

## Molecular scale study of the sorptive fractionation of a fulvic acid by means of ESI-FTMS

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### Introduction

Building a comprehensive and realistic model of the interactions that occur between mineral (nano-)particles of soils, sediments and rivers, and complex mixtures of organic compounds such as humic substances (HS) requires knowledge at the molecular level on the fractionation of these substances that is induced by sorption at mineral surfaces. We addressed here, by means of electro-spray ionisation (ESI) mass spectrometry with ultrahigh resolution, the molecular level fractionation of a reference fulvic acid (SRFA) during its sorption at alumina surface -taken as a model for surfaces of natural Al oxide hydrates-.

### Results

Examination of ESI(-)-MS spectra of native SRFA solution, and of supernatant collected in SRFA sorption experiment at acidic pH, provided clear evidence for a process of sorptive fractionation of SRFA, with the ~5700 compounds identified in native solution being partitioned between solution and surface of alumina to very varying degrees. The quantitatively sorbed molecules were found to belong both to the family of tannins and to that of polycyclic aromatic compounds, and had as main characteristics a weak H/C ratio (<1 and <0.5, respectively) and aromatic character. Most of hydrolysable tannins was quantitatively sorbed.

Compounds showing the highest affinity for alumina surface exhibited thus aromatic structures with multiple oxygenated functionalities. There was observed a remarkably good negative correlation between the degree of sorption of a molecule within a CH<sub>2</sub>-series and its number of CH<sub>2</sub> groups, and positive correlation between degree of sorption of a molecule within a COO-series and number of CO<sub>2</sub> groups, which indicated that molecule acidity is a main parameter governing sorption of SRFA compounds at acidic pH. The results suggest that sorptive fractionation of SRFA is controlled by competitive reactions for proton binding and binding at surface Al(III) that involve functional groups of SRFA molecules.