

# Trends and signals in decadal resolved carbon isotopes from the Spanish Pyrenees

O. Konter<sup>1</sup>, S. Holzkämper<sup>1+2</sup>, G. Helle<sup>3</sup>, U. Büntgen<sup>4</sup> & J. Esper<sup>1</sup>

<sup>1</sup> Department of Geography, Johannes Gutenberg University, Becherweg 21, 55099 Mainz, Germany

<sup>2</sup> Department of Physical Geography and Quaternary Geology, Stockholm University, 10691 Stockholm, Sweden

<sup>3</sup> German Centre for Geosciences, Climate Dynamics and Landscape Evolution, Dendro Laboratory, Potsdam, Germany

<sup>4</sup> Swiss Federal Research Institute WSL, 8903 Birmensdorf, Switzerland

E-mail: o.konter@geo.uni-mainz.de

## Introduction

The Mediterranean Basin is considered to be a hotspot of global warming, associated with severe impacts on both bio-ecological and socio-economical systems (IPCC 2007). Several dendroclimatological studies have been carried out in the Pyrenees, where robust temperature signals are predominantly retained from nearby altitudinal treeline ecotones (Büntgen et al. 2010). Büntgen et al. (2008) analyzed maximum latewood densities (MXD) from a high-elevation sampling site in the Spanish Pyrenees and reconstructed May-September temperatures back to medieval times. Despite the commonly used tree ring width (TRW) and MXD parameters (Büntgen et al. 2010, Dorado Liñán et al. 2012), carbon isotopic ratios also showed promising results in different locations and became an important proxy of past climate variability (overview in Treydte et al. 2007). In the Pyrenees, climatic signals retained in stable carbon isotopes include both summer precipitation and temperature (Andreu et al. 2008, Dorado Liñán et al. 2011). Carbon fractionation procedures within trees and their impact on low-frequency trends are not well understood, as variations in the amount and isotopic composition of atmospheric CO<sub>2</sub> as well as climate variations are simultaneously incorporated in tree rings (Farquhar et al. 1982, Feng & Epstein 1995, Kürschner 1996, Treydte et al. 2004, McCarroll & Loader 2004, Helle & Schleser 2004). Analyses of low-frequency changes in tree ring stable isotopes are constrained by the work load required to produce annually resolved  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  time series from single trees. Esper et al. (2010) established decadal resolved, millennial-length  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  records to analyze long-term trends in tree ring isotope data. These data have, however, not being calibrated against instrumental time series, a procedure explored here.

We present six decadal resolved carbon isotope records spanning the 1901-2009 period, derived from *Pinus uncinata* trees originating from the same sampling site as used in Esper et al. (2010). These single-tree  $\delta^{13}\text{C}_{\text{raw}}$  time series are transformed considering various correction methods (Feng & Epstein 1995, Kürschner 1996, McCarroll & Loader 2004) and calibrated against climate data to assess the reconstruction potential of the millennial-length carbon isotope data from the region.

## Material and Methods

### *Study site and sampling strategy*

The altitude of the selected treeline site, located near Gerber Lake at the northern border of the "D'Aigüestortes Estany de Sant Maurici" Spanish National Park in the Central Pyrenees, west of Andorra, ranges from 2314 to 2380 m asl. The prevailing tree species is *Pinus uncinata*, a shade-intolerant conifer tree in the open forest ecotone. Tree height varies between 3-6 m, and diameter at breast height ranges from 0.25-1.08 m.

In June 2010 twenty-three *Pinus uncinata* trees were selected at the aforementioned treeline site. The selection of the pine individuals was based on the estimated tree ages, to establish a dataset including only trees of similar or comparable age throughout the calibration period. Since dry-dead

material was rare, the selection focused on material from living trees. The sampled trees have no access to ground water.

Four cores (0.5 cm diameter) were sampled from each tree in a radial configuration at breast height, two diametrically parallel and two diametrically perpendicular to the slope, whenever possible.

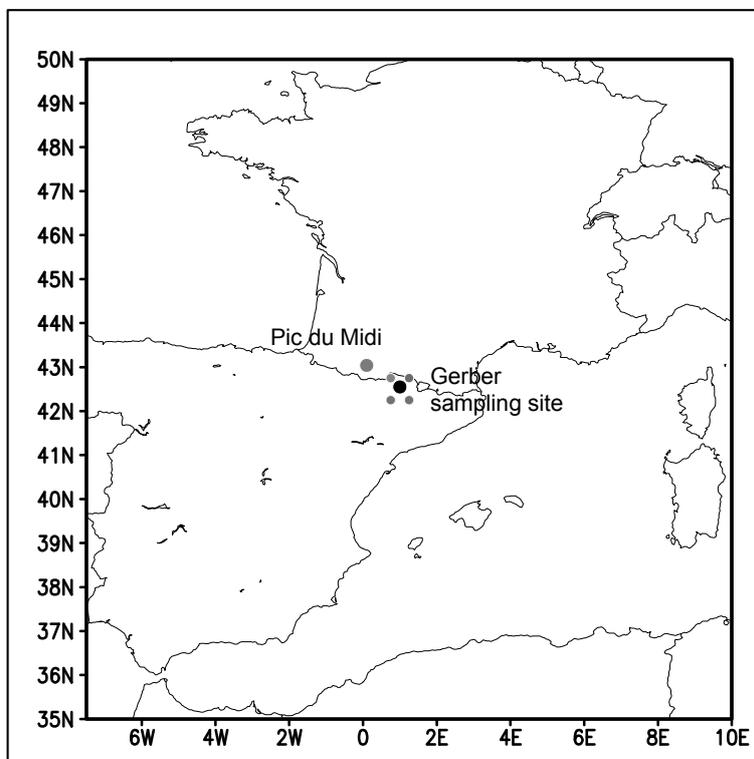


Figure 1: Study area; Gerber sampling site shown in black, gridded climate data in grey, and Pic du Midi station in grey (large dot).

#### Tree ring width and stable isotope measurements

Core samples were cut lengthwise and vertically to the wood fiber to maintain plain surfaces. Tree ring widths were measured using TSAP-WinTM Professional (Rinn et al. 2007), cross-dated using CoFeCha (Holmes 1983), and detrended using the Regional Curve Standardization technique (RCS, Esper et al. 2003) within ARSTAN (Cook 1985).

A subset of six trees was selected and each tree ring, from 1901-2009, sectioned with a scalpel. For isotopic measurements, two core samples were merged to represent a single tree, i.e. two cut samples (from the same year) were joined. From this basic wood material  $\alpha$ -cellulose was extracted following procedures established by Green (1963) and advanced by Loader (1996). Homogenization of the  $\alpha$ -cellulose samples was achieved by using an ultrasonic technique (Laumer et al. 2009). Samples were freeze-dried prior to analyzing carbon isotope ratios using an IsoPrime (GV Instruments, Manchester, UK) Isotope Ratio Mass Spectrometer (IRMS) with an interfaced elemental analyzer (Fisons NA 1500 NC) on a continuous carrier gas flow, operated at the *GeoForschungsZentrum (GFZ) Potsdam*.

The resulting annual values, expressed relative to the international VPDB standard in per mill (‰), were transformed to decadal, no mass weighted values by calculating 10-year-means (1901-1910, ..., 1991-2000; except 2001-2009 representing only 9 values) to transform the explored climate signal to the millennial long, decadal resolved time series displayed in Esper et al. (2010). Six  $\delta^{13}\text{C}$  time series representing individual trees (two radii per tree) and consisting of eleven decadal values from 1901 to 2009 are used in this assessment.

### *Physiological fractionation and correction*

Anthropogenic fossil fuel burning since the beginning of industrialization has led to a declining trend of  $\delta^{13}\text{C}$  in atmospheric  $\text{CO}_2$  and is also reflected in tree ring  $\delta^{13}\text{C}_{\text{raw}}$  values (Farquhar et al. 1982, McCarroll & Loader 2004, Treydte et al. 2007). This non-climatic decreasing trend inherent in the tree ring data is corrected by applying a procedure detailed in McCarroll and Loader (2004); the dataset is referred to as  $\delta^{13}\text{C}_{\text{atm}}$  hereinafter. As the increased atmospheric  $\text{CO}_2$  concentration also influences plant metabolism – through stronger discrimination against the heavier  $^{13}\text{C}$  isotope – we additionally corrected the  $\delta^{13}\text{C}_{\text{raw}}$  values following suggestions by Kürschner (1996, hereinafter  $\delta^{13}\text{C}_K$ ) and Feng & Epstein et al. (1995, hereinafter  $\delta^{13}\text{C}_{\text{FE}}$ ).

### *Climate data and calibration*

Climate signals of the TRW,  $\delta^{13}\text{C}_{\text{atm}}$ ,  $\delta^{13}\text{C}_K$ , and  $\delta^{13}\text{C}_{\text{FE}}$  were assessed using Pearson product-moment correlation coefficients calculated over the 1901-2009 period, including 11 decadal values. Temperature data from the Pic du Midi station (2,862m asl, 43°04'N, 0°09'E), and gridded precipitation (CRU TS 3.1, Mitchell & Jones 2005) and PDSI data (Dai et al. 2004) are considered. To calibrate climate data against the decadal resolved isotope data, decadal arithmetic means were calculated for all climate variables. Since the availability of climate data of the most recent decade varies (temperature 1901-2005, precipitation 1901-2009, PDSI 1901-2005), the period from 2001-2009 represents varying number of values (temperature: 5 values, precipitation: 9 values, PDSI: 5 values).

## **Results and Discussion**

### *Stable isotope data*

The individual stable isotope time series show a remarkable offset among single trees (Fig. 2). Mean values of single trees range from -21.75 ‰ to -23.90 ‰ ( $\delta^{13}\text{C}_{\text{raw}}$ ) and offsets increase up to >3 ‰ during several periods. Whereas these differences do not alter substantially in the different corrections, interseries correlations increase from 0.23 for  $\delta^{13}\text{C}_{\text{atm}}$  to 0.69 for  $\delta^{13}\text{C}_K$  and 0.93 for  $\delta^{13}\text{C}_{\text{FE}}$ . These changes are associated with the common and most important increasing trends added throughout the corrections. The common declining trend inherent in  $\delta^{13}\text{C}_{\text{raw}}$  is removed in the  $\delta^{13}\text{C}_{\text{atm}}$  data. The additional correction for physiological fractionations caused an overall positive low-frequency trend in  $\delta^{13}\text{C}_K$  – and even more so in  $\delta^{13}\text{C}_{\text{FE}}$ , altering the correlations to eventually > 0.9.

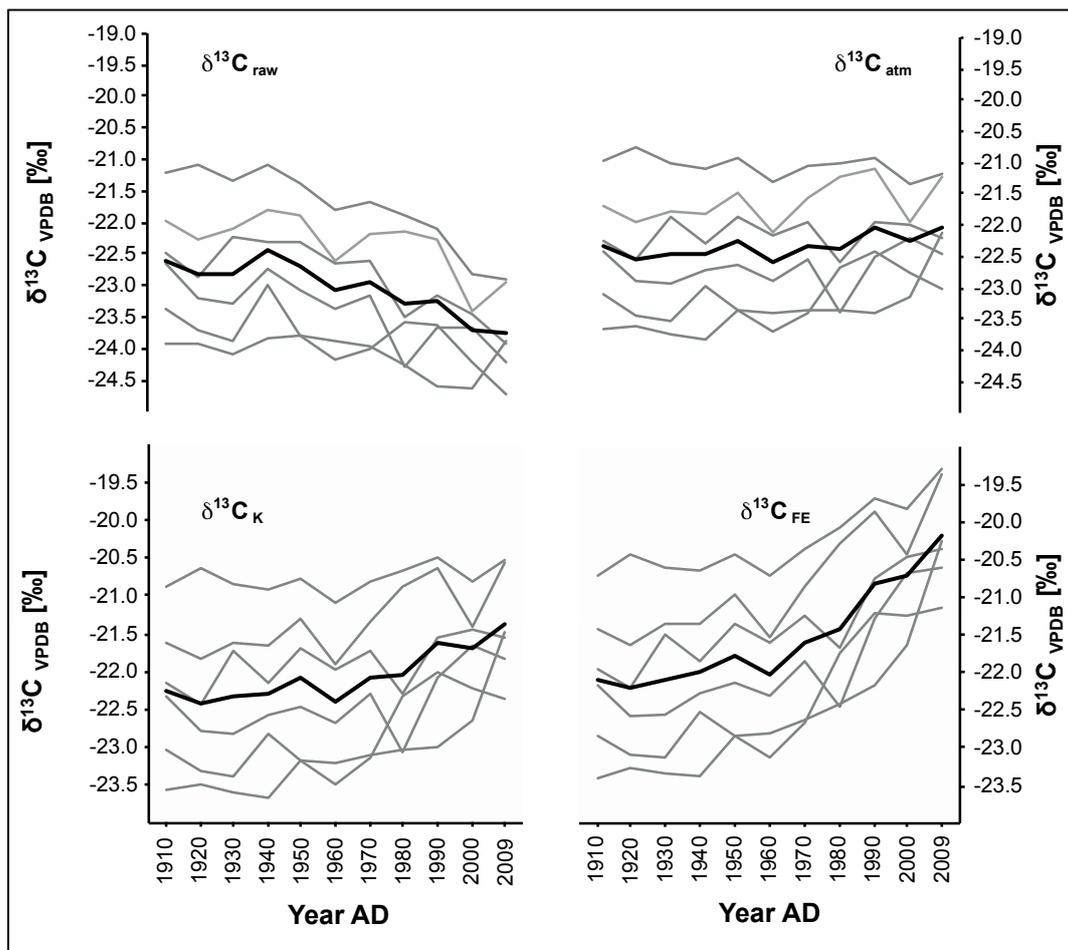


Figure 2: Decadally resolved carbon isotope data. Grey lines indicate individual trees, black lines their arithmetic means, for the  $\delta^{13}\text{C}_{\text{raw}}$ ,  $\delta^{13}\text{C}_{\text{atm}}$ ,  $\delta^{13}\text{C}_{\text{K}}$ , and  $\delta^{13}\text{C}_{\text{FE}}$  data.

### Climate signals

Since the  $\delta^{13}\text{C}_{\text{raw}}$  data contain a well-known non-climatic trend, climate/growth relationships are estimated between  $\delta^{13}\text{C}_{\text{atm}}$ ,  $\delta^{13}\text{C}_{\text{K}}$ ,  $\delta^{13}\text{C}_{\text{FE}}$  and monthly temperature anomalies, precipitation sums, and mean PDSI values (Fig. 3). Most significant results are revealed among the carbon isotope data and summer temperatures, particularly during July ( $p < 0.001$ ). The strongest association is detected between  $\delta^{13}\text{C}_{\text{K}}$  and July-September mean temperatures ( $r=0.94$ , 1901-2009 period). Whereas the influence of precipitation seems overall negligible (except for a 95% significant signal in April), PDSI shows coherent negative correlations up to  $r=-0.88$  ( $p < 0.001$ ) likely driven by the longer-term temperature variations.

The strong coherence between  $\delta^{13}\text{C}_{\text{FE}}$  and (summer) temperatures points to the low-frequency trends, inherent in temperature and largely absent from precipitation, as the key variable influencing the correlation results. The relationships between carbon isotope and climate data vary according to their low-frequency loadings:  $\delta^{13}\text{C}_{\text{FE}}$  (in contrast to  $\delta^{13}\text{C}_{\text{atm}}$ ) correlates significantly with PDSI due to the common low-frequency trends inherent in both datasets. Consequently,  $\delta^{13}\text{C}_{\text{atm}}$  correlates better with precipitation, compared to  $\delta^{13}\text{C}_{\text{K}}$  and  $\delta^{13}\text{C}_{\text{FE}}$ . All significance levels mentioned in the text are not corrected for lag-1 autocorrelation, which are 0.23 for  $\delta^{13}\text{C}_{\text{atm}}$ , 0.76 for  $\delta^{13}\text{C}_{\text{K}}$ , 0.93 for  $\delta^{13}\text{C}_{\text{FE}}$ , and 0.47 for July-September mean temperature, for example. After reduction of the degrees of freedom due to lag-1 autocorrelation,  $\delta^{13}\text{C}_{\text{atm}}$  values still exceed the 99.9 % confidence level when correlated with July-September temperatures ( $r=0.90$ ), in contrast to  $\delta^{13}\text{C}_{\text{K}}$  and  $\delta^{13}\text{C}_{\text{FE}}$  data.

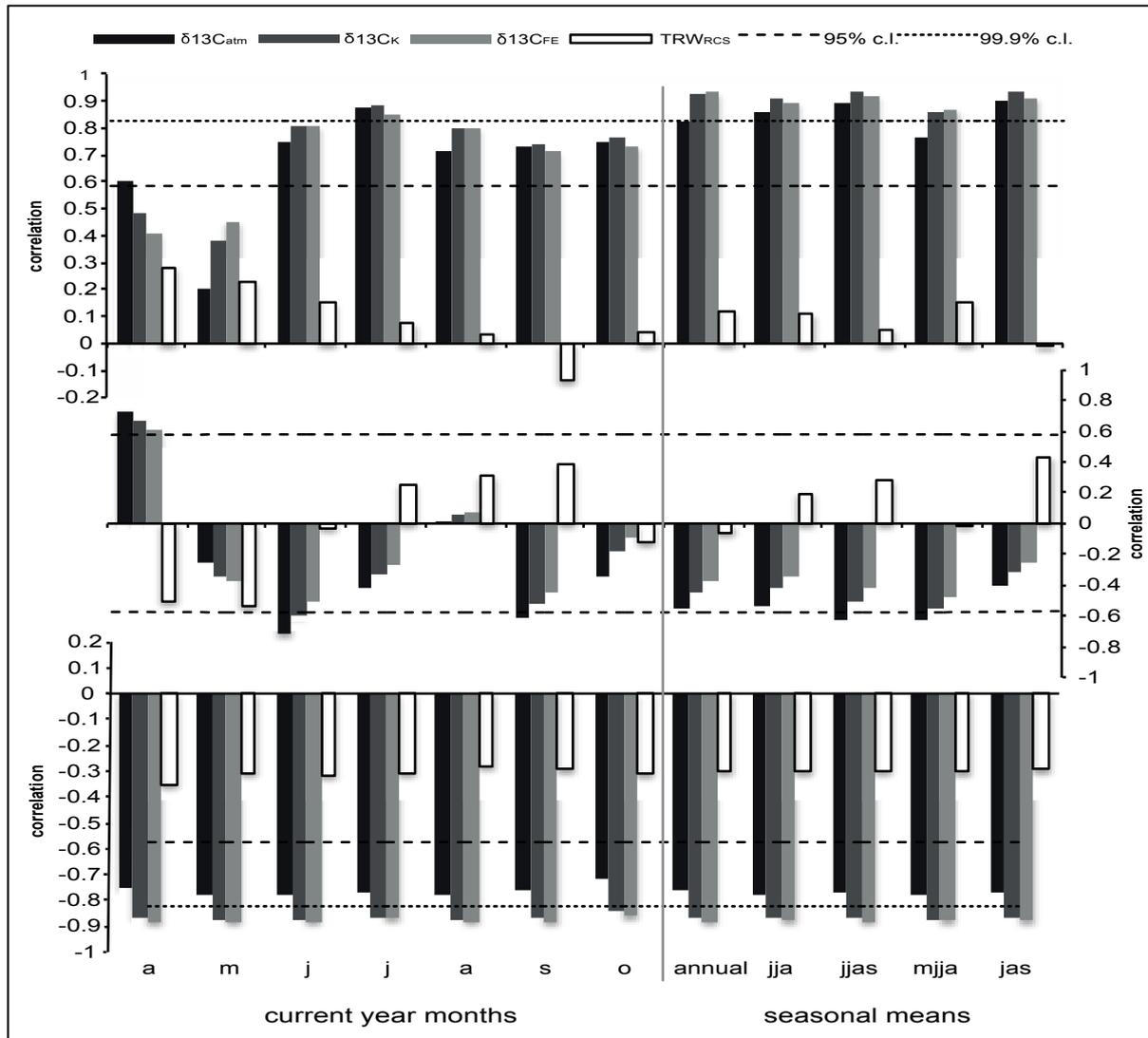


Figure 3: Growth-climate relationships. Monthly and seasonal correlation coefficients between  $\delta^{13}\text{C}_{\text{atm}}$  (black),  $\delta^{13}\text{C}_{\text{K}}$  (grey), and  $\delta^{13}\text{C}_{\text{FE}}$  (light grey) versus temperature (top panel), precipitation (middle), and PDSI (bottom) over the 1901-2009 period. Dashed curves indicate the 95% (bold) and 99% significance levels. These are not corrected for lag-1 autocorrelation effects; for corrected values, see text.

### Spurious trends

The inter-tree offsets shown in this study do not alter the mean values functions (the chronologies), since replication ( $n=6$ ) does not change throughout the calibration period (1901-2009). However, an inter-tree range of 2-3 ‰ can cause spurious trends within carbon isotope datasets, if replication changes over time – which is a typical feature of longer term tree ring records (Esper et al. 2002). To illustrate this effect, we omitted the first three decadal sets of two individual time series and additionally the last three decadal sets of two different time series, as if the dataset would contain two individuals covering the 1901-1980 period and two individuals covering the 1940-2009 period (as well as two trees covering the full 1901-2009 period) (Fig. 4). The replication of this new data is consequently reduced from six to four trees at the beginning (1901-1930) and the end (1980-2009) of the calibration period, which still is considered to be an adequate and representative amount of individuals for isotope based climate evaluations (Leavitt and Long 1984). During the period represented by all individuals (1940-1980) the original data and mean remain unaltered. This setup mirrors tree core composition and age structure changes typical to

long-term chronologies (Treydte et al. 2009, Seftigen et al. 2011, Gagen et al. 2011). The resulting mean chronologies (see the black curves in Fig. 4), however, indicate entirely different low-frequency trends as a result of our data treatment. These spurious trends are the consequence of the substantial level differences of individual stable carbon isotope time series that do not cover the exact same period. The cause for these differing trends would remain unknown – and the trends perhaps interpreted as environmental signals – if the wood samples would have been pooled before isotope measurement. Removing the substantial level differences of individual time series by calculating anomalies to the individual mean values prior to producing a chronology could contribute to verify trends inherent in the data and, thus, could help to avoid discarding data of low-replicated periods.

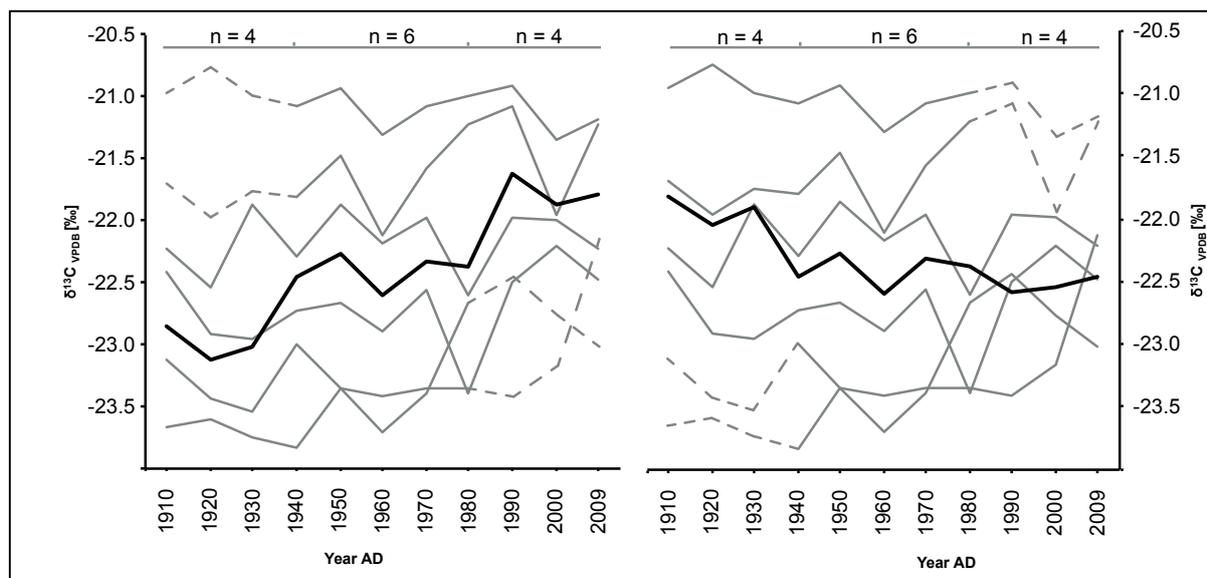


Figure 4: Changing  $\delta^{13}\text{C}_{\text{atm}}$  mean curves (black) as a consequence of removing decadal sets of individual trees (grey, see main text). Dashed lines indicate omitted data; left panel: early high and late low decadal values of two individual time series omitted; right panel: early low and late high decadal values of two individual time series omitted.

## Conclusions

Decadally resolved carbon isotope measurements capture climate signals in the 20<sup>th</sup> century, enabling a calibration setup for reconstruction purposes. Especially summer temperature variations are reflected in tree ring stable carbon isotopes, displayed in correlation values of  $r=0.90$  ( $p<0.001$ ) between July-September temperature anomalies and  $\delta^{13}\text{C}_{\text{atm}}$  values. Stomata aperture and subsequent isotopic fractionation in the leaves are driven by temperature, while precipitation is of a minor importance to the pine trees from the high-elevation Gerber site.

Commonly applied corrections of the carbon isotope data increase the low-frequency trends of  $\delta^{13}\text{C}$  time series. The increased trends alter the relationship to climate indices:  $\delta^{13}\text{C}_K$  and  $\delta^{13}\text{C}_{FE}$  show higher correlations to climate indices that also incorporate low-frequency trends. The increasing autocorrelation affect the degrees of freedom, however, a feature that is particularly significant with decadal resolved data.

More analyses of the physiological processes are needed to clarify which correction is indeed recommended. In the Spanish Pyrenees, the Kürschner approach ( $\delta^{13}\text{C}_K$ ) results in the closest association with temperature data, while the Feng & Epstein approach ( $\delta^{13}\text{C}_{FE}$ ) seems to overestimate the low-frequency trend compared to temperature.

Low-frequency trends within carbon isotope data can also be caused by changes in replication and need careful analyses. In this study, tree replication is stable ( $n = 6$ ) over the entire 1901-2009

calibration period. It is concluded that the displayed low-frequency stable carbon isotope trends reflect the increasing temperatures since the beginning of the 20<sup>th</sup> century.

## References

- Andreu, L., Planells, O., Gutierrez, E., Helle, G., Schleser, G.H. (2008): Climatic significance of tree ring width and  $\delta^{13}\text{C}$  in a Spanish pine forest network. *Tellus B* 60, 771-781.
- Büntgen, U., Frank, D., Grudd, H., Esper, J. (2008): Long-term summer temperature variations in the Pyrenees. *Climate Dynamics* 31: 615-631.
- Büntgen, U., Frank, D.C., Trouet, V., Esper, J. (2010): Diverse climate sensitivity of Mediterranean tree ring width and density. *Trees* 24: 261-273.
- Briffa, K.R., Jones, P.D., Bartholin, T.S., Eckstein, D., Schweingruber, F.H., Karlén, W., Zetterberg, P., Eronen, M. (1992): Fennoscandian summers from AD 500: temperature changes on short and long timescales. *Climate Dynamics* 7: 111–119.
- Cook, E. R. (1985), A time series analysis approach to tree ring standardization, Ph.D. dissertation, 171 pp., Univ. of Ariz., Tucson.
- Dai, A., Trenberth, K. E., Qian, T. (2004): A global dataset of Palmer Drought Severity Index for 1870–2002: Relationship with soil moisture and effects of surface warming. *Journal of Hydrometeorology* 5: 1117-1130.
- Dorado Liñán, I., Gutiérrez, E., Heinrich, I., Andreu-Hayles, A., Muntán, E., Campelo, F., Helle, G. (2011): Age effects and climate response in trees: a multi-proxy tree ring test in old-growth life stages. *European Journal of Forest Research* 131: 933-944.
- Dorado Liñán, I., Büntgen, U., Gonzalez-Rouco, F., Zorita, E., Montavez, J.P., Gomez-Navarro, J.J., Brunet, M., Heinrich, I., Helle, G., Gutiérrez, E. (2012): Estimating 750 years of temperature variations and uncertainties in the Pyrenees by tree ring reconstructions and climate simulations. *Climate of the Past* 8: 919-933.
- Esper, J., Cook, E.R., Schweingruber, F.H. (2002): Low-frequency signals in long tree ring chronologies and the reconstruction of past temperature variability. *Science* 295: 2250-2253.
- Esper, J., Cook, E.R., Krusic, P.J., Peters, K., Schweingruber, F.H. (2003): Tests of the RCS method for preserving low-frequency variability in long tree ring chronologies. *Tree ring Research* 59: 81-98.
- Esper, J., Frank, D.C., Battipaglia, G., Büntgen, U., Holert, C., Treydte, K., Siegwolf, R., Saurer, M. (2010): Low-frequency noise in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  tree ring data: A case study of *Pinus uncinata* in the Spanish Pyrenees. *Global Biogeochemical Cycles* 24: doi: 10.1029/2010GB0037772.
- Farquhar, G.D., O'Leary, M.H., Berry, J.A. (1982): On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves. *Australian Journal of Plant Physiology* 9: 121-137.
- Feng, X., Epstein, S. (1995): Carbon isotopes of trees from arid environments and implications for reconstructing atmospheric CO<sub>2</sub> concentration. *Geochimica et Cosmochimica Acta* 59, 12: 2599–2608.
- Fritts, H.C. (1976): *Tree Rings and Climate*. Blackburn Press. 567 p.
- Gagen, M., Zorita, E., McCarroll, D., Young, G.H.F., Grudd, H., Jalkanen, R., Loader, N., Robertson, I., Kirchhefer (2011): Cloud response to summer temperatures in Fennoscandia over the last thousand years. *Geophysical Research Letters* 38: doi: 10.1029/2010GL046216, 2011.
- Green, J.W. (1963): Wood Cellulose. In Whistler, R.L. (Ed.), *Methods of Carbohydrate Chemistry* III. Academic Press. pp. 9-21.
- Helle, G., Schleser, G.H. (2004): Interpreting climate proxies from tree rings. In: Fischer, H., Floeser, G., Kumke, T., Lohmann, G., Miller, H., Negendank, J.F.W., von Storch, H. (Eds.), *The climate in Historical Times, Towards a synthesis of Holocene proxy data and climate models*. Springer Verlag. pp. 129-148.

- Holmes, R.L. (1983): Computer-assisted quality control in tree ring dating and measurement. *Tree ring Bulletin* 43, 69-78.
- IPCC (2007): *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Kürschner, K. (1996): Leaf stomata as biosensors of paleoatmospheric CO<sub>2</sub> levels. Utrecht, 160 p.
- Laumer, W.; Andreu, L.; Helle, G.; Schleser, G. H.; Wieloch, T.; Wissel, H. (2009): A novel approach for the homogenization of cellulose to use micro-amounts for stable isotope analyses. *Rapid Communications in Mass Spectrometry* 23, 13: 1934-1940.
- Leavitt, S.W., Long, A (1984): Sampling strategy for stable isotope analysis of tree rings in pine. *Nature* 311: 145-147.
- 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. *Chemical Geology* 136, 313-317.
- McCarroll, D., Loader, N.J. (2004): Stable isotopes in tree rings. *Quaternary Science Reviews* 23: 771-801.
- Mitchell, T.D., Jones, P.D. (2005): An improved method of constructing a database of monthly climate observations and associated high-resolution grids. *Int. J. Climatology* 25: 693-712, Doi: 10.1002/joc.1181.
- Rinn, F., 2007. TSAP - WinTM Professional. *Zeitreihenanalyse und Präsentation für Dendrochronologie und verwandte Anwendungen. Benutzerhandbuch*, Heidelberg: 56 pp.
- Seftigen, K., Linderholm, H.W., Loader, N., Liu, Y., Young, G.H.F. (2011): The influence of climate on <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O ratios in tree ring cellulose of *Pinus sylvestris* L. growing in the central Scandinavian Mountains. *Chemical Geology* 286: 84-93.
- Treydte, K., et al. (2007): Signal strength and climate calibration of a European tree ring isotope network, *Geophysical Research Letter*, 34: doi: 10.1029/2007GL031106.
- Treydte, K., Frank, D.C., Saurer, M., Helle, G., Schleser, G.H., Esper, J. (2009): Impact of climate and CO<sub>2</sub> on a millennium-long tree ring carbon isotope record. *Geochimica et Cosmochimica Acta* 71: 4635-4647.