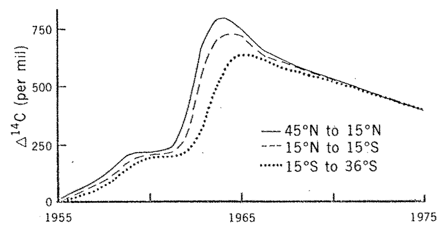

Fig. 4. Values of $\Delta^{14}C$ for atmospheric CO_2 from 1950 through 1975. The large increase over the steady-state value ($\Delta^{14}C = 0$) was the result of radiocarbon produced during nuclear weapons tests (*33*).

the atmospheric $^{14}C/C$ ratio caused by this dilution has been recorded by tree rings. The decrease between 1850 and 1950 was about 2.4 percent (*5*, *28*).

This reduction was only about one-fifth of the amount expected had there been no communication with other reservoirs (*5*, *28*, *29*). The observation thus requires that, since their release as CO_2 to the atmosphere, the fossil fuel carbon atoms have mixed with a carbon reservoir five times larger than the atmosphere alone. Whittaker and Likens (*30*) have estimated that the living biosphere has a carbon mass 1.35 times that in the atmosphere and that its mean replacement time is 16 years. In the 28 years that the average fossil fuel CO_2 molecule has had to wander, a mass of biospheric carbon about 1.1 times that in the atmosphere has been replaced by new growth. The combined reservoir consisting of the atmosphere plus the living biosphere would thus give a carbon mass 2.1 times that in the atmosphere alone. A layer of ocean water 425 m thick (75 + 275 + 75 m) contains 5.6 times as many carbon atoms as the atmosphere. Had this reservoir completely exchanged its carbon with the atmosphere, then the total reservoir (replaced living biosphere plus exchanged ocean plus atmosphere) would have a carbon mass 7.8 times that in the atmosphere. This value exceeds the observed value of 5 ± 1. The problem lies with the ocean reservoir. If a small, well-stirred reservoir of surface seawater is placed in contact with the atmosphere, its isotopic equilibration time will be 10 (the mean Revelle factor) times longer than its chemical equilibration time (*22*). Because the carbon content of the available ocean reservoir is not small compared to that of the carbon content of the atmosphere, the actual time constant ratio is smaller than 10 (*22*). The calculations of Oeschger *et al.* (*8*) show that, whereas as of 1950 the surface ocean had reached 85 percent of chemical equilibrium with the excess CO_2 in the atmosphere, it had reached only one-third of isotopic equilibrium. Moreover, the measured bomb ^{14}C content of the surface ocean carbon in 1972 was only about one-third of that for atmospheric carbon (*31*). Hence the reservoir of oceanic carbon equilibrated with the atmosphere will be only about one-third of that estimated from the characteristic depth of fossil fuel CO_2 penetration. Taking one-third of 5.6 (that is, 1.9) atmospheric carbon masses and combining it with the mass of atmospheric and exchanged biospheric carbon, one obtains 4.0 atmospheric masses. This value lies within the permissible range (5 ± 1).

The Suess effect is unlikely to put more stringent constraints on the ocean mixing depth for the following reasons:

1) As the fraction of isotopic equilibrium in surface ocean water is a nearly linear function of the gas exchange rate, the uncertainty in this rate does constitute an important source of error for carbon isotopic budgets.

2) There may be a significant contribution of nonliving organic material to the exchangeable reservoir (soil organics are being replaced on the time scale of centuries).

3) As the $^{14}C/C$ ratio in atmospheric CO_2 decreased by 2 percent during the 200-year period prior to 1850 (*32*), the assumption that it remained constant since 1950 is certainly open to question.

Thus, although the observed Suess effect is broadly consistent with the accepted size of the living biosphere and the depth to which the ocean has mixed during the fossil fuel era, it does not place a primary constraint on ocean modeling.

The other cross-check arises from the distribution of bomb radiocarbon between the ocean and the air. As of 1955, bomb-produced ^{14}C became measurable in the atmosphere (*33*); between 1952 and 1964, the atmospheric $^{14}C/C$ ratio almost doubled (*33*). Since 1965, it has slowly declined and is now only about 40 percent higher than it was in 1950 (Fig. 4) (*33*).

Measurements made as part of the GEOSECS program show that the bomb radiocarbon concentration in the surface ocean carbon averaged about 33 percent of that in the atmospheric carbon (*27*). This ratio is a function of both the air-sea gas exchange rate and the vertical mixing rate within the sea. In Table 4 the ratio of bomb ^{14}C in the surface ocean carbon to bomb ^{14}C in atmospheric carbon is given as a function of the gas exchange rate and the mean mixing depth (assuming infinitely rapid mixing to this depth and no transfer to deeper levels). Several combinations of mixing depth and exchange rate can reproduce the observed ratio. The bomb ^{14}C distribution is equally sensitive to both of these parameters and provides a measure of their product. The important point is that the combination of the tritium-derived mixing depth and the gas exchange coefficient adopted here (16 mole m^{-2} $year^{-1}$) have the required product. Thus the distribution of bomb-produced ^{14}C between air and surface seawater is consistent with the model used to distribute the fossil fuel CO_2. Once the vertical distribution of bomb-produced radiocarbon within the sea as obtained by the GEOSECS program becomes available, this tracer can be used to independently define the mixing rate and the gas exchange rate.

Table 4. Prediction of the ratio of the bomb-produced radiocarbon in carbon from the surface ocean to that in carbon from the atmosphere (as of 1973) for various choices of mixing depth and gas exchange rate.

CO_2 exchange rate (mole m^{-2} $year^{-1}$)	Mixing depth (m)		
	190	380	570
10	0.29	0.16	
16	0.48	0.29	0.20
24		0.50	0.37

One other potential cross-check should be mentioned. It is conceivable that the net flux of CO_2 into the sea could be directly monitored as a result of measurements of the difference between the partial pressure of CO_2 gas in the atmosphere and that in the surface ocean and of the gas exchange rate at a number of ocean stations. The CO_2 fluxes determined in this way could then be averaged to take into account regional and seasonal variations. The expected oceanwide average pCO_2 difference between atmosphere and ocean can be calculated as follows: If 40 percent of the CO_2 produced by fossil fuel burning each year is indeed entering the sea, then the net CO_2 flux must currently average 0.4 mole m^{-2} $year^{-1}$. The average exchange flux of CO_2 to the sea is 16 mole m^{-2} $year^{-1}$. Thus the difference between the atmospheric and surface ocean pCO_2 (*34*) must be

$$\Delta pCO_2 = \frac{0.4}{16} \times 320 \times 10^{-6}\,\text{atm} = 8\ \mu\text{atm}$$

The best estimate of ΔpCO_2 (as of 1973) is 8 ± 8 μatm (*35*).

The following considerations make flux measurements by this approach difficult:

1) The current experimental error on air-sea ΔpCO_2 measurements is about ± 3 μatm.

2) The sea surface pCO_2 ranges from

220 to 420 μatm (Fig. 5). The pCO_2 changes 4.5 percent per degree Celsius (*36*). During blooms, the rate of fixation of carbon by plants can become as high as the gas exchange rate (*37*). Large seasonal changes in the surface water pCO_2 are to be expected at any given high latitude location as a result of seasonal cycles in temperature and plant productivity. The response time of the oceanic mixed layer to equilibration with the atmosphere lies in the range of several months to several years (*17*). Hence the seasonal pattern in pCO_2 of high latitude surface waters is bound to be complex and will have to be monitored if a valid integration is to be performed.

3) Air injection supersaturations of several percent are not uncommon for gases such as nitrogen and argon (*38-40*). Translated to CO_2, partial pressure excesses of 3 to 10 μatm might be expected as a result of this effect alone.

If this cross-check is ever to be effectively carried out, a decade of preparation and measurements will be required. It is a complex task.

Dissolution of Marine Sedimentary Carbonate Minerals

The surface ocean is supersaturated (*41*) with respect to the mineral calcite by a factor of 5.5 in the warm equatorial oceans and by a factor of 2.5 in the cold polar oceans (Fig. 6). For the mineral aragonite, the saturation factor ranges from 3.7 to 1.7. This supersaturation persists to considerable depths (Fig. 7) (*42*). Using the depth distribution of tritium as a rough guide to the depth distribution of fossil fuel CO_2, we have estimated the change in the CO_3^{2-} content between 1850 and today. This calculation suggests that fossil fuel CO_2 has not yet penetrated into the sea far enough to alter the natural rate of calcite dissolution (that is, it is confined to waters supersaturated with calcite). For aragonite, there may be a thin band of Pacific sediments that formerly was in supersaturated water but now is in undersaturated water. We estimate that the area of sediments so affected constitutes no more than 0.1 percent of the sea floor. Much of this sediment is free of carbonate minerals. Thus, accelerated dissolution of neither calcite nor aragonite from shallow marine sediments can currently be enhancing the uptake of CO_2 by the sea.

Figure 8 shows the concentrations of CO_3^{2-} and total dissolved CO_2 as a function of the partial pressure of CO_2 in a typical tropical seawater at 24.0°C. The tropical surface ocean water will not become undersaturated with respect to aragonite and calcite until the partial pressure of CO_2 is increased to 5.3 and 8.5

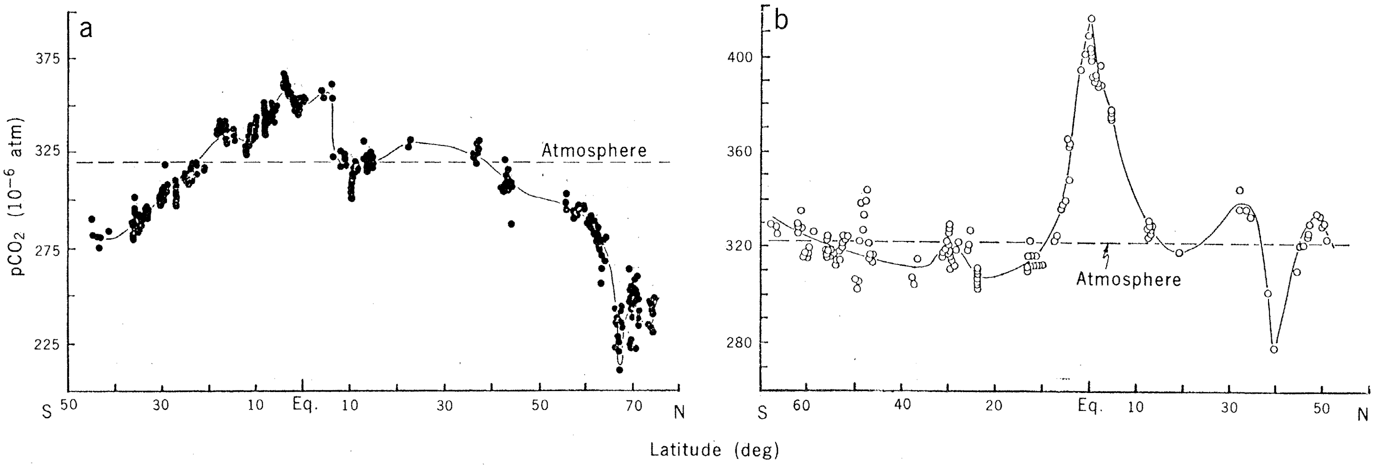

Fig. 5. Partial pressure of CO_2 (pCO_2) exerted by the surface ocean water and that in the marine atmosphere along the GEOSECS tracks: (a) the Atlantic western basin data obtained between August 1972 and January 1973; (b) the central Pacific data along the 180° meridian from October 1973 to February 1974. The equatorial areas of both oceans give up CO_2 to the atmosphere, whereas the northern North Atlantic is a strong sink for CO_2.

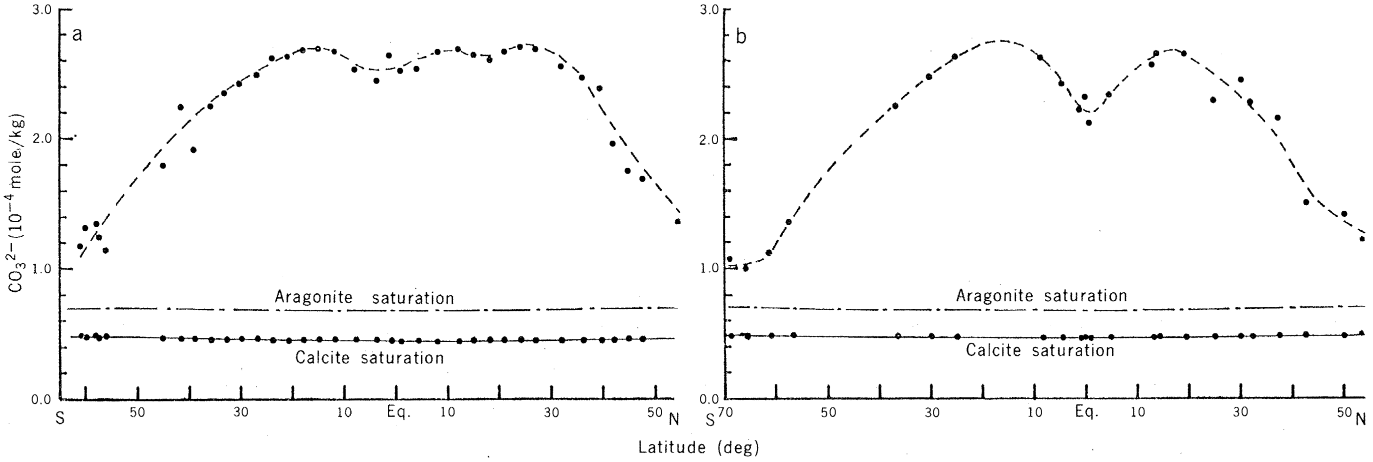

Fig. 6. Concentration of CO_3^{2-} in the surface ocean water along the GEOSECS tracks: (a) the Atlantic western basin data obtained from August 1972 through January 1973; (b) the central Pacific data obtained from October 1973 through February 1974 along the 180° meridian. The concentrations of CO_3^{2-} in equilibrium with calcite and aragonite are shown to illustrate that the surface waters of both oceans are supersaturated with respect to these calcium carbonate minerals by two to five times. The calcite solubility values are based on Ingle *et al.* (*57*), and the aragonite value is 1.48 times the calcite value.

times, respectively, the present atmospheric value. Such a condition is not likely ever to be reached and certainly not during the next several decades.

Broecker and Takahashi (*43*) have shown that the dissolution of even the most vulnerable deep-sea sediments (namely, those in the northern Atlantic) will not become a significant contributor to ocean uptake for at least a century. Thus, whereas the dissolution of calcite (and to some extent of aragonite) are necessary components of oceanic models for the era after the exhaustion of fossil fuels, they need not be considered in budgets for the last few decades or in budgets for the next few decades.

Garrels (*44*) has raised the interesting possibility that the high magnesian calcite (magnesium content of 11 to 13 mole fraction), which constitutes a major fraction of the carbonate in shallow-water sediments, is very close to saturation with seawater. In fact, he gives reasons to believe that the magnesium content of these carbonates may be that corresponding to exact saturation with mean preindustrial surface seawater. If so, then the decrease in the CO_3^{2-} content of the surface ocean water (15 to 20 micromoles per kilogram) caused by the increase in the atmospheric CO_2 content from 1850 to the present has subjected this material to dissolution. We estimate that the area of the ocean floor shallow enough to be affected and rich enough in carbonate minerals is no more than about 2 percent (that is, 7×10^{12} m^2). If we were to apply the Holocene rates of calcite dissolution observed for deep-sea sediments (*43*) subjected to the same CO_3^{2-} undersaturation ($\sim$ 10 μmole/kg), we would obtain a rate of 0.7×10^{12} mole of dissolution per year. As the current production rate of fossil fuel CO_2 is about 300×10^{12} moles per year, this process can be significant (it removes at least 10 percent of the fossil fuel CO_2) only if the rate of dissolution of high-magnesian calcite is at least 40 times faster than that for deep-sea calcite subjected to the same extent of undersaturation.

On the other hand, if the high-magnesian calcite is recrystallized to a lower magnesian calcite which is in equilibrium with current seawater, then no net release of CO_3^{2-} would occur. In this case, magnesian calcite can have no effect on the fate of fossil fuel CO_2. Until more research has been done on the geographic distribution, solubility, and dissolution kinetics of high-magnesian calcite, this mineral must remain a low probability candidate for the missing sink.

We do not see any likelihood that the amount of excess CO_2 stored within the sea is appreciably greater than that calculated on the basis of existing models. The answer to the controversy outlined above must lie with the biosphere. Current forest cutting and burning must be more or less balanced by expanded storage of organic matter in the remaining forest, in soils, and in shallow-water sediments. These possibilities are discussed below.

Phosphorus Matching

Garrels *et al.* (*45*) have pointed out that any phosphate released to the aqueous environment by the activities of man (soil fertilization, water softeners in detergents, sewage) tends to be incorporated by plants and ultimately converted into organic residues which accumulate in sediments. These residues have atomic ratios of carbon to phosphorus ranging from 100 to 600. Thus, the release of phosphorus leads to a sequestering of CO_2 from the atmosphere. Mackenzie (*46*) has noted that the fossil fuel burned and the total phosphorus mined on a global basis are currently in approximately the ratio of carbon to phosphorus found in terrestrial plants; this result suggests that perhaps all the CO_2 from the combustion of fossil fuel during recent years could potentially have been stored as woody organic detritus. Unfortunately, we lack information about the fate of the phosphorus being mined and about

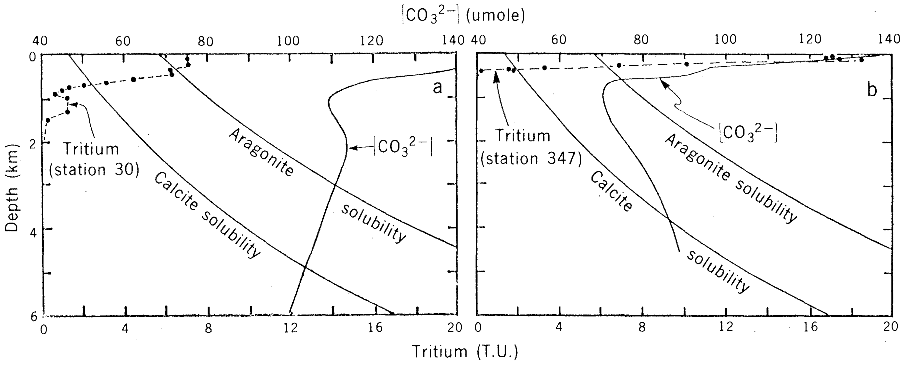

Fig. 7. Concentration of CO_3^{2-} and tritium (in tritium units, T.U.) as a function of depth at the GEOSECS stations in the North Atlantic and the eastern equatorial Pacific oceans. The tritium data at stations 30 and 347 were obtained by Ostlund *et al.* (*27*) and represent the tritium distribution in September 1972 and June 1974, respectively. The solubility curves for aragonite and calcite are based on Ingle *et al.* (*57*), and a volume change of − 35.6 cm^3 for dissolution of calcite. The intersections of the solubility curves and the CO_3^{2-} concentration curves indicate the saturation depth for the respective minerals. (a) In the North Atlantic, tritium has penetrated to a depth of about 1500 m. This indicates that the fossil fuel CO_2 has not reached below this level, and the aragonite and calcite saturation depths are not affected by fossil fuel CO_2. (b) In the eastern equatorial Pacific, tritium has penetrated to about 400 m in 10 years. Since the aragonite saturation depth is quite shallow ($\sim$ 500 m) in this area, fossil fuel CO_2 will soon begin to affect the aragonite saturation depth.

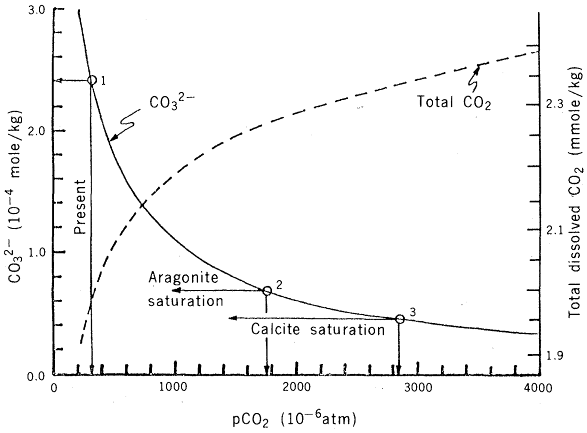

Fig. 8. Total dissolved CO_2 and the CO_3^{2-} concentration as a function of the partial pressure of CO_2(pCO_2) in a typical tropical ocean surface water at 24.0°C with a salinity of 35.0 per mil and an alkalinity of 2.32 milliequivalent per kilogram. The numbers indicate the following conditions: *1*, present-day surface ocean water; *2*, water at equilibrium with aragonite; and *3*, water at equilibrium with calcite. The pCO_2 in the atmosphere must increase to 1760 and 2850 μatm, respectively, before surface seawater becomes undersaturated with respect to aragonite and calcite. Thus, the tropical oceans will not become undersaturated with respect to aragonite and calcite until the atmospheric pCO_2 is increased to 5.3 and 8.5 times its present value, respectively. The apparent dissociation constants of carbonic acid determined by Mehrbach *et al.* (*54*), that of boric acid determined by Lyman (*55*), and the solubility of CO_2 gas in seawater determined by Weiss (*56*) have been used for the calculations.

the mean carbon/phosphorus ratio in organic residues formed. Stumm (*47*) has estimated the quantities of fertilizer and municipal waste phosphorus which reach natural waters in Europe (~ 7 percent of the total applied as fertilizer and produced as municipal waste). Using this data compiled for Europe and the average amount of phosphorus mined in the world since the mid-1950's (~ 0.25×10^{12} mole/year) (*47*) and assuming a carbon/phosphorus ratio of 250/1, the sink for fossil fuel CO_2 stored with anthropogenic phosphorus released to natural waters would be somewhat less than 2 percent of the total combustion source.

Most of the phosphorus mined is used as fertilizer and remains bound in soils. This phosphorus is generally thought to be inorganically bound and therefore does not contribute to the removal of atmospheric CO_2. However, as the actual data available in support of this generalization are quite meager, it is possible that the amount of CO_2 removed in this manner is significantly greater than 2 percent of the fossil fuel consumed.

Forest and Soil Storage of Carbon

The major active reservoirs of biospheric carbon are the forests and soil humus. The forests contain 1.3 ± 0.3 times the amount of carbon in the atmosphere (*30*) and the soil humus 4 ± 2 times this amount (*31, 48*). As a result of man's efforts in agriculture and forestry, these reservoirs have undergone considerable change and cannot in any sense be considered to be at steady state. In addition to these changes in land use, man has released to the atmosphere large amounts of plant nutrients (fixed nitrogen and gaseous carbon) and plant toxins (sulfuric acid, heavy metals, pesticides). The overall response of the nonagricultural terrestrial biosphere to these releases is not known. Forest cutting and burning during the last two decades do not constitute the only perturbation to this system; rather, it is the only perturbation that lends itself to ready quantification.

To get a feeling for the overall effects of land use, we must assess the temporal effect of the following alterations; forest to farm, farm to forest, and forest to forest. As forests store more living carbon than farmland by more than an order of magnitude (*30*) and since forest soils generally contain more humus than the farmland generated by their cutting, forest-to-agriculture and agriculture-to-forest transitions involve large net shifts of carbon between the atmosphere and the terrestrial biosphere. Where forests are cut and allowed to regrow, there is a temporary transfer of carbon from the biosphere to the atmosphere. Depending on the biomass of the second-growth forest, the net long-term change could be either positive or negative.

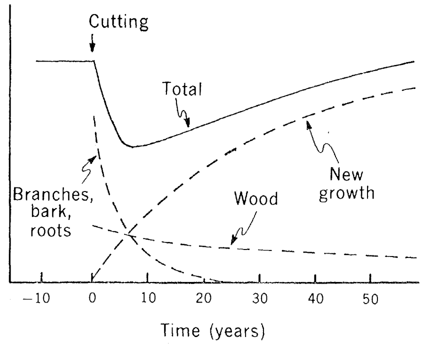

Fig. 9. Hypothetical response of the biomass in a forest cut for lumber and then allowed to regrow.

Figure 9 shows diagrammatically the nature of these transitions. In order to quantify this diagram, details specific to any given site would be needed. Was the wood present burned, used for paper, or used for structures? How long does it take for the roots to decay? Does a significant net oxidation of soil humus accompany the temporary removal of forest cover? How rapidly is the forest biomass reestablished? How rapidly is the lost soil humus replaced? How do the new steady-state forest biomass and soil humus content differ from those that prevailed at the time of cutting?

If we are to assess the net effect of land use during the period from 1958 to the present, we must consider not only the cutting and burning of forests but also the recovery of forested lands cut or burned at earlier times. The implication of the most extreme estimates of biomass reduction is that during the period from 1958 to the present forest carbon losses due to cutting and burning greatly exceeded forest gains resulting from regrowth. In our opinion, the significance of regrowth has not been adequately treated. The main value of the discussions of biomass destruction up to now has been to point out that, because forests are being destroyed at a rate that is not negligible in comparison to that at which fossil fuels are being burned, changes in the forest biomass must be considered in carbon budgeting. We believe that at this time it is possible to place only very uncertain limits on the net change. Assessing the forest biomass on the basis of a consideration of only the rate of cutting and burning is similar to evaluating a person's financial position on the basis of an examination of his expenditures. Our own analysis suggests that annual decreases in the global forest biomass of the order of 1 percent or more are unreasonable and cannot be supported by the available data (*49*).

There are two ways in which the actual changes might be estimated. The first would be to combine response functions like those in Fig. 9 with historical land use data. The cutting history for most of the world's forested land could be reasonably well reconstructed. If adequate response functions could be generated, then one could determine the net effect of tampering with forested land by summing the current response of all the affected parcels of land. Only through this procedure would it be possible to determine that the change in the mass of wood occurred during the period from 1958 to the present. To our knowledge, such an integration has never even been attempted.

The history of the soil humus biomass will prove more difficult to obtain. Presently, the independent estimates for the gross photosynthesis rate (*50*) and for the total soil respiration rate of the terrestrial ecosystem can only be balanced within 25 percent (*48*). Ten percent of the land is now subject to agriculture. This amount has not changed greatly during this century. Nevertheless, agricultural practice has evolved very rapidly. Changes in the method of plowing, in the crops grown, and in the amount of fertilizer used have certainly altered the humus contents of the agricultural soil. Since these soils contain 0.5 ± 0.2 (*51*) atmospheric carbon masses, a change of 1 percent per decade in this storage would be significant to budgeting. A minimum requirement for progress in this area would be the gathering together of the available soil carbon analyses; the next step would be the analyses of soil samples collected and stored during the last century matched with analyses on present-day samples collected in the same manner from the same sites.

This direct biomass inventory will necessitate an enormous amount of effort. The prognosis for its success will become apparent only after the first such inventory has been attempted. Our guess is that the uncertainty in the results will be sufficiently large to void the use of the inventory for the purpose proposed here. Nevertheless, such an analysis must be attempted before a firm judgment can be made.

In the other approach we take advantage of an integration performed for us by nature. The idea, as outlined by Stuiver (*31*), is to use the record of the atmospheric ratio of the stable carbon isotopes, $^{13}C/^{12}C$, in tree rings as an index of the net transfers of carbon between the biosphere and atmosphere. The logic is as follows. During photosynthesis ^{12}C is fixed more rapidly than ^{13}C. For the C-3 plants which dominate our forests, the fractionation is such that the carbon of the plant matter has a $^{13}C/^{12}C$ ratio lower by 17 ± 2 per mil than the carbon in atmospheric CO_2. Any net storage of carbon in wood or soil will leave behind ^{13}C in the atmosphere, raising its $^{13}C/^{12}C$ ratio. Such atmospheric $^{13}C/^{12}C$ changes are recorded in the tree rings.

The use of this method during the period of interest (1958 to the present) is complicated by the fact that fossil fuel use produces an exactly analogous effect. Coal, oil, and natural gas show the same average ^{13}C depletion as contemporary wood and soil humus. Fortunately, we can use the Suess effect (described above) to estimate the fossil fuel influence. Unlike modern vegetation and soils which have $^{14}C/^{12}C$ ratios within a few percent of the atmospheric value, fossil fuel CO_2 is free of ^{14}C. Thus, as shown by Stuiver (*31*), this problem can be circumvented. This principle is explained graphically in Fig. 10.

Several other difficulties will have to be faced in estimating biomass changes from isotope data on tree rings. One is that the change in the $^{13}C/^{12}C$ ratio in atmospheric CO_2 is unlikely to be the only source of variation in the $^{13}C/^{12}C$ ratio in any given tree. There are already indications that the fractionation during photosynthesis is temperature-dependent (*52*). Such efforts could be countered by measuring the $^{13}C/^{12}C$ ratios of trees from a variety of areas showing different temperature histories (as recorded by thermometers at nearby meteorological stations). The Northern Hemisphere is subject to substantial seasonal variations in the CO_2 concentration [4 to 6 parts per million (ppm) at Hawaii and 14 ppm at Point Barrow, Alaska (*53*)]. As these changes reflect photosynthesis and respiration by land plants, there is a corresponding isotope effect (± 0.4 per mil at Hawaii and ± 1.0 per mil at Point Barrow). Hence the $^{13}C/^{12}C$ ratio in organic matter produced during different parts of the growing season will differ. Changes in the ratio of spring to summer growth would cause further complication on the record. The noise thus introduced could either be averaged out or avoided by the use of Southern Hemisphere trees, since the seasonal variation in CO_2 concentrations south of the equator is only 1.5 ppm (*53*). Heartwood may differ in its $^{13}C/^{12}C$ from sapwood. This may be true for cellulose (the best choice for ^{13}C monitoring) as well as for whole wood. As in the earlier case, there are ways around this problem if enough trees are investigated and the results carefully analyzed and interpreted. Finally, other growth characteristics which influence the $^{13}C/^{12}C$ ratio in cellulose may vary with environmental conditions or even with the age of the tree. The answer lies in the thoughtful analyses of many trees.

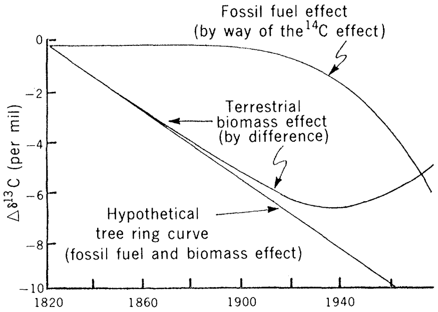

Fig. 10. Hypothetical $^{13}C/^{12}C$ tree ring record (bottom curve) over the past 160 years, similar to that obtained by Stuiver (*31*). The upper curve is the expected curve if only fossil fuel CO_2 were causing the change. The middle curve shows what would have been obtained had there been no fossil fuel consumption, and may be interpreted to mean that the terrestrial biomass decreased from 1820 to about 1930, stayed nearly constant between 1930 and 1940, and increased since 1940.

Conversion of the trends in the $^{13}C/^{12}C$ ratio to a temporal history of terrestrial biomass poses yet another problem. The reason is that, the longer the elapsed time since the transfer of any given batch of carbon from the biosphere to the atmosphere, the smaller is its isotope effect. The reduction is the result of mixing with oceanic and biospheric carbon. We have already seen an example of this effect. The decrease in the $^{14}C/^{12}C$ ratio in tree rings between 1850 and 1950 was only one-fifth of that expected if the fossil fuel carbon atoms had not been traded back and forth by the atmosphere, biosphere, and sea. The extent of this reduction will depend on the time available for mixing. One year after a given biospheric change, nearly the full effect will be seen. Thirty years later, a fivefold reduction will have occurred. One thousand years later, a 60-fold reduction will have occurred. This temporal blurring constitutes a serious deficiency in the ^{13}C approach. For any given observed ^{13}C trend, a number of terrestrial biosphere-atmosphere transfer scenarios could be called upon. In other words, there is no unique deconvolution of the ^{13}C message carried by tree rings. The best way around this problem will probably be to use land use reconstructions to guide the deconvolution.

Stuiver (*31*) has summarized the sparse ^{13}C data available to date. His conclusion is that there is no evidence for any net change in the $^{13}C/^{12}C$ ratio (corrected for the Suess effect) in atmospheric CO_2 between 1945 and the present. However, prior to 1945 the corrected $^{13}C/^{12}C$ ratio showed a continued gradual decrease, interpreted by Stuiver as an indication of a decrease in biomass.

Until many more trees have been studied, Stuiver's conclusion must be taken as tentative. However, the preliminary results are compatible with the usual conclusion of carbon budgeting efforts—namely, that neither a large increase nor a large decrease in the size of the terrestrial biosphere has occurred since 1958.

Conclusions

Our analysis of the carbon budget suggests several conclusions.

1) The ocean-atmosphere model developed by Oeschger and his co-workers (*8*) is consistent with the available data. Hence, their estimate of the uptake of excess CO_2 is as reliable an estimate as can currently be made.

2) There is no compelling reason to believe that the earth's biomass has decreased at a rate comparable to the rate of fossil fuel combustion over the last two decades. Forest cutting and burning estimates provide only an upper limit on the rate of biomass decrease. The regrowth of forests cut in the past may well have compensated for much of the recent cutting. Preliminary ^{13}C results on tree rings suggest that the total biomass has remained about the same over the last two decades (*31*).

Despite the fact that we reject the hypothesis that changes in terrestrial biomass over the last two decades have contributed amounts of CO_2 significant with respect to those generated by the combustion of fossil fuels, the reexamination of the global carbon budget triggered by this claim (*1-4*) makes clear the potential of the biosphere. If we are to reconstruct the atmospheric CO_2 concentrations that prevailed before 1958 or predict future atmospheric CO_2 concentrations, we must consider man's impacts on the biosphere. If, as we conclude, the change in forest biomass over the last two decades has been small, the reason must be a chance compensation of opposed effects rather than an indication that this reservoir is neither big enough nor variable enough to play a key role in atmospheric carbon budgets. Both its size and its complexity testify to its significance.

References and Notes

1. B. Bolin, *Science* **196**, 613 (1977).
2. G. M. Woodwell and R. A. Houghton, in *Global Chemical Cycles and Their Alterations by Man*, W. Stumm, Ed. (Dahlem Konferenzen, Berlin, 1977), p. 61.
3. G. M. Woodwell, R. H. Whittaker, W. A. Reiners, G. E. Likens, C. C. Delwiche, D. B. Botkin, *Science* **199**, 141 (1978).
4. G. M. Woodwell, *Sci. Am.* **238**, 34 (January 1978).
5. W. S. Broecker, Y.-H. Li, T.-H. Peng, in *Impingement of Man on the Oceans*, D. W. Hood, Ed. (Wiley, New York, 1971), p. 287.
6. L. Machta, *Nobel Symp. 20* (1971), p. 121.
7. C. D. Keeling, in *Chemistry of the Lower Atmosphere*, S. I. Rasool, Ed. (Plenum, New York, 1973), p. 251.
8. H. Oeschger, U. Siegenthaler, U. Schotterer, A. Guzelman, *Tellus* **27**, 168 (1975); U. Siegenthaler and H. Oeschger, *Science* **199**, 388 (1978).
9. C. D. Keeling, J. A. Adams, Jr., C. A. Ekdahl, Jr., P. R. Guenther, *Tellus* **28**, 6 (1976).
10. C. D. Keeling, R. B. Bacastow, A. E. Bainbridge, C. A. Ekdahl, Jr., P. R. Guenther, L. S. Waterman, *ibid.*, p. 6.
11. C. D. Keeling, *ibid.* **25**, 174 (1973).
12. C. F. Baes, Jr., H. E. Goeller, J. S. Olson, R. M. Rotty, *Am. Sci.* **65**, 310 (1977).
13. The atmospheric CO_2 concentration is now close to 335 ppm, which is about 45 ppm higher than the preindustrial value reconstructed from the model (*6-8*). Were surface seawater to have maintained equilibrium with this 15 percent increase in the atmosphere pCO_2, its total dissolved inorganic carbon content ($CO_2 + HCO_3^- + CO_3^{2-}$) would have risen 1.5 percent. Modeling suggests that the atmosphere has achieved about 85 percent of equilibrium with the air (*8*). Hence, the actual increase is probably about 1.3 percent.
14. A discussion of how these results were obtained and of their accuracy is given in T. Takahashi, P. Kaiteris, W. S. Broecker, A. E. Bainbridge, *Earth Planet. Sci. Lett.* **32**, 458 (1976). The actual data will appear in the *GEOSECS Atlas Series* (National Science Foundation, Washington, D.C., in press).
15. This is based on a preindustrial atmospheric pCO_2 of 290×10^{-6} atm, a ratio of ocean to global area of 0.71, a mean ocean depth of 3800 m, and a mean dissolved inorganic carbon content for seawater of 2.3 mole m^{-3}.
16. W. S. Broecker and Y.-H. Li, *J. Geophys. Res.* **75**, 3545 (1970). In this paper the isotope fractionation-corrected, atmosphere-surface ocean ΔC^{14} is estimated to be 40 per mil. However, on the basis of the calculation of Oeschger *et al.* (*8*), a correction of 13 per mil made for the surface ocean Suess effect appears to be too large (one-third of the atmospheric Suess effect). A value of 8 per mil is a better choice. Thus we have changed the average difference from 40 to 45 per mil.
17. W. S. Broecker and T.-H. Peng, *Tellus* **26**, 21 (1974).
18. T.-H. Peng, Y.-H. Li, W. S. Broecker, G. Mathieu, A. Bainbridge, *J. Geophys. Res.* **84**, 247 (1979). The diffusive flux, F, of a gas is related to the stagnant film thickness, Z, by $F = D\,\Delta C/Z$, where D is the molecular diffusion coefficient and ΔC is the difference in concentrations across the stagnant film of thickness Z.
19. P. V. Danckwert, *Gas-Liquid Reactions* (McGraw-Hill, New York, 1970), p. 276.
20. B. Bolin, *Tellus* **12**, 274 (1960).
21. R. Berger and W. F. Libby, *Science* **164**, 1395 (1969).
22. W. S. Broecker and T. Takahashi, in preparation.
23. M. Stuiver, *Earth Planet. Sci. Lett.* **32**, 322 (1967).
24. G. S. Bien, N. W. Rakestraw, H. E. Suess, *Bull. Inst. Oceanogr. (Monaco)* **61**, 1278 (1963).
25. This age is obtained by summing the product of the amount of CO_2 produced by fossil fuel burning in a given year and the time elapsed between that year and today, and then dividing the sum by the total amount of CO_2 released over the entire interval.
26. E. Dreisigacker and W. Roether, *Earth Planet. Sci. Lett.*, in press.
27. H. G. Ostlund, H. G. Dorsey, R. Bresher, "Tritium Laboratory data report 5: GEOSECS Atlantic radiocarbon and tritium results" (University of Miami, Miami, 1976).

→ G. J. Fergusson, *Proc. R. Soc. London Ser. A.* **243**, 561 (1958).

29. H. E. Suess, *Science* **122**, 415 (1955).
30. R. Whittaker and G. Likens, in *Primary Productivity of the Biosphere*, H. Lieth and R. H. Whittaker, Eds. (Springer-Verlag, Berlin, 1975), p. 305.
31. M. Stuiver, *Science* **199**, 253 (1978).
32. H. E. Suess, *Nobel Symp. 12* (1970), p. 303.
33. I. U. Olsson and I. Karlen, *Am. J. Sci. Radiocarbon Suppl.* **7**, 331 (1965); T. A. Rafter and B. J. O'Brien, *Proc. 8th Int. Conf. Radiocarbon Dating* **1**, 241 (1972).
34. When the sea-air CO_2 gas exchange is considered, the pCO_2 exerted by seawater should be compared with the pCO_2 in the atmosphere rather than with the concentration of CO_2 in dry air. The concentration of CO_2 in the atmosphere is generally expressed in parts per million by volume (ppmv) in dry air. The partial pressure of CO_2, pCO_2, is related to the volumetric concentration C_{CO_2} by the relation; $pCO_2 = C_{CO_2}(P_b - pH_2O \cdot h)$, where P_b is the total barometric pressure, pH_2O is the partial pressure of water vapor in air, and h is the relative humidity. At normal sea level, P_b is approximately 1 atm, pH_2O ranges from 0.006 atm at 0°C to 0.04 atm at 30°C, and h is about 75 percent. Thus, the numerical value of pCO_2 in air is generally a few percent smaller than the numerical value of the concentration. For example, the mean atmospheric CO_2 concentration over the Atlantic Ocean in 1973 was 327 ppmv in dry air, whereas the mean pCO_2 in the Atlantic air was 320 μatm.
35. T. Takahashi, W. S. Broecker, L. A. Prince, A. E. Bainbridge, in preparation.
36. T. Takahashi, P. Kaiteris, W. S. Broecker, *Earth Planet. Sci. Lett.* **32**, 451 (1976).
37. J. H. Ryther, in *The Sea*, M. N. Hill, Ed. (Interscience, New York, 1963), vol. 2, p. 347.
38. H. Craig, R. F. Weiss, W. B. Clarke, *J. Geophys. Res.* **72**, 6165 (1967).
39. R. H. Bieri, *Earth Planet. Sci. Lett.* **10**, 329 (1971).
40. H. Craig and R. F. Weiss, *ibid.*, p. 289.
41. T. Takahashi, *Cushman Found. Foraminiferal Res. Spec. Publ.* **11**, 11 (1975).
42. W. S. Broecker and T. Takahashi, *Deep-Sea Res.* **25**, 65 (1978).
43. _____, in *The Fate of Fossil Fuel CO_2 in the Oceans*, N. Andersen and A. Malahoff, Eds. (Plenum, New York, 1977), pp. 213-241.
44. R. M. Garrels, oral presentation at the Energy Research and Development Administration (ERDA) Environmental Effect of Carbon Dioxide from Fossil Fuel Combustion Workshop, Miami Beach, Fla., March 1977.
45. R. M. Garrels, T. T. Mackenzie, C. Hunt, *Chemical Cycles and the Global Environment* (Kaufman, Los Altos, Calif., 1975).
46. F. T. Mackenzie, paper presented at the 169th annual meeting of the American Chemical Society, Baltimore, 1975.
47. W. Stumm, *Water Res.* **7**, 131 (1973).
48. W. H. Schlesinger, *Annu. Rev. Ecol. Syst.* **8**, 51 (1977).
49. Northern temperate and boreal forests contain approximately 40 percent of the global forest biomass. From data we have examined, it is not unreasonable to estimate that the annual growth of the biomass of these forests has been a few tenths of 1 percent over the past two decades. There is certainly no documented indication of significant decrease. If global forest biomass had decreased over this period by 1 percent per year or more as claimed by Woodwell (*4*) and no significant net decrease of temperate and boreal forests occurred, then tropical forest biomass (the bulk of the remaining 60 percent) must have declined at a rate of nearly 2 percent per year. Over 20 years (1958 to the present), this would demand that somewhere between one-third and one-half of all of the tropical forest biomass had disappeared. Most of the tropical forest biomass today is in the drainage basins of the Amazon and the Zaire, and the same was true in the late 1950's. These forests do not appear to have suffered destruction on anything near the scale that would be required by a 1 percent per year decline of global biomass.
50. W. A. Reiners, *Brookhaven Symp. Biol.* **24**, 368 (1973).
51. Agricultural land constitutes about 10 percent of all land; we assume that it contains 10 percent of all soil carbon.
52. A. T. Wilson and M. J. Grinsted, *Nature (London)* **265**, 133 (1977).
53. L. Machta, K. Hanson, C. D. Keeling, in *The Fate of Fossil Fuel CO_2 in the Oceans*, N. Andersen and A. Malahoff, Eds. (Plenum, New York, 1977), pp. 131-144.

→ C. Mehrbach *et al.*, *Limnol. Oceanogr.* **18**, 897 (1973).

55. J. Lyman, thesis, University of California, Los Angeles (1957).

→ R. F. Weiss, *Mar. Chem.* **2**, 203 (1974).

57. S. E. Ingle, C. H. Culberson, J. E. Hawley, R. M. Pytkowicz, *Mar. Chem.* **1**, 295 (1973).

58. Discussions at the Dahlem Konferenzen in Berlin, Germany (November 1976) and at the ERDA Fossil Fuel CO_2 Conference in Miami Beach, Fla. (March 1977), stimulated us to write this article. Since then, discussion with S. Schneider, R. M. Garrels, F. T. Mackenzie, D. H. Holland, and M. B. McElroy have been particularly helpful. This work has been supported by a grant from the International Decade of Ocean Exploration Program of the National Science Foundation (OCE 76-04245A). Lamont-Doherty Geological Observatory Contribution No. 2893.