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

TSUNG-HUNG PENG, WALLACE S. BROECKER, HANS D. FREYER, AND SUSAN TRUMBORE

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 Deschger 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 $\times$ 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 $^{13}$CO$_2$ variations on a global scale. The selection of isolated trees far from urban areas for $^{13}$C analysis should minimize this effect. Changes in the $^{13}$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 ($\alpha_{RuDP}$) 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

---

1 Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.
2 Lamont-Doherty Geological Observatory, Palisades, New York 10964.
3 Nuclear Research Center, Jülich, West Germany.

Copyright 1983 by the American Geophysical Union.

Paper number 3C0129.
0148-0227/83/003C-012S00.00
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, 1979; 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 ocean, 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 $^{13}C$ 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 $^{13}C$ 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 $\pm7\%$) from

### Table 1. Summary of CO$_2$ Emissions from Terrestrial Ecosystems

| Investigator       | Annual Input (x 10$^{15}$ mol year$^{-1}$) | Cumulative Input (x 10$^{15}$ mol) |
|--------------------|--------------------------------------------|-----------------------------------|
| Bolin [1977]       | 0.8 $\pm$ 0.5 $^\dagger$                  | 5.8 $\pm$ 2.5 (1800–1975) $^\dagger$ |
| Adams et al. [1977]| 4.2 $^\dagger$                             |                                   |
| Sturier [1978]     | 1.0 $^\ddagger$                            |                                   |
| Woodwell et al. [1978]| 8.3 $\pm$ 6.7 $^\dagger$              |                                   |
| Wong [1978]        | 0.8 $^\dagger$                             |                                   |
| Waggener [1978]    | 12.4 $^\dagger$                            |                                   |
| Freyer [1978]      | 5.8 $^\dagger$                             |                                   |
| Siegenthaler et al. [1978]| 13.7 $\pm$ 2.6 (1860–1974) $^\dagger$ |                                   |
| Hampicke [1979]    | 2.5 $\pm$ 1.3 $^\dagger$                  |                                   |
| Seller and Czutsen [1980]| 0 $\pm$ 1.7 $^\dagger$             |                                   |
| Moore et al. [1981]| 2.9 $\pm$ 1.1 $^\dagger$                  |                                   |
| This paper         | 1 $^\ddagger$                             | 20 (1850–1975) $^\dagger$          |

*$^\dagger$Based on $^{13}C$ data for tree rings.  
$^\ddagger$Based on biomass change data.  
$^\ddagger$Based on C13 data for tree rings.
![Image](https://via.placeholder.com/150)

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

| Record Number | Reference                  | Location             | Species (Number of Trees Analyzed) | Coniferous (C) or Deciduous (D) |
|---------------|----------------------------|----------------------|-----------------------------------|---------------------------------|
| 1             | Francey [1981]             | Tasmania             | Athrotaxis selaginoides (1)        | C                               |
| 2             | Francey [1981]             | Tasmania             | Athrotaxis selaginoides (1)        | C                               |
| 3             | Francey [1981]             | Tasmania             | Athrotaxis selaginoides (1)        | C                               |
| 4             | Freyer [1979a]             | Black Forest, West Germany | Pinus silvestris (1)              | C                               |
| 5             | Freyer [1980]              | Cave Junction, Oregon | Pseudotsuga menziesii (1)         | C                               |
| 6             | Freyer [1981]              | Muddus National Park, Sweden | Pinus silvestris (1)              | C                               |
| 7             | Harkness and Miller [1980] | Jotunheimer, Norway  | Pinus silvestris (1)              | C                               |
| 8             | Wilson [1978]              | White Mountains, California | Pinus ponderosa (1)               | C                               |
| 9             | Lerman and Long [1980]     | Flagstaff, Arizona   | Quercus robur (5)                 | D                               |
| 10            | Freyer [1981]              | Spessart Forest, West Germany | Quercus robur (5)                 | D                               |
| 11            | Francey [1981]             | Tasmania             | Athrotaxis selaginoides (1)        | C                               |
| 12            | Francey [1981]             | Tasmania             | Athrotaxis selaginoides (1)        | C                               |
| 13            | Francey [1981]             | Tasmania             | Athrotaxis selaginoides (1)        | C                               |
| 14            | Francey [1981]             | Tasmania             | Phyllocladus asplenifolius (1)    | C                               |
| 15            | Rebello and Wagener [1976] | Southern Highlands, Brazil | Aurorocaria angustifolia (1)      | C                               |
| 16            | Tans and Mook [1980]       | Drenthe, Netherlands | Quercus rubra (1)                 | D                               |
| 17            | Tans and Mook [1980]       | Drenthe, Netherlands | Quercus rubra (1)                 | D                               |
| 18            | Tans and Mook [1980]       | Drenthe, Netherlands | Quercus rubra (1)                 | D                               |
| 19            | Tans and Mook [1980]       | Drenthe, Netherlands | Quercus rubra (1)                 | D                               |
| 20            | Freyer [1979a]             | Spanish Pyrenees, French Atlantic Coast, Azores | Quercus lusitanica (2)            | D                               |
| 21            | Freyer [1979a]             | North Carolina       | Quercus rubra (3)                 | D                               |
| 22            | Freyer [1979b]             | Eifel, West Germany  | Quercus petraea (1)               | D                               |
| 23            | Freyer and da Silva [1979] | Mauna Kea Mountain, Hawaii | Myoporum sanswicerise (2)         | D                               |
| 24            | Bender and Berge [1981]    | Madison, Wis.       | Quercus macrocarpa (3)            | D                               |
| 25            | Stuiver [1978]             | Olympic Peninsula, Washington | Pseudotsuga menziesii (1)         | C                               |
| 26            | Grinsted et al. [1970]     | White Mountains, California | Pinus luscarpa (2)                | C                               |
| 27            | Pearman et al. [1976]      | North Tasmania       | Anthrotaxis selaginoides (1)       | C                               |
| 28            | Pearman et al. [1976]      | North Tasmania       | Anthrotaxis selaginoides (1)       | C                               |
| 29            | Galimov [1976]             | Permal District, U.S.S.R. | Spruce (1)                        | C                               |
| 30            | Galimov [1976]             | Permal District, U.S.S.R. | Spruce (1)                        | C                               |
| 31            | Farmer and Baxter [1974]   | Forest of Dean, England | Quercus robur (1)                 | D                               |
| 32            | Farmer and Baxter [1974]   | Glengarry Forest, Scotland | Larix decidua (1)                 | D                               |
| 33            | Farmer [1979]              | Cape Cod, Mass.      | 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 CO$_2$ contribution.

This temporal history of forest-soil CO$_2$ 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
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 CO₂ 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 CO₂ 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

$$I = \rho_{CO2}^{atm} F$$

and the evasion rate from the relationship

$$E = \rho_{CO2}^{surf\ ocean} F$$

where $F$ 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. 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.

Fig. 4. Multi-box model used to calculate CO2 uptake and carbon isotope dilution. A description is given in the text.
The value of $F$ 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 $F$ is

$$F = 40 \text{ mol m}^{-3} \text{ atm}^{-1} \times 4.0 \times 365 \text{ m year}^{-1} = 5.8 \times 10^4 \text{ mol m}^{-2} \text{ year}^{-1} \text{ atm}^{-1}$$

At an atmospheric CO$_2$ pressure of $280 \times 10^{-6}$ 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:

$$K_{\text{thermocline}} = 1.6 \text{ cm}^2 \text{ s}^{-1} (100 \text{ to } 700 \text{ m})$$
$$K_{\text{deep sea}} = 0.5 \text{ cm}^2 \text{ s}^{-1} (700 \text{ to } 3800 \text{ m})$$
$$F_{\text{deep water}} = 50 \times 10^6 \text{ m}^3 \text{ s}^{-1}$$
$$h_{\text{deep water source}} = 1000 \text{ m}$$

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)**
  - mass = $5.8 \times 10^{15}$ mol
  - $\tau = 4$ years
- **Nonwoody parts tree + detritus/decomposers (L.B. 2)**
  - mass = $9.8 \times 10^{15}$ mol
  - $\tau = 1.92$ years
- **Woody parts tree (L.B. 3)**
  - mass = $37.7 \times 10^{15}$ moles
  - $\tau = 25$ years
- **Soil carbon**
  - mass = $93.4 \times 10^{15}$ mol
  - $\tau = 100$ 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
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 
ratio 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 
adegradately 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 $21 \times 10^{-6}$ atm. The model yields an increase 
of $23 \times 10^{-6}$ 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 is related 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 equilibrium [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 Sie- 
genthaler 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

\begin{table}[h]
\centering
\caption{Distribution of Bomb $^{14}$C in the Ocean}
\begin{tabular}{|c|c|}
\hline
\textbf{Inventory} & \textbf{Model} \\
\hline
$3.14 \pm 0.35 \times 10^{28}$ atm & $3.02 \times 10^{28}$ atm \\
Mean $\delta^{13}$C surface water & $160 \pm 15$‰ \\
& $172$‰ \\
\hline
\end{tabular}
\end{table}

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

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig8}
\caption{Fig. 8. Forest and soil CO$_2$ input time history based on the 
deconvolution of Freyer’s tree ring based atmospheric $^{14}$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.}
\end{figure}
Fig. 9. The sensitivity of the deconvolution to changes in the forest-soil CO₂ 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 C¹³/C¹² 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 C¹³ trend for Freyer’s δ¹³C versus time curve is consistent with direct measurements on atmospheric CO₂ samples collected over the past two decades [see Freyer and Belacy, 1983].

The atmospheric CO₂ 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 x 10⁻⁶ atm. This is to be compared with a 23 x 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 CO₂ 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 C¹³. The dilution of the C¹³ anomaly generated by earlier inputs has almost exactly balanced the anomaly generated by the forest and soil CO₂ 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 $^{13}$C DATA FOR DISTINGUISHING AMONG BASIC HYPOTHESES**

To show the sensitivity of the $^{13}$C 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 al., 1983] we compared the $^{13}$C 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 $^{13}$C decline rather than the amplitude of its decline.

**PREANTHROPOGENIC ATMOSPHERIC CO$_2$ 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 $^{13}$C data...
and for the $^{13}$C/$^{12}$C-based forest-soil contribution, the early measured value of Chen and Millero [1979].

The scenario derived from Freyer's data yields a pre-1800 PCO$_2$ of 243 x $10^{-6}$ atm. As can be seen, the comparison 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 trend in atmospheric CO$_2$ content from 1958 to present.

While we have not yet constructed what we consider to be an adequate two-dimensional (2-D) model which takes up CO$_2$ from regions where thermocline and deep water isopycnal 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] land-use 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.'

**Acknowledgments.** We benefited from discussions with J. White, T. Takahashi, and W. R. Emanuel. We also thank W. R. Emanuel and T. J. Blasing for reviewing this manuscript. At Oak Ridge National Laboratory, research was supported jointly by the National Science Foundation's Ecosystem Studies Program under Interagency Agreement DEB 8115316 and the Carbon Dioxide Research Division, Office of Energy Research, U.S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corpo-
References

Adams, J. A. S., M. S. M. Mantovani, and L. L. Lundell, Wood versus fossil fuel as a source of excess carbon dioxide in the atmosphere: A preliminary report, *Science*, 196, 54–56, 1977.

Bacastow, R. B., and C. D. Keeling, Atmospheric carbon dioxide concentration and the observed air borne fraction, *SCOPE 16, in Carbon Cycle Modelling*, edited by B. Bolin, pp. 103–112, John Wiley, New York, 1981.

Baertschi, P., Die Fraktionierung der Kohlenstoff isotopen bei der Absorption von Kohlendioxid, *Helv. Chim. Acta.*, 35, 1030–1036, 1952.

Bender, M. M., and A. J. Berge, Carbon isotope records in Wisconsin trees, *Tellus*, 34, 500–504, 1981.

Bolin, B., Changes of land biota and their importance for the carbon cycle, *Science*, 196, 613–615, 1977.

Broecker, W. S., A revised estimate for the radiocarbon age of North Atlantic deep water, *J. Geophys. Res.*, 84, 3218–3226, 1979.

Broecker, W. S., T. Takahashi, H. J. Simpson, and T.-H. Peng, Fate of fossil fuel carbon dioxide and the global carbon budget, *Science*, 206, 409–418, 1979.

Broecker, W. S., T.-H. Peng, and R. Engh, Modeling the carbon system, *Radiocarbon*, 22, 565–598, 1980.

Broecker, W. S., T.-H. Peng, and T. Takahashi, A strategy for the use of bomb-produced radiocarbon as a tracer for the transport of fossil fuel CO2 into the deep-sea source regions, *Earth Planet. Sci. Lett.*, 49, 463–466, 1980b.

Chen, C. T., and P. J. Millero, Gradual increase of oceanic carbon dioxide, *Nature*, 277, 205–206, 1979.

Craig, H., The geochemistry of the stable carbon isotopes, *Geochem. Cosmochim. Acta.*, 3, 53–92, 1953.

Craig, H., Carbon-13 in plants and the relationship between carbon-13 and carbon-14 variations in nature, *J. Geol.*, 62, 115–149, 1954.

Emanuel, W. R., G. E. O. Killough, and J. S. Olson, Modeling the circulation of carbon in the world's terrestrial ecosystems, *SCOPE 16, in Carbon Cycle Modelling*, edited by B. Bolin, pp. 335–353, John Wiley, New York, 1981.

Farquhar, G. D., M. H. O'Leary, and J. A. Berry, On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves, *Aust. J. Plant Physiol.*, 9, 121–137, 1982.

Francey, R. J., Tasmanian tree rings belie suggested anthropogenic 14C/12C trends, *Nature*, 290, 232–235, 1981.

Francey, R. J., and D. G. Farquhar, An explanation of the 14C/12C variations in tree rings, *Nature*, 297, 229–231, 1982.

Freyer, H. D., Preliminary evaluation of past CO2 increase as derived from 14C measurements in tree rings, in *Carbon Dioxide, Climate and Society*, edited by J. Williams, pp. 69–78, Pergamon, New York, 1978.

Freyer, H. D., On the 13C record in tree rings, 1, 13C variations in northern hemispheric trees during the last 150 years, *Tellus*, 31, 124–137, 1979a.

Freyer, H. D., On the 13C record in tree rings, 2, Registration of microenvironmental CO2 and anomalous pollution effect, *Tellus*, 31, 308–312, 1979b.

Freyer, H. D., WMO project on research and monitoring of atmospheric CO2, *Rep. 1, Appendix E, WMO, Geneva*, 1980.

Freyer, H. D., and M. de Silva, On the record in tree rings, 3: an experiment simulation, report, Nuclear Res. Center, Jülich, West Germany, 1979.

Freyer, H. D., and N. Belacy, 14C/12C records in northern hemispheric trees during the past 500 years anthropogenic impact and climatic superpositions, *J. Geophys. Res.*, in press, 1983.

Galimov, E. M., Variations of the carbon cycle at present and in the geological past, in *Environmental Biogeochemistry*, vol. 1, edited by J. O. Nriagu, pp. 3–11, Ann Arbor Science, Ann Arbor, Mich., 1976.

Grinsted, M. J., A. T. Wilson, and C. W. Ferguson, 13C/12C ratio variations in *Pinus longaeva* (bristle-cone pine) cellulose during the last millenium, *Earth Planet. Sci. Lett.*, 42, 251–253, 1979.

Hampiecke, U., Net transfer of carbon between the land biota and the atmosphere, induced by man, in *The Global Carbon Cycle*, *SCOPE Rep. 13*, edited by B. Bolin, E. T. Degens, S. Kempe, and P. Ketner, pp. 219–236, John Wiley, New York, 1979.

Harkness, D. B., and B. F. Miller, Possibility of climatically induced variations in the 13C and 14C enrichment patterns as recorded by a 3000-year-old Norwegian pine, *Radiocarbon*, 22, 291–298, 1980.

Houghton, R. A., J. E. Hobbie, J. M. Melillo, B. Moore, B. J. Peterson, G. R. Shaver, and G. M. Woodwell, Changes in the carbon content of terrestrial biota and soils between 1860 and 1980: A net release of CO2 to the atmosphere, *Ecol. Monogr.*, in press, 1983.

Keeling, C. D., Industrial production of carbon dioxide from fossil fuel and limestone, *Tellus*, 25, 1174–1198, 1973.

Keeling, C. D., R. B. Bacastow, and P. Tans, Predicted shift in the 13C/12C ratio of atmospheric carbon dioxide, *Geophys. Res. Lett.*, 7, 505–508, 1980.

Lerman, J. C. and A. Long, Carbon-13 in tree rings: Local or canopy effect?, in *Proceedings International Meeting on Stable Isotopes in Tree Ring Research*, edited by G. C. Jacoby, pp. 22–34, U.S. Department of Energy, Washington, D.C., 1980.

Moore, B. R. D., Boone, J. E. Hobbie, R. A. Houghton, J. M. Melillo, B. J. Peterson, G. R. Shaver, C. J. Vorosmarty, and G. M. Woodwell, A simple model for analysis of the role of terrestrial ecosystems in the global carbon budget, *SCOPE 16, in Carbon Cycle Modelling*, edited by B. Bolin, pp. 365–385, John Wiley, New York, 1981.

Mozes, A., and E. Aubin, Recherches sur la constitution chimique de l'atmosphere, d'apres les experiences de M. le Dr. Hyades, Mission Scientifique du Cap. Horn 1882–1883, Tome III (2), Paris, Gauthier-Villars, 1886.

Nefeli, A., H. Oeschger, J. Schwander, B. Staufuffer, and R. Zumbrun, Ice core sample measurements give atmospheric CO2 content during the last 40,000 years, *Nature*, 295, 220–223, 1982.

Oeschger, H., U. Siegenthaler, U. Schotterer, and A. Gugelmann, A box diffusion model to study the carbon dioxide exchange in nature, *Tellus*, 27, 168–192, 1975.

Pearman, G. J., R. S. Franey, and P. J. B. Fraser, Climatic implications of stable carbon isotopes in tree rings, *Nature*, 260, 771–773, 1976.

Peng, T.-H., W. S. Broecker, G. G. Mathieu, Y.-H. Li, and A. E. Barkridge, Radon evasion rates in the Atlantic and Pacific Oceans as determined during the Geoseas project, *J. Geophys. Res.*, 84, 2471–2486, 1979.

Rebello, A., and K. Wagener, Evaluation of 12C and 13C data on atmospheric CO2 on the basis of a diffusion model for oceanic mixing, in *Environmental Biogeochemistry*, vol. 1, edited by J. O. Nriagu, pp. 13–23, Ann Arbor Science, Ann Arbor, Mich., 1976.

Rotty, R. M., Data for global CO2 production from fossil fuels and cement, in *SCOPE 16, in Carbon Cycle Modelling*, edited by B. Bolin, pp. 121–123, John Wiley, New York, 1981.

Seiler, W., and P. J. Crutzen, Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning, *Clime. Change*, 2, 207–247, 1980.

Shiller, A. M., Calculating the oceanic CO2 increase: A need for caution, *J. Geophys. Res.*, 86, 11083–11088, 1981.

Siegenthaler, U., and K. O. Munnich, 13C/12C fractionation during CO2 transfer from air to sea, in *SCOPE 16, in Carbon Cycle Modelling*, edited by B. Bolin, pp. 249–258, John Wiley, New York, 1981.

Siegenthaler, U., M. Heinmann, and H. Oeschger, Model responses of the atmospheric CO2 level and 13C/12C ratio to biogenic CO2 input in carbon dioxide, in *Climate and Society*, edited by J. Williams, pp. 79–84, Pergamon, New York, 1978.

Stuiver, M., Atmospheric CO2 increases related to carbon reservoir changes, *Science*, 199, 235–258, 1978.

Stuiver, M., and P. D. Quay, Atmospheric 14C changes resulting
from fossil fuel CO$_2$ release and cosmic ray flux variability, Earth Planet. Sci. Lett., 53, 349–362, 1981.

Tans, P. P., and W. G. Mook, Past atmospheric CO$_2$ levels and $^{13}$C/$^{12}$C ratios in tree rings, Tellus, 32, 268–283, 1980.

Wagener, K. 1978. Total anthropogenic CO$_2$ production during the period 1800–1935 from carbon-13 measurements in tree rings, Radiat. Environ. Biophys., 15, 101–111, 1978.

Weiss, R. F., H. G. Ostlund, and H. Craig, Geochemical studies in the Weddell Sea, Deep Sea Res., 26, 1093–1120, 1979.

Wilson, A. T., Pioneer agriculture explosion and CO$_2$ levels in the atmosphere, Nature, 273, 40–41, 1978.

Wong, C. S., Atmospheric input of carbon dioxide from burning wood, Science, 200, 197–200, 1978.

Woodwell, G. M., R. H. Whittaker, W. A. Reiners, G. E. Likens, C. C. Delwiche, and D. B. Botkin, The biota and the world carbon budget, Science, 199, 141–146, 1978.

(Received June 21, 1982; revised December 27, 1982; accepted December 28, 1982.)