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Sequential fatty acid analysis of a peat core covering the last two millennia (Tritrivakely lake, Madagascar): diagenesis appraisal and consequences for palaeoenvironmental reconstruction.

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When studying fatty acids (FAs) organic geochemists classically paid attention either to the "free" fraction or to "bound" compounds commonly released by saponification. However, it is now well established that more detailed information can be obtained by a study of the various pools of FAs that can be released successively by different chemical treatments (e.g. [1]). Following previous geochemical and petrographical work [2], we applied such an approach to the analysis of a peat core section to get additional information on the palaeoenvironment of the study area and its changes during the last 2300 yr. Thus, seven samples from the 1m long upper section of a core taken from the centre of the Tritrivakely maar lake (Madagascar), were successively submitted to solvent extraction, acid hydrolysis and saponification to release their "free", H⁺-labile and OH⁻-labile bound fatty acids, respectively. The main conclusions that can be drawn from this approach can be summarized as follows:

(1) High amounts of "free" and OH⁻-labile FAs (saturated and unsaturated n-FAs, plus i-C₁₆) at the surface of the peat sequence and low amounts in the immediately underlying level indicate rapid hydrolysis of lipid esters inherited from the primary production, followed by slightly slower consumption.

(2) A whole range of OH⁻-labile FAs (diacids, i- and ai-C₁₅, 3-OH-C₁₄) that are almost or even totally absent from the peat surface, but are abundant at the sub-surface before decreasing just below, denote *in situ* secondary production and subsequent decay. All the corresponding compounds are totally missing from the "free" fraction.

(3) Once past the upper levels where FA dynamics are very active in response to primary inputs, secondary production and active diagenesis, most of the H⁺-labile FAs attest to an important but late *in situ* microbial production that rather rapidly slows down with increasing depth. The latter can be considered as a third production.

(4) In contrast, compounds such as i-C₁₅ and ai-C₁₅ acids also released by acid hydrolysis and which are abundant at the sub-surface but vary very irregularly at depth, might

be inherited from consumers acting as secondary producers. As a matter of fact, these compounds maximize at depth at levels (ca. 30 cm and 60 cm) strongly depleted in "free" and OH⁻-labile FAs normally inherited from the primary producers.

(5) High OM preservation conditions (e.g. at ca. 98 cm depth) are indicated by high relative amounts of nearly all compounds especially in the "free" and OH⁻-labile fraction (i.e. inherited from the primary as well as from the secondary producers, consumers included).

6) The comparison of compound concentration profiles permits recognition of whether compounds are related to each other or not, i.e. whether they have the same source (e.g. i- and ai-C₁₅), or be independent.

(7) Sequential FA extraction combined with comparison of depth-related compound concentration profiles constitutes what looks like a molecular stratigraphy approach.

(8) However, the previous statement must also take into account the fact that active molecular dynamics during diagenesis hardly allows the drawing of a reliable geochemical portrait for isolated recent geological samples (sediments or soils) after FA analysis. As formulated in a previous study on lake sediments [3], extensive diagenesis can provoke the disappearance of most fatty acids and thus nearly all give information on the contributing organisms except the latest consumers-producers, i.e. methanotrophs.

References

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