

## **Influence of FA composition on mobility of trace metal elements (TME) in surface waters**

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**Introduction :** Understanding mobility of TME such as lanthanides (Ln) or Uranium (U) in surface waters requires knowledge on TME interactions with natural organic matters such as Fulvic Acids (FA), which are complex mixtures of thousands of organic molecules and are known to bind metals. In this study, we studied FA samples extracted from surface waters having significant contents of U and Ln by using electrospray ionization Fourier Transform mass spectrometry (ESI-FTMS) analysis. The aim was gaining molecular-scale insights into the chemical identity of FA molecules which influence metal mobility.

**Results and conclusion :** Two granitic sites were selected for collection of surface waters (3 samples per site) in deciduous forests and in close vicinity of the U ancient mines of Saint-Hippolyte (SH) and Lachaux (LA) exploited in the 1950s in France. Concentrations of U (0.9 to 3 ppb) and Ln (0.01 to 0.8 ppb) of collected samples were measured by ICP-MS and were found not correlated with concentration of dissolved inorganic carbon ( $<5\text{mg.L}^{-1}$ ) of waters. The samples showed significant concentrations of dissolved organic carbon (DOC) from  $2.5\text{ mg.L}^{-1}$  (LA) up to  $6.7\text{ mg.L}^{-1}$  (SH), suggesting a possible influence of DOC on mobility of U and Ln in these surface waters. The FA were extracted according to the IHSS protocol (DAX 8) and characterized by ESI-FTMS. Examination of ESI(-) spectra showed that FA in SH waters is composed by 2442 molecules. A chemical formula (CHON) could be attributed to 71% of them. Most of the identified molecules were found to have a pronounced aliphatic character, on basis of calculated aromaticity index. The LA sample displayed a high amount of constitutive organic molecules (6732 molecules detected, 73% identified) showing a variety of chemical composition, degree of aromaticity, hydrophobicity and acidity, and of O/C atomic ratio of the molecules. Identified molecules range from poorly-oxygenated condensed aromatics or aliphatics ( $\text{O/C}<0.5$ ;  $\text{H/C}<1$ ) to highly-oxygenated aromatics and aliphatics ( $\text{O/C}>0.5$ ). We suggest that the presence of such highly-oxygenated FA compounds promoting aqueous complexation of TME contribute to the higher concentrations of U and Ln observed in the low-DOC LA surface waters than in the high-DOC SH waters.