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Disentangling the effect of thermal and microbial degradation on the distribution pattern of n-alkanes in sediments: Implication for paleo-fire studies

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Biomass burning is an important component of major biomes as it acts as an ecological forcing factor in controlling the vegetation composition as well as biomass production. Thus long-term paleo-fire records are required to understand the extent to which future fire regimes will affect ecosystem health and the global carbon balance. Unfortunately, paleo-fire proxies such as charcoal analysis, dendrochronology and archaeological relicts are often fragmented and difficult to interpret owing to their poor preservation in the natural archives. To resolve the uncertainties associated with the existing paleo-fire proxies, biomarker-based investigations (n-alkanes) provide a new avenue for gaining insight into the paleo-fire events due to their relatively stable chemical property and source-specific distribution in sediments. For instance, laboratory and field-based experiments have shown that a significant amount of short-chain n-alkanes (predominantly C₁₈) are produced at the expense of long-chain n-alkanes during thermal degradation of plant-derived organic matter. This modification of primary carbon chain-length can thus be used as a tool to decipher paleo-fire events. However, this characteristic distribution pattern of n-alkane in the soil can also result from microbial degradation of plant-derived organic matter. Therefore, it is vital to disentangle the effect of thermal and microbial degradation on the distribution pattern of n-alkane before using it for paleo-fire reconstructions. For this purpose, published n-alkane distribution records from two distinct climatic settings have been compared. The site-A is located in arid Banni grassland, western India (with a history of repeated fire events) whereas, site-B is situated at the sub-humid region of southern peninsular India (Lake Ennamangalam). The n-alkane distribution in both the sites exhibits a dominance of short-chain homologues with prominent even-over-odd preference (EOP). The cross-plot between the relative concentration of C₁₈ (dominant in short-chain) and C₂₉ (dominant in long-chain) homologues shows positive and significant correlation ($R^2 = 0.9$, $p < 0.05$, $n=19$) at site-A, whereas statistically insignificant correlation ($R^2 = 0.2$, $p < 0.05$, $n=19$) has been obtained from site-B. In case of thermal events, production of short-chain n-alkanes (predominantly C₁₈) is related to the temperature-dependent breakdown of long-chain n-alkanes. Subsequently, the concentration of C₁₈ and C₂₉ homologues are expected to be well correlated, as observed in site-A. On the contrary, in a depositional setting dominated by microbial activity, multiple sources of C₁₈ homologue may produce an insignificant correlation, as observed from site-B. Therefore, it can be suggested that short-chain n-alkanes at

site-A are a product of thermal degradation while microbial activity controlled the distribution of short-chain n-alkanes at site-B. This claim is further supported by the ratio between the relative concentration of C_{18} and C_{19} homologues (P_{Factor}) which are much higher at site-A (11 to 62) compared to that of the site-B (1 to 10). Higher production of C_{18} homologue during thermal degradation perhaps is producing the offset in the P_{Factor} values for site-A and B. Our observations will be useful to recognise paleo-fire events that have been previously overlooked owing to the fragmentary nature and limited preservation of existing proxies.