n-Alkane biosynthetic hydrogen isotope fractionation is not constant throughout the growing season in the riparian tree Salix viminalis

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Compound-specific δ2H values of leaf wax n-alkanes have emerged as a potentially powerful paleohydrological proxy. Research suggests terrestrial plant n-alkane δ2H values are strongly correlated with meteoric water δ2H values, and may provide information on temperature, relative humidity, evaporation, and precipitation. This is based upon several assumptions, including that biosynthetic fractionation of n-alkanes during synthesis is constant within a single species. Here we present a multi-isotope study of the n-alkanes of riparian Salix viminalis growing in Norwich, UK. We measured n-alkane δ2H, leaf water δ2H, xylem water δ2H, and bulk foliar δ13C and evaluated the variability of n-alkane δ2H values and net biosynthetic fractionation (εlw-wax) over a whole growing season. S. viminalis n-alkane δ2H values decreased by 40‰between the start of the growing season in April and the time when they stabilized in July. Variation in leaf and xylem water δ2H did not explain this variability. εlw-wax varied from $-$116‰during leaf expansion in April to $-$156‰during the stable phase. This suggests that differential biosynthetic fractionation was responsible for the strong seasonal trends in S. viminalis n-alkane δ2H values. We suggest that variability in εlw-wax is driven by seasonal differences in the carbohydrate source and thus the NADPH used in n-alkane biosynthesis, with stored carbohydrates utilized during spring and recent occurring growing season assimilates used later in the season. This is further supported by bulk foliar δ13C values, which are 13C-enriched during the period of leaf flush, relative to the end of the growing season. Our results challenge the assumption that biosynthetic fractionation is constant for a given species, and suggest that 2H-enriched stored assimilates are an important source for n-alkane biosynthesis early in the growing season. These findings have implications for the interpretation of sedimentary n-alkanes and call for a careful design of calibration studies using contemporary samples.

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