



New ecophysiological information from intramolecular isotope variation: methods, analysis and implications for biogeochemistry

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Conventional isotope applications in ecology and biogeosciences measure isotope ratios (e.g. $\delta^{13}\text{C}$) of whole molecules. However, for primary metabolites large intramolecular isotope variation – isotopomer variation – has long been known. This variation reflects enzyme fractionations and encodes metabolic information.

We will for two example studies present approaches to measure such intramolecular variation, concepts for data analysis, and models to derive physiological interpretations.

First, intramolecular ^{13}C distributions of an annually-resolved *Pinus nigra* chronology. We 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. When glucose units with the observed intramolecular ^{13}C pattern are broken down, CO_2 with strongly differing $\delta^{13}\text{C}$ will be released; affecting isotope signals of atmosphere-biosphere C exchange fluxes. Furthermore, cluster analysis shows that tree-ring glucose exhibits several independent intramolecular ^{13}C signals, which constitute distinct ecophysiological information channels. ^{13}C fractionation by stomata/Rubisco explains only part of isotopomer variation, suggesting that whole-molecule ^{13}C analysis likely misses a large part of the isotope information stored in tree rings.

Second, results from a study of deuterium isotopomers in tree rings. We compare data from growth chamber experiments, FACE studies and tree-ring series covering the anthropogenic CO_2 since industrialization. The increase in CO_2 should have led to increased photosynthesis, but this CO_2 fertilization effect is poorly constrained on long time scales. A substantial part of the expected increase of photosynthesis is due to expected CO_2 -driven suppression of photorespiration. Data will also be compared to herbaceous C_3 species, with the goal to quantify the CO_2 -driven suppression of photorespiration during recent decades.