

## ***Interactive comment on “An Overview on Isotopic Divergences – Causes for instability of Tree-Ring Isotopes and Climate Correlations” by Martine M. Savard and Valérie Daux***

**Martine M. Savard and Valérie Daux**

[martinem.savard@canada.ca](mailto:martinem.savard@canada.ca)

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General comments Reply – We would like to thank referee 1 for the suggestions made during this review.

The manuscript reviews recent development of isotopic dendroclimatology, addressing possible divergence problem in tree-ring  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . In my opinion, this kind work is very important when isotopic dendroclimatology has been paid more attention and plays more important role in high-resolution paleoclimate reconstruction. However, the current manuscript should be reorganized and concentrated in  $\delta^{13}\text{C}$ . Physiological mechanisms between tree-ring  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  are quite different, therefore, compar-

C1

ing with tree-ring  $\delta^{13}\text{C}$ , tree-ring  $\delta^{18}\text{O}$  did not show recognizable effects from rising  $p\text{CO}_2$  (Lines 240-241) and pollution (Lines 424-425). Just as the authors said in Lines 514-515, tree-ring  $\delta^{18}\text{O}$  is a more appropriate proxy for climate reconstruction. And, the phenomenon of divergence between the  $\delta^{18}\text{O}$  and climate is really few worldwide.

REPLY - Regarding presenting the review on  $\delta^{18}\text{O}$  series, indeed, rising  $p\text{CO}_2$  does not create divergence with climate for the  $\delta^{18}\text{O}$  series, as we pertinently explain, but other causes do: change in climatic regimes and pollution (sections 4.1 and 4.3). That is why we judge pertinent keeping the  $\delta^{18}\text{O}$  series in this review (see Table 1).

I also suggest the authors adding one section discussing uncertainty. Isotopic dendroclimatology is a subject based on chemical experiment. Unlike tree-ring width or density, the result of tree-ring  $\delta^{13}\text{C}$  or  $\delta^{18}\text{O}$  measurements are different to verified again from their core or disk samples, due to time consuming and great expense. It is possible to introduce mistakes during many steps of experiments, for example, impure cellulose and unreliable measurements caused by bad condition of the isotope ratio mass spectrometer.

REPLY - Uncertainties do exist for any kind of physical measurement, including tree ring width or density determination. We agree that in isotopic dendroclimatology, the chemical extraction of cellulose and the spectrometric measurements are critical steps. Impure cellulose and unreliable measurements yield bad data, which indeed more than likely diverge from climate. We can introduce a sentence of caution and refer to several papers devoted to good analytical practices (for instance: Loader et al., 1997; Boettger et al., 2007; Wieloch et al., 2011; Kagawa et al., 2015; Andre-Hayles et al., 2019) but we do not think this subject has to be extensively discussed in this paper. Andreu-Hayles, L., Levesque, M., Martin-Benito, D., Huang, W., Harris, R., Oelkers, R., Leland, C., Martin-Fernández, J., Anchukaitis, K.J., Helle, G., 2019. A high yield cellulose extraction system for small whole wood samples and dual measurement of carbon and oxygen stable isotopes. *Chem. Geol.* 504, 53–65. <https://doi.org/10.1016/j.chemgeo.2018.09.007> Boettger, T., Haupt, M., Knöller, K.,

C2

Weise, S.M., Waterhouse, J.S., Rinne, K.T., Loader, N.J., Sonninen, E., Jungner, H., Masson-Delmotte, V., Stievenard, M., Guillemin, M.T., Pierre, M., Pazdur, A., Leuenberger, M., Filot, M., Saurer, M., Reynolds, C.E., Helle, G., Schleser, G.H., 2007. Wood cellulose preparation methods and mass spectrometric analyses of  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and nonexchangeable  $\delta^2\text{H}$  values in cellulose, sugar, and starch: An interlaboratory comparison. *Anal. Chem.* 79, 4603–4612. <https://doi.org/10.1021/ac0700023> Loader, N.J., Robertson, I., Barker, a. C., Switsur, V.R., Waterhouse, J.S., 1997. An improved technique for the batch processing of small wholewood samples to  $\alpha$ -cellulose. *Chem. Geol.* 136, 313–317. [https://doi.org/10.1016/S0009-2541\(96\)00133-7](https://doi.org/10.1016/S0009-2541(96)00133-7) Kagawa, A., Sano, M., Nakatsuka, T., Ikeda, T., Kubo, S., 2015. An optimized method for stable isotope analysis of tree rings by extracting cellulose directly from cross-sectional laths. *Chem. Geol.* 393–394, 16–25. <https://doi.org/10.1016/j.chemgeo.2014.11.019> Wiehloch, T., Helle, G., Heinrich, I., Voigt, M., Schyma, P., 2011. A novel device for batch-wise isolation of  $\alpha$ -cellulose from small-amount wholewood samples. *Dendrochronologia* 29, 115–117. <https://doi.org/10.1016/j.dendro.2010.08.008>

Some other uncertainties also exist. First is sampling strategy. We should understand what kind of tree could be used for climate reconstruction. As recommended by classical “The principle of limiting factors” (Fritts 1976), site selection is very important when one would employ trees to infer climate change. It is also important to isotopic dendroclimatology. Because mixed (deep phreatic water, shallow ground water, precipitation. . .) ground water may disturb tree-ring  $\delta^{18}\text{O}$  (A tree in flowing figure), tree-ring  $\delta^{18}\text{O}$  of B tree only absorb precipitation. Although cellulose  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  could be measured for any tree from any site, but for purpose of climate correlation, it should be carefully selected.

REPLY- Thank you for raising that up. Indeed site selection is a crucial step in paleoclimate research. If trees and/or sites are not well selected, one of the main risks is that their  $\delta^{18}\text{O}$  and/or  $\delta^{13}\text{C}$  isotopic series show no significant relation with climate. In that case, reconstruction is not possible. Therefore, we judge that using poor criteria

C3

for site selection does not have to be dealt with in this paper as we assume that the readership is well aware of the initial step in adequate site selection.

Second uncertainty may be introduced by different samples for measurement (extractive-free samples,  $\alpha$ -cellulose, whole wood or holocellulose). And, for different chemical extraction methods (Green’s method, Brendel’s method. . .). Third uncertainty may be introduced by “pooling” or “not pooling”.

REPLY- Different extraction methods, as well as measurements produced in different laboratories with different spectrometers and procedures, should produce comparable results. There are very few inter-lab calibration experiments. To our knowledge the only study dealing with such a comparison was produced by the ISONET group (Boettger et al., 2007). Another one is in progress in the frame of the THEMES project conducted by one of the two authors (Daux, Andreu-Hayles et al., in progress). These inter-laboratories comparisons show that shifts between isotopic levels exist between laboratories (high correlations but different absolute value) due to different extraction methods, use of different reference materials, different apparatus, etc. However, as long as the data included in an isotopic chronology have all been produced following the same protocols, by the same experimentalists, the data are consistent with one another and if they diverge from climate variations, the cause should be sought elsewhere.

Special comments are as follow.

Lines 13-19, changes on physiology (fo and peplet effect. . .) should be mentioned here.

REPLY- These items are covered in section 2.1. Here we cite the main CAUSES for divergences, not the mechanisms through which they operate. No change to these lines.

Line 32, need a reference

REPLY- We will add D’Arrigo et al., 2008.

C4

Lines 38-42, it is no need to describe growth divergence  
REPLY- The referee probably means lines 38-42. Here we just present some background using growth divergence. No change to these lines.

Line 72, "concentration" is better than "pressure", also in Line 236

REPLY- Atmospheric CO<sub>2</sub> Pressure or pCO<sub>2</sub> are well accepted and widely used. No change to these lines.

Lines 94-95, need references

REPLY- The references covering this topic are through equations 1-3, for which the citations are in the previous text. No change to these lines.

Line 157, 5 year is not enough

REPLY- Understood. The parenthesis underlines the fact that some researcher may opt for longer overlaps. No change to this line.

Lines 175-177, one advantage for tree-ring isotope chronology is no need to detrending. If detrending for the isotope chronology, some climate signals may be lost.

REPLY- We agree. That is exactly what the text explains. No change to these lines.

Line 263, "1850s" is easy to understand than "last 170 years"

REPLY- We will modify the sentence from "of rising pCO<sub>2</sub> of the last 170 years" to: "of rising pCO<sub>2</sub> since 1850."

Line 302, relative humidity and RH, repeat

REPLY- we just present the abbreviation (RH) for relative humidity here. No change to this line.

Line 376, tropic/

REPLY- Tropical is a well accepted English adjective. No change to this line.

C5

Lines 399-412 – multi-proxy approach and more climate noise?

REPLY- We do not understand what the reviewer means. We say the contrary in the text: 'Indeed, combining proxies with the same dominant control, but different secondary controls, tends to accentuate the common climate signal'.

Section 3.3. there is only one sentence to state the situation of cellulose d<sup>18</sup>O (Line 240). I recommend to delete d<sup>18</sup>O discussion in this manuscript. In addition, removing effect of increasing CO<sub>2</sub> from the d<sup>13</sup>C series has been discussed in many literatures. Please shorten this section.

REPLY- It is true that the literature raised the issue abundantly, but there is still no consensus on how to approach and correct the problem. This manuscript designed to be a review article should cover the matter and section 3.3 intend to do just that. Concerning the effects on d<sup>18</sup>O values, it is worth explaining which articles address the potential pCO<sub>2</sub> effects, even if nil or minimal. In addition, referee 2 pertinently suggests to integrate new references to this section. So we decide not to shorten the section.

Table 1, check which one use pooling method.

REPLY- good point. We indicated the studies using pooled series (asterisks in Table 1 that we can provide by means to be indicated by the editorial team), without identifying any specific common factors. Note that many of these studies validated that the use of pooled trees gave similar results to treatments of individual trees later averaged mathematically.

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Interactive comment on Clim. Past Discuss., <https://doi.org/10.5194/cp-2020-28>, 2020.

C6