



Understanding the effects of early degradation on isotopic tracers: implications for sediment source attribution using compound-specific isotope analysis (CSIA)

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Application of compound-specific isotope analysis (CSIA) in sediment fingerprinting source apportionment studies is becoming more frequent, as it can potentially provide robust land-use based source attribution of freshwater sediments. A variety of vegetation-derived organic compounds are considered to be suitable as tracers for CSIA fingerprinting technique, with the most common ones being long-chain fatty acids and *n*-alkanes. However, a rigorous evaluation of tracer conservativeness in terms of isotopic signature stability during detachment and transport processes is essential for the specific application of CSIA. With the aim to identify potential fractionation and thus shifts in tracer signatures during early degradation of organic matter, we analysed concentrations and stable carbon isotopic ratios ($\delta^{13}\text{C}$) of long-chain fatty acids and *n*-alkanes from fresh plant biomass, degraded organic matter (Oi, Oe and Oa horizons) as well as upper mineral soil (A horizon) from various forest types with different humus forms (5 sites). Vegetation was the predominant source of long-chain fatty acids and *n*-alkanes in soils. Additionally, fatty acids in the soils were also produced by the oxidation of other compounds. The bulk $\delta^{13}\text{C}$ values showed continuous enrichment over the degradation gradient from fresh plant material to O – and A horizons, ranging between 3.5‰ and 5.6‰. Compound specific $\delta^{13}\text{C}$ values showed a clear enrichment for both, long-chain fatty acids as well as *n*-alkanes from plant material to O horizon overlying on the mineral soil. However, the compound specific $\delta^{13}\text{C}$ values remained largely unchanged between A horizon and the overlying degraded organic sub-horizon. We also compared compound specific $\delta^{13}\text{C}$ values between two soil particle-sizes (< 2 mm and < 63 μm) within the soils (A horizon) from 4 sites and found no significant differences between them, although the long-chain *n*-alkanes showed comparatively closer isotopic values.

To conclude, because of the relative stability of compound specific $\delta^{13}\text{C}$ signal of long-chain fatty acids and *n*-alkanes during degradation from the fresh plant material to O – and A horizons, our results supports the suitability of these tracers as representative source soil signature in CSIA based sediment source attribution. Furthermore, particle size effects on tracer signature of the bulk soil (< 2 mm) compared to the fine fraction (< 63 μm) seem to be negligible.