



Effect of leaf litter degradation and seasonality on D/H isotope ratios of n-alkane biomarkers

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During the last decade, compound-specific hydrogen isotope analysis of plant leaf-wax and sedimentary n-alkyl lipids has become a promising tool for paleohydrological reconstructions. However, with the exception of several previous studies, there is a lack of knowledge regarding possible effects of early diagenesis on the δD values of n-alkanes. We therefore investigated the n-alkane patterns and δD values of long-chain n-alkanes from three different C3 higher plant species (*Acer pseudoplatanus* L., *Fagus sylvatica* L. and *Sorbus aucuparia* L.) that have been degraded in a field leaf litterbag experiment for 27 months.

We found that after an initial increase of the total long-chain n-alkane mass (up to $\sim 50\%$), decomposition took place with mean turnover times of 11.7 months. Intermittently, the total mass of mid-chain n-alkanes increased significantly during periods of highest mass losses. Furthermore, initially high odd-over-even predominance declined and long-chain n-alkane ratios like n-C31/C27 and n-C31/C29 started to converge to the value of 1. While bulk leaf litter became systematically D-enriched especially during summer seasons (by $\sim 8\text{‰}$ on average over 27 months), the δD values of long-chain n-alkanes reveal no systematic overall shifts, but seasonal variations of up to 25‰ (*Fagus*, n-C27, average $\sim 13\text{‰}$).

These findings suggest that a microbial n-alkane pool sensitive to seasonal variations of soil water δD rapidly builds up. We propose a conceptual model that accounts for the decomposition of plant-derived n-alkanes and the build-up of microbial n-alkanes. Model results are in good agreement with measured n-alkane δD results. Since microbial 'contamination' is not necessarily discernible from n-alkane concentration patterns alone, care may have to be taken not to over-interpret δD values of sedimentary n-alkanes. Furthermore, since leaf-water is generally D-enriched compared to soil and lake waters, soil and water microbial n-alkane pools may help explain why soil and sediment n-alkanes are D-depleted compared to leaves.