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Past atmospheric CO_2 levels and the $^{13}C/^{12}C$ ratios in tree rings

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ABSTRACT

Intra-ring differences of the $^{13}C/^{12}C$ ratio in tree rings are found to be very large in four Dutch trees. In some cases differences were measured over 4 ‰ $\delta^{13}C$. Even the $^{13}C/^{12}C$ ratio averaged over entire rings sometimes still exhibits abrupt jumps of over 1 ‰ in $\delta^{13}C$ from year to year. Significant correlations of $\delta^{13}C$ in tree rings with yearly average temperature and precipitation are found. Responses of the atmosphere to a ^{13}C labelled input of CO_2 are calculated in $3\frac{1}{2}$ box perturbation model, consisting of an atmosphere, a biosphere, an oceanic mixed layer and a leak of the perturbation to the deep seas. The average ^{13}C record obtained from the four trees is interpreted in terms of past biospheric growth and shrinkage by using the $3\frac{1}{2}$ box model.

1. Introduction

A major problem with predictions of the future rise of CO_2 levels due to fossil fuel combustion is that the geochemical models used for these predictions can be validated with only a limited number of recent atmospheric CO_2 data. Another check on the models can be obtained from $^{13}C/^{12}C$ and $^{14}C/C$ ratios and tree rings provide a very long time series of these. If they can be shown to reflect the corresponding global average ratios of the atmosphere during the time of formation of the ring, the timespan covered by experimental data will be greatly expanded.

In particular $^{13}C/^{12}C$ ratios could be used instead of (non-existent) historic CO_2 concentration data. A change in the amount of carbon stored in the long-lived land biota and soil organics produces both a CO_2 and a $^{13}C/^{12}C$ signal in the atmosphere because the carbon locked up in organic matter (to be further called the biota reservoir) is depleted in ^{13}C relative to the atmosphere. At present the largest uncertainties in the modelling of the global carbon cycle seem to be related to the behavior of the biota reservoir (Revelle and Munk, 1977; Woodwell et al., 1978). The study of past $^{13}C/^{12}C$ ratios is of special importance in this respect.

Recently several investigators have used $^{13}C/^{12}C$ in tree rings in trying to establish an atmospheric history of this ratio, typically extending back about one century from the present (Farmer and Baxter, 1974; Freyer and Wiesberg, 1974; Galimov, 1976; Rebello and Wagener, 1976; Stuiver, 1977; Wilson, 1978; Freyer, 1979). From the results obtained so far it is not very clear how to extract the atmospheric trend.

This finding is not surprising since there are many factors that can interfere with the tree's recording of the atmospheric carbon isotopic composition. First of all there is the problem of cyclic enrichment; that is, plants taking up CO_2 that is derived in part from their own respiratory processes and is, therefore, isotopically light (Wickman, 1952). Evidence exists that this effect rapidly becomes smaller at greater tree height and that it is smaller at locations not conducive to vertical air stability (Keeling, 1961). Apart from this problem there can be an effect on the actual fractionation from climatic factors such as temperature and precipitation. If this influence could be quantified we would have a tree palaeothermometer and rain indicator, irrespective of whether the effect stems from a direct termperature dependence of the molecular kinetics of photo-

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synthesis or from some other climatic influence acting through the physical condition of the tree. In the latter case the calibration of the thermometer would probably be of less general validity than in case a direct molecular kinetic effect would be operative. Finally, trees are sampling CO_2 from the lower portion of the atmosphere which has a variable $\delta^{13}C$ and CO_2 content. As the rate of CO_2 uptake by the tree is far from constant, this alone will already result in some variability of the $\delta^{13}C$ values produced by the tree.

We report here another attempt at reconstructing the atmospheric $^{13}C/^{12}C$ ratio from tree rings, with special emphasis on the variations in $\delta^{13}C$ that can be found within a single tree. Correlations of $\delta^{13}C$ with climatic factors will be calculated. Finally the interpretation of an atmospheric record, once it exists, will be treated in terms of changes in the volume of the global biomass.

2. The data

2.1. *Sample selection and preparation*

The trees from which samples were taken are from the province of Drenthe, The Netherlands (Table 1). All were mature, high rise trees that had been felled by a severe storm in November 1972. A 40–50 cm thick slice was taken from the lower portion of the stem of each tree, about 0.5 m above the ground. No samples were cut from the innermost 20 rings, as a precaution against the cyclic enrichment effect mentioned.

First, the chronology of the tree rings was established beyond reasonable doubt. In each tree a comparison of ring patterns of four radial directions showed that no rings were partially missing. Neither could any evidence of double rings be found. The average ring patterns of the trees correlated well with each other and also with the oak chronology of the northern Netherlands. This chronology was established by Brongers (1973) and relates the Dutch oaks to the West German master chronology of E. Hollstein (1965).

Small samples about 80 mg each were cut from individual rings and from different parts within the same ring. From one oak (*Quercus rubra* L.) and from the beech, samples were taken exclusively from the latewood portions of the rings. This was done easily in this case because of the large width of the rings. Most samples were given a chemical pretreatment before total combustion and subsequent measurement on a M86 Varian MAT mass spectrometer. A total of about 600 $\delta^{13}C$ determinations have been performed, not counting duplicate measurements. From the distribution of differences between duplicate measurements of the same sample, the standard deviation of a single analysis caused by the mass spectrometer is estimated at 0.08‰. In the same manner the standard deviation for the entire procedure of pretreatment, combustion and measurement is estimated to be 0.11‰. We checked that no correlation existed of $\delta^{13}C$ both with the weight loss by pretreatment and with the yield of combustion, both varying a few percent, probably because of imperfect drying.

As to the chemical pretreatment of the samples prior to combustion, the following procedures have been applied.

(1) No pretreatment, i.e. combustion to CO_2 of whole wood.
(2) Treatment with successive 4% hydrochloric acid (80 °C, 24 h), 4% sodium hydroxide (80 °C, 24 h), and 4% hydrochloric acid solutions (80 °C, several hours), each step separated by thorough washing with demineralized water. This treatment is routinely applied to most organic samples in the Groningen laboratory (AAA treatment).

Table 1. *Description of trees*

Species	Location
Red oak (*quercus rubra* L.)	Sleen (52°45′ N, 6°45′ E), border of small patch of open forest
Common oak (*quercus robur* L.)	Sleen, along road through pastures
Common oak	Norg (53°4′ N, 6°27′ E), forest border
Beech (*Fagus sylvatica* L.)	Sleen, inside small patch of open forest

(3) Preparation of alpha cellulose, successively obtained by extraction with a 2:1 mixture of benzene–ethanol during several hours, rinsing with ethanol, bleaching by a $NaClO_2$ solution and acetic acid (Green, 1963), followed by treatment with 4% NaOH (80 °C, 24 h) and 4% HCl solution (80 °C, several hours). The last three steps again are separated by washing with demineralized water.

2.2. *Influence of pretreatment on results*

Results obtained from the same samples without pretreatment and with the AAA treatment correlate very well (Figs. 1, 2). The direction in which the samples were taken from the tree slab is shown schematically in the figures. The cellulose fraction of the wood also correlates well with the AAA-treated wood, but is consistently about 1 ‰ heavier (Fig. 3). We see that the pretreatment procedure chosen has no influence on the patterns that can be observed, although the absolute differences resulting from varying pretreatments can be considerable. If not specifically mentioned, all further values reported have been obtained from AAA-treated wood. This was mainly a measure of precaution as ^{14}C measurements on the same wood indicated that there had been a slight radial movement of material from other years of growth, which apparently could be removed by the treatments described (Tans et al., 1978).

2.3. *Patterns within a single tree*

Quercus rubra, a fast-growing oak, has been treated first because of the large width of its rings. Some correlation, though not satisfactory, is shown for samples taken from different radial directions (Fig. 4). The largest difference observed within a

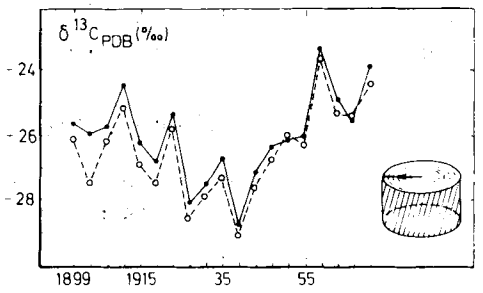

Fig. 1. Quercus rubra L. A comparison of $\delta^{13}C$ measurements of whole wood and the same wood after chemical pretreatment. The direction in which the samples have been taken from the tree has been depicted by a heavy line. Heavy dots, untreated wood, open circles, wood treated with a sequence of hot acid, alkali and acid (AAA pretreatment).

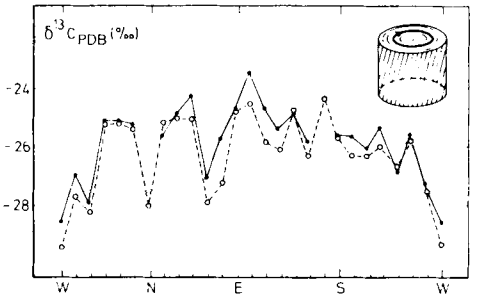

Fig. 2. Quercus rubra L. A comparison of results from whole wood and pretreated wood. Heavy dots, untreated wood; open circles, AAA pretreatment.

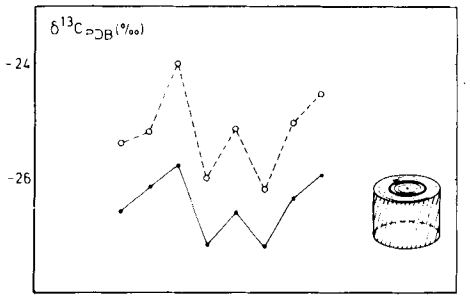

Fig. 3. Quercus robur L. (Sleen). A comparison of results from one ring divided into 8 samples for pure alpha cellulose and AAA pretreated wood. Heavy dots, AAA pretreatment; open circles, alpha cellulose.

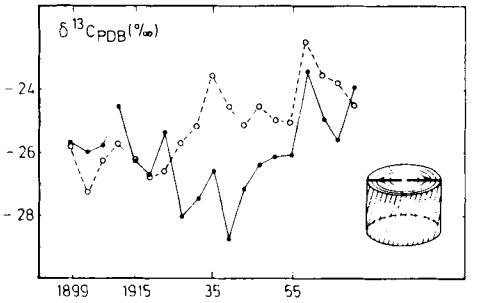

Fig. 4. Quercus rubra L. $\delta^{13}C$ of samples (AAA) in two opposite radial directions. Heavy dots, west side of tree; open circles, east side.

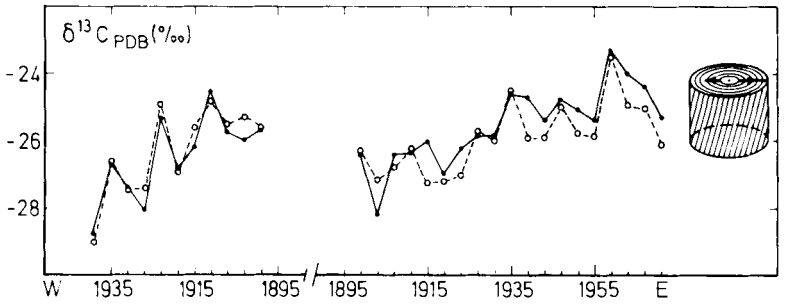

Fig. 5. Quercus rubra L. A comparison of corresponding samples (AAA) separated by a distance of 40 cm in the vertical direction. Heavy dots, upper side of tree slab; open circles, lower side.

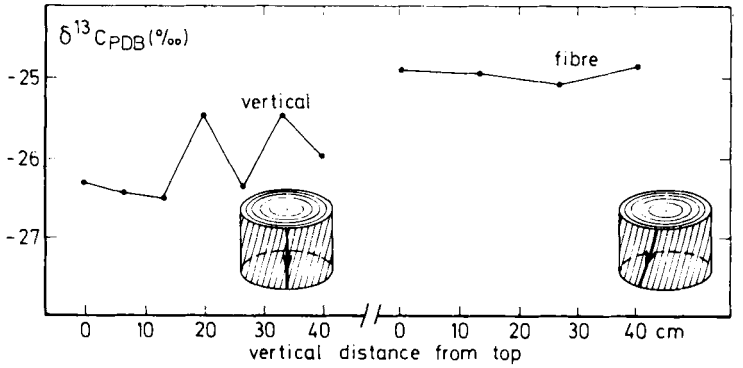

Fig. 6. Quercus rubra L. A detailed picture of $\delta^{13}C$ variations in the vertical direction. AAA pretreated samples. If the sampling follows the fibre very closely, the variation almost disappears.

single year is 4.4‰. Within the same radial direction, however, there is a high correlation between samples taken at a vertical distance of about 40 cm from the top and the bottom of the slab (Fig. 5). However, there is still a discrepancy within a single year of up to 1.3‰. At this point we decided to map the $\delta^{13}C$ patterns of this tree in three dimensions. To proceed, a single ring was sampled in the vertical direction at intervals of 5 cm. The $\delta^{13}C$ values can be seen to fluctuate by up to 0.8‰ (Fig. 6), but close following of the wood fibers reduced this figure to 0.2‰. The fibers were not laid down exactly vertically but as if the tree had responded to a torsional stress. This explains the limited correlation in Fig. 5: each individual fiber appears to have its own $\delta^{13}C$ identity.

As all samples from this tree were taken exclusively from latewood, these findings have a bearing on the current discussion about the isotopic difference between earlywood and latewood and the climatic information that could be extracted from whole tree rings or from the earlywood or latewood portions exclusively (see, for further references, Wigley et al., 1978). It thus seems that the same chemical components taken exclusively from the latewood portion of a single ring still do not yield the same climatic information along the circumference of that ring.

A closer look at one single ring in the circumferential direction reveals a very irregular pattern. The largest difference within the ring of 1938, for instance, is 4.2‰, for 1939 even 4.9‰ (Fig. 7). An excellent correlation, however, exists between the circumferential patterns of consecutive years, still clearly persisting to a ring 7 years older. All these large intra-ring ‰ variations could not be related to intra-ring differences of ring width, that ranged up to a factor of 2, although in a more gradual manner.

For a different tree, *Quercus robur* L., a tree with

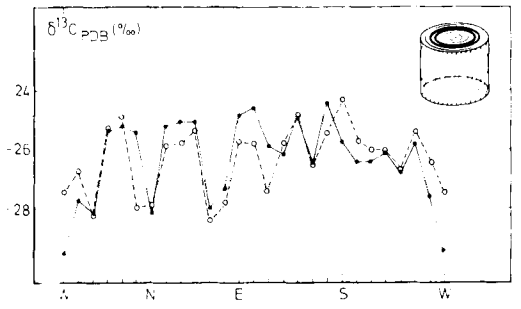

Fig. 7. Quercus rubra L. A comparison of two consecutive rings in the circumferential direction. AAA pretreated samples. Heavy dots, 1939; open circles, 1938.

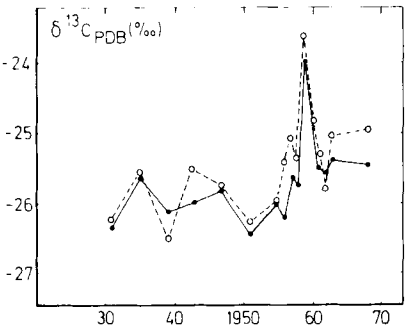

Fig. 8. Quercus rubra L. $\delta^{13}C$ of circumferential average (AAA) samples that have been taken at a vertical distance of 40 cm. Heavy dots, upper side of the tree slab; open circles, lower side.

markedly narrower rings, similar results have been obtained. This time the cellulose fractions were prepared from samples to 2 consecutive years. The 2 years correlate well, but within a single year samples differ up to 2‰.

To explain the intra-ring variations in $\delta^{13}C$, it might be interesting to look into the possibility that the cause is to be found in the roots and in the branch system. The different roots might be subject to different microregimes of water and nutrient supply, influencing $\delta^{13}C$ in the bundle of fibers originating in the roots. Also some branches may experience more radiant heating than others. Another tempting idea would be that there is some translocation of dissolved CO_2 (CO_2 or HCO_3^-) through the roots from the soil to the leaves in varying amounts.

2.4. *$\delta^{13}C$ values for entire rings*

It will be clear from the above results that $^{13}C/^{12}C$ ratios determined from one spot on a tree ring (by taking a core sample) and intended to characterize the ^{13}C fractionation of such a ring might be highly insignificant. It is therefore necessary to scrutinize ^{13}C data—and possibly other isotopes as well—on tree rings on this point. Nevertheless, we might still try to assign a meaningful $\delta^{13}C$ value to specific rings. The close resemblance between patterns of consecutive rings and the isotopic identity of individual vertical fibers suggests that only those isotopic values are meaningful, or better, reproducible, that are averaged along the circumference. In order to test this idea, a total of 12–16 samples were cut from different points along the circumference of one ring and thoroughly mixed before pretreatment and combustion. The same procedure was followed for the same ring, but 40 cm lower in the slab. This procedure was applied to a number of rings (Fig. 8). A second test was performed by mixing the odd-numbered samples apart from the even-numbered. The difference between the odd and the even average samples ranges from 0 to 0.5‰, the average difference being 0.2‰. The distribution of discrepancies between corresponding samples, observed from both tests, does not differ significantly from a normal distribution, so that we can assume the $\delta^{13}C$ values for entire rings, thus obtained, to be normally distributed around their "true" values with an estimated standard deviation of 0.25‰.

2.5. *A $\delta^{13}C$ trend or a tree thermometer?*

Now that we are able to assign reproducible $\delta^{13}C$ values to individual tree rings, it is interesting to intercompare the four trees and look for a $\delta^{13}C$ trend and for the climatic information that they might contain. The final whole-ring $\delta^{13}C$ values are presented in Fig. 9. They represent values for ring-averaged samples.

As has been mentioned in the introduction, the $\delta^{13}C$ values of tree rings depend, in general, on a number of factors: the isotopic composition of the surrounding CO_2, the time of the year photosynthesis takes place, certain climatic factors and most probably a number of other factors that we will group together as the "potential for growth". A very coarse scheme of causal relationships is shown in Fig. 10. The CO_2 content of the atmosphere shows considerable variation not only on a very local basis but also on the mesoscale of the large synoptic weather patterns, due to the activity of

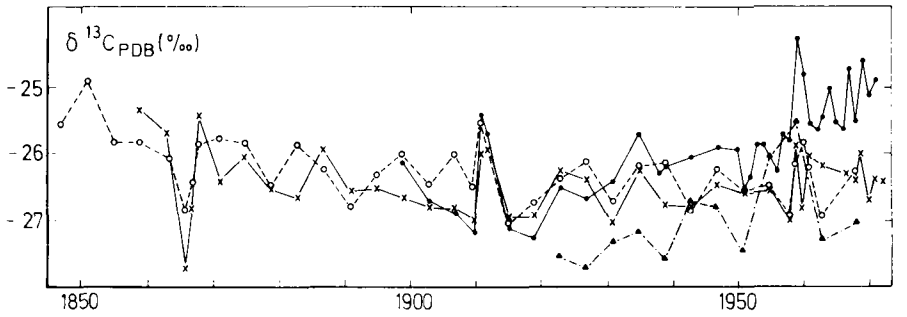

Fig. 9. $\delta^{13}C$ of circumferential average (AAA) samples taken from four different trees in Drenthe, The Netherlands. Heavy dots, *Quercus rubra*; open circles, *Q. robur* (Norg); crosses, *Q. robur* (Sleen); triangles, *Fagus sylvatica*. The estimated (one sigma) error of the $\delta^{13}C$ values is 0.25‰.

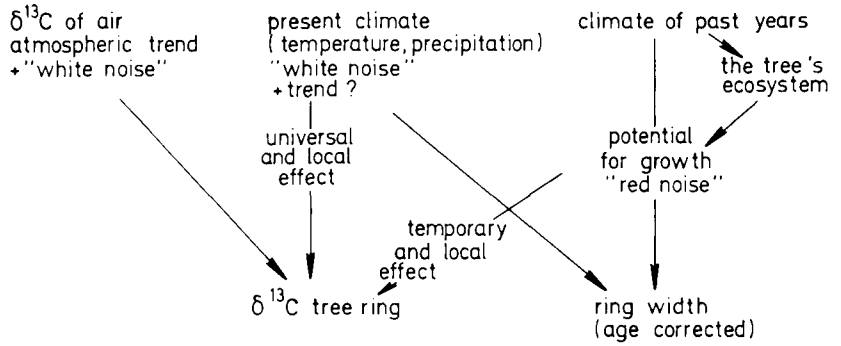

Fig. 10. Simple scheme of causal relationships that have a bearing on carbon isotope fractionation during photosynthesis.

land plants. The air masses "remember" the vegetation of regions they have passed by their changed CO_2 content and $^{13}C/^{12}C$ ratio. Spittlehouse and Ripley (1976) found a variation of up to 7 p.p.m. in the daily minimum CO_2 concentration in summer that they could relate to the varying distance air masses had traveled over land just before reaching their measuring site. As this variation is caused by the activity of the land plants the corresponding $\delta^{13}C$ variation should be up to 0.4‰.

As to the climatic factors, we consider only those that are most important for plant growth, viz. temperature and precipitation. It is evident that the temperature can have a direct net effect on fractionation. Precipitation can act on molecular kinetics through its effect on water stress of the tree. This will result, among things, in more or less stomatal closure and evaporative cooling of the leaves. Finally, the potential for growth represents the integrating effect that prior seasons have on the physical well-being of the tree. The influence on the tree growth of climatic factors prior to the growing season has been described in detail by Fritts (1976). This influence is clearly shown by our trees when autocorrelation functions are calculated from the ring-width curves. The ring widths are found to exhibit simple Markov persistence, with lag-one serial correlation coefficients ranging from 0.50 to 0.85. This general physical state of the tree can have an influence on $\delta^{13}C$, if, for instance, growth starts earlier and is more vigorous in spring, or through different concentrations of growth regulating substances, which may shift the rate limiting step in photosynthesis and hence the fractionation. This effect on fractionation, however, will be of a local and transitory nature. It is possibly related to ring width.

In searching for a trend or for periodicities in a time series, in a manner that presupposes nothing

as to the nature of the non-randomness, power spectrum analysis is very helpful (Mitchell et al., 1966). The spectrum gives a measure of the contribution of each wavelength to the total variance present in the time series. The climatic data used in this paper are seasonal mean temperatures and precipitation data from 1835 to the present from De Bilt, the Netherlands (Labrijn, 1945), at a distance of about 100 km from the location of the trees. The observed ring widths have been converted into an index (Svenonius and Olausson, 1975) that removes the age trend, as the rings of each tree become, on the average, narrower as the tree grows in size and circumference. After the lag-one serial correlation was determined for the ring-width sequences, no frequency component of any tree was found to differ in a significant way from the null continuum for red noise, the "redness" being determined for each tree by its own lag-one serial correlation. As to the climatic data, no trend or periodicity could be shown to differ significantly from the null continuum for white noise. Unfortunately it was not possible to compute the autocorrelation and the power spectrum of the $\delta^{13}C$ sequences of the trees because of lack of a sufficient number of data points and the inhomogeneous character of the time series. The $\delta^{13}C$ values should have been spaced at regular intervals, preferably of 1 year.

In a controlled laboratory study of the effect of temperature and precipitation on isotope fractionation, one would try to keep all other factors constant. With freely growing trees this obviously cannot be done. We can try, however, to approximate the ideal experiment by correlating only first differences, that is, by matching the change in a climatic factor with the change in $\delta^{13}C$ from the previous values in the time series. In this way we keep the influence of the group of factors that has been called "potential for growth" as small as possible. If their influence is real, they will probably tend to mask a more direct relationship of climate with isotope fractionation. They will increase the total variance of $\delta^{13}C$ while their association with climatic factors may either be positive or negative and may differ with time. The first difference correlation of $\delta^{13}C$ with temperature, precipitation and ring-width index has been calculated for each tree separately, and also for the weighted average of the trees. In Table 2 some coefficients are listed for the weighted average, both of direct correlations and of first difference correlations. The level of significance or, in other words, the chance that the same correlation coefficient (or better) is found

Table 2. *Zero order correlations between $\delta^{13}C$, ring width and climate*

		Direct correlation			Correlations of first difference	
^{13}C-ring-width year		Coefficient	Level of significance		Coefficient	Level of significance
T-ppt	winter	0.48	$\ll 10^{-4}$	ΔT-Δppt	0.46	$\ll 10^{-4}$
	spring	−0.09	not sign.		−0.06	not sign.
	summer	−0.36	10^{-4}		−0.35	10^{-4}
	autumn	0.06	not sign.		−0.01	not sign.
	all year	0.13	not sign.		0.05	not sign.
$\delta^{13}C$-T	winter	−0.06	not sign.	$\Delta\delta^{13}C$-ΔT	0.15	10%
	spring	0.25	1 %		0.42	$<10^{-4}$
	summer	0.39	<1 %		0.46	$\ll 10^{-4}$
	autumn	0.23	1 %		0.19	5%
	all year	0.27	<1%		0.48	$\ll 10^{-4}$
δ^{13}-ppt	winter	−0·18	<5%	$\Delta\delta^{13}$-C-Δppt	−0·30	1 %
	spring	−0·07	not sign.		−0·11	not sign.
	summer	−0·26	<1%		−0·48	$\ll 10^{-4}$
	autumn	−0·01	not sign.		−0·09	not sign.
	all year	−0·24	1%		−0·46	$\ll 10^{-4}$
$\delta^{13}C$-ring-width year		−0·09	not sign.	$\Delta\delta^{13}C$-Δring	−0·30	1 %
T-ring-width year		0·07	not sign.	ΔT-Δring	0·04	not sign.
ppt-ring-width year		0·14	1%	Δppt-Δring	0·19	1 %

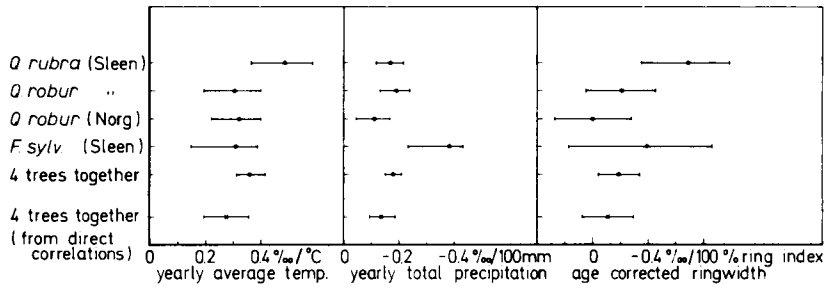

Fig. 11. Estimated second-order regressions of $\delta^{13}C$ on temperature, precipitation and ring width. The regressions have been derived from first differences. A weighted average of the regressions of the four trees is also presented, together with the weighted average of the regressions derived from direct correlations. The error bars correspond to one sigma confidence intervals.

in a sample taken from a normal bivariate population with zero correlation, has also been given. For $\delta^{13}C$ the correlations and levels of significance are much better for a matching of first differences than for a comparison of direct values, as had been expected.

We cannot calculate the (linear) regressions of $\delta^{13}C$ on ring width and on the climatic variables from the variances and convariances found, because these variables are not independent. Their (zero order) correlations are also shown in Table 2. It is seen that it makes no difference whether we match direct values of temperature and precipitation or whether we take first differences, as neither temperature nor precipitation shows a memory effect. We have to determine the correlation between two variables while the other variables are held constant. This is defined as partial correlation and the techniques for calculation have been taken from Kendall and Stuart (1967).

The partial correlations and regressions of $\delta^{13}C$ on ring width, yearly average temperature and total yearly precipitation have been calculated. The estimated regressions and their 68% (one sigma) confidence intervals are shown in Fig. 11. The resemblance between the trees is a clear indication that with $\delta^{13}C$ we indeed have a palaeothermometer of some general validity. This is more nearly true where only two of the trees are of the same species and they have been growing in different environments. However, it is equally obvious that we also have to some degree a palaeo rain gauge, so that we cannot distinguish between the two without invoking the help of other techniques. Both effects are, on the average, of equal magnitude, while the dependence on ring width results to $\delta^{13}C$ variations that are an order of magnitude smaller. The fact that $\delta^{13}C$ in tree rings can be independently and almost equally influenced by temperature and precipitation has been overlooked by most authors searching for a tree palaeothermometer (e.g. Pearman et al., 1976; Wilson and Grinsted, 1977).

Returning to a determination of atmospheric $\delta^{13}C$ from tree rings, we first normalize all $\delta^{13}C$ ring values to a standard yearly average temperature, precipitation and ring width by using the estimated regressions (Fig. 11). In this way the variance of first differences is reduced by a little more than 50%. The estimated standard deviation for whole-ring $\delta^{13}C$ values (0.25‰) accounts for 60% of the variance still remaining, while another 20% is due to the dip in 1866 and the peak in 1912 alone (Fig. 14). Thus we cannot expect to be able to smooth the $\delta^{13}C$ record much further.

A relation of $\delta^{13}C$ with the sapwood–heartwood transition cannot be found in the curves. For the American oak (*Quercus rubra* L.) and the beech (*Fagus sylvatica* L.) the transition took place in the rings of 1962–1964, while in both native oaks (*Quercus robur* L.) the transition was located around 1950.

The extraordinary $\delta^{13}C$ values in 1866 and 1912 we cannot explain at present. They are not coincident with exceptional occurrences in either the climatic temperature and precipitation record, or in the ring-width sequences.

3. The interpretation of an atmospheric ^{13}C trend

A $\delta^{13}C$ trend in time exclusively caused by fossil fuels should resemble an exponential. Such a trend cannot be discerned in the climate-normalized tree ring $\delta^{13}C$ data of Fig. 14. We will now try to better quantify our expectation: to actually calculate it for a simple physical model. The equations defining our model are perturbation equations (Tans, 1979) that describe isotopic exchange between four reservoirs, the atmosphere, the biosphere, the ocean mixed layer and the deep seas. The isotopic exchange is coupled to the exchange of total carbon. These equations are for total carbon:

$$\frac{d}{dt} n_a = -k_3 n_a + k_4 \zeta n_m + \sum_i \gamma_i(t) + \gamma_b(t)$$

$$\frac{d}{dt} n_m = k_3 n_a - k_4 \zeta n_m - k_5 n_m$$

and for the isotopic ratio:

$$N_{bo} \frac{d}{dt} r_b = -k_1 N_{bo} r_b + k_2^* N_{ao} r_a$$

$$N_{ao} \frac{d}{dt} r_a = k_1 N_{bo} r_b - (k_2^* + k_3^*) N_{ao} r_a + k_4^* N_{mo} r_m - \varepsilon_3 (k_3^* R_{ao} n_a - k_4^* R_{mo} \zeta n_m) + \sum_i \gamma_i(t)[R_{\gamma i} - R_{ao}] + \gamma_b(t)[R_{bo} - R_{ao}]$$

$$N_{mo} \frac{d}{dt} r_m = k_3^* N_{ao} r_a - (k_4^* + k_5) N_{mo} r_m + \varepsilon_4 (k_3^* R_{ao} n_a - k_4^* R_{mo} \zeta n_m)$$

The symbols used are defined as follows:

a, b, m	atmosphere, biosphere, mixed layer
(suffix) 0	initial value of variable suffixed
N_i, i = a, b, m	amount of carbon in reservoir i
n_i	perturbation of the above amount
R_i	$^{13}C/(^{12}C + {}^{13}C)$ ratio in reservoir i
r_i	perturbation of the above ratio
k_1, k_2	transfer from biosphere to atmosphere and vice versa
k_3, k_4	transfer from atmosphere to mixed layer and vice versa
k_5	transfer from mixed layer to deep sea
ζ	buffer factor (taken as 10)
k_i^*	^{13}C transfer, corresponding to k_i
$\alpha_i \stackrel{\text{df}}{=} 1 + \varepsilon_i$	k_i^*/k_i, kinetic isotope fractionation factor
γ_i	industrial sources; i = coal, oil, gas, cement
γ_b	net increase or decrease of total global biomass

Admittedly this model is physically very simple. Its use will primarily be to investigate the problems that will have to be solved if we want to reconstruct the atmospheric CO_2 history from a $^{13}C/^{12}C$ time series with any model. The choice of constants closely resembles that of Keeling (1973a) and Oeschger et al. (1975).

The isotopic exchange reactions are treated without approximation in the limit of small perturbations. This is necessary in the case of carbon 13 because fractionation effects are of the same magnitude as the isotopic signal of the input, which itself is the result of isotopic fractionation during photosynthesis.

The flux from the atmosphere to the biosphere and vice versa is taken as constant and independent of the atmospheric CO_2 concentration and as a consequence this exchange only shows up in diluting the isotopic signal in the atmosphere. A decrease or increase in the global biomass can be treated as an extra input to the atmosphere just like the fossil fuels, but with a positive or negative sign respectively and with an isotopic ratio representative of terrestrial plants.

Results are shown in Fig. 12. They are not very sensitive to varying k_1 and k_3. A problem in calculating the expected $\delta^{13}C$ decrease is that it can be sensitive to our choice of ε_3, the kinetic fractionation associated with air–sea transfer, which is essentially unknown. This sensitivity increases when the air and the sea are further removed from equilibrium with each other as is the case when the mixed layer exchanges rapidly with the deeper waters (curves 3, 4 versus 1, 2 in Fig. 12). In our calculations we have varied ε_3 an arbitrary $\pm 8‰$ around the value $-14‰$. The latter value is commonly found when absorbing CO_2 into concentrated alkaline solutions. However, this value may not at all apply to the atmosphere–ocean system where we have movement of dissolved CO_2 instead of the CO_3^{2-} ions in the alkaline case. Furthermore, a significant fraction of the gas

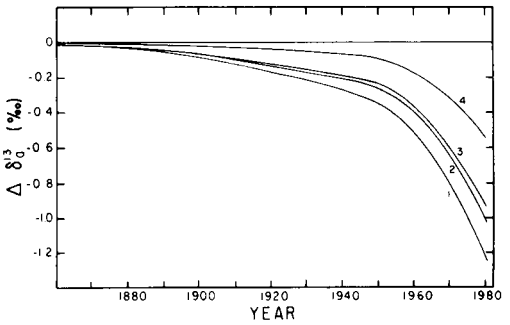

Fig. 12. Calculated effect of fossil fuel combustion on $\delta^{13}C$ changes of atmospheric CO_2. Values assigned to variables as in Table 3 except when mentioned otherwise. Curve 1: $k_5 = \frac{1}{8}$ yr^{-1} and $\varepsilon_3 = -6‰$; 2: $k_5 = \frac{1}{8}$ yr^{-1} and $\varepsilon_3 = -22‰$; 3: $k_5 = \frac{1}{2}$ yr^{-1} and $\varepsilon_3 = -6‰$; 4: $k_5 = \frac{1}{2}$ yr^{-1} and $\varepsilon_3 = -22‰$.

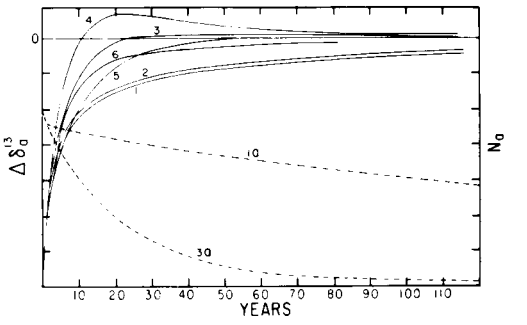

Fig. 13. Calculated response to a spike input at $t = 0$ with $R_{input} = 0.976$. Solid lines: δ^{13}_a; broken lines: n_a. Values assigned to variables as in Table 3 except when mentioned otherwise. Curve 1: $k_5 = \frac{1}{32}$ yr^{-1} and $\varepsilon_3 = -6‰$; 2: $k_5 = \frac{1}{32}$ yr^{-1} and $\varepsilon_3 = -22‰$; 3: $k_5 = \frac{1}{2}$ yr^{-1} and $\varepsilon_3 = -6‰$; 4: $k_5 = \frac{1}{2}$ yr^{-1} and $\varepsilon_3 = -22‰$; 5: $k_1 = \frac{1}{120}$ yr^{-1}, $k_5 = \frac{1}{8}$ yr^{-1} and $\varepsilon_3 = -14‰$; 6: $k_1 = \frac{1}{30}$ yr^{-1} and $k_5 = \frac{1}{8}$ yr^{-1} and $\varepsilon_3 = -14‰$. Curve 1a: $k_5 = \frac{1}{32}$ yr^{-1}; 3a: $k_5 = \frac{1}{2}$ yr^{-1}.

exchange in the real world may take place through air bubbles being swept into the sea surface at higher windspeeds (Kanwisher, 1963), with little or no isotopic fractionation.

More insight into the response characteristics of this model of CO_2 and $^{13}C/^{12}C$ exchange will be gained by calculating the response to a spike input (Fig. 13) of labeled CO_2, starting at $t = 0$.

The disturbance of total carbon equilibrates fast with the disturbance of the mixed layer but is only relatively slowly removed from the atmosphere (Fig. 13, curves 1a, 3a) due to the buffer factor, which prevents the ocean surface from taking up much CO_2. Kinetic isotope effects do not play a role when the atmosphere is in equilibrium with the sea surface as should be expected (Fig. 13, curves 1, 2) but they can be very important in the case of a fast turnover of the mixed layer (Fig. 13, curves 3, 4). It is interesting to note that in the case of k_5 (mixed layer to deep sea transfer) = 1/2 yr^{-1} and ε_3 (kinetic air to sea fractionation) = $-22‰$ the original $\delta^{13}C$ disturbance changes sign after about 10 years due to the fact that in this case the sea surface takes up the ^{12}C component of the added carbon much faster than the ^{13}C component.

On a 100-year time scale the total CO_2 content of the atmosphere acts more or less like an integrating filter for CO_2 inputs and losses while the isotopic ratio signal is removed from the atmosphere an order of magnitude more rapidly. In principle both the total CO_2 content and the $^{13}C/^{12}C$ ratio of the atmosphere could be used to reconstruct a history of biospheric gains and losses.

But the $^{13}C/^{12}C$ ratio is more sensitive to fast transients and can be used only for periods of steady input to (or loss from) the atmosphere if model variables like ε_3 and k_5 have been established to a fair accuracy on the basis of independent data. Furthermore, the $^{13}C/^{12}C$ ratio of the atmosphere when the entire carbon exchange system is at steady state (R_{a0}) has to be very well known, because a constant atmospheric $^{13}C/^{12}C$ ratio does not imply the absence of net biospheric gains or losses. Depending on the real value of R_{a0} the atmospheric CO_2 content could in such a case be either increasing or decreasing at an almost steady rate.

4. The inverse problem

The actual reconstruction of the past atmospheric CO_2 concentration from an atmospheric $^{13}C/^{12}C$ record on the assumption that the variations have been caused, apart from fossil fuel combustion, by biospheric changes is an example of an inverse problem: the output is known and the input that caused it has to be determined. The procedure consists of three steps: the inference of a continuous record of past atmospheric $^{13}C/^{12}C$ ratios from a source of data such as tree rings, the choice of parameters of a global carbon exchange model and the actual solution of the equations that describe the inverse problem.

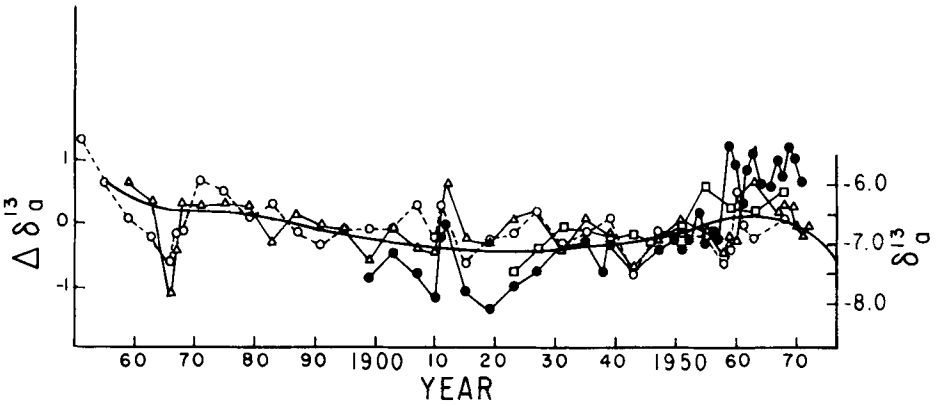

Fig. 14. $\delta^{13}C$ of tree rings normalized to an average yearly temperature of 9 °C, a total precipitation of 700 mm/yr and a standard ring thickness. Symbols are the same as in Fig. 9. The ^{13}C values of each tree have been expressed as deviations from their own individual average (left scale). The heavy full curve is a smoothed cubic spline fit through the data, where each tree has been given equal weight. It can be though to represent the atmosphere (right scale) when the isotopic composition of atmospheric CO_2 is known in 1977 (Keeling et al., 1979).

4.1. *Past atmospheric $^{13}C/^{12}C$ variations*

The tree rings that have been measured to date still show much divergence and we do not yet have enough criteria to make a judgment on their validity and representativeness. For the purpose of this article we will take the line drawn through the date of our four trees (Fig. 14) as representing the atmospheric $^{13}C/^{12}C$ history. However, it should be stressed that we do not claim that the real history actually did follow our curve. We will try to determine what conclusions can or cannot be drawn from such an isotopic time record. The curve of Fig. 14 has been obtained by fitting a smoothed cubic spline through the data (Reinsch, 1967) while giving equal weight to all trees. The $\delta^{13}C$ decrease between 1956 and 1978 has been determined to be -0.55 ± 0.13‰ by actual direct atmospheric measurements (Keeling et al., 1979). The fitted curve was forced to reproduce this decrease by assigning a low $\delta^{13}C$ value with a high weight to 1979.

Table 3. *Model parameters to reconstruct a history of biota growth and shrinkage and atmospheric CO_2 levels from $^{13}C/^{12}C$ data*

Parameter	Preferred value
N_{ao}	615·6 gigaton C
N_{mo}/N_{ao}	1·2
N_{bo}/N_{ao}	2·5
k_3^{-1}	7·7 yr
k_5^{-1}	6·5 yr
k_1^{-1}	60 yr
ζ	10
R_y/R_s	0·976 (coal) 0·974 (oil) 0·960 (gas) 1·000 (cement)
R_{bo}/R_s	0·975
R_{ao}/R_s	0·9935
R_s	isotopic ratio of PDB standard
Fossil fuel input	from Keeling (1973b) and Rotty (1973)

4.2. *Equations for the inverse problem*

Again the model of Section 3 will be employed. The choice of parameters is given in Table 3. They have been chosen such that the time response of the model will closely resemble the box diffusion model of Oeschger et al. (1975) for a characteristic frequency of $1/30\ y^{-1}$.

In a linear box model the course in time of all the boxes is uniquely determined from the initial conditions and the input function. Conversely if the initial conditions of the system and the time behaviour of one box is known, the input can be derived in a unique way in case the input is known to be confined to one box.

If the isotopic composition of the input is known, then also the isotopic ratios in all boxes are uniquely determined. Conversely if both the concentration and the isotopic ratio of one box are

known, then the input and its isotopic composition can be uniquely derived. But if only the time record of the isotopic ratio of one box is known, the input can still be reconstructed in a unique way by making an assumption on the isotopic ratio of the input. This is tantamount to reconstructing historic CO_2 levels since they follow directly from the input once that has been established.

The above remarks can be read from the equations for the inverse problem that are given below. They are identical to those of Section 3 except that R_a is now to be regarded as the independent variable whereas the source function has become a dependent variable. For the isotopic case with R_a, the atmospheric isotopic ratio, as the independent variable they are:

$$\begin{pmatrix} 0 \\ N_{b0}\dfrac{d}{dt}r_b \\ N_{m0}\dfrac{d}{dt}r_m \end{pmatrix} + \begin{pmatrix} 1 & k_1 & k_4^* \\ 0 & k_1 & 0 \\ 0 & 0 & k_4^* + k_5 \end{pmatrix}$$

$$\times \begin{pmatrix} \text{Source}^* \\ N_{b0}r_b \\ N_{m0}r_m \end{pmatrix} = \begin{pmatrix} k_2^* + k_3^* \\ k_2^* \\ k_3^* \end{pmatrix} N_{a0}r_a +$$

$$+ \begin{pmatrix} N_{a0}\dfrac{d}{dt}r_a \\ 0 \\ 0 \end{pmatrix} + \begin{pmatrix} \varepsilon_3 \\ 0 \\ \varepsilon_4 \end{pmatrix}$$

$$\times (k_3^* R_{a0} n_a - k_4^* R_{m0} \zeta n_m)$$

where the isotopic input is defined as:

$$\text{source}^* = \sum_i \gamma_i(t)[R_{\gamma i} - R_{a0}] + \gamma_b(t)[R_{b0} - R_{a0}]$$

The notation has been kept the same as in Section 3. As these equations are formulated directly in terms of isotopic ratios R, they are particularly well suited for the solution of this type of inverse problem where no concentrations but only ratios are known initially. These equations can be Laplace transformed and the 3×3 matrix inverted. After back transformation to the time domain, we have to obtain the solution in a reiterative manner because of the terms with ε_3 and ε_4 which require a knowledge of n_a and n_m. The starting point is to set n_a and n_m equal to zero and obtain isotopic source terms which lead to chemical source terms if we assume values $(R_{b0} - R_{a0})$ and $(R_i - R_{a0})$ for the isotopic ratio of the source terms. The first approximation to n_a and n_m is then calculated from the chemical source terms. Now the next approximation to the isotopic source is obtained from the inverse equations with the first approximation to n_a and n_m inserted in them and so on. This procedure has been tested to be rapidly converging.

4.3. *Results and discussion*

The input from the biosphere to the atmosphere between 1855–1977 is obtained from our $\delta^{13}C$ curve by subtracting the (known) amount of fossil fuels from the total source function as calculated. Under varying assumptions the most persistent features (Fig. 15) are a net release of carbon from the biosphere during the last part of the nineteenth century and the first half of this century, changing to a net uptake around 1950 which comes to a halt in very recent years. This general behavior could already have been more or less guessed from the tree ring curve (Fig. 14) which is especially true for the sharp rise and fall of $\delta^{13}C$ between 1950 and 1980.

But how sensitive are the results to the assumptions that we have to make? Our equations have been formulated in terms of perturbations from steady-state values and if we consider perturbations for the atmosphere we have to also consider them for the other reservoirs in contact with the atmosphere: the biosphere and the ocean mixed layer. We have to prescribe initial values (for 1855, when the calculation starts) to the $\delta^{13}C$ perturbation from steady state of the biosphere and the mixed layer. These initial values result from previous interactions that we do not know. In this respect we could think of changes in the storage of carbon by plants and their fractionation due to historic climatic variations such as the little ice age.

In this connection an inconsistency can be noted in our equations because the isotopic labeling of the

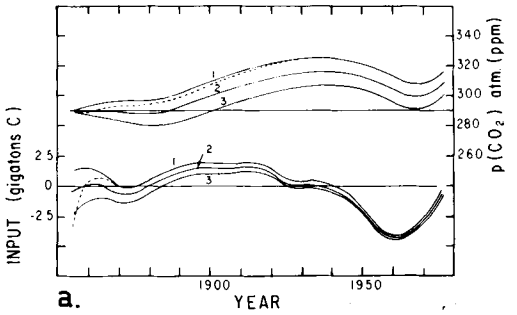

Fig. 15a. Release of carbon (in gigaton/yr, left scale) from the biota to the atmosphere and atmospheric CO_2 levels (in p.p.m.v., right scale) as calculated from $\delta^{13}C$ of tree ring curve (Fig. 14). Sensitivity to assumptions on initial (1855) values of r_b and r_m. Curve 1: $r_{bI} = +0.5‰$, $r_{mI} = 0‰$; 2: $r_{bI} = 0‰$, $r_{mI} = 0‰$; 3: $r_{bI} = -0.5‰$, $r_{mI} = 0‰$. Broken line: $r_{bI} = +0.5‰$, $r_{mI} = -0.5‰$. All curves $n_{aI} = 0$, $n_{mI} = 0$, $\varepsilon_3 = -14‰$ and preferred values of Table 3. (Subscript I for initial value.)

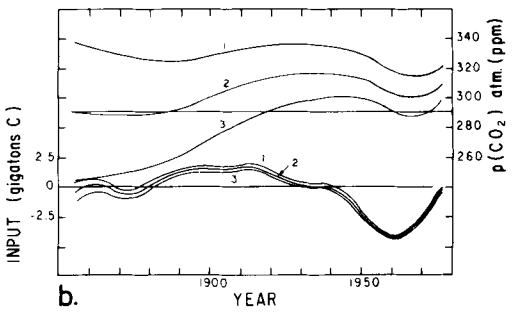

Fig. 15c. Sensitivity to assumptions on the location of floating tree-ring curve with respect to zero perturbation level (steady state) of atmosphere. Curve 1: tree-ring average (TRA) equals $r_a = 0$; 2: TRA $-0.2‰$ equals $r_a = 0$; 3: TRA + $0.2‰$ equals $r_a = 0$. Sensitivity to assumptions on kinetic fractionation during air to sea transfer. Curve a: $\varepsilon_3 = -6‰$; $\varepsilon_3 = -22‰$. All curves: initial values set to 0 and preferred values of Table 3.

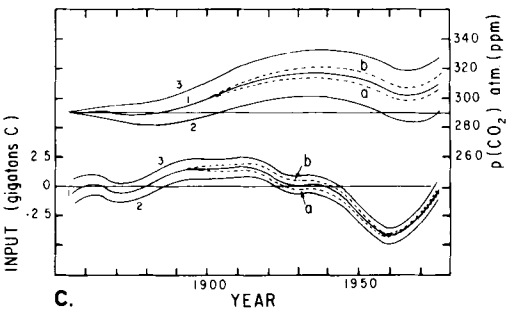

Fig. 15b. Sensitivity to assumptions on initial (1855) values of N_a. Curve 1: $n_{aI} = 10^5$ GT; 2: $n_{aI} = 0$ GT; 3: $n_{aI} = -10^5$ GT. All curves $r_{bI} = r_{mI} = 0$, $\varepsilon_3 = -14‰$ and preferred values of Table 3.

source has always been assumed to be constant. However, a change of this labeling by $0.5‰$ is not of much consequence since our calculation of the source would be affected to only 3% ($\simeq 0.5‰/18‰$). On the other hand, the atmospheric $^{13}C/^{12}C$ ratio will be appreciably affected by its exchange with the biota. If we assume the biota to have a below steady state $^{13}C/^{12}C$ value, this exchange will also tend to lower the atmospheric ratio. Our calculated source has to counter this tendency since the atmospheric $^{13}C/^{12}C$ has already been fixed by the observations. As the source term is only the small difference between two large fluxes of carbon entering and leaving the biota, it can be affected to a fair amount by our assumption on the initial value of r_b (r_{bI}). In Fig. 15a we assumed r_{bI} to vary $\pm 0.5‰$ and the resulting differences in the computed source functions are shown, together with the historic CO_2 levels that go with them. The calculated input difference levels off with an e-fold time approximately equal to the average assumed age (60 yr) of the biota. As the $\delta^{13}C$ perturbations of the mixed layer are short lived, the mixed layer initial condition does not have much influence on the results (Fig. 15a, broken line).

Very different curves of the historic CO_2 level (Fig. 15b) are found to be consistent with our $\delta^{13}C$ curve depending on the assumed initial perturbation of the atmosphere, ± 45 p.p.m. CO_2. A zero perturbation has always been assumed to correspond to a level of 290 p.p.m. The effect of a different initial (and unknown!) CO_2 level on the inferred CO_2 level of later years dies out only very slowly with a decay time approximately equal to the decay time of a total CO_2 perturbation of the atmosphere (Fig. 13).

A crucial assumption in interpreting tree ring $\delta^{13}C$ records is how they relate to the deviation of $\delta^{13}C$ of the atmosphere from its steady-state value. Each tree ring curve is displaced by a certain amount from the atmospheric curve it is intended to represent. The displacement can be different for each tree and we hope that it is at least (on the average) constant in time. Any curve from tree rings that extends into the second part of the

twentieth century can be fixed to directly measured atmospheric $^{13}C/^{12}C$ ratios. In our case the average of the trees would then be located at $\delta^{13}_{a} = -6.65‰$ However, it would be purely accidental if this number were the actual atmospheric steady-state value. Therefore, whether we assign absolute or relative numbers to a tree ring derived curve does not help us in establishing how far from steady state each curve actually is because we do not know where the atmosphere is at present with respect to steady state.

In Fig. 15c we show the result of shifting the assumed atmospheric steady state $\pm 0.2‰$ from the average of the trees. The computed input from the biota to the atmosphere between 1840 and 1940 totals 55 ± 45 gigatons of carbon for these cases. The reason being that a constant nonsteady state $\delta^{13}C$ value can be maintained only by a continuous source or drain of labeled CO_2 and results therefore in considerable differences in CO_2 level.

The effect of varying the kinetic air to sea isotopic fractionation factor, represented by ε_3, has also been shown in Fig. 15c (broken lines). The effect is larger the further the system is removed from steady state (mostly during fast transients).

Up to this point no use has been made of direct atmospheric CO_2 measurements during the latter part of the nineteenth century (Callendar, 1958) and at Mauna Loa Observatory (Keeling et al., 1976). If we could be confident that our $\delta^{13}C$ curve tracked the atmosphere accurately, these direct CO_2 data would constitute a powerful tool to determine steady-state values of both the atmospheric CO_2 concentration and its $^{13}C/^{12}C$ ratio. The average CO_2 slope between 1890 and 1970 would give us the steady-state $^{13}C/^{12}C$ ratio (Fig. 15c) and taking other values for the steady-state CO_2 concentration would shift the entire CO_2 curve parallel up and down until it fits with the Mauna Loa observations. It is to be remembered at this point that our calculations deal only with perturbations.

The behavior of our $\delta^{13}C$ curve can in no way be made to fit the observed CO_2 record at Mauna Loa. This inconsistency is caused by the enormous jump in $\delta^{13}C$ values during the late fifties of one tree, *Q. rubra*. However, deleting this tree from the record would not be a very scientific procedure since we would then be selecting results instead of samples. Once we have decided that certain samples are the proper ones to analyze, we are allowed to delete them afterwards only in case we can prove that the results are invalid either on the basis of experimental mistakes or because an as yet unknown mechanism is discovered which renders them invalid.

5. Conclusions

The assessment of small changes with time in a diverse and not well-defined reservoir of carbon as the earth biosphere, including soil organics, is an immensely complex task. Yet its importance for the global carbon cycle in general and future atmospheric CO_2 burdens in particular is obvious. It therefore seems to be a fortuitous circumstance that nature provides for a well-defined and very well-mixed reservoir, the atmosphere, in which she performs the integration for us.

However, the sampling instruments that we have at our disposal for historic $^{13}C/^{12}C$ ratios and CO_2 levels, trees, are complicated organisms that are not dedicated to this task. It may still take a large effort before we understand how trees as atmospheric samplers change their calibration. More specifically, they apparently can produce values that differ up to 5 per mil in $\delta^{13}C$ in neighboring spots in the same ring. The fractionation averaged over an entire ring can display sudden year-to-year jumps exceeding 1 per mil in $\delta^{13}C$ that do not seem to be related to ring thickness, climatic variables or growth phenomena like the heartwood–sapwood transition. Similar but smaller and more gradual changes in fractionation will in almost all cases go unnoticed and be mistaken for an atmospheric $^{13}C/^{12}C$ trend. Therefore, at the present state of knowledge about isotopic fractionation in tree rings the only way to guard against such apparent changes in fractionation seems to be to average a very large number of trees. When we know more about the causes of these variations in fractionation it might be possible to select species and sites where the fractionation is much less variable.

When it comes to interpreting the record that has been obtained in terms of historic CO_2 levels, our calculations show that the average of the trees should be obtained to great precision, in the vicinity of $0.1‰$ in $\delta^{13}C$. Part of this precision could be obtained by reducing the variance displayed by individual trees by an optimal use of correlations that in many cases will exist with climatic (and

other) variables. Related to the requirement of precision is that the record should be as homogeneous as possible. In other words, great attention has to be given that no shifts of the "calibration" enter the record when trees are combined that span different time periods.

It is very important that a very long record be obtained so as to reduce the influence of our uncertainty about the initial conditions. Typically the record would have to start 100 years before the period we are interested in.

6. Acknowledgments

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REFERENCES

Brongers, J. A. 1973. Dendrochronological investigations of recent oak (*Quercus* sp.) in the Netherlands. *Berichten Rijksdienst Oudheidk. Bodemonderzoek 23*, 459–464.

Callendar, G. S. 1958. On the amount of carbon dioxide in the atmosphere. *Tellus 10*, 243–248.

Farmer, J. G. and Baxter, M. S. 1974. Atmospheric carbon dioxide levels as indicated by the stable isotope record in wood. *Nature 247*, 273–275.

Freyer, H. D. and Wiesberg, L. 1974. Dendrochronology and ^{13}C content in atmospheric CO_2. *Nature 252*, 757.

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

Fritts, H. C. 1976. *Tree rings and climate.* London: Academic Press.

Galimov, E. M. 1976. Variations of the carbon cycle at present and in the geological past. In *Proc. 2nd Int. Symp. on Environmental Biogeochemistry, Vol. 1* (ed. J. O. Nriagu). Ann Arbor, Mich.: Ann Arbor Science Publishers, 3–11.

Hollstein, E. 1965. Jahrringchronologische Datierung von Eichenhölzern ohne Waldkante. *Bonner Jahrbücher 165*, 12–27.

Kanwisher, J. 1963. Effect of wind on CO_2 exchange across the sea surface. *J. Geophys. Res. 68*, 3921–3927.

Keeling, C. D. 1961. The concentration and isotopic abundances of carbon dioxide in rural and marine air. *Geochim. Cosmochim Acta 24*, 277–298.

Keeling, C. D. 1973a. The carbon dioxide cycle: reservoir models to depict the exchange of atmospheric carbon dioxide with the oceans and land plants. In *Chemistry of the lower atmosphere* (ed. S. I. Rasool). New York, London: Plenum, 251–329.

Keeling, C. D. 1973b. Industrial production of carbon dioxide from fossil fuels and limestone. *Tellus 25*, 174–197.

Keeling, C. D., Bacastow, R. B., Bainbridge, A. E., Ekdahl, C. A., Guenther, P. R., Waterman, L. S. and Chin, J. F. 1976. Atmospheric carbon dioxide variations at Mauna Loa observatory, Hawaii. *Tellus 28*, 538–551.

Keeling, C. D., Mook, W. G. and Tans, P. P. 1979. Recent trend in the $^{13}C/^{12}C$ ratio of atmospheric carbon dioxide. *Nature 277*, 121–123.

Kendall, M. G. and Stuart, A. 1967. *The advanced theory of statistics, Vol. 2.* London: Charles Griffin, 278–345.

Labrijn, A. 1945. Het klimaat van Nederland gedurende de laatste 2½ eeuw. Thesis, Univ. of Utrecht, The Netherlands. (In Dutch.)

Mitchell, J. M., Dzerdzeevski, B., Flohn, H., Hofmeyr, W. C., Lamb, H., Rao, K. N. and Wallen, C. C. 1966. *Climatic change.* W.M.O. Tech. Note 79, Geneva.

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

Pearman, G. I., Francey, R. J. and Fraser, P. J. B. 1976. Climatic implications of stable carbon isotopes in tree rings. *Nature 260*, 771–772.

Rebello, A. and Wagener, K. 1976. Evaluation of ^{12}C and ^{13}C data on atmospheric CO_2 on the basis of a diffusion model for oceanic mixing. In *Proc. 2nd Int. Symp. on Environmental Biogeochemistry, Vol. 1* (ed. J. O. Nriagu). Ann Arbor, Mich.: Ann Arbor Science Publishers, 13–23.

Reinsch, C. H. 1967. Smoothing by spline functions. *Num. Math. 10*, 177–183.

Revelle, R. and Munk, W. H. 1977. The carbon dioxide cycle and the biosphere. In *Energy and climate*, Ch. 10. Wash, D.C.: National Academy of Sciences, 140–158.

Rotty, R. M. 1973. Commentary on an extension of calculative procedure for CO_2 production. *Tellus 25*, 508–516.

Spittlehouse, D. L. and Ripley, E. A. 1977. Carbon dioxide concentrations over a native grassland in Saskatchewan. *Tellus 29*, 54–65.

Stuiver, M. 1978. Atmospheric carbon dioxide and carbon reservoir changes. *Science 199*, 253–258.

Svenonius, B. and Olausson, E. 1975. The variations in

annual rings of trees. Some methodical problems. *Geol. Föreningens i Stockholm Förhandl. 97*, 174–179.

Tans, P. P., de Jong, A. F. M. and Mook, W. G. 1978. Chemical pretreatment and radial flow of ^{14}C in tree rings. *Nature 271*, 234–235.

Tans, P. P. 1980. On calculating the transfer of carbon 13 in reservoir models of the carbon cycle. To appear in *Tellus*.

Wickman, R. E. 1952. Variations in the relative abundance of the carbon isotopes in plants. *Geochim. Cosmochim. Acta 2*, 243–254.

Wigley, T. M. O., Gray, B. M. and Kelly, P. M. 1978. Climatic interpretation of $\delta^{18}O$ and δD in tree rings. *Nature 271*, 92–94.

Wilson, A. T. 1978. Pioneer agriculture explosion and CO_2 levels in the atmosphere. *Nature 273*, 40–41.

Wilson, A. T. and Grinsted, M. J. 1977. $^{12}C/^{13}C$ in cellulose and lignin as palaeothermometers. *Nature 265*, 133–135.

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

УРОВНИ CO_2 В ПРОШЛОМ И ОТНОШЕНИЕ $^{13}C/^{12}C$ В КОЛЬЦАХ ДЕРЕВЬЕВ

Найдено, что различие в отношениях $^{13}C/^{12}C$ очень велики между кольцами для четырех голландских деревьев. В некоторых случаях превышали 4‰ для $\delta^{13}C$. Даже отношения $^{13}C/^{12}C$, осредненные по всем кольцам, все еще проявляли резкие скачки свыше 1‰ в содержании $\delta^{13}C$ от года к году. Найдены значительные корреляции величины $\delta^{13}C$ в кольцах с годично осредненными температурой и осадками. Реакция атмосферы на ввод CO_2, помеченный ^{13}C, вычислялась для модели возмущений из 3½ боксов, состоящей из атмосферы, биосферы, перемешанного слоя океана и отвода возмущения в глубокие слои океана. Временной ряд концентраций ^{13}C, осредненный по 4 дереьям, интерпретируется с помощью названной модели в терминах роста и уменьшения биосферы в прошлом.