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A remarkable relationship of the stable carbon isotopic compositions of wood and cellulose in tree-rings of the tropical species *Cariniana micrantha* (Ducke) from Brazil

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ABSTRACT

The stable isotopes of carbon were analysed in total wood and cellulose from the tree-rings of the tropical wood species *Cariniana micrantha* (Ducke). The aim was to examine the isotopic relationship between total wood and its cellulose over the last two and a half centuries. Although the correlation for the whole time period is very high ($r = 0.96$) it is remarkable that different sub-periods deviate strongly from this close relationship. Consequently, a good correlation from the subset of a longer isotopic record cannot necessarily prove its validity for the whole record. The study indicates that changes of the carbon isotopes of cellulose and of total wood show sometimes during short sub-periods different isotope patterns presumably caused by different environmental effects. Thorough calculations indicate that strong variations within the isotopic record especially changes of the isotopic level along a chronology lead to high correlations between $δ^{13}C_{\text{wood}}$ and $δ^{13}C_{\text{cel}}$. Contrary thereto subsections with low isotopic variability lead to low correlations. The results imply that long term trends provide similar patterns. Therefore, if long term trends are of interest such as e.g. in climate reconstruction then total wood can be analysed in favour of cellulose, thus saving a tremendous amount of work. However, if short term aspects from a longer record are of interest, cellulose and total wood may sometimes provide different information. In addition it is hypothesized that during intervals of low isotopic variability the proportions of the various wood components may change relative to each other, leading for certain time intervals to different isotope patterns.

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1. Introduction

In recent decades, numerous carbon isotope studies in tree-rings have been performed with the objective to reconstruct climate variations of the past. Tree-ring chronologies represent unique terrestrial archives with annual resolution which can absolutely be dated and go back for hundreds, sometimes thousands of years (e.g. Freyer and Belacy, 1983; Pilcher et al., 1984; Briffa et al., 1990; Lipp et al., 1991; Zetterberg et al., 1996; Lindholm et al., 1999).

In the early days of stable carbon isotope investigations, use was made of total wood (e.g. Craig, 1954; Farmer and Baxter, 1974; Libby et al., 1976). However, with the observation that total wood and cellulose and in general the various wood components differ in their isotopic composition (Wilson and Grinstead, 1977; Yildiz, 1995; Borella et al., 1998; Zimmermann, 1998; Loader et al., 2003; Harlow et al., 2006; Szymczak et al., 2011; Gori et al., 2013), most investigators started to extract cellulose for the purpose of climate reconstruction. The main argument was, to prevent any distortion of the isotopic records due to changing proportions of the different wood components relative to each other. As such if any individual component is analysed a climate signal should remain uninfluenced by changing proportions of the tree-ring components. This raises the question of whether or not the proportion of the different wood components is generally constant over the life span of a tree. Up to now this has tacitly been assumed in most isotope investigations in which total wood has been used although this is not proven.

The main wood components, namely carbohydrates, comprising holocellulose (including α-cellulose and hemicelluloses) and lignin, show differences in their carbon isotopes of several permil (Wilson and Grinstead, 1977; Borella et al., 1998; Loader et al., 2003). Although α-cellulose and hemicelluloses represent by far the largest proportion of wood (on average 65–75%), the high carbon content of lignin as compared to carbohydrates which is almost 50% higher (Kürschner and...
2. What may be the reason if a correlation of the stable carbon isotopes between cellulose and total wood is changing in time?

3. What plant physiological reactions may be responsible for the decoupling of a correlation in a particular time period? Are the two components, i.e. cellulose and total wood (presumably lignin), responding differently to certain environmental changes and as such provide in part independent information? For example, does the proportion of cellulose to total wood change as a tree matures?

4. What are the implications of a non stable correlation between the carbon stable isotopes of cellulose and total wood for climate reconstructions?

The present study is a first approach by which in a tropical tree the correlation between cellulose and wood will be investigated for a longer time period, namely a period of about 253 years. This investigation addresses primarily points 1, 2 and 4 of the above listed points.

2. Material and methods

The investigation centred on tree material which was collected from the ‘terra firme’, the inundation free tropical rain forest, north of Manaus, Brazil. For the present study, a tree species was selected which shows frequently far more than 200 years of age. *Cariniana micrantha* (Ducke) is known to reach ages of up to 500 years (Anhuf et al., 2013) and, most important, shows tree-rings although they are not always distinct. In some cases they become incoherent or indistinguishable and may thus cause big challenges for trustworthy chronological reconstructions. Therefore, thin section investigations of some time intervals were added for which the corresponding δ¹³C values were measured in order to substantiate tree-ring borders (Verheyden et al., 2004; Pons and Helle, 2011). We are, however, aware that the exact number of tree-rings cannot be given here especially with regard to false rings and wedging rings. A sufficient number of individuals for successful dendrochronological cross-dating could not be sampled. Nevertheless, tree rings have been counted repeatedly and the period covered is well in the order of two and a half centuries. In view of the question discussed, namely whether or not total wood and cellulose do always show the same isotopic pattern, the exact length of the chronological sequence is irrelevant.

2.1. Material

Samples of *C. micrantha* (Ducke) were collected within the Reserve of Cuieiras (Reserva Biológica do Cuieiras, better known as ZF2) some 60 km north of Manaus. Cores were collected at breast height (≈1.3 m) using a 12 mm diameter increment borer. The trees are growing in the ‘terra firme’, an area which shows a distinct dry period of 2 to 3 months with less than 100 mm precipitation per month. This dry period occurs generally between June and November and is sufficient in length to bring the cambial activity to a standstill (Worbes, 1999). Accordingly, growth is interrupted for a short time, thus leading mostly to visible tree-rings.

First tree-ring inspections were undertaken at the INPA (Instituto Nacional das Pesquisas da Amazônia) at Manaus which indeed demonstrated the visibility of tree-rings. On a scale from 0 to 3, characterizing the quality of tree-ring visibility, with the best visibility given by 3, the clarity of tree-rings for *C. micrantha* (Ducke) is given by 1.5. Consequently, the recognition of tree-ring borders is partly difficult, justifying the additional analysis of isotopic thin section investigations.

For the present investigation a period with 253 counted tree rings, i.e. years, was chosen encompassing the time interval from 1750 to 2007. This represents the outer part of the tree, i.e. the sap wood including a restricted part of the heartwood. The age of the investigated tree was well above 253 years. *C. micrantha* (Ducke) has a diffuse porous wood structure, like the European beech (*Fagus sylvatica*). Contrary to the situation for diffuse porous species of temperate climate zones, the number of large vessels does not vary much along a tree ring. Hence, density across the tree-
rings of *C. micrantha* (Ducke) is practically constant. Therefore, a differentiation in early wood (EW) and late wood (LW) was not possible. Moreover, no anatomy-based definition for early wood and late wood exists for diffuse porous broadleaf tree species in contrast to the clear definition formulated for coniferous species (Mork, 1928; Denne, 1989). Thus, no effort was made to define any increment which might symbolize the EW section of a tree-ring, although the initial wood development and subsequently the associated δ13C value may be influenced by the environmental conditions of the previous year (Hill et al., 1995). Even highly resolved intra-annual increments on the basis of isotope values do not allow defining the border between EW and LW. Thus, the investigation was based on wood material consisting of the whole annual increment. This implies that the carry-over of stored photoassimilates, i.e. of reserves, from the previous year may induce iso-13C value may be in-13C values of thin sections are well suited for the veri-13C values of thin sections are well suited for the verification of indistinct or almost invisible tree-ring boundaries of tropical trees (see also Verheyden et al., 2004). The selected sequence was chosen to demonstrate that thin sections do sometimes also raise questions regarding tree-ring boundaries. The interval between 1782 and 1783 could well represent two years with an additional boundary indicated by the question mark in Fig. 1, although the δ13C increase is not very strong (merely 0.3‰). An additional tree-ring was, however, ruled out by additional careful visual inspections. Moreover, the start of the 1784 boundary is questionable. Unfortunately additional measurements were not possible due to the very low amount of available material. Nevertheless, there is no doubt about the existence of the 1784 boundary at the data point no. 67, and thus the uncertainty for the start of the 1784 ring is 280 μm.

Consequently, the tree-ring boundaries of *C. micrantha* (Ducke) were reasonably recognized by the microscopic and the intra-annual isotopic analyses, allowing the further discussion of the inter-annual variability over the last two and a half centuries.

3.2. δ13C values of total wood and its cellulose

As known from many investigations the δ13C values of cellulose are enriched by 1‰ to almost 4‰ relative to total wood (Schleser, 1992; Marshall and Monserud, 1996; Borella et al., 1998; Zimmermann, 1998; Loader et al., 2003; Ferrol and Voltas, 2005; Dietz, 2006; Roden and Farquhar, 2012). Fig. 2 documents the δ13C difference between total wood and the corresponding cellulose for the investigated *C. micrantha* (Ducke) covering the last two and a half centuries. The mean difference between the two data sets is 1.5 ± 0.36‰ by which total wood is depleted relative to cellulose, corroborating published data of trees from the temperate zones. It is, however, remarkable that the variations are not statistically distributed around the mean. For more than 100 years of the initial part of the chronology an unusual almost sinusoidal like pattern is observed which is superseded by an erratic phase and a minimum during the period from 1900 to 1950 followed by a slight increase for the last 50 years. The solid black line represents a 2-year moving average.

The similarity of the trends between cellulose and total wood was tested by correlating the two data sets. In view of the question raised at the beginning, this could give an answer as to whether or not cellulose and total wood can equally well be used for reconstructions of past environmental changes. The relationship between δ13C values of
cellulose and total wood of the whole chronology is shown in Fig. 3 yielding a correlation coefficient of $r = 0.96$. This is rather convincing for preferring total wood to cellulose for climate reconstructions.

### 3.3. Stability of the correlation between total wood and cellulose for selected time windows

For reconstructing the environment of the past it is common practice to calibrate a set of isotope data from a longer record with available meteorological data (see e.g. Schollaen et al., 2013) and try to validate this result by taking the succeeding data set of the chronology, reconstruct the accompanying meteorological data by using the calibration results and compare them with the corresponding yet existing environmental data. In most regions, records of accessible meteorological data sets are rather short. More than 100 to 120 years for calibration and validation are rarely available. The main point is that in isotope research a successfully i.e. reasonably well correlated sequence although limited in length is normally assumed to be valid for the whole record under investigation. Logically, similar considerations have to be accepted for the relationship between total wood and cellulose: A satisfying, statistically sound correlation, although short in length, should be valid for a whole record preferably for the entire lifetime of a tree.

A first test was made by subdividing the last 100 years of the available record of *C. micrantha* (Ducke) in two 50 year sequences and comparing their correlations, notwithstanding the fact that the correlation between total wood and cellulose is high for the whole record of the two and a half centuries. The results are shown in Figs. 4 and 5 which document the correlations for the periods of 1955 to 2007 and 1905 to 1955, respectively. It is surprising to see that the correlations differ substantially. While during the period from 1955 to 2007, total wood and cellulose correlate well (Fig. 4, $r = 0.92$), the correlation for the period from 1905 to 1955 (Fig. 5) breaks almost completely down with a correlation coefficient of only $r = 0.05$. On the basis of this result, the correlation was investigated by using a moving interval length of 50 years over the existing 253 years period of the *C. micrantha* (Ducke). The result is shown in Fig. 6 (upper curve) with ages representing the middle of the interval. The correlation intervals of Figs. 4 and 5 are marked as grey circles in Fig. 6 representing two contrasting situations representing very low and very high $r$-values, respectively. This shows that the correlation of the carbon isotopes between total wood and its cellulose is only constant during specific time intervals. At particular intervals, there seems to exist a decoupling of the two data sets. Two aspects seem to be responsible for these phenomena: Firstly, a strong isotopic shift of the chronology from one isotopic level to another, shown simultaneously for cellulose and total wood. Such level changes are also seen in carbon isotope chronologies by other authors of tropical trees (see e.g. Ballantyne et al., 2011), reasons for this phenomenon are manifold: e.g. penetration of a tree’s crown through the canopy into the free atmosphere, or clearing of a tree’s surrounding through storm, fire or age (see e.g. van der Sleen et al., 2014). Thus, subsets like the first 80 years of the correlation curve from Fig. 6 (upper curve), showing a highly variable isotopic sequence for cellulose and total wood, characterized by their strong standard deviations (Fig. 6, lower curve) will automatically result in high correlations. Secondly, changes of the chemical composition of various wood components relative to each other along a broadly constant isotopic level of the

![Fig. 2](image1.png)

**Fig. 2.** The difference of the $\delta^{13}C$ values from total wood and cellulose presented as $\Delta \delta^{13}C_{\text{wood-cel}}$ for *C. micrantha* (Ducke) covering the time period from 1755 to 2007. On the average total wood is depleted by $1.5 \pm 0.36\%$ relative to its cellulose. Solid line represents a 2 year moving average.

![Fig. 3](image2.png)

**Fig. 3.** The relation of $\delta^{13}C_{\text{cel.}}$ values between total wood and cellulose of *C. micrantha* (Ducke) for the time period from 1755 to 2007. The correlation coefficient is $r = 0.96$.

![Fig. 4](image3.png)

**Fig. 4.** The relation of $\delta^{13}C$ values of total wood and cellulose for the period of 1955 to 2007. This data set represents the final values of the isotopic sequence given in Fig. 3. The correlation coefficient is $r = 0.92$. 

![Fig. 5](image4.png)

**Fig. 5.** The correlation of $\delta^{13}C$ values between total wood and cellulose for the selected time windows.
chronology, showing a low isotopic standard deviation. Such sequences with low moving standard deviations as from 1850 to 1930 (based on interval centres) may inherently include a mixture of the lowest and rather high correlations. Reasons might be changing compositions of wood components relative to each other during the vegetation period or transfer of material across the tree-ring border into the subsequent tree-ring. It is clear that a reconstruction of δ13Ccel based on the δ13Cwood of the interval 1905 to 1955 will not reflect the general picture of the ups and downs of δ13Ccel over the whole time horizon, i.e. the whole isotopic record. Currently it is unclear as to whether or not these are unusual effects which cannot be generalized or whether certain environmental situations may indeed induce such behaviour pattern. The result obtained needs further investigations because it raises a number of questions for the interpretation of carbon isotopes in tree-rings. Total wood and cellulose might as such sometimes record different environmental episodes, both being of interest for reconstructions.

3.4. Correlations from time windows of low isotopic variability

3.4.1. Influence of varying wood compositions in tree-rings during tree growth

It is still open for discussion why during intervals of relatively stable isotopic variations, i.e. low standard deviation of sequences from total wood and cellulose, correlations may either be low or high. One hypothesis is an environmentally induced variable change of various wood components relative to each other.

Since different wood components show partly strong differences in their carbon isotope composition, changing proportions of components will alter the trend of total wood δ13C values as compared to δ13C values of any of the wood components. It should be noted that for example late wood of oaks produces a higher content of methoxy groups than early wood, indicating that even within an annual ring the composition of lignin may vary which certainly has an influence on the relative composition of these constituents, i.e. cellulose and lignin (Sitte et al., 1998). This may in part explain the intra-annual variation in δ13C values (Helle and Schleser, 2004).

In a first simple exercise it will be assumed that wood is just composed of cellulose and lignin. From numerous investigations it is justified to infer a constant isotopic difference between cellulose and lignin of 3.5‰ (e.g. Wilson and Grinsted, 1977), such that δ13Ccel = δ13Clig + 3.5‰. The relative percentage of cellulose and lignin in the corresponding wood will be given by fcel and flig, respectively. Here cellulose comprises a-cellulose and hemimcelluloses because they show largely similar isotopic values. In addition Ccel and Clig shall represent the proportions of carbon in either molecule. Under these conditions the overall proportion of carbon mass, Pcel, in the corresponding wood regarding cellulose (including hemielluloses) is Pcel = fcel * Ccel. Similarly the proportion of carbon mass from lignin is Plig = flig * Clig.

For the present assessment it is assumed that wood is composed of 70% cellulose and 30% lignin (e.g. Narayamurthi and Das, 1955; Pettersen, 1984), with cellulose Ccel consisting of 44% carbon and lignin Clig consisting of 66% carbon. As such it follows that the proportion of carbon mass of cellulose in the total wood mass is: Pcel = 0.70 * 0.44 = 0.31 and the carbon mass of lignin from the total wood mass is Plig = 0.30 * 0.66 = 0.20, respectively. Thus, the percentage of total carbon in total wood is Pcel + Plig = 31% + 20% = 51%. With these preconditions δ13Cwood of total wood is given by:

\[
\delta^{13}C_{\text{wood}} = \left( \delta^{13}C_{\text{cel}} \right)_{\text{hi}} = \left[ P_{\text{cel}} * \delta^{13}C_{\text{cel}} + P_{\text{lig}} * \delta^{13}C_{\text{lig}} \right] / \left( P_{\text{cel}} + P_{\text{lig}} \right)
\]

(1)

\[
\delta^{13}C_{\text{wood}} = \delta^{13}C_{\text{cel}} - 3.5 * \left( \delta^{13}C_{\text{lig}} \right)_{\text{hi}} / \left( P_{\text{cel}} + P_{\text{lig}} \right)
\]

(2)

\[
\Delta\delta^{13}C_{\text{wood-cel}} = \delta^{13}C_{\text{wood}} - \delta^{13}C_{\text{cel}} = -3.5 * \left( \delta^{13}C_{\text{lig}} \right)_{\text{hi}} / \left( P_{\text{cel}} + P_{\text{lig}} \right)
\]

(3a)

leading to a value of:

\[
\Delta\delta^{13}C_{\text{wood-cel}} = -1.37\%.
\]

(3b)

Thus, a constant enrichment of 1.37‰ for cellulose relative to wood is inferred. Although this corroborates the above given average result for C. micrantha (Ducke) of 1.5 ± 0.36‰, the assumptions used are probably not exactly those of the investigated tree species. The main point is, however, that Δδ13Cwood-cel is not constant (see Fig. 2) as would have to be expected according to Eqs. (3a) and (3b). The difference of Δδ13Cwood-cel varies substantially between −0.8 and −2.0‰ which is far beyond the error margins of the experimental analyses.

An alternative to this outcome is that the percentages of cellulose and lignin are not constant with tree growth. For the present situation
it will be assumed that the cellulose content (α-cellulose and hemicellul-oloses) of wood \( f_{\text{cel}} \) will vary between 60% and 80% (Shimizu, 1990).

Thus, from Eqs. (1) to (3) it follows, keeping in mind that \( f_{\text{cel}} + f_{\text{lig}} = 1 \):

\[
\Delta \delta^{13}C_{\text{woof}} - \Delta \delta^{13}C_{\text{cel}} = -3.5 + (1 - f_{\text{lig}}) \left( \Delta \delta^{13}C_{\text{lig}} + \Delta \delta^{13}C_{\text{extr}} \right) / (1 + \Delta \delta^{13}C_{\text{lig}}).
\]

(3c)

This leads to \( \Delta \delta^{13}C_{\text{woof}} - \Delta \delta^{13}C_{\text{cel}} \) values ranging from \(-1.75\%\) to \(-0.95\%\), respectively.

The difference of \( \delta^{13}C_{\text{woof}} - \delta^{13}C_{\text{cel}} \) documented in Fig. 2 as \( \Delta \delta^{13}C_{\text{woof}} - \Delta \delta^{13}C_{\text{cel}} \) varies primarily in the interval as deduced above. Only during the time periods from 1910 to 1925 and roughly 1950 to 1980 the \( \Delta \delta^{13}C_{\text{woof}} - \Delta \delta^{13}C_{\text{cel}} \) values are lower than \(-1.75\%\), in some cases being below \(-2\%\). Thus, the derivation leads smoothly to a satisfactory result, although wood contains hardly up to 40% lignin. 30–35% lignin is generally the upper limit for woody structures (Sakakibara, 1990) despite the fact that up to 36% are reported for some softwood species (Shimizu, 1990).

Tropical wood contains mostly higher lignin content than hardwood of temperate-zones which rarely reaches as much as 30%. In tropical wood even 38% lignin has been measured in some cases (Petterson, 1984). E.g. *Eperua bijuga* Mart. ex Benth./Muirapiaranga from Brazil showed values of 38% for lignin and only 53% for carbohydrates. *Cedrela odorata* L. from Mozambique showed 33% for lignin and 55% for carbohydrates. This indicates that in many tropical trees extractives have to be more important as compared to temperate-zone wood. Up to 20% of extractives were measured for wood of tropical trees (Petterson, 1984). Additionally, it is known that extractives can even be exchanged between adjacent annual rings such as resins (Tans et al., 1978). Other constituents such as Ca-oxalate are known to show occasionally very substantial number of consecutive years, they were rather abundant, evidence from stable isotope ratios in EW and LW of annual growth rings of oak trees from temperate climates occurs at the expense of stored carbohydrates laid down in the previous year (Hill et al., 1995). This documents that young leaves switch to current photosynthetic products for current cellulose production only if they are becoming net exporters of photosynthates. Therefore, synthesis of EW in deciduous trees from temperate climates occurs at the expense of stored carbohydrates laid down at the end of the previous season. It is commonly assumed that carbon is mainly stored as starch which is then converted to sucrose for transport to the growing wood tissue. In these cases the seasonal isotopic signatures of the preceding year due to changes of its total wood composition caused by transfer of certain chemical compounds (e.g. sucrose) to the current year. On the other hand this transfer will then influence the isotopic composition of the current year.

Evidence from stable isotope ratios in EW and LW of annual growth rings from oak stem tissue indicates that EW bears the isotope signature of stored carbohydrates laid down in the previous year (Hill et al., 1995). This documents that young leaves switch to current photosynthetic products for current cellulose production only if they are becoming net exporters of photosynthates. Therefore, synthesis of EW in deciduous trees from temperate climates occurs at the expense of stored carbohydrates laid down at the end of the previous season. It is commonly assumed that carbon is mainly stored as starch which is then converted to sucrose for transport to the growing wood tissue. In these cases the seasonal isotopic signatures of the preceding year will influence the isotopic signature of the current year, thus distorting the climatic signal of each year. Regarding time series of isotope records from such trees will automatically lead to significant autocorrelation effects which can only be suppressed, at least to a considerable part, if late wood is selected for tree-ring isotope records. Therefore, isotope chronologies of oak trees will normally be restricted to LW. As a matter of fact, investigations do unfortunately not exist which have documented the importance of choosing LW in favour of total ring wood to circumvent contributions of isotopic signature transfer from preceding years. In addition no data exist giving definite proof that LW data are uninfluenced by previous years’ environmental signatures. Frequently, except
for oak trees, tree-ring isotope investigations are based on whole ring wood information, especially in case of very narrow rings.

The situation is, however, different for tropical trees because in many cases they keep their leaves all year round, indicating that photosynthates are continuously being produced although the photosynthetic activity may vary during the year. *Cariniana micrantha* (Ducke) belongs to these tree species which are evergreen. Therefore, the question of transfer, i.e. the usage of stored photosynthates for later wood production is difficult to answer especially because it is not possible to determine a border between EW and LW. No studies are presently available which have thoroughly dealt with this problem. At first sight we cannot rule out that at particular seasonal periods a certain mechanism of substrate carry over exists. Nonetheless, it is questionable if a differentiation in EW and LW is meaningful for evergreen tropical trees.

### 4. Conclusion

The carbon isotopes of cellulose and total wood from the tree-rings of the tropical wood species *C. micrantha* (Ducke) were analysed. The investigation covered a time period of about 253 years, ranging from 1755 to 2007. In view of the questions raised it has finally to be concluded that the carbon isotope correlation between total wood and its cellulose is not stable in time. For *C. micrantha* (Ducke) it is therefore not justified to extrapolate the correlation properties from a particular time interval to any other time interval of the isotope chronology. In general, high correlations will preferably be encountered for chronological subsets in which the isotopic signature varies strongly changing from a certain level to another one. Contrary thereto changes of the chemical composition of wood constituents along relatively stable iso- tope levels with low standard deviation may result in low correlations. For this reason it is essential to use micro-amounts for stable isotope analyses.

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