Are sediment-derived long-chain *n*-alkanes a reliable paleoenvironmental indicator?

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In soil, the distribution and carbon isotopic composition of *n*-alkane ($d^{13}C_{n\text{-}alk}$) is extremely source-specific. In general, terrestrial higher plants are primary producers of long-chain *n*-alkanes (C_{27}-C_{33}) while short-chain *n*-alkanes (C_{14}-C_{20}) are mainly contributed from microorganisms with distinct $d^{13}C_{n\text{-}alk}$ values. Hence, the distribution and $d^{13}C$ values of *n*-alkane in sediments have been primarily used to characterize the source(s) of organic matter in a given depositional environment as well as to gain insight into paleoenvironmental conditions. However, very little is known about post-depositional modification of plant-derived long-chain n-alkanes within the soil. Therefore, the present study aims to understand the factors affecting the distribution and $d^{13}C$ values of long-chain *n*-alkanes in the soil as well as evaluate their potential as paleoenvironmental indicators. In this context, three soil profiles developed within an oxbow lake setting from the lower Gangetic plain, West Bengal, India has been used. The *n*-alkanes exhibit a bimodal distribution suggesting contributions from both terrestrial higher plants and soil microbes. The concentration of long-chain *n*-alkanes (C_{27}-C_{33}) within the soil profiles decreases with depth, indicating a significant loss of biomarkers during soil-forming processes. In the soil profiles, the $d^{13}C_{n\text{-}alk}$ values exhibit a high degree of variability across the higher molecular weight homologues (C_{27}-C_{33}). On the contrary, the $d^{13}C_{n\text{-}alk}$ values of the modern C_3 and C_4 plants from the study area show minimal variation (~2‰) in the isotopic composition across its homologues (C_{27}-C_{33}). This suggests that the observed variation in the $d^{13}C_{n\text{-}alk}$ values in the soil is a result of microbial degradation of *n*-alkanes during its transfer from leaves to soil. Additionally, the inter-homologue variation in the $d^{13}C_{n\text{-}alk}$ values shows an increasing trend with depth (from 6.0‰ to 9.6‰) suggesting that older soil samples have undergone more microbial alteration compared to the younger ones. As the $d^{13}C$ values of higher molecular weight homologues (C_{27}-C_{33}) have been primarily used to estimate the relative abundance of C_3 and C_4 plants in the past, significant inter-homologue variations in the $d^{13}C_{n\text{-}alk}$ values can result in erroneous paleovegetational interpretations. Therefore, the present study suggests that caution must be exercised while using *n*-alkanes as a paleoenvironmental indicator as the variations in $d^{13}C_{n\text{-}alk}$ values in sediments is a cumulative product of temporal changes in the vegetation composition and post-depositional modifications experienced by the biomarker.

Keywords: Biomarker, Carbon Isotope, Microbial degradation, Paleoenvironment

