n-alkane biosynthetic fractionation is not constant in field-grown Salix

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Compound-specific δ^2H values of terrrestrial plant *n*-alkanes have emerged as a potentially powerful paleohydrological proxy. Research suggests *n*-alkanes are strongly correlated with meteoric waters, and may provide information on temperature, relative humidty, evaporation, and precipitation. However, these findings are based upon several assummptions, one of which is biosynthetic fractionation (ε_{bio}) is constant within a single species. Here we present a whole-growth season study of the *n*-alkanes of field-grown Salix. Using a multi-isotope and conceptual model approach, with measurements of bulk foliar $\delta^{13}C$, *n*-alkane δ^2H, leaf water $\delta^{18}O$ and δ^2H, and xylem water δ^2H, we test the consistency of *n*-alkane δ^2H values, and ε_{bio}, over the course of a whole growth season.

The results suggests Salix *n*-alkanes are "locked in" after 13-weeks, exhibiting a ~40 ‰ ^2H-depletion from the start of flush to the "locked in" phase in July. Empricially derived, and model-estimated ε_{bio} significantly varies with time. With derived ε_{bio} showing significantly less fractionation during leaf flush (-116 ‰ in April, vs. -156 ‰ in the locked in phase). The enriched $\delta^{18}O$ and δ^2H leaf water values suggest the stomata are functioning normally during leaf flush. While stable and ^{13}C-enriched bulk foliar $\delta^{13}C$ values during the same period suggest the leaves are not metablically mature enough to produce organic matter from current photsynthates. These results challenge the assumption that ε_{bio} is constant for a given species, and suggest ^2H-enriched stored assimilates are an important hydrogen source for *n*-alkane biosynthesis during leaf flush. These findings have implications for the interpretation of sedimentary *n*-alkanes and call for a carefull design of calibration studies using contemporary samples.