^{13}Carbon-Isotope Decrease in Annual-Rings of Twentieth-Century Trees

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The steadily increasing global carbon dioxide concentration is further recognized through the decreasing trend of ^{13}C/^{12}C isotopic ratio in the annual rings of twentieth-century trees. The decrease is averaged to about 0.012 per mil per year which is attributed not only as due to anthropogenic fossil-fuel burning but also to the man's impact on the land pattern.

Introduction

The longterm increase of carbon dioxide in the atmosphere resulting from fossil-fuel burning (Fossil CO$_2$) and through man's changing of landbiota (Biospheric CO$_2$) is known to be registered in the wood of tree-rings. Both fossil-fuel and biospheric carbon dioxide are marked with a ^{13}C isotope deficit of about $-18‰$ (on the PDB scale) against the background atmospheric carbon dioxide. The fossil-fuels are however completely decayed with respect to ^{14}C isotope. A decrease of ^{14}C/^{12}C in the atmospheric carbon dioxide therefore indicates an increase through fossil-fuel sources only, whereas ^{13}C/^{12}C decrease reflects both anthropogenic and biospheric emissions into the atmosphere. The trees absorb carbon dioxide from the atmosphere during the process of photosynthesis and build up sugars which are converted among others into the wood components like cellulose, hemicellulose, lignin etc. Each ring therefore gives a representative record of the isotopic composition of the atmosphere at the time of the formation of the ring.

Method

A single wood component (cellulose in this case) is used throughout the investigation since each component has its characteristic carbon isotope ratio and also the relative fractions of the components in each

ring may not be constant over the entire age of a tree (Wagener and Rebello [1]). Two ring samples are used throughout. Cellulose (which is 40–50% of whole wood) is extracted out of the wood according to methods described by Sohn and Reiff [2] and Kürschner and Popik [3]. In this way an acid hydrolysis of the cellulose and the use of organic reagents are avoided. The cellulose is burnt to carbon dioxide gas in a special combustion apparatus (modified after Craig, [4]) in an atmosphere of pure oxygen at a constant pressure of 150 torr at 800 ± 50 °C. The isotope ratios are measured in a double focussing massspectrometer Micromass 602C in comparison with a standard carbon dioxide gas of known isotopic composition. The relative isotopic change is expressed in conventional δ^{13}C units

$$\text{where } \delta^{13}\text{C (‰)} = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{wood}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \times 1000.$$

All ^{13}C data are converted to the PDB scale because of its wide usage as the reference scale.

Results and Discussion

The analysed trees (a total of 7) came from three different research Stations in North Carolina USA. The exact locations and their climatic characteristics are extensively described in de Silva [5]. The trees were so selected that they were not influenced by any unwanted local disturbances which may cause anomalous ^{13}C oscillations. For each analysed tree the δ^{13}C values over its entire time of record (1900–1975) were calculated as deviations from its tree-specific value which is the average δ^{13}C for the period 1930–1959. This period is selected arbitrarily but however any anomalous values due to juvenile and any possible aged effects are in this way avoided. The tree specific δ^{13}C values are given in Table I.

Table I. Tree-specific δ^{13}C-values of the analysed trees and their localities in North-Carolina, USA

Tree art	Locality	δ^{13}C$_{\text{PDB}}$
1. *Pinus serotina*	Wilmington	– 26.40
2. *P. virginiana*	Reidsville	– 25.29
3. *Populus alba*	Reidsville	– 23.75
4. *Quercus alba*	Reidsville	– 23.89
5. *Q. rubra*	Reidsville	– 25.24
6. *Q. rubra var. borealis*	Waynesville	– 23.73
7. *Q. alba*	Waynesville	– 25.40

Diagram 1. $\delta^{13}C$ decrease in *Pinus serotina* during the period 1890–1975 and the corresponding ring widths. The juvenile effect is to be observed during the period 1890–1910.
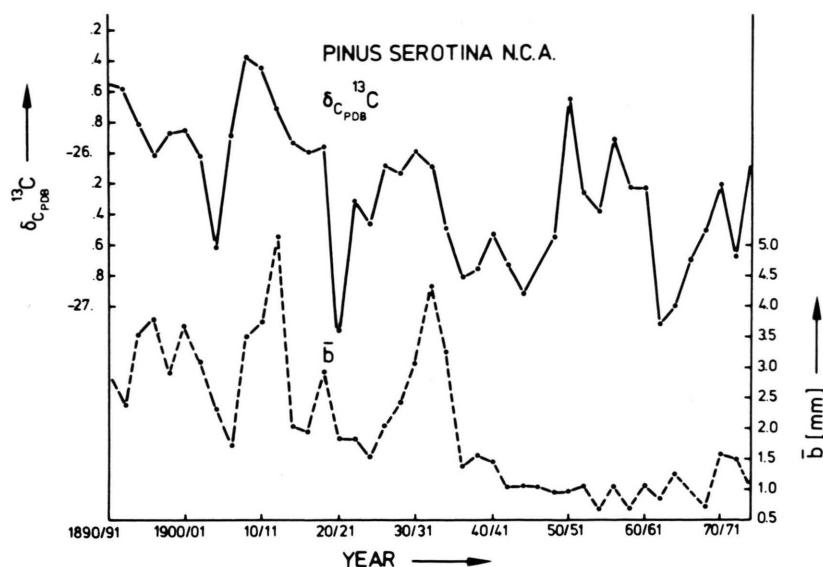
The trees at their young stages are known to show decreasing ^{13}C values due to reabsorption of the respiratory carbon dioxide which is depleted in ^{13}C isotope in comparison to atmospheric back-ground carbon dioxide. As the tree grows the mixing of the respiratory and the atmospheric carbon dioxide under the tree canopy is enhanced and the tree begins to register the atmospheric carbon dioxide. This effect is to be seen in diagram 1.

All samples were taken at a height of about one meter from the ground. It is shown however that the $\delta^{13}C$ variations of different samples taken at varying heights from the same tree but with the same number of rings starting from the pith, lie within the experimental range of error (5), (see Table II). This indicates that there is no noticeable change in the isotopic fractionation as the distance between the place of sugar production and its place of deposition in the annual-rings along the trunk increases. This is to be expected if the sugars are transported through the phloem sieve tubes according to a mass transfer mechanism. The radius of investigation is found to be of less significance contrary to earlier observations (de Silva [5]).

Diagram 2 shows the trend of the ^{13}C decrease for this century as obtained by averaging the $\delta^{13}C$ data of all analysed trees (all $\delta^{13}C$ values are given in de Silva [5]). The form of the curve confirms former measurements at other regions (Farmer and Baxter [6], Freyer and Wiesberg [7], Stuiver [8]). An overall ^{13}C decrease is to be recognised with a well marked interruption during the period 1940–1955. The mean $\delta^{13}C$ during the periods 1900–1920, 1930–1940, 1955–1970 decreases with almost linear slopes.

An increasing trend is to be seen between 1940–1955 interval, a trend observed by many other
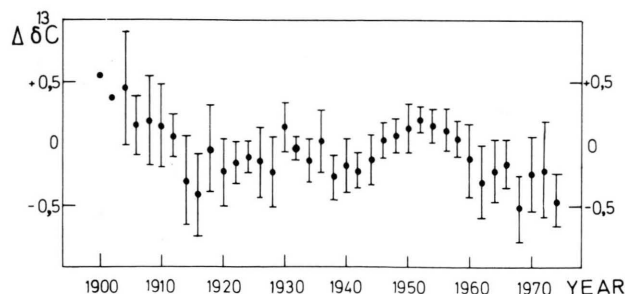

Diagram 2. Averaged $\delta^{13}C$ values of 7 trees from North Carolina, USA, plotted as deviations from the average of their tree-specific values calculated for the period 1930–1959.

Table II. Average $\delta^{13}C$-values of samples taken at three different heights from the stem of *Pinus sylvestris*. Each sample includes twenty-five rings counted from the pith towards the bark.

Position of sample (distance above ground)	$\delta^{13}C_{PDB}$
1 meter	-24.84 ± 0.11
2 meters	-24.89 ± 0.13
3 meters	-24.79 ± 0.18

authors (Stuiver [8]). The exact cause of this effect is not established but increasing global temperatures which reached their maximum in 1940 could have caused a reflux of ocean carbon dioxide into the atmosphere and alongwith a ^{13}C enrichment.

When fitted with a linear regression curve a ^{13}C decrease of 0.012‰ per year is observed. Extrapolation upto 1850 gives a total ^{13}C decrease of $-1.8‰$ for the period of industrialisation. This decrease exceeds what could be attributed alone to the fossil-fuel emissions of carbon dioxide into the atmosphere even if 50% of the excess carbon dioxide dissolves in the ocean. Therefore other carbon dioxide emission sources have to be recognised. According to Wilson [10] an almost world-wide explosion of pioneer agriculture during the latter half of the nineteenth century released one and a half times the total amount released through fossil-fuel burning upto 1950. The fraction of this biospheric carbon dioxide that remained in the atmosphere depleted the $\delta^{13}C$ of the atmosphere by 0.9‰. It is clear that man's contribution to the increasing carbon dioxide concentrations through agricultural practices is of comparable magnitude to that released by the consumption of fossil-fuels. However, before we can draw conclusions to their amounts more data extending to the pre-industrial time are needed. Furthermore the carbon dioxide exchange processes between the atmosphere, biosphere and ocean should be reviewed.

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