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A Deconvolution of the Tree Ring Based $\delta^{13}C$ Record

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We assumed that the tree-ring-based $^{13}C/^{12}C$ record constructed by Freyer and Belacy (1983) to be representative of the fossil fuel and forest-soil induced $^{13}C/^{12}C$ change for atmospheric CO_2. Through the use of a modification of the Oeschger et al. ocean model, we have computed the contribution of the combustion of coal, oil, and natural gas to this observed $^{13}C/^{12}C$ change. A large residual remains when the tree-ring-based record is corrected for the contribution of fossil fuel CO_2. A deconvolution was performed on this residual to determine the time history and magnitude of the forest-soil reservoir changes over the past 150 years. Several important conclusions were reached. (1) The magnitude of the integrated CO_2 input from these sources was about 1.6 times that from fossil fuels. (2) The forest-soil contribution reached a broad maximum centered at about 1900. (3) Over the 2 decade period covered by the Mauna Loa atmospheric CO_2 content record, the input from forests and soils was about 30% that from fossil fuels. (4) The $^{13}C/^{12}C$ trend over the last 20 years was dominated by the input of fossil fuel CO_2. (5) The forest-soil release did not contribute significantly to the secular increase in atmospheric CO_2 observed over the last 20 years. (6) The pre-1850 atmospheric p_{CO_2} values must have been in the range 245 to 270 × 10^{-6} atmospheres.

INTRODUCTION

With the publication of a paper by *Bolin* [1977] a controversy began regarding the contribution of the terrestrial biosphere and soils to the rise in atmospheric CO_2 content observed over the last 20 years. Bolin pointed out that the CO_2 released as a result of deforestation and of the agricultural manipulation of soils could not be taken as negligible when compared with CO_2 released through the combustion of fossil fuels. Other investigators followed up this idea (see summary in Table 1). While most agree with Bolin's basic conclusion, a few have gone much further and proposed that the forest-soil contribution over the last 20 years has equaled or even exceeded that from fossil fuels. Geochemists, interested in fossil fuel CO_2 uptake by the sea, have, on the other hand, generally been critical of the contemporary forest-soil contribution estimates because their models fall somewhat short of explaining the difference between the amount of CO_2 produced by fossil fuel burning since 1958 and the amount of excess CO_2 accumulated in the atmosphere since 1958. Hence, they see no place to store the CO_2 coming from forests and soils [*Broecker et al.*, 1979]. They are sufficiently confident in their models to preclude entirely those scenarios that involve large forest-soil releases. Only if pushed to the limits of their credibility could these models accommodate even the modest amounts of forest-soil CO_2 suggested by Bolin.

When this debate arose, the most promising approach to its resolution appeared to be through the $^{13}C/^{12}C$ record for atmospheric CO_2 contained in tree rings. *Stuiver* [1978] was the first to derive from such a record the magnitude of historical forest-soil atmospheric release. As summarized in Table 1, his estimates of the rate and total magnitude of the release were comparable with those of Bolin. Subsequent ^{13}C work, although based on a larger data base and interpreted by using more rigorous models, has not significantly altered Stuiver's original estimate.

In addition to those authors claiming success in obtaining a meaningful ^{13}C record (see Table 1), there are quite a number who have obtained records divergent to the expected trend. We have attempted to summarize all this work in Table 2 and in Figure 1. A quick look at these summaries certainly does not raise one's confidence in the $^{13}C/^{12}C$ approach. Clearly, the changing atmospheric $^{13}C/^{12}C$ ratio cannot be the only source of variability in the carbon isotope ratios for the wood formed in a single tree. Other factors contributing to variability in the $^{13}C/^{12}C$ ratio include (1) local fluctuations in the ^{13}C content of the CO_2 used by the tree, (2) ring-to-ring variations in the chemical makeup of the wood, and (3) environmentally influenced changes in the net rate of CO_2 uptake by the plant. Any attempt to isolate the effect of global changes in atmospheric CO_2 content on the $\delta^{13}C$ record in tree rings must correct for, or at least minimize, these three factors.

CO_2 derived from respiration or automobile exhaust is depleted in ^{13}C when compared with average atmospheric CO_2. Plants using this depleted CO_2 would not be reliable recorders of $\delta^{13}CO_2$ variations on a global scale. The selection of isolated trees far from urban areas for $\delta^{13}C$ analysis should minimize this effect. Changes in the $\delta^{13}C$ of whole wood due to variations in the ratio of cellulose to lignin and extractives can be eliminated by analyzing only cellulose. The effects of environmental variability of the $^{13}C/^{12}C$ ratio in tree rings are the most difficult to correct for, since they change the isotopic fractionation associated with photosynthesis.

The recent model of carbon isotope fractionation by C3 plants [*Farquhar et al.*, 1982] envisions that diffusion of atmospheric CO_2 into intercellular leaf spaces causes a kinetic fractionation. This kinetic fractionation is followed by further isotopic separation during carboxylation of RuDP. $^{13}CO_2$ diffuses more slowly in air than $^{12}CO_2$ ($\alpha_{diffusion}$ = 0.9955). The magnitude of the fractionation by RuDP (α_{RuDP}) is not well determined; G. D. Farquhar (personal communication) places it at 0.97.

The rate of diffusion of CO_2 through the leaf stomata is controlled by the CO_2 partial pressure gradient between the leaf interior and the atmosphere. The sizes of the stomatal openings adjust according to variations in relative humidity, irradiance, and temperature, thereby controlling the size of the CO_2 reservoir within the leaf. The activity of RuDP

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TABLE 1. Summary of CO_2 Emissions from Terrestrial
Ecosystems

Investigator	Annual Input* 1960–1975 ($\times 10^{14}$ mol year^{-1})	Cumulative Input* ($\times 10^{15}$ mol)
Bolin [1977]	0.8 ± 0.5†	5.8 ± 2.5 (1800–1975)†
Adams et al. [1977]	4.2†	—
Stuiver [1978]	1.0‡	10 (1850–1950)‡
Woodwell et al. [1978]	8.3 ± 6.7†	—
Wong [1978]	0.8†	—
Wagener [1978]	—	14.2 (1800–1935)‡
Freyer [1978]	—	5.8 (1860–1974)‡
Siegenthaler et al. [1978]	—	13.7 ± 2.6 (1860–1974)‡
Hampicke [1979]	2.5 ± 1.3†	—
Seiler and Crutzen [1980]	0 ± 1.7†	—
Moore et al. [1981]	2.9 ± 1.1†	—
This paper	1‡	20 (1850–1975)‡

*As of present, the contribution from fossil fuel burning is about 5
$\times 10^{14}$ mol year^{-1}, and the total fossil fuel CO_2 release since
industrialization is about 13 $\times 10^{15}$ mol.
†Based on biomass change data.
‡Based on C13 data for tree rings.

carboxylation determines how much of that internal reservoir will be converted to glucose. The final isotopic composition of the plant tissue will be determined by diffusion or carboxylation, which limits the amount of CO_2 assimilated by the plant. If diffusion alone limits the assimilation rate, all of the CO_2 that diffuses into the leaf is eventually fixed as glucose, and the diffusion fractionation will dominate:

$$\left(\frac{^{13}C}{^{12}C}\right)_{plant} = \left(\frac{^{13}C}{^{12}C}\right)_{atm} \alpha_{diff}$$

However, if diffusion is rapid when compared with carboxylation, no CO_2 concentration gradient will exist across the stomata, and the $\delta^{13}C$ of the plant will depend only on the enzyme fractionation

$$\left(\frac{^{13}C}{^{12}C}\right)_{plant} = \left(\frac{^{13}C}{^{12}C}\right)_{atm} \alpha_{enzy}$$

Trees, as C3 plants, have $\delta^{13}C$ values that fall in between the two extremes. Thus, environmental factors that change the ratio of diffusion resistance to carboxylation resistance change the $^{13}C/^{12}C$ ratio of the plant (see Figure 2). Farquhar et al. [1982] and Francey and Farquhar [1982] attribute much of the $\delta^{13}C$ variability observed in C3 plants to the effects on stomatal geometry of changing irradiance, relative humidity, and temperature.

Careful selection of trees that are isolated, not water stressed, and experience relatively consistent growing season temperatures may be sufficient to minimize environmental effects on the $\delta^{13}C$ of tree ring cellulose. Such trees would theoretically yield the best record of global $\delta^{13}C$ changes in atmospheric CO_2. However, Francey [1981], selecting trees largely according to the above criteria, did not obtain the trend in $\delta^{13}CO_2$ which would be expected from fossil fuel addition.

With this in mind, we ranked (Figure 1) each of the existing records for material (M), site (S), and climate (C). A cross indicates that the record is deficient with regard to this criterion. On the basis of these criteria, only nine (reference numbers 5, 6, 7, 15, 20, 21, 22, 23, and 24) fully qualify. In

constructing his composite curve, Freyer used seven of these records (5, 6, 7, 20, 21, 23, and 24) and 11 of those not fulfilling the full set of criteria (4, 8, 16, 17, 18, 19, 26, 29, 30, 31, and 33). In Figure 3 we compare Freyer's composite with that based only on the nine records fulfilling all the criteria set forth above. For those records in Figure 1 that include the juvenile stages of tree growth, a systematic increase in ^{13}C with time is often observed. This 'juvenile effect' has been attributed to either reassimilation of respired CO_2 that has accumulated beneath the forest canopy [Freyer, 1979a] or to reduced CO_2 assimilation rates due to lower irradiance near the forest floor [Francey and Farquhar, 1982]. To eliminate the inclusion of juvenile effects in the composite, the first 20–30 years of growth for each tree were excluded during averaging. The specific deletions are noted in the caption to Figure 3.

As can be seen, the 2-decade-averaged curves, although disagreeing in detail, show the same linear decline from 1850 to 1970. Also shown in this figure is a comparison between the Freyer composite and trees selected only for material and site (i.e., the climate criterion is dropped). In this case, most of the same records are used, and, hence, curves are nearly the same. The remaining two comparisons are for composites of the cellulose records and all 32 of the records. As can be seen, the inclusion of these additional records decreases the amplitude of the 1850–1970 decrease. We present these comparisons so that the reader has some feeling for the impact of the selection process on the shape and amplitude of the past 1850 $^{13}C/^{12}C$ decline.

DECONVOLUTION PROCEDURE

The technique we use was first suggested by Siegenthaler et al. [1978]. Indeed, their preliminary calculations led these authors to foresee the main conclusions drawn here. They state, 'We find that not only the amount of biospheric CO_2 is important, but, because of the time-dependent flow into the oceans, also the time of release into the atmosphere, i.e., the history of the biospheric CO_2 production is essential. If a large input pulse occurred only a few decades ago, it is still influencing the present CO_2 level by providing a decreasing atmospheric baseline, since CO_2 is still being taken up by the ocean.'

The logic behind the ^{13}C approach is as follows. Both fossil fuel CO_2 and forest-soil CO_2 have $\delta^{13}C$ values averaging about -26 ‰. The pre-1850 atmosphere had a value of about -6 ‰. Thus addition of CO_2 from either source will decrease the atmospheric $\delta^{13}C$ value. The situation is complicated by the fact that the carbon atoms from fossil fuels and forest-soil will mix with carbon atoms in the ocean and in the forest-soil reservoir. Only if the dilution caused by this mixing can properly be accounted for is the $^{13}C/^{12}C$ record for the atmosphere useful. A proponent of the large forest-soil contribution might argue that because the dilution correction is based on the same models used for the ocean uptake calculations, we are only perpetuating some basic inadequacy in these models. We will show that this is not the case.

Once the dilution model has been selected (we will discuss this selection in the next section), the next step is to calculate the $^{13}C/^{12}C$ time history for atmospheric CO_2, assuming that the only perturbation has come through the addition of fossil fuel CO_2 to the system. As the time history of these inputs is accurately known (i.e., to ±7%) from

TABLE 2. Summary of ^{13}C Records for Tree-Ring Series

Record Number	Reference	Location	Latitude-Longitude	Species (Number of Trees Analyzed)		Coniferous (C) or Deciduous (D)
1	*Francey* [1981]	Tasmania	42°S, 145°E*	*Athrotaxis selaginoides*	(1)	C
2	*Francey* [1981]	Tasmania	42°S, 145°E*	*Athrotaxis selaginoides*	(1)	C
3	*Francey* [1981]	Tasmania	42°S, 145°E*	*Athrotaxis selaginoides*	(1)	C
4	*Freyer* [1979a]	Black Forest, West Germany	49°N, 9°E*	*Pinus silvestris*	(1)	C
5	*Freyer* [1980]	Cave Junction, Oregon	43°10'N, 123°3'W	*Pseudotsuga menziesii*	(1)	C
6	*Freyer* [1981]	Muddus National Park, Sweden	67°0'N, 20°12'E	*Pinus silvestris*	(5)	C
7	*Harkness and Miller* [1980]	Jotunheimer, Norway	60°30'N, 9°0'E	*Pinus silvestris*	(1)	C
8	*Wilson* [1978]	White Mountains, California	37°30'N, 118°0'W*	*Pinus longaeva*	(1)	C
9	*Lerman and Long* [1980]	Flagstaff, Arizona	35°N, 111°40'W	*Pinus ponderosa*	(1)	C
10	*Freyer* [1981]	Spessart Forest, West Germany	50°0'N, 9°18'E	*Quercus robur*	(5)	D
11	*Francey* [1981]	Tasmania	42°S, 145°E*	*Athrotaxis selaginoides*	(1)	C
12	*Francey* [1981]	Tasmania	42°5, 145°E*	*Athrotaxis selaginoides*	(1)	C
13	*Francey* [1981]	Tasmania	42°S, 145°E*	*Athrotaxis selaginoides*	(1)	C
14	*Francey* [1981]	Tasmania	42°S, 145°E*	*Phyllocladus asplenifolus*	(1)	C
15	*Rebello and Wagener* [1976]	Southern Highlands, Brazil	22°S, 45°W*	*Aurorocaria angustifolia*	(1)	C
16	*Tans and Mook* [1980]	Drenthe, Netherlands	52°45'N, 6°45'W	*Quercus rubra*	(1)	D
17	*Tans and Mook* [1980]	Drenthe, Netherlands	52°45'N, 6°45'W	*Quercus robur*	(1)	D
18	*Tans and Mook* [1980]	Drenthe, Netherlands	53°4'N, 6°27°W	*Quercus rubra*	(1)	D
19	*Tans and Mook* [1980]	Drenthe, Netherlands	53°4'N, 6°27°W	*Fagus sylvatica*	(1)	D
20	*Freyer* [1979a]	Spanish Pyrenees, French Atlantic Coast, Azores	40–50°N, 0–10°W*	*Quercus lusitanica*	(2)	D
				Quercus robur	(3)	D
				Quercus maritima	(2)	C
				Platanus acerifola	(1)	
21	*Freyer* [1979a]	North Carolina	34–37°N, 76–83°W*	*Quercus rubra*	(2)	D
				Quercus albra	(2)	D
				Populus alba	(1)	D
				Pinus virginia	(1)	C
				Pinus serotina	(1)	C
22	*Freyer* [1979b]	Eifel, West Germany	50°40'N, 6°40'E	*Quercus robur*	(3)	D
				Quercus petracea	(1)	D
				Fraxinus excelsior	(1)	D
23	*Freyer and da Silva* [1979]	Mauna Kea Mountain, Hawaii	19°50'N, 155°30'W	*Myoporum sanswicerise*	(2)	D
24	*Bender and Berge* [1981]	Madison, Wis.	43°15'N, 89°30'W	*Quercus macrocarpa*	(3)	D
25	*Stuiver* [1978]	Olympic Peninsula, Washington	47°46'N, 124°06'W	*Pseudotsuga menziesii*	(1)	C
26	*Grinsted et al.* [1979]	White Mountains, California	37°30'N, 118°W*	*Pinus longaeva*	(2)	C
27	*Pearman et al.* [1976]	North Tasmania	41°40'S, 146°5'E*	*Anthrotaxis selaginoides*	(1)	C
28	*Pearman et al.* [1976]	North Tasmania	41°40'S, 146°5'E*	*Anthrotaxis selaginoides*	(1)	C
29	*Galimov* [1976]	Permal District, U.S.S.R.	58°N, 55°E*	Spruce	(1)	C
30	*Galimov* [1976]	Permal District, U.S.S.R.	58°N, 55°E*	Spruce	(1)	C
31	*Farmer and Baxter* [1974]	Forest of Dean, England	51°48'N, 2°37'W	*Quercus robur*	(1)	D
32	*Farmer and Baxter* [1974]	Glengarry Forest, Scotland	57°01'N, 4°51'W	*Larix decidua*	(1)	D
33	*Farmer* [1979]	Cape Cod, Mass.	41°34'N, 70°38'W	American elm	(1)	D

*Latitudes and longitudes are approximate.

historic records [*Keeling*, 1973; *Rotty*, 1981], this calculation can be done in a straightforward manner. The δ^{13}C change obtained in this way is subtracted from the record obtained from measurements on tree rings. The residual ^{13}C/^{12}C anomaly is then assumed to represent the forest and soil CO₂ contribution.

This temporal history of forest-soil CO₂ input is then obtained by iteration. An estimate of the time history is made. The ^{13}C/^{12}C anomaly generated by this history is calculated and compared with the residual ^{13}C/^{12}C anomaly. The history is then adjusted in such a way as to improve the match between the calculated and the observed residual. Another run is carried out. As the shape of the observed smoothed residual is simple, this procedure proves quite effective. A good match can be achieved after only a few iterations. Once a good match is obtained, its sensitivity to
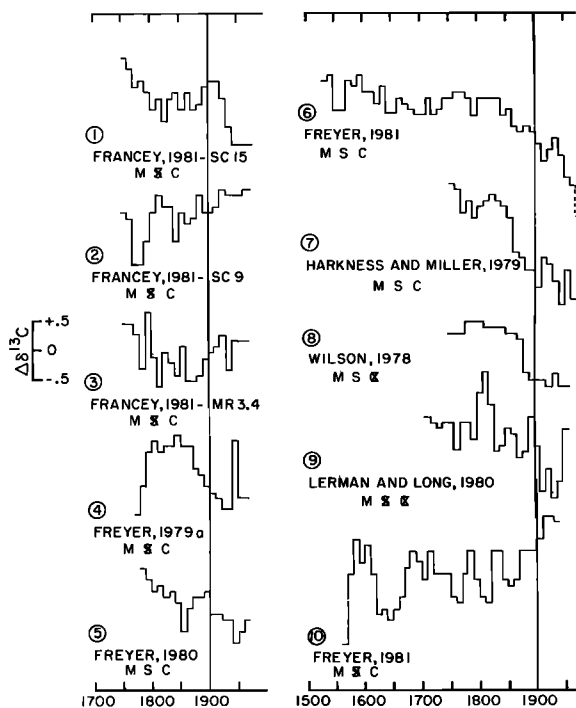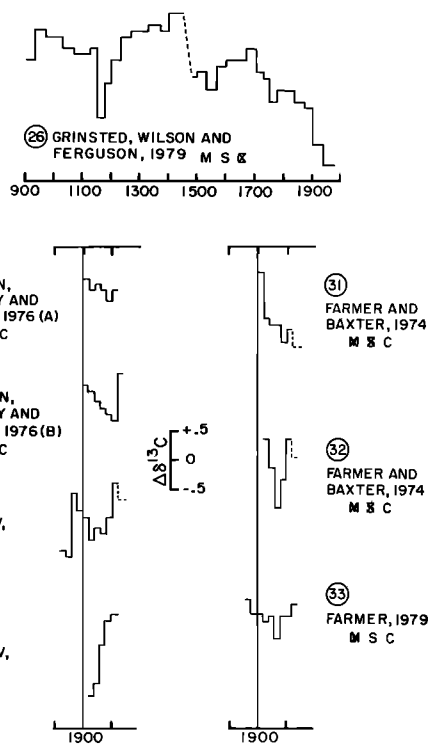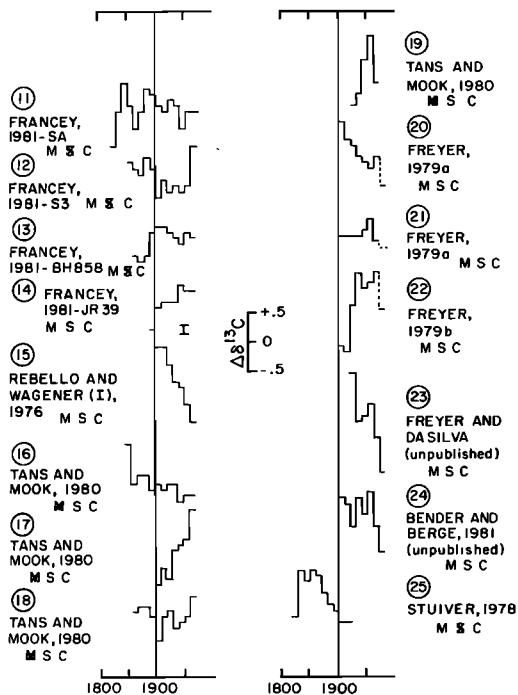
Fig. 1a

Fig. 1c

Fig. 1b

Fig. 1. A summary of the published $^{13}C/^{12}C$ records for individual trees. Decadal averages are given rather than individual analyses. All are given on the same time and $\delta^{13}C$ scales. Because of the species-to-species, climate-to-climate, site-to-site variations in the absolute $^{13}C/^{12}C$ ratio only, the relative values are shown. M, S, and C stand for material, site, and climate. Where the analyses was made on whole wood rather than cellulose, the M is crossed. Where the tree was located within a forest, the S is crossed. Where the site experiences an annual dry period, the C is crossed. In each case the reference is given.

changes in the input time history is assessed by making systematic modifications in the input function.

MODEL

Our calculations are made by using a modification of the *Oeschger et al.* [1975] model. Their model is a one-dimensional representation of the ocean. It includes CO_2 exchange between a well-mixed atmosphere and a well-mixed surface ocean reservoir and diffusive mixing into the waters lying below the mixed layer. The thickness of the mixed layer is taken to be close to that observed in the real ocean (~100 m). The CO_2 exchange rate and coefficient of vertical eddy diffusion are based on the distribution of natural radiocarbon in the system. Isotope exchange with the terrestrial biosphere is accomplished by treating this reservoir as four separate well-mixed boxes and assigning a single exchange time with the atmosphere for each box.

Our model is shown in Figure 4. It differs from that of *Oeschger et al.* [1975] in the following ways.

1. We include the oceanic photosynthesis-respiration cycle. It should be noted, however, that the inclusion of this cycle does not significantly alter the result. We include it to overcome an often invoked (but not justified) criticism of the Oeschger model.

2. We include the production of deep water. A loop is inserted that brings intermediate water to the surface in the polar region, increases its density, and sends it back to the bottom of the model ocean. From here it upwells to intermediate depth, completing the cycle. Because this cycle mixes the deep sea, the coefficient of vertical diffusivity below the level from which the source water is drawn (i.e., ~1000 m) is reduced to about one-half the value chosen by Oeschger et al. Again, this modification eliminates a supposed deficiency in the Oeschger model but does not significantly alter its response to the anthropogenic effects of interest.

3. The rate of vertical eddy diffusivity in the main thermocline (i.e., above the depth of the deep water source) is increased over the value adopted by *Oeschger et al.* [1975] so as to be consistent with the penetration of bomb-produced tritium as determined by the GEOSECS program. The distribution of this tracer provides a better measure than does natural ^{14}C of the extent to which substances penetrate the thermocline on a time scale of several decades. This is the most important of the modifications we have made.

4. We represent the living terrestrial biosphere (L.B. boxes in Figure 4) with three well mixed reservoirs with differing time constants. We do not include CO₂-induced growth factor for these reservoirs because we are trying to account for the change in the forest and soil carbon reservoir size by the $^{13}C/^{12}C$ record deconvolution. The change in the sizes of these reservoirs is sufficiently small that there is no need to include the change in their dilution capacity with time. Were these changes to be included in the iterative procedure, they would not in any way affect the conclusions we draw.

5. We include the isotope dilution capacity of soil carbon.

6. *Keeling et al.* [1980] pointed out that the result of the type of deconvolution carried out here is dependent on the kinetic isotope fractionation factor for CO₂ entering the sea. We adopt the value of 0.998 suggested by *Siegenthaler and Munnich* [1981] rather than that of 0.986 as derived in strongly alkaline solutions [*Baertschi*, 1952; *Craig*, 1953, 1954]. However, we compare both values to show the sensitivity of isotopic fractionation factor.

CALIBRATION OF THE MODEL

The CO₂ invasion rate is calculated for each model time step from the relationship

$$I = p_{CO_2}{}^{atm} I^o$$
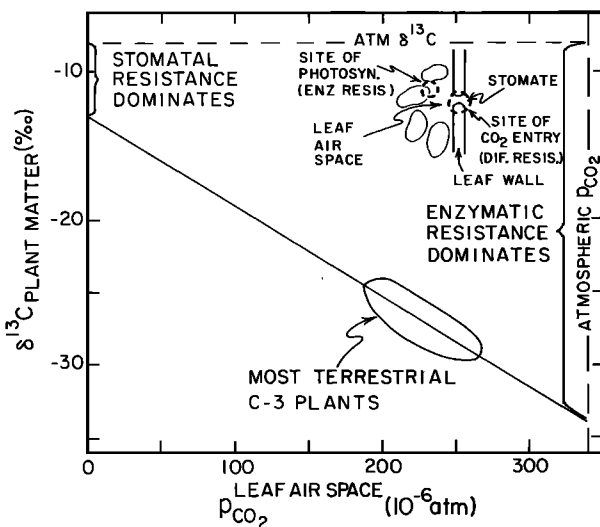
and the evasion rate from the relationship

Fig. 2. Relationship between the $\delta^{13}C$ for the cellulose in C-3 plants as a function of the leaf space CO₂ partial pressure (as documented by *Farquhar et al.* [1982]). If this pressure is near the atmospheric value, then the enzymatic fractionation dominates. If this pressure is very low, the fractionation associated with diffusion through the stomatal openings into the leaf air space must dominate. Although the exact position of the line has yet to be pinned down, the approximate trend has been established.
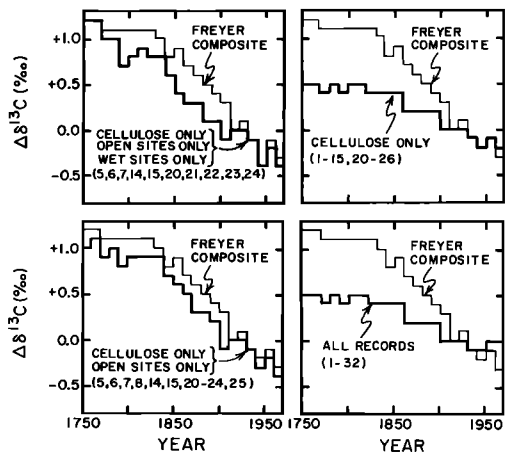
Fig. 3. Comparisons of the decade-averaged composite for the trees selected by *Freyer and Belacy* [1983] with similar composites for all the trees in Figure 1 (bottom right), for those trees where cellulose was analyzed (top right), for those open site trees where cellulose was analyzed (bottom left), and for those trees from non-dry-period open sites where cellulose was analyzed (top left). The numbers designate the trees included in each group (see Figure 1). To exclude juvenile effects during averaging, the first few decades of some of the records summarized in Figure 1 were dropped. These include records 14, 15, 20, 21, 22, 31, 32 (first 20 years dropped) and 4, 25, 29, 30 (first 30 years dropped). The remaining records either extended at least 20 years before 1750 or already excluded juvenile effects when originally published.

$$E = p_{CO_2}{}^{surf\ ocean} I^o$$

where I^o is the rate of invasion per square meter of sea surface per atmosphere of CO₂ pressure. Prior to the onset of the anthropogenic perturbations, I and E (averaged over the sea surface) are assumed to have been equal. Today, of course, I must be somewhat larger than E to accommodate the flow of fossil fuel and forest-soil CO₂ into the sea.
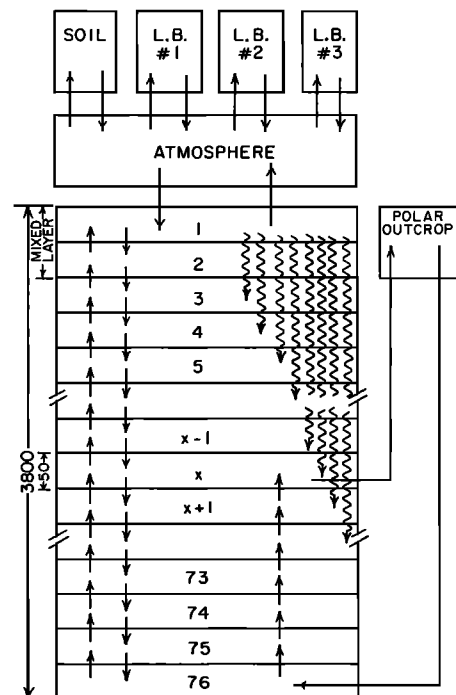
Fig. 4. Multi-box model used to calculate CO₂ uptake and carbon isotope dilution. A description is given in the text.
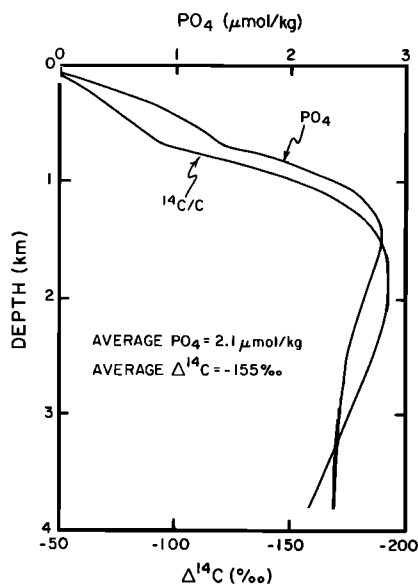
Fig. 5. Phosphate and $^{14}C/^{12}C$ ratios as a function of depth in the model ocean. These curves match satisfactorily the laterally averaged results of the GEOSECS surveys.

The value of Γ is obtained from the radon measurements obtained during the GEOSECS program. These measurements yield an average piston velocity of 2.8 m d^{-1}. Because the molecular diffusivity of CO_2 is 1.43 times that of radon, if the stagnant film model is adopted its piston velocity must be 4.0 m d^{-1}. The solubility of CO_2 gas in sea water at one atmosphere pressure and 20°C is 40 moles m^{-3}. Hence, the value of Γ is

$$\Gamma = 40 \text{ mol m}^{-3} \text{ atm}^{-1} \times 4.0 \times 365 \text{ m year}^{-1}$$

$$= 5.8 \times 10^4 \text{ mol m}^{-2} \text{ year}^{-1} \text{ atm}^{-1}$$

At an atmospheric CO_2 pressure of 280 × 10^{-6} atm, this corresponds to an invasion rate of 17 mol m^{-2} $year^{-1}$. This value is consistent with the distribution of natural radiocarbon in the atmosphere-ocean system.

The coefficients for vertical eddy diffusion for the thermocline and deep sea, the flux of deep water, and the depth from which the source of deep water drawn are chosen to fit the mean penetration depth of bomb-produced tritium at the time of the GEOSECS survey and the mean depth distribution of natural radiocarbon. The values obtained are as follows:

$$K_{\text{thermocline}} = 1.6 \text{ cm}^2 \text{ s}^{-1} \text{ (100 to 700 m)}$$

$$K_{\text{deep sea}} = 0.5 \text{ cm}^2 \text{ s}^{-1} \text{ (700 to 3800 m)}$$

$$F_{\text{deep water}} = 50 \times 10^6 \text{ m}^3 \text{ s}^{-1}$$

$$h_{\text{deep water source}} = 1000 \text{ m}$$

The depth from which the source water for deep sea ventilation strongly influences the $^{14}C/^{12}C$ ratio in bottom water. Were a shallower depth chosen, this model value would exceed the observed value. Furthermore, the depth obtained in this way is consistent with our knowledge of the real ocean. The source for the deep water forming in the northern Atlantic has been shown to be water from the depth range 0.7–1.1 km [Broecker, 1979]. That for deep water forming in the Weddell Sea is even greater [Weiss et al., 1979].

The particulate cycle is designed to reproduce the mean

profile for PO_4 in the sea. All the phosphate reaching the surface sea is incorporated into organic debris with a C/P ratio of 105 which falls to the thermocline and deep sea where it is destroyed releasing the PO_4 to solution. The depth distribution of this oxidation is set to yield the vertical distribution of PO_4 in the sea. This cycle of organic material in the sea is assumed to have suffered no anthropogenic alteration.

The sizes and response times for the various terrestrial carbon reservoirs are selected to be consistent with our knowledge of these reservoirs [Emanuel et al., 1981]. They are as follows:

Ground vegetation (L.B. 1)

$$\text{mass} = 5.8 \times 10^{15} \text{ mol}$$

$$\tau = 4 \text{ years}$$

Nonwoody parts tree + detritus/decomposers (L.B. 2)

$$\text{mass} = 9.8 \times 10^{15} \text{ mol}$$

$$\tau = 1.92 \text{ years}$$

Woody parts tree (L.B. 3)

$$\text{mass} = 37.7 \times 10^{15} \text{ moles}$$

$$\tau = 25 \text{ years}$$

Soil carbon

$$\text{mass} = 93.4 \times 10^{15} \text{ mol}$$

$$\tau = 100 \text{ years}$$

While uncertainties exist in all these estimates, fortunately the reservoirs play only a minor role when compared with the ocean in the dilution of the carbon isotope anomalies.

This model yields a mean penetration depth for tritium of 374 m as of January 1973, which is to be compared with the area weighted value of 375 m observed during the Atlantic and Pacific surveys. The depth profiles of natural ^{14}C and of phosphorous yielded by the model are shown in Figure 5. They are consistent with the horizontally averaged depth distributions observed during the GEOSECS surveys.

CROSSCHECKS ON THE MODEL

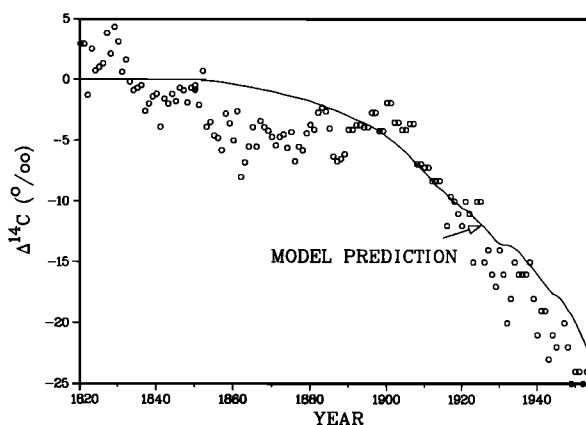Fortunately, not all the information we have was used in the calibration of the model. There are three sources we can

Fig. 6. Comparison between the model-derived Suess effect curve (solid line) and the observed $^{14}C/^{12}C$ trend for atmospheric CO_2 as reconstructed by Stuiver and Quay [1981] from measurements on tree rings (points).

TABLE 3. Distribution of Bomb ¹⁴C in the Ocean

	Observed	Model
Inventory	$3.14 \pm 0.35 \times 10^{28}$ atm	3.02×10^{28} atm
Mean $\Delta^{14}C$ surface water	160 ± 15 ‰	172 ‰

use as crosschecks. The first is the decline in the atmospheric $^{14}C/^{12}C$ ratio over the last 100 years. As the releases of forest and soil CO^2 do not have any significant impact on the $^{14}C/^{12}C$ ratio of atmospheric CO_2, this decline should be mainly the result of the release of fossil fuel CO_2 (which contains no ^{14}C). As shown in Figure 6, our model yields a very good fit to tree-ring ^{14}C records obtained by *Stuiver and Quay* [1981]. The one criticism of this crosscheck is that part (10–15%) of the decline could be the result of changes in the rate at which ^{14}C atoms were generated in the earth's atmosphere [see *Stuiver and Quay*, 1981]. If we were to use Stuiver and Quay's suggested correction for changes in the production rate of natural radiocarbon, then either a higher diffusivity for the upper water column or a higher invasion rate of CO_2 across the air-sea boundary would be required to yield the smaller $^{14}C/^{12}C$ decline.

A second crosscheck is provided by the distribution of bomb-produced ^{14}C as measured during the Atlantic and Pacific GEOSECS surveys. As shown by *Broecker et al.* [1980a], the combination of the integrated amount of bomb ^{14}C in the sea and the mean bomb ^{14}C concentration in surface water carbon provide a check on both the vertical mixing rate in the upper ocean and the rate of CO_2 invasion across the air-sea interface. The comparison between the model and observed values are listed in Table 3. The differences lie within the uncertainty of the observations.

Thus, while both the Suess effect and bomb effect are adequately explained by our model, there is an indication that the model may slightly underestimate the rate of dilution of carbon isotope anomalies by the sea. This possibility should be kept in mind in the discussions that follow.

The third crosscheck is based on a comparison between the CO_2 increase in the atmosphere observed by Keeling and his coworkers [*Bacastow and Keeling*, 1981] from 1958 to 1979 and that predicted from the model based on fossil fuel CO_2 production alone. The observed increase over this 20 year period is 21×10^{-6} atm. The model yields an increase of 23×10^{-6} atm. As inclusion of forest-soil CO_2 production would likely increase the model prediction, the short fall suggests that the model ocean is not taking up enough CO_2 (or that the CO_2 enhancement of forest growth is significant).

An important point must be raised here. Two models of differing geometry that equally well match all the isotope distributions need not take up the same amount of CO_2. The reason for this geometry dependence relates to the fact that the resistance posed by the air-sea interface is smaller for the uptake of excess CO_2 than for the carbon isotope equilibration [see *Broecker et al.*, 1980b]. The one-dimensional model by necessity eliminates an important phenomena taking place in the real ocean. Isopycnal horizons rise toward the surface at latitudes greater than 30°. During cold winter months they outcrop at the surface. As mixing along these horizons is quite rapid, this outcropping provides a means of circumventing vertical mixing resistance. As shown by *Siegenthaler et al.* [1978], a model including these outcrops and calibrated to satisfy the distribution of natural ^{14}C would take up somewhat more fossil fuel CO_2 than would the
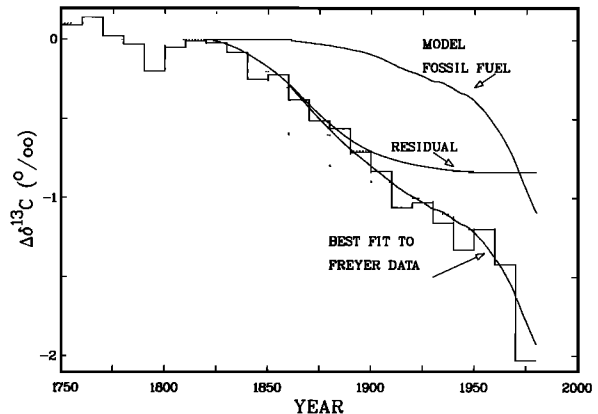

Fig. 7. Forest and soil CO_2 contribution (solid curve marked residual) to the decline in atmospheric $^{13}C/^{12}C$ ratio as obtained by subtracting the model-derived contribution of fossil fuel CO_2 (solid curve marked model fossil fuel) from the actual atmospheric $^{13}C/^{12}C$ decline as reconstructed by *Freyer and Belacy* [1983] (solid step curve) and as obtained here by using only open site trees on which cellulose was analyzed (dotted lines).

conventional one-dimensional (1-D) model adopted here. Thus, while our model comes close to satisfying the available crosschecks, there is an indication that its CO_2 uptake by the ocean may be somewhat low because entry along outcropping isopycnals is not permitted in a 1-D model.

DECONVOLUTION

The tree-ring-based $^{13}C/^{12}C$ record obtained by *Freyer and Belacy* [1983] is shown in Figure 7. Also shown in this figure is the fossil fuel CO_2 contributions to this change calculated from the model. The residual (i.e., that portion of the $^{13}C/^{12}C$ change not explained by input of fossil fuel CO_2) is also shown. We attribute this residual to the input of forest and soil CO_2.

In Figure 8 is shown the best estimate of the time history of the forest-soil CO_2 input needed to generate the residual shown in Figure 7. The degree of fit to the Freyer and Belacy ^{13}C record is shown in Figure 9. Also shown in Figure 9 are the effects changing the amplitude and the timing of the forest-soil scenario. The purpose of this figure is to provide the reader with an idea of the sensitivity of this kind of
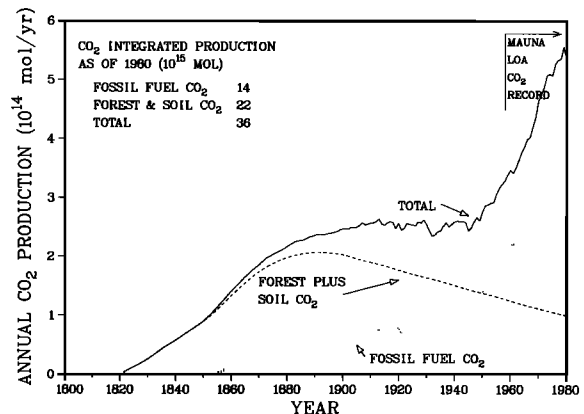

Fig. 8. Forest and soil CO_2 input time history based on the deconvolution of Freyer's tree ring based atmospheric $^{13}C/^{12}C$ curve. Shown for comparison are fossil fuel CO_2 input time history and the sum of these two contributions. As can be seen, the integrated forest-soil contribution exceeds the fossil fuel contribution by a factor of 1.6.
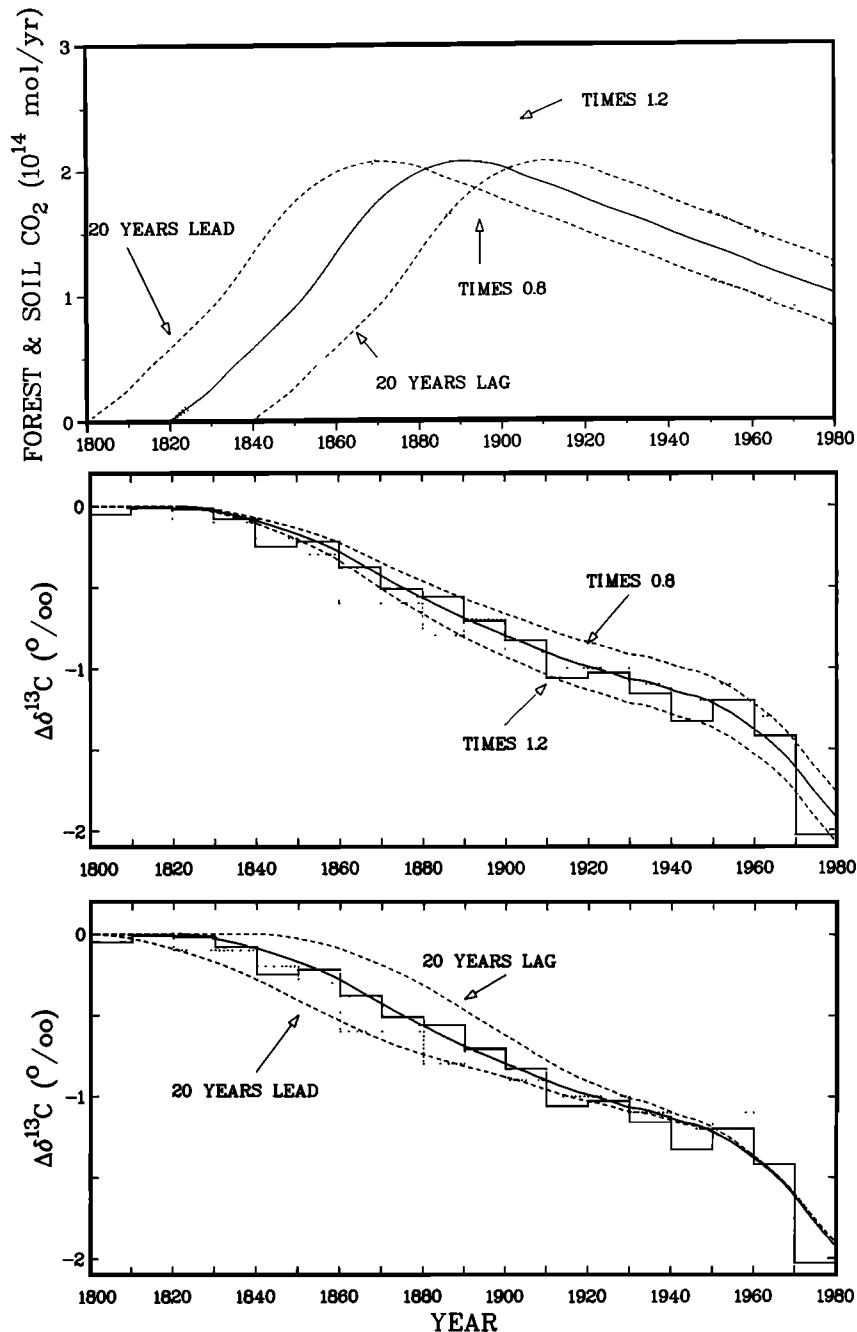
Fig. 9.   The sensitivity of the deconvolution to changes in the forest-soil CO_2 input scenario is depicted by shifting the preferred scenario forward and backward in time by 20 years and by changing its amplitude by plus and minus 20% (see top panel). As shown in the middle and bottom panels, the changes in the forest-soil contribution created by these scenario changes are about at the resolution of the C^{13}/C^{12} record.

analysis. It should be emphasized that our deconvolution should be considered as a 20-year running mean for this input. Clearly, we could create scenarios with 2-decade or less time-scale variability about the smooth scenario we have adopted that would equally well match the observations. The tree-ring curve does not provide a sufficiently detailed record to permit these second-order features to be deconvolved. It should be pointed out that the recent ^{13}C trend for Freyer's $\delta^{13}C$ versus time curve is consistent with direct measurements on atmospheric CO_2 samples collected over the past two decades [see *Freyer and Belacy*, 1983].

The atmospheric CO_2 anomaly generated by the forest-soil scenario alone is shown in Figure 10. As can be seen its

contribution over the last 20 years (i.e., the period of time over which a reliable atmospheric record exists) is only about 4×10^{-6} atm. This is to be compared with a 23×10^{-6} atm change computed by using the model for the fossil fuel contribution over this interval of time. This is one of the important consequences of the shape we obtain for the forest-soil scenario. Uptake by the ocean of CO_2 released from forest and soils in earlier years has almost exactly balanced the new production from this source during the last 20 years. As can be seen in Figure 7, the same is true for ^{13}C. The dilution of the ^{13}C anomaly generated by earlier inputs has almost exactly balanced the anomaly generated by the forest and soil CO_2 input over the last 20 years. This
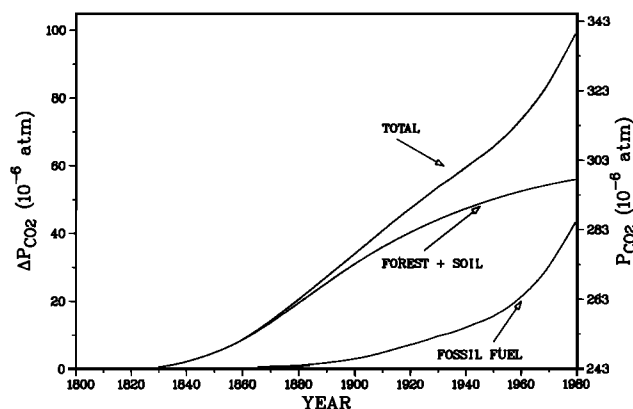
Fig. 10. Atmospheric CO_2 pressure versus time as obtained from the combined forest-soil and fossil fuel CO_2 inputs (curve marked total). Also shown are the separate contributions of the two components. As can be seen over the 20-year period for which we have an atmospheric CO_2 record, the trend is dominated by the fossil fuel CO_2 contribution.

removes the point of contention between the ocean modelers and the biosphere historians. As long as the relaxation of the anomalies generated by even larger emissions of forest-soil CO_2 in the past balance the inputs over the last 2 decades, releases of forest-soil CO_2 do not aggravate the situation for the ocean modelers.

IMPORTANCE OF THE AIR TO SEA KINETIC ISOTOPE FRACTIONATION FACTOR

To assess the importance of the kinetic fractionation factor used for the CO_2 entering the sea we have completed the deconvolution using the value of -14 ‰ for the strongly alkaline solutions (opposed to the Siegenthaler and Munnich [1981] value of -2 ‰). The comparison is shown in Figure 11. Use of the less realistic fractionation factor raises the amplitude of the needed forest-soil input by about 20% without changing the shape.

SENSITIVITY OF ¹³C DATA FOR DISTINGUISHING AMONG BASIC HYPOTHESES

To show the sensitivity of the ¹³C record in distinguishing between the merits of the latest forest-soil scenario deconvolved from the tree-ring record (this paper) and the latest forest-soil scenario derived from land-use data [Houghton et
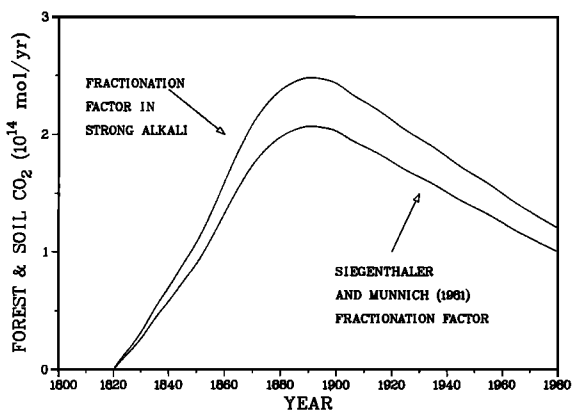

Fig. 11. Comparison of the forest-soil CO_2 input function, using the -14 ‰ kinetic fractionation factor (in strong alkaline solution) for CO_2 taken up by the sea with that for the -2 ‰ factor proposed by Siegenthaler and Munnich [1981]. The calculations in this paper were all carried out by using the latter value.
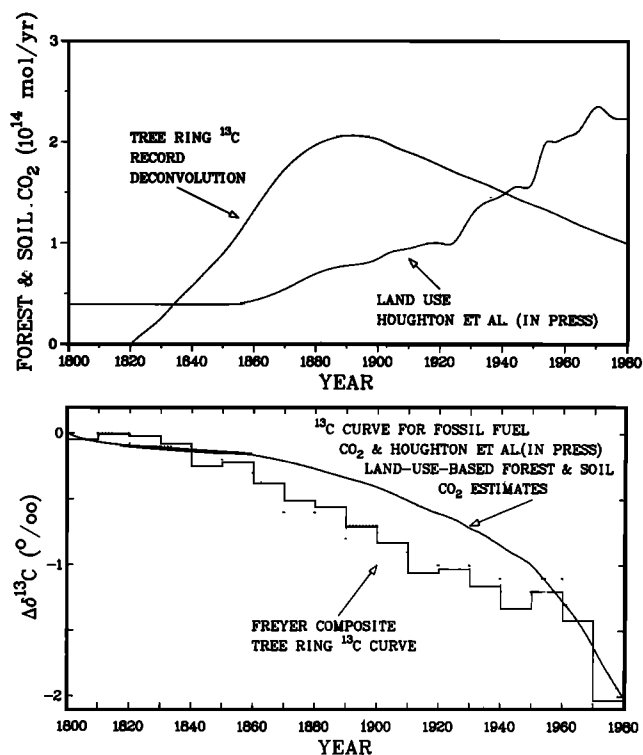

Fig. 12. Contrast between the ¹³C/¹²C derived forest-soil CO_2 scenario obtained in this paper with that based on land use and stored carbon response functions obtained by Houghton et al. [1983]. The atmospheric ¹³C/¹²C response for the land use scenario is compared with the response obtained from the ¹³C/¹²C records. While the amplitudes are the same, the shapes are quite different.

al., 1983] we compared the ¹³C curves calculated (using the model) with the Freyer composite curve in Figure 12. As the two forest-soil CO_2 scenarios differ in their shape rather than in their integrated input, the difference lies in the shape of the ¹³C decline rather than in the amplitude of its decline.

PREANTHROPOGENIC ATMOSPHERIC CO₂ CONTENT

The preanthropogenic atmospheric CO_2 concentration is calculated by using the amount of forest-soil CO_2 release history derived from the deconvolution of tree ring ¹³C data
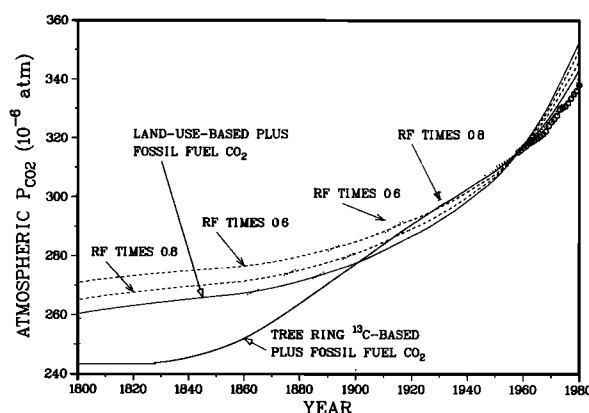

Fig. 13. Comparison of the atmospheric CO_2 pressure time histories for ¹³C/¹²C based and land-use-based forest-soil scenarios. Both are constrained to pass through the atmospheric value of 315.5 $\times 10^{-6}$ atm for 1958. Note that the land-use curve is far steeper than the actual atmospheric increase (1958 to present), while the ¹³C/¹²C-based curve has only a slightly steeper increase. The effect of reducing the Revelle factor to 0.8 and to 0.6 is shown for each of these scenarios.
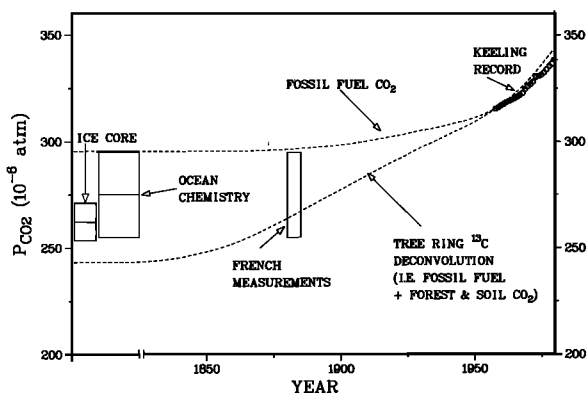
Fig. 14.   Summary of estimates of the pre-1900 atmospheric CO_2 content. Included are the model based curves for no forest-soil input and for the $^{13}C/^{12}C$-based forest-soil contribution, the early measurements by the French [Muntz and Aubin, 1886], the ice core derived value of Neftel et al. [1982], and the ocean chemistry derived value of Chen and Millero [1979].

and the fossil fuel CO_2 release history derive from coal, oil, and natural gas production data. In these model calculations the curve is forced through the observed p_{CO_2} value of 315.5 ppm for 1958. As shown in Figure 13, the scenario derived from Freyer ^{13}C data yields a pre-1800 p_{CO_2} of 243 × 10^{-6} atm. The scenario derived from land-use data predicts the pre-1800 p_{CO_2} of 260 × 10^{-6} atm. Fossil fuel CO_2 production alone yields a value of 295 × 10^{-6} atm. As can be seen, the Houghton et al. [1983] scenario produces a far larger than observed post-1958 atmospheric CO_2 rise.

As stated above, the ocean model might yield too low a ratio of excess CO_2 uptake to carbon isotope dilution. The reason is that the one-dimensional model maximizes the importance of mixing relative to gas exchange resistance. While we have not yet constructed what we consider to be an adequate two-dimensional (2-D) model which takes up CO_2 in regions where thermocline and deep water isopycnals outcrop, we can get a sense of the importance of this type of model modification by arbitrarily increasing the thermodynamic capacity of surface sea water for fossil fuel CO_2 uptake (i.e., by reducing the Revelle factor). Such a change permits the model to take up more fossil fuel CO_2 without altering its isotope dilution characteristics. In Figure 13 we show p_{CO_2} versus time curves for Revelle factors of 0.8 and 0.6 the one used in the model. The same modifications are also shown for the Houghton et al. [1983] land-use scenario. These calculations show that to bring the CO_2 record generated by the model for the ^{13}C based forest-soil scenario into agreement with the Keeling curve, the thermodynamic capacity for excess CO_2 must be increased by 60%. Even this increase would not bring the model prediction for the Houghton et al. [1983] scenario into concordance with observation.

Finally, we compare these CO_2-versus-time curves with other sources of information (see Figure 14). During the early 1880s, the French made a series of atmospheric CO_2 content measurements on an expedition through the Atlantic Ocean [Muntz and Aubin, 1886]. Unfortunately, there is no way to evaluate their absolute accuracy. Neftel et al. [1982] report a value of 271 ± 9 ppm for the CO_2 content of the atmosphere about 600 years ago, based on CO_2 to air ratios in gases released from the bubbles in Greenland ice cores.

Finally, Chen and Millero [1979] estimate from measurements on 'old' ocean water that the preanthropogenic CO_2 content was 275 ± 20 ppm. As pointed out by Shiller [1981], the approach taken by these authors is subject to many serious pitfalls. Thus, while all the methods give consistent values, none is reliable enough to permit a firm answer to be given regarding the magnitude of the forest-soil contribution to the build-up of atmospheric CO_2.

CONCLUSIONS

Unfortunately, the data in hand still are not adequate to settle the controversy between terrestrial biologists who estimate the forest-soil CO_2 contribution from land use and carbon inventory response data and geochemists who model the ocean uptake of excess CO_2. $^{13}C/^{12}C$ results which many hoped would serve to resolve the dilemma are still not adequate for the task. If future work bears out Freyer's composite $^{13}C/^{12}C$ curve, then the terrestrial biologists will have been proven correct in their estimate that the total amount of excess CO_2 from forests and soils has over the last 200 years exceeded that from fossil fuels. However, they will have been shown to be incorrect in their contention that the forest-soil CO_2 contribution has had a strong influence on the trend in atmospheric CO_2 content from 1958 to present.

Aspects of the problem still needing investigation are as follows:

1.   Further work must be done to identify and eliminate sources of 'noise' in the tree ring $^{13}C/^{12}C$ record. This is still the most powerful approach to the problem. The recent work of Farquhar et al. [1982] and Francey and Farquhar [1982] toward developing a simple theory to explain carbon isotope fractionation by plants is an important step toward understanding the meaning of the $^{13}C/^{12}C$ record in tree rings.

2.   The effect of outcropping isopycnal horizons on the ability of the ocean to take up excess CO_2 (while not changing its carbon isotope dilution response) must be investigated. If this is to be done, 2-D ocean models must replace the current 1-D models.

3. CO_2 partial pressure estimates from ice cores and from old photographs of solar spectra must be fully exploited.

4.   The concept that land use impacts on the forest and soil carbon inventory followed population growth (at least until the early 1950s) must be reexamined. It is possible that the great expansion of grazing land which accompanied colonization had a greater impact than the expansion of human population.

5.   The possibility that the biomass in the world's unimpacted forests and soils has shown a recent increase due to anthropogenic CO_2, nitrogen, and phosphorus fertilization must be examined. The land-use approach disregards this countering influence. While being cut back around the 'edges,' the forests may be becoming more lush in the 'middle.'

ration, Environmental Sciences Division Publication 2125. At Lamont-Doherty Geological Observatory, the financial support came from Department of Energy grant DE-AC02-79EV10041C and subcontract UCC 19X-22237C with Oak Ridge National Laboratory. LDGO contribution 3451.

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