Comparative analysis of molecular biomarkers in the sediments of two artificial urban lakes in Orléans, France

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The onset of the Anthropocene, a new geological Era characterized by human activities being the dominant geological process affecting the Earth surface, will soon be defined by the International Commission on Stratigraphy in 1950 AD (Zalasiewicz, 2015). For palaeoenvironmentalists, the Anthropocene opens a new and very exciting challenge: decrypt geological archives by using various tracers over unusual time scales (days, seasons, years, decades) and take into account the major forcing factor: human activities. As for longer time periods and more natural contexts, organic geochemistry will have to contribute and will be confronted to emerging issues: (1) to which extent organic tracers and proxies developed for longer time scales, in more natural ecosystems, can be transferred and applied in hyper-anthropized socio-ecosystems such as urban areas?; (2) human activities produce novel materials and organic compounds such as emerging pollutants that could be readily considered as novel tracers for a large set of socio-economic concerns, thus establishing new connections between paleoenvironmentalists and researchers engaged into pollution studies.

We have analysed molecular biomarkers preserved in the sediments of two artificial lakes of Orléans: Lac de l'Université (LU) and Lac de l'Orée de Sologne (LOS) in order to determine their potential as sedimentary archives, through the presence of both sedimentary accumulations and specific tracers in order to reconstruct the recent history of their surroundings, and evaluate to which extent molecular imprints reflect local environmental conditions. Those two lakes collect local rainwaters and were clean out around 1990. Only few centimetres could be collected in LOS whereas LU afforded 30 cm constituted by 6 cm of sand with gravels (TOC<0.1 %; Tmax >400°C), then 16 cm of black organic clay and finally 8 cm of greenish organic clay (TOC> 5%, IH>400 mgHC/COT, IO~150 mgO_2/COT, Tmax>400°C).

The strong contribution of vascular plants to the sediment is not only attested by Rock-Eval values but also by the distribution of n-alkanes that maximize at *n*-C_{27} with a strong odd/even predominance. In LOS minor amounts of short-chain n-alkanes attest to a bacterial/algal contribution. The ketone fraction afforded a large diversity of compounds such as pentacyclic triterpenones (taraxerone, β- and α-amyrenones, germanicone, lupanone, glutinone and friedelin). In addition, LOS sample displayed abietic acid and a series of four methoxy-serratenes (two dimethoxy and two keto-methoxy; LeMilbeau et al., 2013). LOS sample was also characterized by the presence of four compounds of which the mass spectra displayed M^+ at m/z 378 or 392 and intense m/z at 199 and 225 that are interpreted as diagenetic derivatives of pentacyclic triterpenes bearing a ketone function (Tris-nor-olea-trien-2-one, Tris-nor-ursa-trien-2-one, Bis-nor-olea-trien-2-one and Bis-nor-ursa-trien-2-one). The alcohol fraction contained the alcohol equivalent to triterpene ketones such as taraxerol, β-, δ- and α-amyrins, germanicol and glutinol, as well as a keto-methoxy-serratene and a hydroxy-methoxy-serratenes in LOS. Again, LOS displayed original pentacyclic triterpenes constituted by diketo Δ^{12} (Bandaranayake, 1980) and $\Delta^{12,17(18)}$ (Schnell et al., 2012) derivatives with an ursane and an oleanane structure. We also detected aromatic a series of compounds of which the mass spectra display M^+ at m/z 360, 390 and 404 that could correspond to derivatives of pentacyclic triterpenes with one or two ketone functions (Le Milbeau, 2005; Le Milbeau et al., 2010).

The molecular imprints of sediments in these two urban lakes provide preliminary information on the application of molecular biomarkers in highly anthropized systems. First, we detected few traces of pollutant contamination such as fossil hydrocarbons. The picture is off course incomplete since we did not adapt our methods to analyse other organic compounds such as drugs or pesticides. Second, the molecular imprint is very similar to those depicted in more natural environments with a classical n-alkanes distribution, various pentacyclic triterpenes and their derivatives. Third, we detected original structures such as diketone or ketoaromatic derivatives of pentacyclic triterpenes. A precise study of their sources and diagenetic pathway could be of interest for their broader application in paleoenvironmental studies. Finally, its is worthwhile noting that distinct imprints between the two lakes attest to local differences in the surroundings. For example, LOS sediments contain abietic acid and methoxy-serratenes. This is consistant with the presence of Pinaceae in LOS catchment whereas no Pinaceae is to note in the immediate vicinity of LU.

Although the thickness of the sedimentary pile did not satisfy our expectations in order to reconstruct the recent history of urban lakes surrounding, our study confirm that molecular biomarkers in such a context constitute robust tracers of local/immediate environmental conditions.

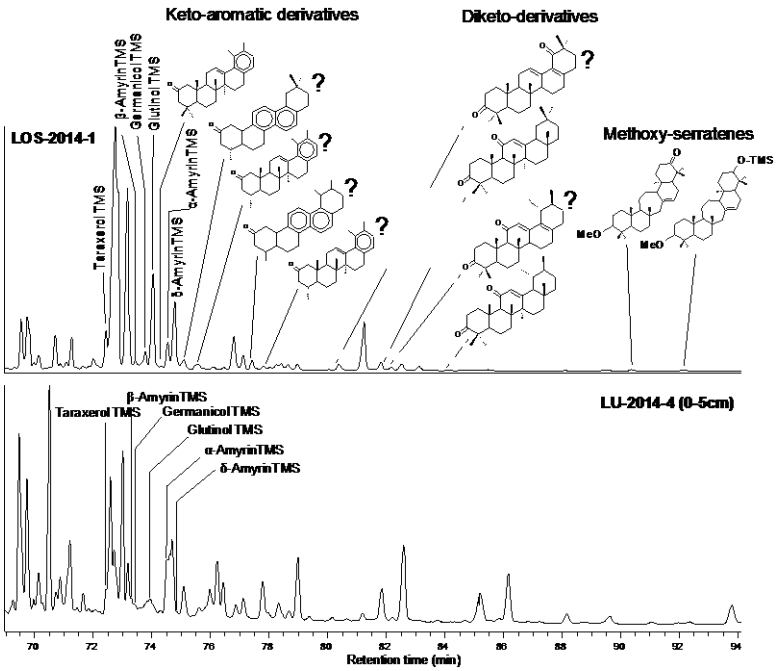

Fig. 1. Distribution of pentacyclic triterpenes and their derivatives in the alcohol fractions of LOS and LU samples.

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