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Tree-ring cellulose exhibits several distinct intramolecular 13C signals

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Stable carbon isotopes are a key tool in biogeosciences. Present applications including compound-specific isotope analysis measure $^{13}C/^{12}C$ ratios ($\delta^{13}C$) of bulk material or of whole molecules. However, it is well known that primary metabolites also show large intramolecular ^{13}C variation – also called isotopomer variation. This variation reflects ^{13}C fractionation by enzyme reactions and therefore encodes metabolic information. Furthermore, $\delta^{13}C$ must be considered an average of the intramolecular ^{13}C distribution.

Here we will present (1) methodology to analyse intramolecular ^{13}C distributions of tree-ring cellulose by quantitative ^{13}C NMR (Chaintreau et al., 2013, Anal Chim Acta, **788**, 108-113); (2) intramolecular ^{13}C distributions of an annually-resolved tree ring chronology (*Pinus nigra*, 1961-1995); (3) isotope parameters and terminology for analysis of intramolecular isotope time series; (4) a method for correcting for heterotrophic C redistribution.

We will show that the intramolecular ^{13}C distribution of tree-ring cellulose shows large variation, with differences between isotopomers exceeding 10‰Thus, individual ^{13}C isotopomers of cellulose constitute distinct ^{13}C inputs into major global C pools such as wood and soil organic matter. When glucose units with the observed intramolecular ^{13}C pattern are broken down along alternative catabolic pathways, it must be expected that respired CO_2 with strongly differing $\delta^{13}C$ will be released; indicating that intramolecular ^{13}C variation affects isotope signals of atmosphere-biosphere C exchange fluxes. taking this variation into account will improve modelling of the global C cycle.

Furthermore, cluster analysis shows that tree-ring glucose exhibits several independent intramolecular ^{13}C signals, which constitute distinct ecophysiological information channels. Thus, whole-molecule ^{13}C analysis likely misses a large part of the isotope information stored in tree rings. As we have shown for deuterium (Ehlers et al., 2015, PNAS, **112**, 15585), intramolecular isotope signals allow tracing plant acclimation over centuries, and intramolecular ^{13}C distributions will also improve our understanding of ^{13}C signatures of global C fluxes.