

MICROWAVE-ASSISTED HYDROLYSIS INVESTIGATION OF THE SPATIO-TIME VARIABILITY OF RIVERINE ORGANIC MATTER IN THE SEINE BASIN

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Organic matter (OM) of natural waters plays a major role in the global cycles of carbon and nitrogen at several levels. In particular, its role is of main importance on the geochemistry of metallic or organic micro-pollutants since it potentially influences their speciation and bioavailability. Additionally, from an operational point of view, it is a key parameter in drinking water treatment.

To extend our knowledge about riverine OM and within the frame of the *Piren-Seine* French project, it was thus decided to trace sources of OM (*allochthonous* vs *autochthonous*, *natural* or *anthropic*) in several rivers of the Paris Basin (namely, the Seine, the Marne and the Oise) in order to investigate their spatio-time variability.

Twenty-two samples of particulate OM (POM) were collected through filtration of riverine waters from various places of the Seine, the Marne and the Oise watersheds, during two sampling campaigns corresponding to low and flood water periods (summer of 2012 and winter of 2013, respectively). These samples were analyzed using solid state CPMAS ¹³C NMR to determine their chemical functionalities, and through Curie point thermally assisted hydrolysis and methylation with tetramethylammonium hydroxyde (TMAH) coupled with GC-MS (CuTHM-GC-MS) to investigate their chemical composition at the molecular level. Comparison of the solid state ¹³C NMR spectra obtained for a given sampling site at low water vs flood water led to distinguish three main groups of samples, based on the relative abundance of aliphatic carbons with respect to polysaccharidic carbons: (i) samples exhibiting a strong relative decrease in the polysaccharide content reflecting an input of more humified OM during the flood (Fig. 1a), (ii) samples showing a strong increase in the polysaccharide content reflecting an input of fresher OM during the flood (Fig. 1b) and, (iii) samples characterized by carbohydrates and aliphatic signals of similar abundances whatever the sampling period (Fig. 1c).

The CuTHM-GC/MS traces of thermolysates revealed the presence of methoxy and dimethoxy aromatic compounds attributed to lignin and/or tannins, and various aliphatic linear compounds consisting mainly in the methylated derivatives of C_{16:0} and C_{18:0} mid-chain hydroxyalkanoic acids, even C_{16:0} to C_{24:0} ω-hydroxyalkanoic acids, even and odd C_{12:0} to C_{28:0} alkanolic acids, C_{9:0} and C_{16:0} alkanedioic acids, and even C_{16:0} to C_{26:0} alkan-1-ols which reflect a higher plant contribution (wax esters, cutin/suberin biopolymers). Nevertheless, contrary to ¹³C NMR spectra, products directly related to polysaccharides could not be detected in the CuTHM pyrolysates. Moreover, based on the relative abundance of the pyrolysis constituents, CuTHM-GC/MS and ¹³C NMR data could not be fully correlated. It therefore appeared necessary to investigate in more detail the hydrophilic constituents of these samples.

To this end, ten selected POM samples were analyzed using a recently developed alternative sequential microwave (MW)-assisted acid (HCl) and base (TMAH) hydrolysis (Allard and Derenne, 2009, 2013). Indeed, it has been reported that microwave energy interacts efficiently with the polar moieties of the macromolecular structure and is able to disrupt such polar bonds. At each step, the residues were investigated using CPMAS ¹³C NMR and CuTHM-GC-MS, and both organic and aqueous extracts were analyzed by GC-MS with

previous derivatization to focus on monosaccharides, 2-amino sugars and amino acids. Semi-quantitation of released compounds was performed using internal normalization.

The organic phases resulting from the MW-assisted acid hydrolysis showed besides cutin/suberin derivatives in low amount, the presence in various relative amount, of degraded sugars and mainly lignin derivatives. Aqueous phases allowed the identification of undegraded sugars (both hexoses and pentoses) and amino acids. Selective removal of polysaccharides and lignin derivatives proved that MW-assisted acid hydrolysis favors the cleavage of interunit linkages of the ether type. This trend was well confirmed by the relative decrease of lignin markers observed on the pyrolysates of the acid residues. Conversely, there was no significant evolution for the cutin/suberin derivatives, but they are selectively released upon the MW-assisted base hydrolysis as shown by the chromatograms of the organic phases and the pyrograms of the base residues. As expected, the MW-assisted hydrolysis upon basic conditions promotes the cleavage of ester linkages.

In addition, it was measured, from the acid and base residues, that 18 to 80% and 11 to 90% of the organic C were released through MW-assisted acid hydrolysis and MW-assisted base hydrolysis, respectively.

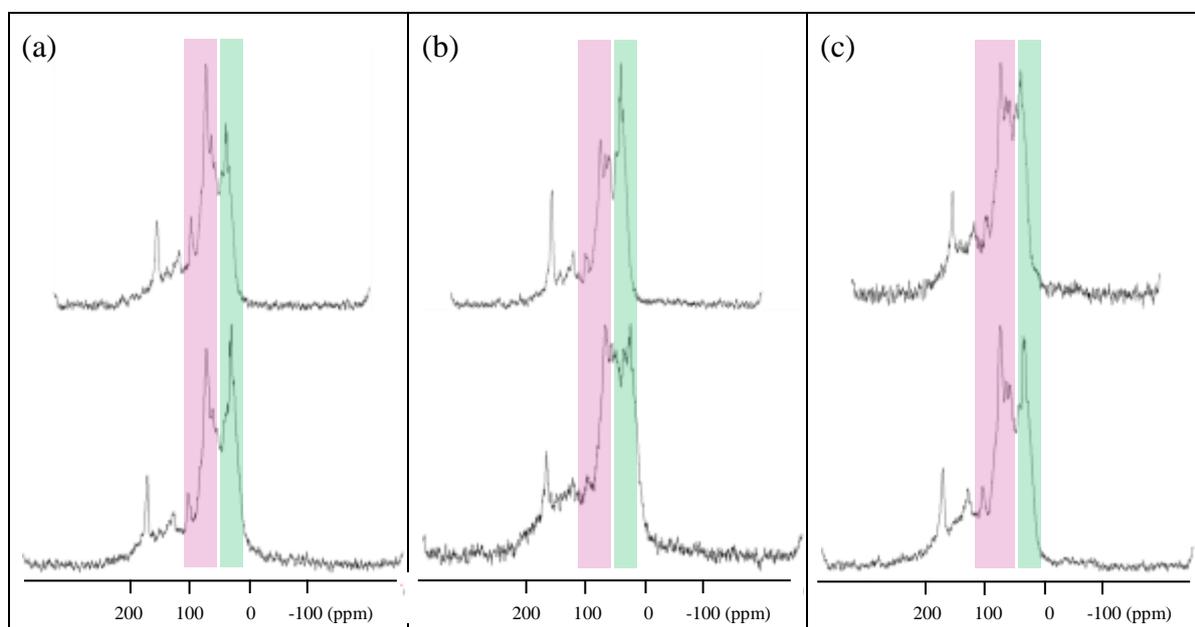


Figure 1: three main groups of samples identified by solid state CPMAS ^{13}C NMR, based on the relative abundance of aliphatic carbons (green area) with respect to polysaccharidic carbons (pink area), at low water (top) vs flood water (bottom).

This proof of concept highlights the efficiency of sequential MW-assisted hydrolysis coupled with GC/MS to characterize OM at the molecular level in riverine environments. Indeed, some noticeable extraction yields of the organic fractions were obtained and this technique appears especially suitable for the identification of hydrophilic compounds and to distinguish ether-bound from ester-bound moieties.

References

- Allard, B. and Derenne, S., 2009. Microwave assisted extraction and hydrolysis: An alternative to pyrolysis for the analysis of recalcitrant organic matter? Application to a forest soil (Landes de Gascogne, France). *Organic Geochemistry* 40, 1005-1019.
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