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Effect of mineral surface properties (alumina, kaolinite) on the sorptive fractionation mechanisms of soil fulvic acids: Molecular-scale ESI-MS studies

Guillaume Fleury *, Mirella Del Nero, Rémi Barillon

Institut Pluridisciplinaire Hubert Curien, UMR7178 Université de Strasbourg/CNRS, 23 rue du Loess, 67037 Strasbourg, France

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Abstract

We addressed the effects of mineral surface properties (kaolinite versus Al-oxide) on the sorption-driven fractionation of a soil fulvic acid (FA) at acidic pH, mainly by means of ESI(−)-FTMS analysis of initial and supernatant solutions of FA sorption batch experiments. The MS data provided clear molecular-scale evidence of distinct mechanisms and molecular parameters controlling the FA fractionation upon its sorption on clay and oxide surfaces, respectively.

Identification of sorbing and not-sorbing FA compounds in kaolinite-solution systems revealed a weak fractionation among members of $-CO_2$ series of aliphatics or not-condensed aromatics (NCAs) at pH 3.8, and almost no sorption of poorly-oxygenated polycyclic aromatic compounds (PACs) and NCAs. This first molecular-scale description of a FA fractionation in a clay-solution system suggests that H-bonding with low affinity sites (aluminol/silanol) on the basal planes of the clay particles is the main mechanism of sorption. Due to the predominance of such weak and poorly-selective mechanism, the sorption of aliphatic and NCA molecules bearing oxygenated functionalities was prevented at pH 5, due to dissolved Al competing successfully for their coordination.

In contrast, a strong FA fractionation was observed onto alumina, with a preferential retention of PACs and highly-oxygenated aliphatics and NCAs. The major part of the poorly oxygenated aliphatics was left in solution. The sorption degree of NCAs and aliphatics was strongly correlated with molecular acidity. For PACs and poorly-oxygenated NCAs, the sorption was driven by reactions of surface ligand exchange (for the most oxygenated compounds) or by hydrophobic interactions (for the least oxygenated compounds).

Keywords: Humic substances; Kaolinite; Alumina; Fractionation; Mass spectrometry

1. INTRODUCTION

Humic substances (HSs) like fulvic acids (FAs) are complex heterogeneous mixtures of thousands of biochemically stable polymeric substances (Aiken et al., 1985) which are ubiquitous in all terrestrial surface systems and which account for a great part of organic carbon in soils. HSs show a variety in the composition, structure and reactivity of their constituents and functional groups (Swift, 1989; Plancque et al., 2001). It has long been known that HSs have the ability to interact with metals (Dobbs et al., 1989; Tipping, 2002; Milne et al., 2003; Janot et al., 2013), organic pollutants (Rebhun et al., 1996) and surfaces of (nano) particles of clays and Al- or Fe-oxyhydroxides (Ochs et al., 1994; Schlautman and Morgan, 1994; Feng et al., 2005; Janot et al., 2013), with the sorption of HSs resulting in its chemical fractionation between minerals and solution (Meier et al., 1999; Zhou et al., 2001; Reiller

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* Corresponding author.
E-mail address: guillaume.fleury@iphc.cnrs.fr (G. Fleury).

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et al., 2006). Sorption-driven fractionation of HSs is expected to influence surface characteristics (reactivity, sorption capacity, charge) of minerals, dispersion behavior of suspended nanoparticles which are potential pollutants' carriers, and metal binding capacity of dissolved organic matter in many geochemical systems (Ochs et al., 1994; Schlautman and Morgan, 1994; Yang et al., 2013). Understanding of the fractionation of HS during the sorption at surfaces of mineral particles is thus of interest in many environmental issues including sorption/mobility of trace metal elements in soils and aquatic systems. It has some implications on the evaluation of the impact on health of the release of pollutants in the ecosystems and on the safety assessments of remediation processes of polluted soils or radioactive waste repositories in geological formations (Loffredo and Senesi, 2006; Bryan et al., 2012).

Building a comprehensive description of the coupled cycles of organic matter and pollutants in natural systems requires some basic knowledge of the fractionation trends exhibited by HSs during their sorption at mineral surfaces relevant to soils and waters, as well as a thorough understanding of the mechanisms and molecular parameters driving the fractionation – which is still lacking. Speaking in a general way, several mechanisms of sorption of HSs onto minerals were proposed, including surface ligand exchange, specific adsorption, electrostatic interactions, hydrophobic effects, H-bonding and metal-ion bridging (Ochs et al., 1994; Schlautman and Morgan, 1994). In many studies, HSs were considered as bulk materials bearing polar functionalities and spectroscopic/modeling evidence was given that carboxyl functional groups of HS (Fu et al., 2005; Ghosh et al., 2009) are involved in the macroscopic sorption of HS at surfaces of iron or aluminum oxide minerals and that the contribution of phenol groups increases with pH (Filius et al., 2003; Claret et al., 2008). In the last two decades, there has also been a growing interest in getting a detailed understanding of the behavior of HSs during their sorption at (nano) mineral – solution interfaces. Many spectroscopic evidences were provided that a strong sorptive fractionation takes place between the diverse classes of organic compounds of a humic substance (e.g. Meier et al., 1999; Claret et al., 2008; Ghosh et al., 2009). It was reported that the hydrophobic fractions of FAs and/or the organic molecules with high contents in aromatic moieties activated by oxygenated functionalities were preferentially sorbed- as compared to aliphatic fractions- on the surfaces of metallic oxide minerals (Meier et al., 1999; Zhou et al., 2001; Kaiser, 2003; Claret et al., 2008). Moreover, several studies combining size-exclusion-chromatography and spectroscopy analysis have revealed a size fractionation of fulvic or humic acids during their sorption at several mineral surfaces (e.g. Hur and Schlautman, 2004), which was explained by structural trends in the molecular weight fractions (degree of aromaticity, functionalities...) and the underlying sorption processes. Since recently, the development of an advanced technique, namely ultra-high resolution Fourier transform mass spectrometry (FTMS), has offered unique opportunities for identifying the molecules constitutive of a HA or FA (e.g. Kujawinski et al., 2002a; D'Andrilli et al., 2010) and for approaching the issue of the HS-metallic oxide-solution interactions at the molecular scale (Reiller et al., 2006; Galindo and Del Nero, 2014, 2015). Published FTMS data for the characterization of HSs (Plancque et al., 2001; Stenson et al., 2002; Sutton and Sposito, 2005) have supported the model proposed by Wershaw (1993) and by Engebretson and von Wandruszka (1994), and recently revived by Piccolo (2001) and Plancque et al. (2001), which describes an HS as a supramolecular association of small organic entities ("building blocks" of ca. 500 Da for FAs) assembled via weak bonds. This model has led to view an HS as a complex mixture of thousands of polycarboxylates of distinct molecular weight, degree of aromaticity or acidity, and chemical reactivity. Recently, the ESI-FTMS technique was applied by our research team to the identification of sorbing (and not sorbing) molecules of an aquatic fulvic acid (Galindo and Del Nero, 2014), and of a terrestrial humic acid (Galindo and Del Nero, 2015) during experiments of HS-alumina-solution interactions. A striking result was an inverse correlation existing between the degree of sorption of a molecule within a CH_2 series and its number of CH_2 groups, and a positive correlation between the degree of sorption and the number of CO_2 groups in a COO series, for homologous series containing up to nine members. In agreement with previous experimental work by Evanko and Dzombak (1998) on simple organic acids and modeling work by Janot et al. (2012) suggesting that enhanced sorption with increasing number of carboxyl groups was due to changes in compound acidity, the correlations observed for FA by ESI-FTMS provided for the first time a molecular scale evidence that the sorptive fractionation of complex mixtures of thousands of organic compounds as fulvic acids was controlled by molecule acidity, which was remarkable. These ESI-FTMS findings also strongly supported that the FA subunits, held together by hydrophobic forces and hydrogen bonding, were disrupted during sorption because of strong FA-alumina surface interactions via surface ligand exchange mechanism, which was consistent with the concept of supramolecular assembly for HS (Piccolo, 2001; Piccolo et al., 2010). Hydrophobic interactions were moreover found to be a mechanism cooperating to the sorption onto alumina of the poorly-oxygenated polycyclic aromatic compounds (PACs) of a terrestrial HA, with the degree of molecule hydrophobicity influencing the degree of molecule sorption.

In contrast to the metallic oxide systems, very few information is available on the sorption-driven fractionation of HSs onto clay minerals and no molecular scale description of the process has been reported so far. Unlike for iron or aluminum (hydr)oxides, the aliphatic fractions of a humic acid were found to be more prone to sorption on the surface of kaolinite and montmorillonite than the aromatic fractions (Wang and Xing, 2005; Ghosh et al., 2009). Such contrasting results between metallic oxides and clays have pointed the need to acquire detailed knowledge of the molecular characteristics and the sorption mechanisms driving HS sorptive fractionation in clay mineral – solution systems, which are relevant to many geochemical systems. In particular, such knowledge is critically needed for developing a comprehensive understanding of the sorptive frac-