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The hydrogen isotopic composition of plant carbohydrates – Advancement in methods and interpretation

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The hydrogen isotopic composition (δ^2H) of plant organic matter is considered as a potential proxy for hydro-climatic conditions, plant physiology, and metabolic pathways. However, the information that is imprinted on δ^2H of photosynthetic assimilates (i.e., sugars), carbon storage (i.e., starch) and plant biomass (i.e. cellulose) is barely understood so far, mainly due to methodological constraints. Here we present a novel high-throughput method that allows accurate and precise analyses of δ^2H values in various plant carbohydrates. The new method is based on an equilibration between water vapor of a known isotopic composition and hydroxyl group of carbohydrate molecules at 130°C in metal chamber, which is performed before the actual IRMS measurement. The equilibration allows for mathematical corrections and the determination of the non-exchangeable carbon-bound hydrogen isotopic composition in plant carbohydrates, containing the actual meaningful information. Initial applications under controlled conditions showed clear δ^2H differences among plant types differing in their photosynthetic pathways (e.g. C3, C4, CAM) and carbohydrate classes (e.g. sugars, starch, and cellulose) within each plant type. We also tested phylogenetic differences among 73 tree species in a common garden experiment to create a baseline knowledge for further tree-ring applications. We observed large phylogenetic δ^2H variation over 100‰, with clear δ^2H difference between angio- and gymnosperms, but not between deciduous and evergreen species. Finally, results from controlled-environment tobacco experiments showed that δ^2H variation in plant carbohydrates can be explained by differences in the primary carbon metabolism. Yet, δ^2H values of lipids in the same experiments did not carry a metabolic signal, suggesting strong difference in the metabolic origin of H atoms between lipids and carbohydrates. The different response of the two compound classes may help to better understand metabolic fluxes and plant responses to changing environmental conditions and may improve their reconstruction. Given the recent methodological advancement and interpretation of hydrogen isotopes patterns in plant carbohydrates, we predict a fast increase in δ^2H applications on various dateable geological and ecological archives such as tree-rings, lake-sediment plant macrofossils, or peatlands to investigate plant responses to climatic or non-climatic extremes, carbon allocation and starvation, and tree mortality.