



Spatio-temporal variability of the molecular fingerprint of soil dissolved organic matter in a headwater agricultural catchment

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Dissolved organic matter (DOM) is implied in (i) ecosystem services such as the support of biodiversity, (ii) the alteration of the drinkable water quality by formation of trihalomethane and (iii) the transfer of micropollutants from soils to rivers. Moreover, since DOM connects soils and oceans that are interacting with the atmosphere, understanding its biogeochemistry will help in investigating the carbon cycle and in creating strategies to mitigate climate change.

DOM in headwater stream ecosystems is mainly inherited from allochthonous inputs with different reservoirs being mobilized during storm and interstorm events at the scale of an hydrological year. Those changes in DOM reservoirs, if accompanied by composition and reactivity changes, may impact DOM ecosystem services and drinking water production processes. Elucidating the compositional changes due to changes in the source of DOM in rivers has thus become an important axis of DOM research.

The aim of this study is to test the ability of the molecular tools of the organic geochemistry and more specifically the combination of thermochemolysis and gas chromatography – mass spectrometry (THM-GC-MS) to (i) link the variability of the river DOM composition to different DOM reservoirs in catchment soils and (ii) provide hypothesis on the nature and the mechanisms of formation (microbial growth, litter decomposition) of those reservoirs. This analytical method seems particularly adapted since it allows the differentiation between vegetal and microbial inputs and the determination of the extent of the biodegradation process of biomolecules such as lignin. To test this method, the molecular fingerprint of soil DOM has been investigated in the wetland area of a small (500 ha) agricultural catchment (the so-called Kervidy-Naizin catchment) located in Brittany, western France. The soil DOM was sampled fortnightly at three depths using zero-tension lysimeters during the hydrological year 2010–2011. The samples were freeze-dried and analyzed for their molecular composition using THM-GC-MS. Three chemical classes of compounds were investigated including lignin, polysaccharides and fatty acids.

The combination of those results at the molecular scale with the results of investigations on spectroscopic (specific UV absorbance at 254 nm, SUVA) fingerprints, the isotopic ($\delta^{13}C$) fingerprint of DOM and the hydrological data (water table depth) has highlighted (i) the correlation between molecular and bulk scales investigated using the SUVA and the proportion of lignin markers and (ii) the evolution of the molecular composition of soil DOM related to the changes of the water table depth, which could be linked to the mobilization of different reservoirs and/or to the succession of different mechanisms of production governed by the changes in hydrological regimes. This study highlights THM-GC-MS as a valuable tool to investigate the molecular composition of DOM. By differentiating the vegetal and the microbial components of DOM, it allows the investigation of the sources and mechanisms of DOM formation. Finally, its application to a catchment with hydrological data emphasizes the hydrological regime as a main driver of the evolution of the molecular composition of DOM.