

## Seasonal variation of NOM composition in Vosgian freshwaters: a molecular scale ESI-FTMS study

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### Introduction

Natural organic matter (NOM) is a significant component of freshwaters affecting biogeochemical cycling of metals. Various inputs (natural and anthropic) in aquatic ecosystems contribute to the chemical complexity and to the variability in composition and reactivity of dissolved NOM, including fulvic acids (FA). To better understand the effect of NOM on metal mobility, we determined the molecular composition of FA, and its seasonal variation, in freshwaters by means of electro-spray ionisation mass spectrometry (ESI-FTMS).

### Results

Samples were collected at different seasons of year 2016 in two connected rivers in "La Petite Pierre" valley (France) which is covered by hardwoods and/or conifer trees. FAs were extracted and purified using DAX resin (IHSS procedure). Molecular formula of organic molecules constitutive of FA were extracted from ESI(-)-FTMS data. Aromaticity index calculations led to define three classes of FA molecules, namely condensed aromatics (AC), aromatics (A) and aliphatics (AL). Molecular compositions were reported in Van Krevelen (VK) diagrams (H/C atomic ratio vs O/C ratio). Molecules (1580) common to all samples were mainly AL ( $O/C < 0.8$  and  $H/C < 1.6$ ) and a few molecules of the types A ( $O/C < 0.7$ ) and hydrogenated AC ( $O/C < 0.5$ ). At end of winter, additional 1957 compounds -distributed in all three classes- were identified, especially on a VK diagram region gathering poorly hydrogenated and highly oxygenated A and AL ( $0.5 < O/C < 0.9$ ). At end of rainy period (spring), FAs are made up by the common compounds and by 1760 additional low-oxygenated molecules (AL:  $O/C < 0.7$ ; AC:  $O/C < 0.3$ ). End of summer favored mainly low-oxygenated ( $O/C < 0.5$ ) and highly hydrogenated ( $H/C < 1.8$ ) AL compound. All of these poorly-oxygenated compounds disappeared at beginning of winter. The data obtained showing a season dependency of FA composition suggested seasonal changes in dissolved FA chemical reactivity, which may coincide with variations in metal concentrations observed for these waters.