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

5

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24 **ABSTRACT**

25

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

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

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

44

45 **Key words:** humic substances; kaolinite; alumina; fractionation; mass spectrometry

46

47 1. INTRODUCTION

48

49 Humic substances (HSs) like fulvic acids (FAs) are complex heterogeneous mixtures of thousands of
50 biochemically stable polymeric substances (Aiken et al., 1985) which are ubiquitous in all terrestrial surface
51 systems and which account for a great part of organic carbon in soils. HSs show a variety in the composition,
52 structure and reactivity of their constituents and functional groups (Swift, 1989; Plancque et al., 2001). It has
53 long been known that HSs have the ability to interact with metals (Dobbs et al., 1989; Tipping, 2002; Milne et
54 al., 2003; Janot et al., 2013), organic pollutants (Rebhun et al., 1996) and surfaces of (nano) particles of clays
55 and Al- or Fe-oxyhydroxides (Ochs et al., 1994; Schlautman and Morgan, 1994; Feng et al., 2005; Janot et al.,
56 2013), with the sorption of HSs resulting in its chemical fractionation between minerals and solution (Meier et
57 al., 1999; Zhou et al., 2001; Reiller et al., 2006). Sorption-driven fractionation of HSs is expected to influence
58 surface characteristics (reactivity, sorption capacity, charge) of minerals, dispersion behavior of suspended
59 nanoparticles which are potential pollutants' carriers, and metal binding capacity of dissolved organic matter
60 in many geochemical systems (Ochs et al., 1994; Schlautman and Morgan, 1994; Yang et al., 2013).
61 Understanding of the fractionation of HS during the sorption at surfaces of mineral particles is thus of interest
62 in many environmental issues including sorption / mobility of trace metal elements in soils and aquatic
63 systems. It has some implications on the evaluation of the impact on health of the release of pollutants in the
64 ecosystems and on the safety assessments of remediation processes of polluted soils or radioactive waste
65 repositories in geological formations (Loffredo and Senesi, 2006; Bryan et al., 2012).

66 Building a comprehensive description of the coupled cycles of organic matter and pollutants in natural
67 systems requires some basic knowledge of the fractionation trends exhibited by HSs during their sorption at
68 mineral surfaces relevant to soils and waters, as well as a thorough understanding of the mechanisms and
69 molecular parameters driving the fractionation -which is still lacking-. Speaking in a general way, several
70 mechanisms of sorption of HSs onto minerals were proposed, including surface ligand exchange, specific
71 adsorption, electrostatic interactions, hydrophobic effects, H-bonding and metal-ion bridging (Ochs et al.,
72 1994; Schlautman and Morgan, 1994). In many studies, HSs were considered as bulk materials bearing polar
73 functionalities and spectroscopic/modeling evidence was given that carboxyl functional groups of HS (Fu et
74 al., 2005; Ghosh et al., 2009) are involved in the macroscopic sorption of HS at surfaces of iron or aluminum
75 oxide minerals and that the contribution of phenol groups increases with pH (Filius et al., 2003; Claret et al.,

76 2008). In the last two decades, there has also been a growing interest in getting a detailed understanding of the
77 behavior of HSs during their sorption at (nano) mineral - solution interfaces. Many spectroscopic evidences
78 were provided that a strong sorptive fractionation takes place between the diverse classes of organic
79 compounds of a humic substance (e.g. Meier et al., 1999; Claret et al., 2008; Ghosh et al., 2009). It was
80 reported that the hydrophobic fractions of FAs and/or the organic molecules with high contents in aromatic
81 moieties activated by oxygenated functionalities were preferentially sorbed –as compared to aliphatic
82 fractions- on the surfaces of metallic oxide minerals (Meier et al., 1999; Zhou et al., 2001; Kaiser, 2003;
83 Claret et al., 2008). Moreover, several studies combining size-exclusion-chromatography and spectroscopy
84 analysis have revealed a size fractionation of fulvic or humic acids during their sorption at several mineral
85 surfaces (e.g. Hur and Schlautman, 2004), which was explained by structural trends in the molecular weight
86 fractions (degree of aromaticity, functionalities...) and the underlying sorption processes. Since recently, the
87 development of an advanced technique, namely ultra-high resolution Fourier transform mass spectrometry
88 (FTMS), has offered unique opportunities for identifying the molecules constitutive of a HA or FA (e.g.
89 Kujawinski et al., 2002; D’Andrilli et al., 2010) and for approaching the issue of the HS-metallic oxide-
90 solution interactions at the molecular scale (Reiller et al., 2006; Galindo and Del Nero, 2014; Galindo and Del
91 Nero, 2015). Published FTMS data for the characterization of HSs (Plancque et al., 2001; Stenson et al., 2002;
92 Sutton and Sposito, 2005) have supported the model proposed by Wershaw (1993) and by Engebretson and
93 von Wandruszka (1994), and recently revived by Piccolo (2001) and Plancque et al. (2001), which describes
94 an HS as a supramolecular association of small organic entities (“building blocks” of ca. 500 Da for FAs)
95 assembled via weak bonds. This model has led to view an HS as a complex mixture of thousands of
96 polycarboxylates of distinct molecular weight, degree of aromaticity or acidity, and chemical reactivity.
97 Recently, the ESI-FTMS technique was applied by our research team to the identification of sorbing (and not
98 sorbing) molecules of an aquatic fulvic acid (Galindo and Del Nero, 2014), and of a terrestrial humic acid
99 (Galindo and Del Nero, 2015) during experiments of HS-alumina-solution interactions. A striking result was
100 an inverse correlation existing between the degree of sorption of a molecule within a CH₂ series and its
101 number of CH₂ groups, and a positive correlation between the degree of sorption and the number of CO₂
102 groups in a COO series, for homologous series containing up to nine members. In agreement with previous
103 experimental work by Evanko and Dzombak (1998) on simple organic acids and modelling work by Janot et
104 al. (2012) suggesting that enhanced sorption with increasing number of carboxyl groups was due to changes in

105 compound acidity, the correlations observed for FA by ESI-FTMS provided for the first time a molecular
106 scale evidence that the sorptive fractionation of complex mixtures of thousands of organic compounds as
107 fulvic acids was controlled by molecule acidity, which was remarkable. These ESI-FTMS findings also
108 strongly supported that the FA subunits, held together by hydrophobic forces and hydrogen bonding, were
109 disrupted during sorption because of strong FA–alumina surface interactions via surface ligand exchange
110 mechanism, which was consistent with the concept of supramolecular assembly for HS (Piccolo, 2001;
111 Piccolo et al., 2010). Hydrophobic interactions were moreover found to be a mechanism cooperating to the
112 sorption onto alumina of the poorly-oxygenated polycyclic aromatic compounds (PACs) of a terrestrial HA,
113 with the degree of molecule hydrophobicity influencing the degree of molecule sorption.

114 In contrast to the metallic oxide systems, very few information is available on the sorption-driven
115 fractionation of HSs onto clay minerals and no molecular scale description of the process has been reported so
116 far. Unlike for iron or aluminum (hydr)oxides, the aliphatic fractions of a humic acid were found to be more
117 prone to sorption on the surface of kaolinite and montmorillonite than the aromatic fractions (Wang and Xing,
118 2005; Ghosh et al., 2009). Such contrasting results between metallic oxides and clays have pointed the need to
119 acquire detailed knowledge of the molecular characteristics and the sorption mechanisms driving HS sorptive
120 fractionation in clay mineral – solution systems, which are relevant to many geochemical systems. In
121 particular, such knowledge is critically needed for developing a comprehensive understanding of the sorptive
122 fractionation of FAs in the various types of soils (rich in metal oxi-hydroxides or in clays).

123 In this study, we addressed the effects of mineral surface properties, i.e., clay versus aluminum oxide, on the
124 molecular scale fractionation of a terrestrial FA during its sorption at mineral surface by mean of
125 complementary techniques, traditional batch experiments, electro-kinetic measurements and electrospray
126 ionization FTMS. The systems under investigation included an extracted FA (PPH) and kaolinite or alumina
127 as a model sorbent taken as being representative of Al (hydr)oxides or clays in soils, respectively. First, batch
128 sorption experiments and on-line electrophoretic mobility measurements were performed in PPH-containing
129 mineral suspensions for studying the pH-dependency of sorption of PPH onto alumina and kaolinite and for
130 gaining insights into surface charges of PPH-loaded particles. The use of a LTQ Orbitrap XL hybrid mass
131 spectrometer allowed deriving the exact elemental composition of the molecules of PPH present in the
132 solution before and after contact with the metal oxide or the clay mineral, for experiments performed under
133 acidic and middle acidic solutions (pH 3.5 and 5.0, respectively). The molecular approach was used to retrieve

134 the distinct orders of relative affinity of the FA molecules for the surface of a clay and a metallic oxide,
135 respectively, and to explore the relations existing between chemical characteristics of the PPH molecules
136 (such as number of CO₂ functionalities, degree of aromaticity or acidity...) and their degree of relative
137 sorption onto mineral. The molecular-scale results presented here represent a significant contribution to our
138 understanding of the fractionation trends of a terrestrial FA during its sorption onto a clay mineral, and of the
139 sorption mechanisms involved, and highlight the strong effects of mineral surface properties on the
140 fractionation behavior of terrestrial fulvic acids.

141

142 **2. EXPERIMENTAL SECTION**

143

144 **2.1. Materials**

145

146 The fulvic acid denoted as “PPH” was extracted from a soil sample collected in a beech forest developed on
147 sandstone, near La Petite-Pierre, Bas-Rhin, France. The extraction was carried out by using the International
148 Humic Substances Society (IHSS, St. Paul, MN, USA) standard method for isolation of soil fulvic acids. This
149 method, excerpted from Sparks et al. (1996), uses XAD-8 resin adsorption to isolate such acids. Due to the
150 chemical properties of the resin, the fulvic acids used here only contain hydrophobic organic compounds.
151 Stock solutions of PPH fulvic acid were prepared and stored frozen in the dark until used.

152 Alumina colloids were Alfa Aesar's α -Al₂O₃ crystallites (chemical purity: 99.95%, surface area: 7.6 m²/g)
153 with a particle size of 280 nm as determined by dynamic light scattering ($[\alpha\text{-Al}_2\text{O}_3] = 2.5 \text{ g.L}^{-1}$, particle size
154 determined in % of intensity, $w_{50\%} = 90 \text{ nm}$, polydispersity index = 0.12). The kaolinite sample used was the
155 standard sample KGa-1b provided by The Clay Minerals Society. This sample was characterized by Pruett
156 and Webb (1993), who reported a particle distribution of 57.8% < 2 μm and 32.0% < 0.5 μm , as well as a
157 surface area of 11.7m².g⁻¹. This value for surface area of kaolinite has been used as such and no attempt was
158 made to determine again this value.

159 All solutions were prepared using reagent grade chemicals and ultra-pure water (purity > 18 M Ω .cm).

160

161 **2.2. Experimental setup**

162

163 Experiments of FA sorption at acidic pH and 298K on alumina and kaolinite were carried out for analysis of
164 the supernatants by ESI(-)-FTMS and study of the mineral surface characteristics on FA sorptive
165 fractionation. The experiments were carried out at $\text{pH } 3.8 \pm 0.1$ and 4.9 ± 0.1 for both minerals.

166 Alumina and kaolinite suspensions were prepared in individual PEHD tubes with solid-to-solution ratios of 25
167 and 15 g.L^{-1} , respectively. These values of solid-to-solution ratios were chosen so that the surface areas of
168 alumina and kaolinite used in the experiments fall in the same range of values (ca. 170 and $150 \text{ m}^2/\text{L}$,
169 respectively). Efforts were made to adjust the concentration of PPH added in the individual tubes, so that the
170 values of FA-to-mineral ratios (r) of all experiments fall within a narrow range ($r \sim 5 \text{ mg C/g}$, or more
171 precisely, $r \sim 0.6$ and 0.8 mgC/m^2 of mineral for sorption of FAs on kaolinite and alumina, respectively). No
172 attempt was made to fix the ionic strength of the initial experimental solutions, as background salts were
173 previously observed to alter considerably the ESI-MS response. After shaking of the tubes for 24 hours at
174 298K, the final pH values of the suspensions were measured. The suspensions were then centrifuged at 8000
175 rpm during 2.5 hours for solution-colloid separation and the supernatants were collected. Aliquots were taken
176 for measurements of dissolved organic carbon, DOC, using a Shimadzu TOC $-V_{\text{CPH}}$ analyzer, and of
177 dissolved aluminum content using Inductively Coupled Plasma Mass Spectrometry (quantification limit:
178 $5.3 \mu\text{g/L}$). All the remaining supernatant solutions were adjusted (using a 0.01M HCl solution) to a same pH
179 value of 3.8 ± 0.1 prior to ESI-MS analysis. Such an acidification procedure allows a direct comparison of the
180 datasets obtained for the different experiments (as pH is known to affect ionization of compounds during ESI-
181 MS analysis). An exception was however made for the supernatant of the PPH-kaolinite sorption experiment
182 at pH 5.0, which was analyzed as collected because the ESI(-)MS spectra obtained for the acidified
183 supernatant sub-sample were found to be of very poor quality due to the amount of salt introduced in the
184 sample to obtain a pH of 3.8. It is to be noted that the ESI-MS data obtained from an analysis at pH 5.0 cannot
185 be straightforwardly compared to those obtained from analysis at pH 3.8.

186 Complementary series of batch experiments were performed to study the macroscopic sorption of FA as a
187 function of pH and to perform on-line electro-kinetic measurements of the FA-containing suspensions of
188 kaolinite or alumina. Same procedure as that described above was used, except that an aliquot of sample was
189 taken before centrifugation for particle electrophoretic mobility (EM) measurements, which were carried out
190 using dynamic light scattering with a Malvern Zetasizer Nano ZS instrument. Values reported for EM
191 correspond to mean values calculated on the basis of three replicates of a same measurement. Sorption

192 isotherms and EM values in the pH range 3.5-7 were determined for the alumina – PPH systems ($r = 5-10$
193 mgC/g). For the kaolinite – PPH system, both the effect of pH and ratio r on the percent of FA sorption and
194 EM of particles were investigated (r value up to 50 mgC/g).

195

196 **2.3. ESI-MS instrumentation and data analysis**

197

198 **2.3.1. Instrumentation and acquisition parameters**

199

200 A Thermo Scientific LTQ Orbitrap hybrid mass spectrometer was used for the analysis in ESI negative
201 ionization mode of native FA solutions and supernatants. Negative ion ESI appears to be the most appropriate
202 ionization mode for the analysis of anionic compounds such as fulvic acids, which are already partly pre-
203 ionized in solution. Ultra-pure water was used as the electrospray solvent as other solvents have been found to
204 alter the FA properties (Piccolo et al., 2001). The samples were infused directly into the ESI source with a
205 spray voltage of 3.5 kV at a flow rate of $10 \mu\text{L}\cdot\text{min}^{-1}$, and were analyzed in negative ion mode. Nitrogen was
206 used as the drying and spraying gas. For each acquisition, 100 scans (2s/scan) were co-added using Xcalibur
207 software. The Orbitrap MS was externally calibrated in negative ion mode on the 50-2000 m/z range using a
208 LTQ/FT-Hybrid ESI Calmix solution, for a mass accuracy better than 3 ppm. Instrument operating parameters
209 (capillary voltage and temperature, tube lens voltage) were optimized one after the other for an optimal
210 transmission of higher m/z ions. It was found that modifying the instrumental parameters did not affect
211 important characteristics of spectra such as ion distribution, charge state or mass spacing patterns. The source
212 capillary was finally held at -50 V and 275 °C, and a voltage of -240 V was applied to the tube lens.

213 All ESI(-) mass spectra were recorded in the ranges 120-400 m/z and 400-798 m/z in order to improve the
214 mass accuracy in the region of low masses as well as the signal-to-noise ratio (S/N) for compounds having the
215 highest values of m/z in samples.

216

217 **2.3.2. Elemental formula determination**

218

219 Elemental formulae were assigned to the measured m/z values using the Xcalibur software. The following
220 criteria were chosen for assignment of molecular formulas to the peaks detected on the mass spectra:

- 221 – Signal-to-noise ratio of peak > 4,
 222 – Mass accuracy better than 3 ppm,
 223 – Application of the following ranges: $^{14}\text{N} \leq 1$; $^{16}\text{O} \leq 50$; $^{12}\text{C} \leq 200$; $^1\text{H} \leq 600$ (N, O, C and H being
 224 respectively the number of Nitrogen, Oxygen, Carbon and Hydrogen atoms).
 225 – $0,2\text{C} \leq \text{H} \leq 2\text{C} + 3$
 226 Double Bond Equivalent $\frac{2+2\text{C}-\text{H}+\text{N}}{2} \geq 0$

227

228 Elemental analyses showed that the PPH sample contains low amounts of Nitrogen (< 3% w/w). Sulfur and
 229 Phosphorus contents were assumed negligible (<1% w/w). Odd m/z values correspond to even mass, and
 230 relate to chemical formulae with even number of nitrogen atoms. As the nitrogen content in the sample does
 231 not exceed a few percent, we assumed that compounds peaking at odd m/z primarily contain C, H and O
 232 atoms. All possible formula attributable to a given odd m/z value were thus calculated by considering only C,
 233 H and O atoms. Due to low nitrogen content in HS, species peaking at even m/z were considered to contain at
 234 most one N atom, in addition to C, H and O atoms. Ions corresponding to ^{13}C isotopes and elemental formulae
 235 that did not match the above criteria were not taken into account.

236

237 2.3.3. *Van krevelen diagrams*

238

239 The Van Krevelen (VK) diagram plots the H/C ratio vs. the O/C ratio of a molecule and is an effective
 240 graphical method for displaying complex data from NOM analysis by ultrahigh-resolution mass spectrometry
 241 (Kim et al., 2003). On the VK diagrams, the identified compounds are classified into three categories on basis
 242 of their value of Aromaticity Index (A.I.) proposed by Koch and Dittmar (2006). The authors proposed a
 243 modified formula for calculating A.I., considering that half of the oxygen is σ -bound:

$$\text{Aromaticity Index (A.I.)} = \frac{1 + \text{C} - \frac{\text{O}}{2} - \frac{\text{H}}{2}}{\text{C} - \frac{\text{O}}{2} - \text{N}}$$

244 They defined two threshold values of AI to distinguish between three categories of compounds, i.e., between
 245 compounds having an unambiguous polycyclic aromatic structure (PACs, having $0.67 < \text{A.I.}$), a not-
 246 condensed aromatic structure (NCAs, having $0.5 < \text{A.I.} < 0.67$), and a more or less pronounced aliphatic

247 character (A.I. < 0.5).

248

249 **2.3.4. Definition of I**

250

251 In order to explore the mechanisms of the sorptive fractionation of FAs, we used the parameter I defined by
252 Galindo and Del Nero (2014). The value of I for a given ion is equal to the ratio of the normalized peak
253 intensity of this ion in the supernatant (after sorption) on the normalized peak intensity of the ion in the initial
254 solution (before sorption), with the normalization being made to the sum of the intensities of all the ions
255 (Total ion current, TIC) of the considered solution. Trends in the values of I for compounds in a FA supply
256 information on trends existing in the orders of relative affinity of compounds for the mineral surface: the
257 lower the value of I of a FA ion, the higher its relative affinity (by comparison with that of the other detected
258 FA ions) for the surface of the mineral. Ions with $I = 0$ are totally sorbed at the surface of mineral, and ions
259 with $I \neq 0$ are distributed between the surface and the solution.

260 It is well known that the intensity of an ion on a mass spectrum not only depends on its concentration but also
261 on its ionization efficiency and on the matrix, i.e. on the number, the quantity and the structure of the other
262 ions present in the sample. A simple dilution of initial FA solution can thus possibly have an effect on the
263 relative peak intensities of the ions in the solution. As bulk concentration of PPH is lower in the supernatants
264 collected at the end of the sorption experiments than in the native PPH solution (due to PPH sorption at the
265 surface of the minerals), it is necessary to determine the effect of such a sorption-driven decrease in solution
266 concentration on the I values of the FA ions and to differentiate it from the effect on I of the sorptive
267 fractionation process itself. To this end, we compared the ESI(-)MS spectra recorded for initial PPH solution
268 at pH 3.8 and at pH 4.9 used in the experiments to those obtained for PPH native solutions diluted by a factor
269 2, and we calculated the “I values” of the FA ions resulting from a pure dilution of samples. Dilution by a
270 factor of 2 was chosen because approximately 50% of total organic carbon was found to be removed from
271 solution during the experiments of PPH sorption onto alumina and kaolinite. It was found (cf. Fig. A1 in the
272 Appendix) that all PPH ions display I values equal to 0.85 ± 0.15 due to dilution effect only (except for the
273 400-798 m/z range at pH 3.8 where the values were equal to 1.05 ± 0.15). Applying these results of the
274 dilution tests to the interpretation of the I values of ions derived from the sorption experiments, it can be
275 considered that a value of I lower than 0.7 (or 0.9 for the range 400-798 m/z range at pH 3.8) indicate a rather

276 good sorption of an ion on the mineral surface, while ions showing values comprised between 0.7 and 1 (or
277 0.9 and 1.2 for the range 400-798 m/z range at pH 3.8) are poorly sorbed or not sorbed at all, and ions
278 showing values higher than 1 (or 1.2) are not sorbed at all during the experiment.

279

280 3. RESULTS

281

282 3.1. Macroscopic description of the FA-mineral systems

283

284 Fig. 1 shows the percentage of organic carbon of PPH sorbed onto alumina or kaolinite as a function of pH,
285 for different FA/mineral ratios (r). The results are as follows.

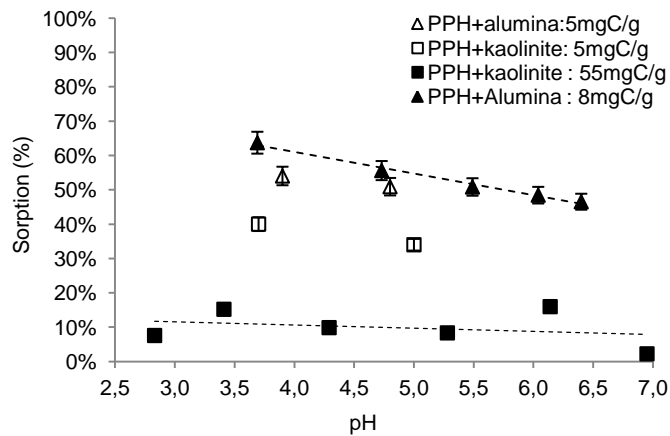
286 Regarding alumina, first, the sorption isotherm obtained for PPH indicate a slight pH-dependency of the
287 sorption, i.e., a slight decrease of the percentage of sorption with increasing pH. Such a decrease with
288 increasing pH value is consistent with an increase of the rate of deprotonation of both the reactive groups of
289 the FA molecules and the aluminol sites on the surface of alumina. It has been widely reported that the
290 carboxyl and phenol functional groups of FAs exhibit wide distributions of pK values, which are mostly lower
291 than 4 for carboxyl groups (e.g. Ritchie and Perdue, 2003) and higher than 8 for phenol moieties (e.g. Gu et
292 al., 1995). Moreover, the IEP of the alumina particles used here was previously found to be equal to 8.5 (Del
293 Nero et al., 2010). An increase of the deprotonation with pH thus has the effect of diminishing electrostatic
294 attractions between aluminol sites on the mineral surface and FA molecules, which is unfavorable to a close
295 approach of the organic molecules to the vicinity of the surface. Thus, such features may lead to a slight
296 decrease of the percentage of macroscopic sorption with pH observable in Fig. 1. The results of EM
297 measurements performed on the systems investigated are presented on Fig. 2. The data show a sign reversal of
298 the surface charge of the suspended alumina particles in the presence of PPH, evidencing that the FA-alumina
299 interactions are not of electrostatic nature only but involve the formation of inner-sphere fulvate complexes on
300 the surface of alumina. Chemical sorption is indeed the only sorption process capable of inducing such a sign
301 reversal (Fairhurst and Warwick, 1998).

302 Fig. 1 shows that PPH has a lower overall affinity for the kaolinite surface than for the alumina surface (cf.
303 data at $r= 5\text{mgC/g}$). There also appeared that the percentage of PPH sorption decreases with an increase of the
304 PPH / kaolinite ratio (cf. data at $r= 5$ and 55 mgC/g). Such a feature indicates that multiple sites on the mineral

305 surface were involved in the sorption of the PPH molecules and/or several types of surface complexes of very
 306 distinct values of formation constant were formed. The former hypothesis is consistent with results of many
 307 previously published studies reporting the existence of weak surface sites at basal planes of kaolinite particles
 308 and of strong sites (high-affinity sites) at edges and/or defects of kaolinite(Sverjensky and Sahai, 1996). The
 309 high-affinity sites existing in limited amounts onto the kaolinite particles might be saturated in our
 310 experiments at low surface loadings of FA. High-affinity sites have long been reported to be protonated under
 311 acidic and neutral pH conditions whereas the early deprotonation of basal aluminol sites (Wieland and
 312 Stumm, 1992) is (partly) responsible for an overall negative surface charge of kaolinite (e.g. data on Fig. 2
 313 obtained in the absence of FA). EM measurements reported in Fig. 2 shows that the sorption of the PPH
 314 molecules imparts negative charges to the kaolinite surface, which is consistent with involvement of the high-
 315 affinity sites in the sorption.

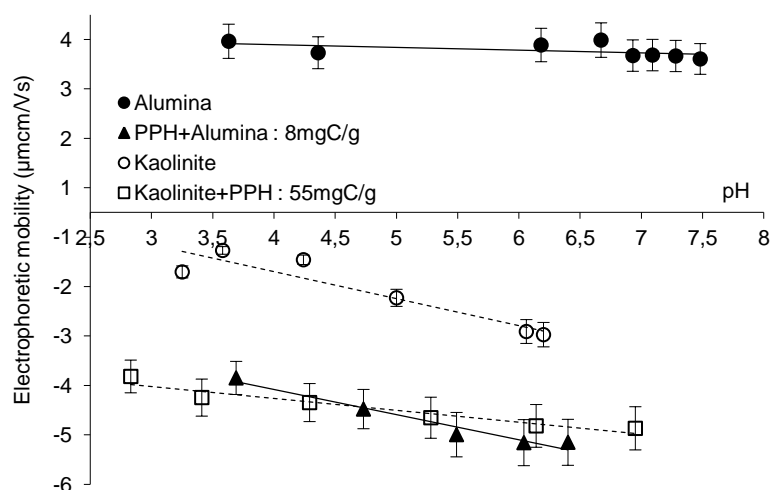
316 In summary, surface properties of mineral have an effect on the macroscopic behavior of sorption of FA at
 317 acidic/near neutral pH, which highlights a need for further understanding their effect on the fractionation of
 318 FA.

319



320

321 **Fig. 1:** Sorption isotherms of organic carbon obtained for different PPH-to-mineral ratios in alumina or
 322 kaolinite suspensions.



323

324 **Fig. 2:** Electrophoretic mobility (EM) of alumina or kaolinite particles as a function of final pH of mineral-
 325 solution suspensions, in the absence of PPH or at different PPH-to-mineral ratios.

326

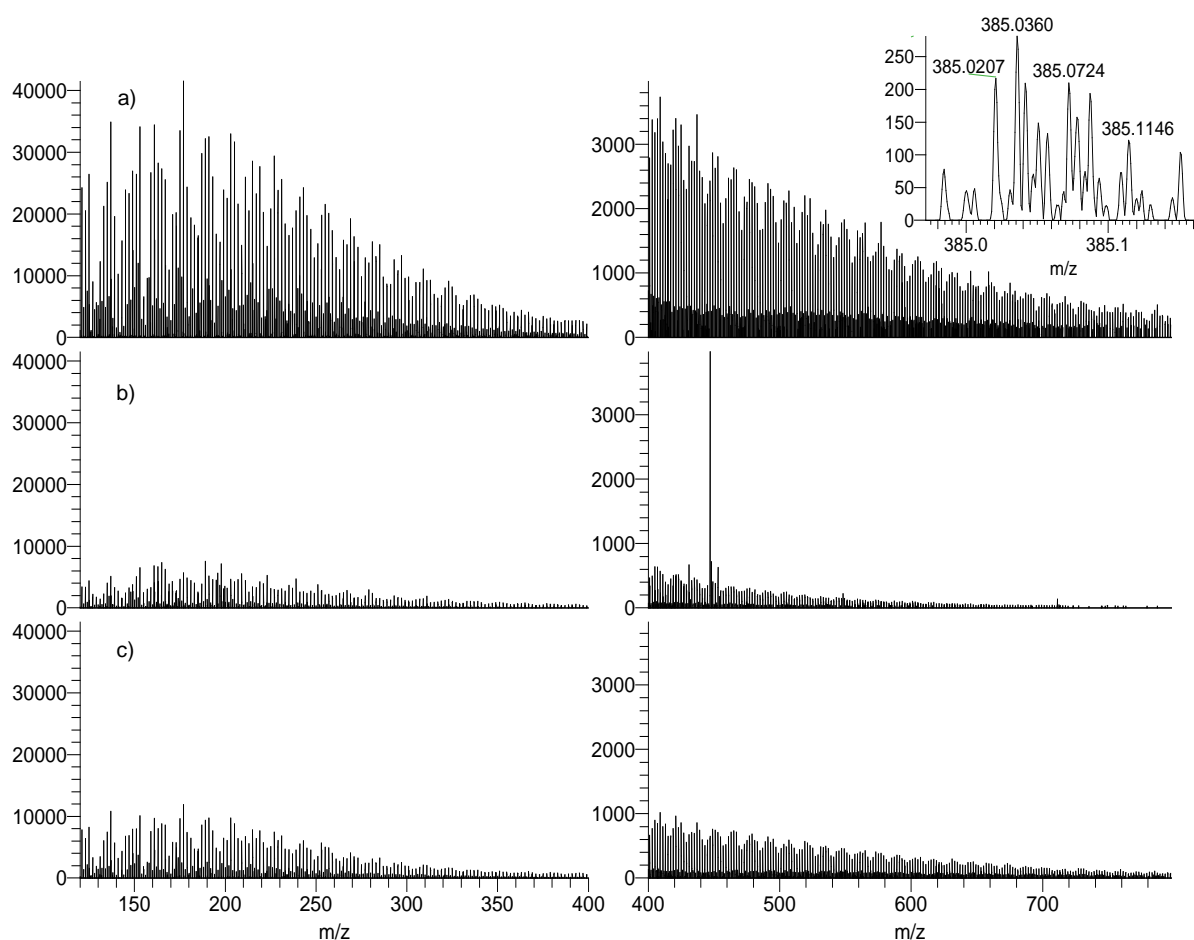
327 3.2. ESI(-)-FTMS spectra of initial solution of PPH and chemical formula assignments

328

329 The full mass spectrum recorded in the mass range 120-2000m/z for the native solution of PPH, using the
 330 negative ionization mode, showed a mono-modal distribution of peaks lying between 120-800m/z (cf. Fig. A2
 331 in the Appendix). The presence on our mass spectra of peaks at m/z<800 only is globally consistent with
 332 previously published ESI-MS spectra of fulvic acids, which exhibit compounds of molecular weight no higher
 333 than a few kDa (Piccolo, 2001; Sutton and Sposito, 2005; Reemtsma, 2009). Several authors have underlined
 334 that their mass spectrometry data support the view of HS as being a supramolecular assembly, which can be
 335 dissociated during ionization in the ESI probe, in particular when high voltages are applied to the transfer
 336 optics (Piccolo et al., 2010). Fig. 3 shows the ESI(-) mass spectra recorded for the native solution of PPH in
 337 the ranges 120-400 m/z and 400-798 m/z. Circa 1725 and 1190 peaks were detected with S/N > 4 in the
 338 aforementioned mass ranges, respectively. The spectra display peaks of high intensity at odd-integral values
 339 of m/z and peaks of lower intensity at even-integral values of m/z, with the latter peaks having been reported
 340 in previously published studies to correspond to either the ¹³C-containing isotopes of the odd m/z ions or to
 341 components containing one nitrogen atom (Brown and Rice, 2000; Leenheer et al., 2001; Stenson et al., 2002;
 342 Kim et al., 2003). No spacing equal to (1.0034/n)m/z (with n = 2, 3...) was detected between the mono-
 343 isotopic peak and the corresponding peak for the one ¹³C-containing isotope, showing that no multiply
 344 charged species were generated in the ESI probe during analysis of PPH. The PPH mass spectra display a

345 common 14.0156 amu repeating unit due to the existence of homologous series of species differing by $-CH_2$
346 groups (Stenson et al., 2003; Reemtsma et al., 2008; Hertkorn et al., 2008), as reported previously for spectra
347 of DOM analyzed by using FT-ICR MS (Stenson et al., 2002; Stenson et al., 2003; Reemtsma et al., 2008;
348 Hertkorn et al., 2008). Homologous $-CH_2$ series identified for PPH by Kendrick mass analysis were found to
349 contain up to 14 molecules, which suggests that the $-CH_2$ group is an important constitutive element in the
350 structure of FAs (e.g. Fig. A3 in the Appendix). Numerous homologous series were observed and accounted
351 for the large number of different basic structures in PPH, similar to what was reported for DOM samples
352 (Kujawinski, Hatcher, et al., 2002).

353



354

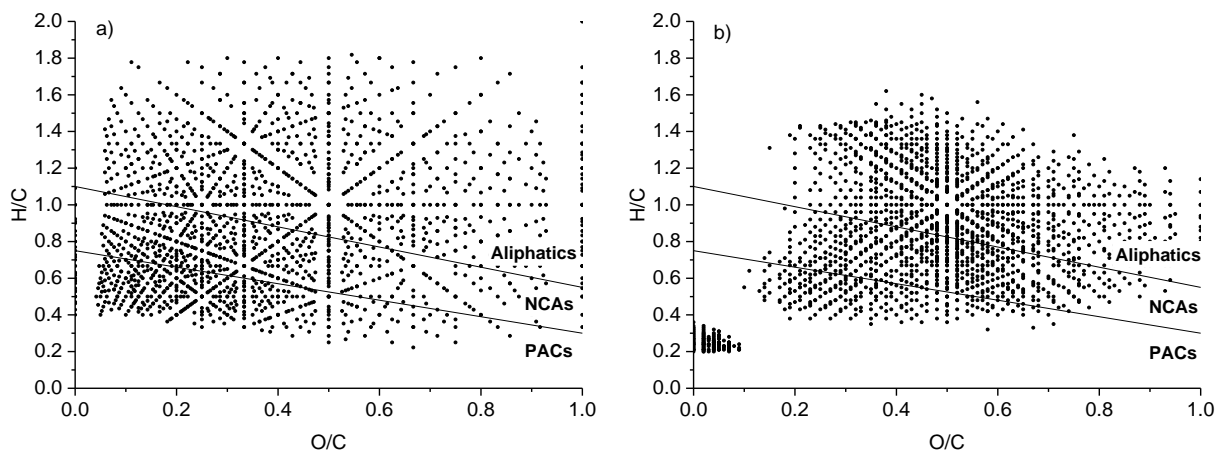
355 **Fig. 3:** Negative ion ESI mass spectra in the ranges 120-400 m/z and 400-798 m/z of PPH native solution (a),
356 and of the supernatants of PPH sorption experiments (pH = 3.8 ± 0.1) onto alumina (b), and kaolinite (c).

357

358 Chemical formulae were assigned to 74% and 98% of the PPH compounds detected with $S/N > 4$ in the mass
359 ranges 120-400 m/z and 400-798 m/z, respectively. Fig. 4 shows that the chemical compositions of PPH
360 compounds are distributed in a wide region of the VK diagrams and belong to the three following categories,

361 i.e., polycyclic aromatic compounds (PACs), not-condensed aromatics (NCAs), and compounds of aliphatic
362 character. Such VK diagrams with a wide distribution of compounds is somehow contrasting with most of
363 those previously published for soil humic substances (Rice and MacCarthy, 1991; D'Andrilli et al., 2015)
364 showing data-points gathered in more restricted areas of O/C. However, there are observed in Fig. 4b and Fig.
365 4a two sets of points that show slightly stronger densities and are mainly made up of strongly oxygenated
366 ($0.5 < O/C < 0.8$) NCAs or aliphatics with $H/C < 1.1$ and of poorly oxygenated PACs with $0.1 < O/C < 0.35$ (as
367 well as a few NCAs with $H/C < 0.8$), respectively.

368



369

370 **Fig. 4:** VK diagram showing elemental formulae assigned to ESI(-) FTMS peaks detected at pH = 3.8 on the
371 ranges 120-400 m/z (a) and 400-798m/z (b) for the PPH native solution.

372

373 3.3. Molecular-scale study of the sorptive fractionation of PPH

374

375 3.3.1. Influence of mineral surface characteristics

376

377 At first examination, ESI(-) spectra provide strong evidence that PPH fractionated during the sorption process.
378 Fig. 3b and Fig. 3c report spectra of supernatants collected in PPH sorption experiments which were
379 conducted at $pH\ 3.8 \pm 0.1$ (and PPH-to-solid ratio of 5mgC/g) and which led to 63% and 40% sorption of
380 organic carbon onto α -alumina and kaolinite, respectively (Fig. 1). The total ion currents recorded for the
381 mass spectra of the supernatants were lower than those recorded for the initial solution. Moreover, peak
382 intensities were lower in the mass spectra of the supernatants than in those of PPH. Circa 19% and 11% of
383 compounds detected with $S/N > 4$ on the PPH mass spectra were not detected on the supernatants' spectra,

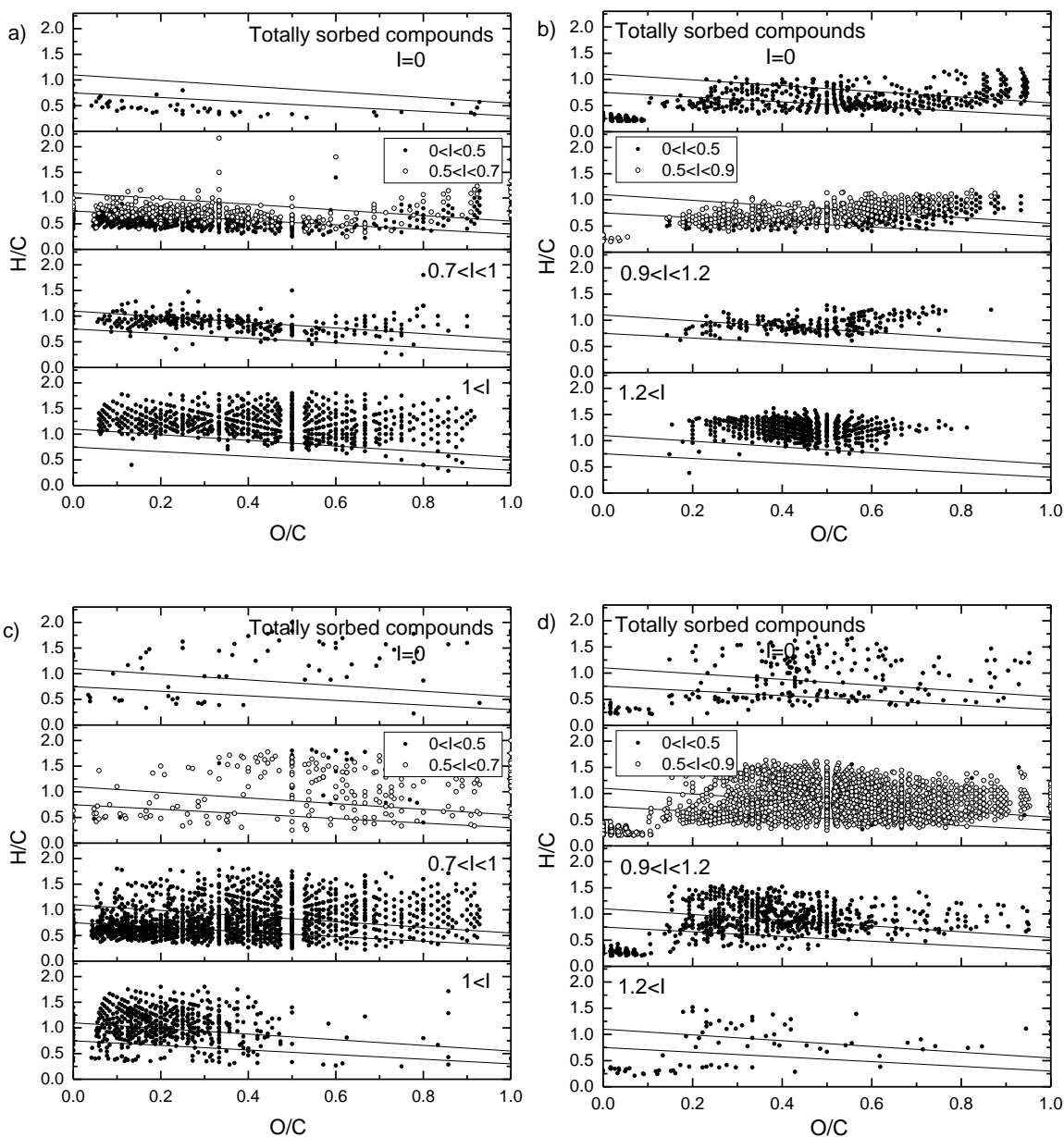
384 indicating that the compounds were totally sorbed on the surfaces of alumina and kaolinite during the
385 experiments, respectively. On the contrary, some ions were detected on the mass spectra of the supernatants
386 only. This phenomenon has already been reported by Reiller et al. (2006) and Galindo and Del Nero (2015) in
387 their ESI MS studies of sorption of HA onto hematite and HSs onto alumina, respectively. Actually, the
388 intensity of an ion on a mass spectrum not only depends on its concentration but also on its ionization
389 efficiency and on the matrix, i.e. on the number, the quantity and the structure of the other ions present in the
390 sample. A possible explanation for the detection of some ions in the supernatants' spectra only is that ions
391 undetectable in the native solutions of PPH because of matrix complexity might be ionized more efficiently in
392 the conditions of the supernatants' matrixes due to combined effects of their low sorption onto minerals and of
393 a release of the ionization charge upon preferential sorption of certain PPH compounds. In summary,
394 important features of the spectra were that the extent of the lowering of peak intensities from initial solution to
395 supernatants was varying considerably with the considered ion -going from a peak disappearance to a
396 lowering higher than that of the TIC-, and with the type of mineral. Hence, the degree of sorption of a PPH
397 compound was dependent on both the type of compound and the characteristics of mineral surface.

398

399 VK diagrams in Fig. 5 provide information on the order of relative affinity of PPH molecules (sorted as a
400 function of their values of I) for the surfaces of alumina and kaolinite. A main result is that PPH is strongly
401 fractionated between mineral surfaces and solution. Some compounds of low values of I ($0 < I < 0.7$ in Figs. 5a,c
402 and $0 < I < 0.9$ in Fig. 5b,d) are well sorbed, while those of highest values of I ($I > 1$ in Figs. 5a,c and $I > 1.2$ in
403 Fig. 5b,d) are unambiguously not sorbed at all. Compounds of intermediate values of I are only poorly sorbed
404 or even not sorbed at all (cf. section 2.3.4. for detailed explanation). The fact that distinct ions show very
405 different degrees of sorption on alumina is a first indication that the supramolecular FA structure is not
406 preserved during sorption on this mineral surface, i.e. that the sorption involves relatively strong forces that
407 are likely to modified to some extent the assembly of building blocks holding together thanks to weak
408 cohesion forces. Another main result is that the sorption scheme of PPH onto alumina and kaolinite appear to
409 be quite different.

410 Clear overall trends are observed for alumina (Figs. 5a,b). Firstly, the affinity of a PPH compound for the
411 surface decreases with an increase of its H/C ratio. Secondly, PACs are totally sorbed ($I=0$) or have a high
412 affinity for the surface ($I < 0.5$) whereas NCAs and aliphatic compounds exhibit a wide range of I, with the

413 latter compounds showing the largest distribution. For NCAs, the cloud of data-points is moved towards lower
414 values of O/C with increasing values of I, which suggests that increasing amounts of oxygenated
415 functionalities for these molecules increases their affinity for the surface. For the aliphatic compounds, the
416 cloud of data-points is displaced towards both lower values of O/C and higher values of H/C, which suggests
417 that the amount of oxygenated functionalities and/or the length (or number) of aliphatic chains are parameters
418 influencing the affinity for surface. Finally, all the strongly oxygenated molecules ($O/C > 0.6$) amongst NCAs,
419 and the H-depleted molecules ($H/C < 1.2$) amongst aliphatics, show a high affinity for the surface of alumina.
420 Differences existing between the sorptive fractionation patterns of PPH in the alumina suspension and
421 kaolinite suspension (Fig. 5c,d) are rather striking. Firstly, the totally sorbed compounds ($I = 0$) are fewer for
422 kaolinite than for alumina and they are moreover dispersed over a wide region of VK diagram. Secondly, no
423 effect of the H/C ratio on the sorption is observed. Unlike for alumina, compounds showing an affinity for the
424 surface of kaolinite extend to aliphatic compounds of intermediate O/C and high H/C -and include as well the
425 same compounds as those displaying a high affinity for alumina, such as NCAs with $O/C > 0.4$ and aliphatics
426 with $O/C > 0.6$ (together with some PACs of $0.2 < O/C < 0.6$)-. It is also to be noted that most of the
427 compounds sorbed onto kaolinite show I values in a narrow range ($0.5 < I < 0.9$). All these features clearly
428 indicate that the surface of kaolinite is weakly selective, and that unlike for alumina, the supramolecular
429 structure of the FA is likely to be globally preserved during sorption onto kaolinite. Thirdly, another striking
430 difference between kaolinite and alumina is that a great part of PACs, including those having weak O/C ratios,
431 are only slightly sorbed or not sorbed at all onto kaolinite (Fig. 5c, $0.7 < I < 1$). All the differences described
432 above suggest that different molecular characteristics and sorption mechanisms are influencing the sorptive
433 fractionation of PPH onto kaolinite and alumina.
434



435

436

437 **Fig. 5:** VK diagrams for PPH compounds sorted as a function of their relative affinity for the surface of
 438 alumina at pH 3.9 (a,b) and for the surface of kaolinite at pH 3.7 (c,d) for the ranges 120-400m/z and 400-
 439 798m/z, respectively.

440

441 3.3.2. Relative affinity order for mineral surfaces of PPH compounds in $-\text{CO}_2$ and $-\text{CH}_2$ series

442

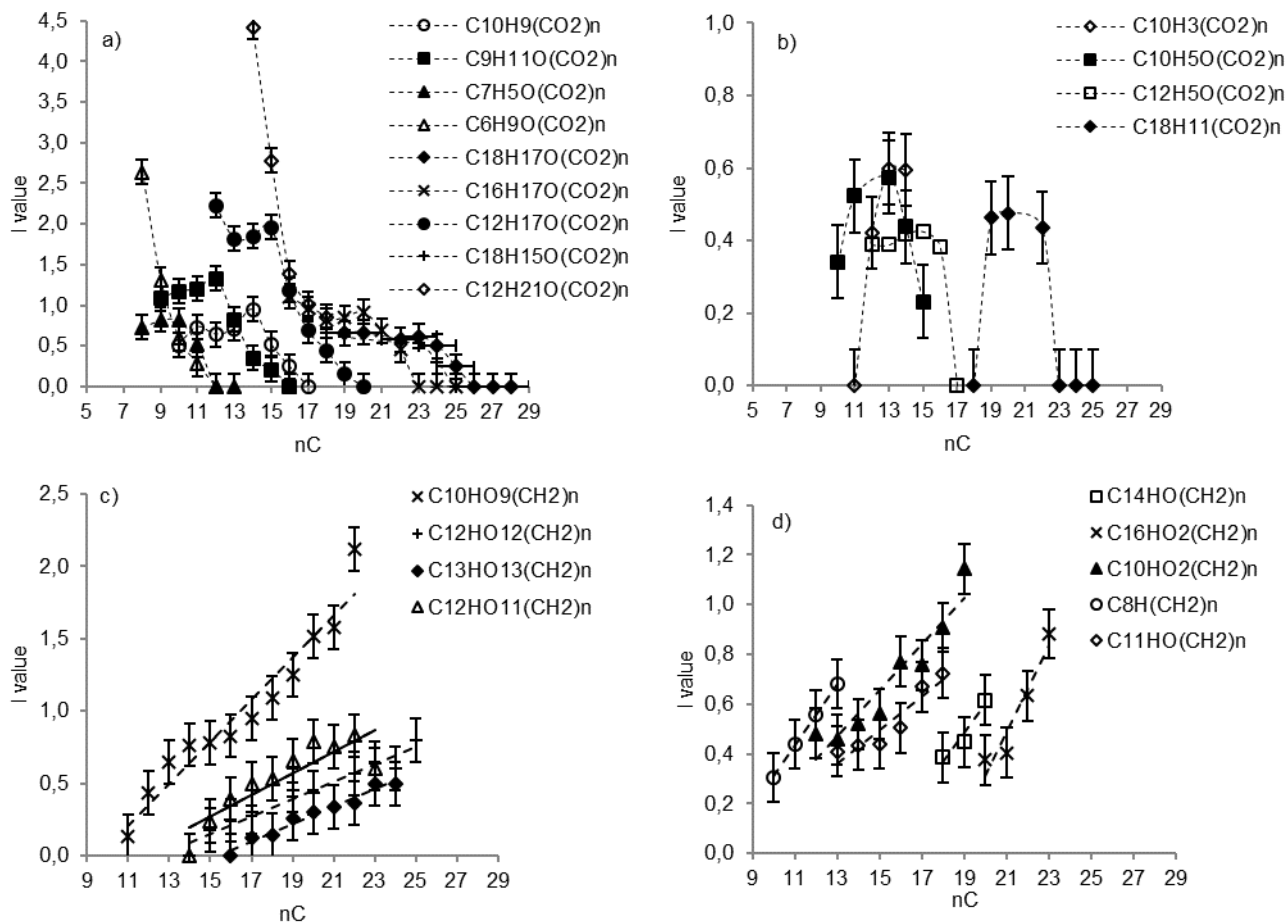
443 Relations existing between the sorption degree of a molecule in a $-\text{CO}_2$ series and its number of CO_2 groups,
 444 as representative for the number of carboxyl functionalities, or between the sorption degree of a molecule in $-\text{CH}_2$
 445 series and its number of $-\text{CH}_2$ groups, as representative for length/number of aliphatic chains, were
 446 investigated to gain further information on the mechanisms involved in the sorption of PPH onto alumina and

447 kaolinite. $-\text{CO}_2$ series or $-\text{CH}_2$ series are made up by compounds whose chemical formula differ only by their
448 number of CO_2 or CH_2 , respectively.

449

450 Figs. 6a,b report, for alumina-solution systems at pH 3.9, the evolution of I as a function of number of carbon
451 atoms (n_c) of PPH compounds in $-\text{CO}_2$ series of aliphatic compounds or oxygenated NCAs compounds
452 ($\text{O}/\text{C}>0.2$), and in $-\text{CO}_2$ series of PACs or poorly-oxygenated NCAs, respectively. Figs. 6c,d refer to the
453 results obtained for the $-\text{CH}_2$ series. A striking result is the difference in the n_c -I relations existing between the
454 two sets of series. For the aliphatic compounds or the NCAs with $\text{O}/\text{C}>0.2$ (Fig.6a), the $-\text{CO}_2$ series show an
455 inverse correlation between the value of I and the number of carbon atoms, n_c . This indicates that the degree
456 of sorption of a molecule in the series is directly related to its number of carboxyl groups. For the $-\text{CH}_2$ series,
457 a sharp increase of I with n_c was observable (Fig. 6c) indicating that the affinity for surface of a molecule
458 within a series decreases with an increasing of the length/number of aliphatic chains. Such remarkable and
459 monotonous n_c -I relations, which were observed for all the $-\text{CO}_2$ / $-\text{CH}_2$ series investigated, suggest that a
460 single mechanism controls the degree of sorption onto alumina of aliphatic compounds and oxygenated
461 NCAs. The fact that distinct molecules of a same $-\text{CO}_2$ / $-\text{CH}_2$ series display very different degrees of sorption
462 -some being totally sorbed ($I = 0$) and others being not sorbed at all ($I > 1.2$)- clearly indicate that the
463 supramolecular structure of the FA existing in solution is greatly modified during sorption. Probably, the
464 sorption implies strong forces which compete efficiently against the weak cohesion forces of the
465 supramolecular assemblies, leading to different sorption behaviors for the distinct FA building blocks at the
466 surface of alumina. Regarding the PACs and the poorly-oxygenated NCAs, more complex features were
467 observed. The degree of sorption of a molecule within a $-\text{CH}_2$ series was found to be only weakly correlated
468 with its number of CH_2 groups (only a small increase of I with n_c is observable in Fig. 6d). In contrast, $-\text{CO}_2$
469 series showed a noticeable and not monotonous evolution of I with n_c . Indeed, bell-shaped curves were
470 observed: the last members of the $-\text{CO}_2$ series showed a decrease of I with an increase of n_c while the first
471 members of the series showed the opposite (Fig. 6b). Hence, PACs and NCA compounds with $\text{O}/\text{C}<0.2$ show
472 different sorption trends according to their molecular O/C ratio, which suggests that within a $-\text{CO}_2$ series of
473 compounds two different mechanisms of sorption (at least) operate, one favoring the retention of molecules
474 containing some oxygen and another favoring the retention of molecules depleted in oxygen.

475



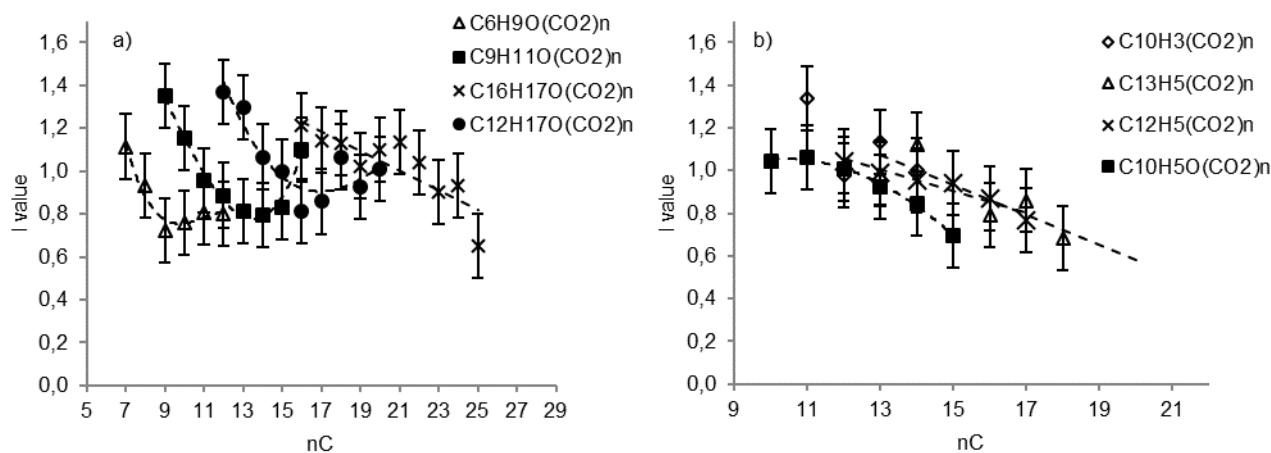
476

477 **Fig. 6:** Evolution of value of I of PPH compounds as a function of number of carbon atoms (n_C) for aliphatics
 478 and NCAs with $O/C > 0.2$ in $-\text{CO}_2$ (a) and $-\text{CH}_2$ (c) series, and for NCAs depleted in oxygen and PACs in $-\text{CO}_2$ (b) and $-\text{CH}_2$ (d) series, in alumina-solution systems at pH 3.9.

480

481 Figs. 7a,b show, for kaolinite-solution systems at pH 3.7, plots of I versus n_C for $-\text{CO}_2$ series of aliphatic
 482 compounds or oxygenated NCAs compounds ($O/C > 0.2$) and for $-\text{CO}_2$ series of PACs or poorly-oxygenated
 483 NCAs, respectively. The same series as those described above for alumina were considered for kaolinite. The
 484 most striking result is that the values of I for $-\text{CO}_2$ series of aliphatics or highly oxygenated NCAs (Fig. 7a)
 485 are in a very limited range, showing that all compounds in a series have almost a similar relative affinity for
 486 the surface of kaolinite. Such a trend in kaolinite-solution systems is also visible for the $-\text{CO}_2$ series of PACs
 487 and oxygen-depleted NCA molecules (Fig. 7b). These results contrast markedly with those reported above for
 488 the surface of alumina, for which values of I varied largely amongst compounds of a $-\text{CO}_2$ series (cf. Figs.
 489 6a,b). It is also to be noted that, in the PPH-kaolinite system, none of the $-\text{CO}_2$ series investigated showed
 490 well-sorbed molecules with values of I lower than 0.5. All these results confirm that the clay surface is less
 491 selective than the Al-oxide surface and that molecular characteristics such as number of $-\text{CO}_2$ groups and/or

492 number/length of aliphatic chains are not determining parameters regulating the sorptive fractionation of PPH
493 onto kaolinite.
494



495
496 **Fig. 7:** Evolution of the values of I within $-\text{CO}_2$ series of aliphatics or NCAs with $\text{O}/\text{C} > 0.2$ (a), and $-\text{CO}_2$
497 series of NCAs depleted in oxygen and PACs (b), after sorption of PPH onto kaolinite at pH 3.7.

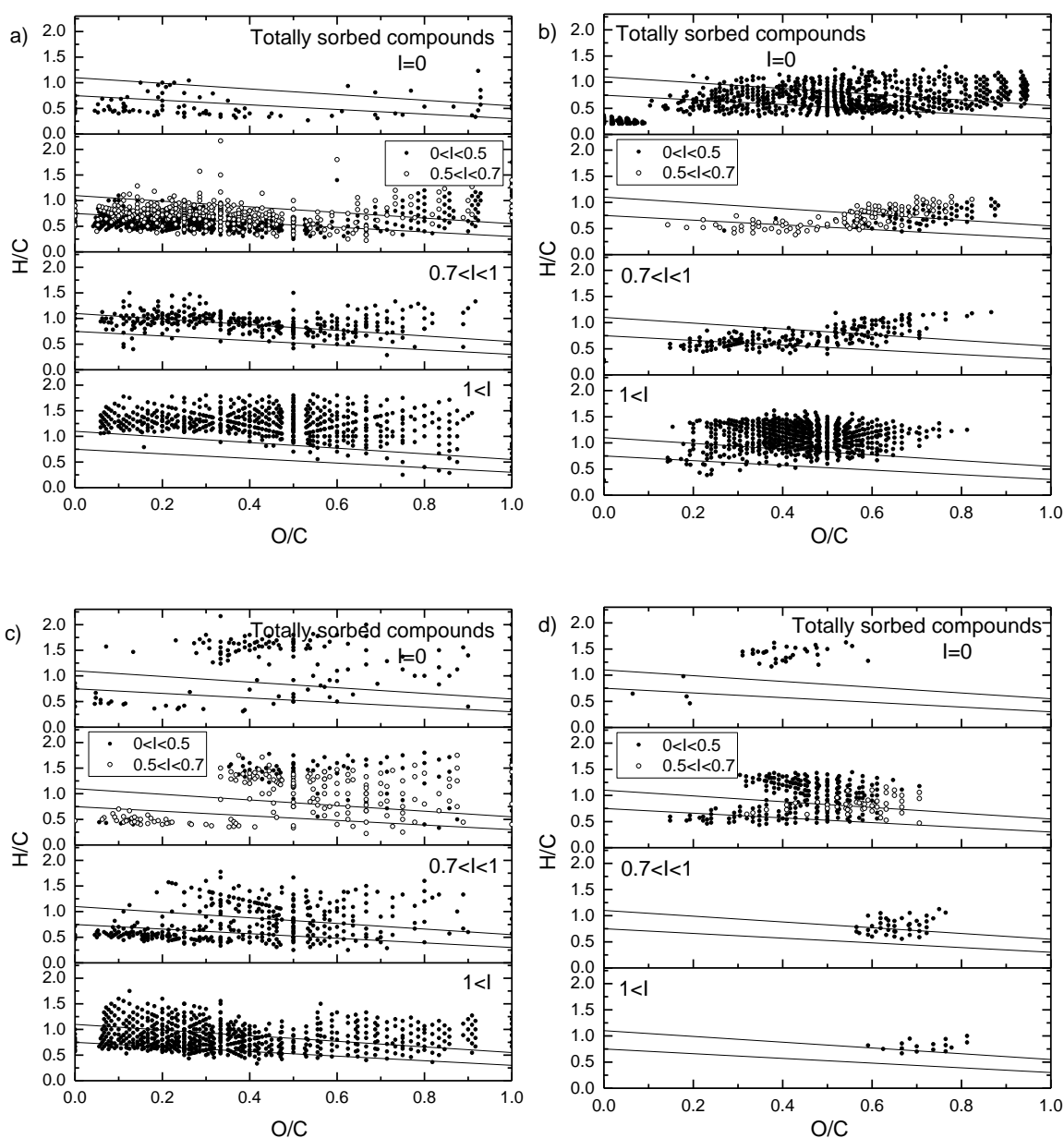
3.3.3. Effect of pH on the sorptive fractionation of PPH

500
501 Regarding the sorption onto alumina, it appears that the relative affinities of PPH molecules for the surface do
502 not change significantly in the acidic pH range 3-5, as shown by comparing VK diagrams obtained for the
503 system at pH = 4.8 (Figs. 8a,b) and at pH = 3.9 (cf. Figs. 5a,b). Correlations observed at pH 4.8 between the
504 degree of molecule sorption and molecular parameters within $-\text{CO}_2$ or $-\text{CH}_2$ series (data not shown) were
505 similar to those described for the pH 3.9 (cf. paragraph 3.3.2).

506
507 Regarding the sorption onto kaolinite, it is first to be noted that fewer compounds are represented on the VK
508 diagrams reporting the relative affinities of PPH molecules for surface at pH 5.0 (Figs. 8c,d) than at pH 3.7
509 (Figs. 5c,d). This is due to the fact that supernatants for the kaolinite-PPH-solution systems had to be analyzed
510 at pH 5.0 (cf. section 2.2), which leads to an alteration of the MS response (for illustrative purposes, compare
511 VK diagrams of native PPH solution analyzed at pH 3.8 in Fig. 4 and at pH 5.0 in Fig. A4 in the Appendix).
512 Despite fewer compounds are detected for the native solution of PPH at pH 5.0 than at pH 3.8, some key
513 trends in the pH-dependency of the sorption of PPH onto kaolinite can still be determined. Some highly
514 oxygenated aliphatics and NCAs are poorly sorbed at pH 5.0 (while they display a good affinity for the

515 surface at pH 3.7). This suggests the existence of a process that competes against sorption at pH 5.0 and tends
 516 to keep these highly oxygenated molecules in solution. Interestingly, the final concentration of dissolved
 517 aluminum in kaolinite-PPH suspensions at pH 5.0 was found to be ca. four times higher than in kaolinite
 518 suspensions without PPH (cf. Fig. A5 in the Appendix). This supports the formation in kaolinite-PPH systems
 519 of solution complexes implying the most oxygenated aliphatic and NCA compounds and the dissolved
 520 aluminum originating from the dissolution of kaolinite.

521



522

523

524 **Fig. 8:** VK diagrams for PPH compounds sorted as a function of their relative affinity for the surface of
 525 alumina at pH 4.8 (a,b) and for the surface of kaolinite at pH 5.0 (c,d) for the ranges 120-400m/z and 400-
 526 798m/z, respectively.

527

528 4. DISCUSSION

529

530 A main finding is that the trends in the sorptive fractionation of PPH in kaolinite-solution systems are very
531 different than those observed for alumina, in the present work or in previously published studies of molecular-
532 scale alumina-HS-interactions (Galindo and Del Nero, 2014; Galindo and Del Nero, 2015). Such a finding
533 provides strong evidence that the mineral surface properties are a key parameter governing the sorptive
534 fractionation of HS.

535 All the results obtained at the molecular scale for the kaolinite-solution system suggest that the sorption of
536 PPH onto kaolinite is mostly the result of a weakly selective mechanism. For example, the dispersion of the
537 totally sorbed PPH compounds over a wide region of VK diagram and the closeness of the I values of the
538 molecules in $-CO_2$ series well exemplify that the number of CO_2 groups in a molecule and, more generally,
539 molecular acidity, have a slight influence on the degree of sorption of NCAs and aliphatics onto kaolinite.
540 These features rule out a substantial contribution to PPH sorption of a surface ligand exchange mechanism
541 between the hydroxyl groups existing on the kaolinite surface and the carboxyl groups of PPH. Though, it has
542 been widely reported that high affinity aluminol sites on singly coordinated oxygens at edges and steps of
543 kaolinite surface have chemical properties close to the surface sites of alumina (e.g. Kummert and Stumm,
544 1980). These sites probably have a strong affinity for the highly oxygenated compounds of PPH but are not
545 numerous enough to have a measurable effect on the overall sorptive fractionation pattern of PPH.

546 Based upon the structure of fulvic acid molecules, which have numerous functional groups with hydrogens
547 bound to heteroatoms (N, O), hydrogen bonding seems to be a good candidate because such a mechanism is
548 not as selective as surface ligand exchange. Hydrogen bonding well accounts for the lack of preferential
549 sorption observed amongst all aliphatics and NCA molecules of $O/C > 0.2$ (Fig. 5d). Sorption of most of PPH
550 compounds, including the hydrogenated compounds, may thus imply aluminol or silanol groups existing on
551 the doubly coordinated oxygens located on the basal planes of kaolinite, which are poorly selective sites
552 expected to be involved in weak sorption mechanisms such as hydrogen bonding. Probably, such weak
553 sorption mechanisms do not compete efficiently against the cohesion forces of the supramolecular FA
554 assemblies. The supramolecular structure would thus be globally preserved during sorption, accounting for the
555 similar affinities of the different FA compounds for the surface of kaolinite. Implication of these low affinity

556 sites not only accounts for a weak fractionation amongst members of $-\text{CO}_2$ series of aliphatics or NCAs
557 during their sorption onto kaolinite, but also for the very low degree of sorption of PACs. No positive n_c -I
558 correlation were observed in kaolinite-solution systems for $-\text{CO}_2$ series of PACs with low O/C ratios,
559 suggesting a poor contribution of hydrophobic interactions between PACs and kaolinite surface. Possibly, the
560 rather limited degree of sorption onto kaolinite of the PACs bearing oxygenated functionalities (due to low
561 amounts of high affinity surface aluminol sites) resulted in few amounts of hydrophobic domains available, in
562 the first layer of PPH molecules sorbed at the clay surface, for further interactions with hydrophobic moieties
563 of NCAs and PACs of low O/C present in solution. Moreover, the first layer of sorbed compounds is only
564 weakly bonded on the basal planes of the kaolinite surface, preventing a strong attach of poorly-oxygenated
565 PACs on the surface.

566 Implication of the low affinity sites on the basal planes of kaolinite also accounts for the pH-dependency of
567 the sorption of the highly oxygenated aliphatic and NCA compounds of PPH. A decrease of the degree of
568 sorption of these molecules at pH 5.0 results from their complexation with aluminum in solution competing
569 against their sorption at the surface of the mineral. Indeed, an increase in pH value induces the deprotonation
570 of both the aluminol/silanol groups on the basal planes of kaolinite, as well as of the carboxyl groups of PPH.
571 Such a deprotonation has the effect of preventing hydrogen bonding of PPH molecules on the kaolinite
572 surface sites, and of decreasing the degree of sorption of the highly oxygenated aliphatic and NCA
573 compounds. Moreover, the deprotonation of the carboxyl groups of these molecules also favors the formation
574 of FA-aluminum complexes in solution. The pH-dependency of the sorption of highly oxygenated aliphatic
575 and NCA compounds in PPH is thus the result of both these processes.

576 The molecular-scale findings on the sorptive fractionation trends of PPH during sorption at the clay surface
577 are quite contrasting with those observed for the alumina-solution-PPH systems, for which molecules showing
578 the highest affinity for the mineral surface are the PACs and the highly oxygenated compounds amongst
579 aliphatics or NCAs. For the latter compounds, strong evidence is provided that a single mechanism controls
580 their sorption at the alumina surface, as shown, for example, by the remarkable positive correlations existing
581 for PPH compounds in CO_2 series between the degree of sorption of a molecule and its molecular O/C ratio.
582 Highly-oxygenated NCA and aliphatic compounds carry multiple carboxyl and phenol groups which are well
583 known to be involved in ligand exchange reactions (specific adsorption) with surface aluminol groups, e.g.
584 (Schlautman and Morgan, 1994). The positive correlation observed between affinity for the surface of alumina

585 and number of carboxyl groups of a PPH compound in a $-\text{CO}_2$ series even includes molecules containing up to
586 5 groups or more (e.g. Fig. 6). As discussed in previously published papers by our team (Galindo and Del
587 Nero, 2014), it is unlikely that more than three of carboxyl groups of a molecule are involved simultaneously
588 in multiple bonding with aluminol groups at the surface of alumina. The concomitant increase of affinity for
589 alumina surface and $n\text{CO}_2$ of compounds in CO_2 -series of the types highly-oxygenated NCAs or aliphatics is
590 thus due likely to a change in molecule acidity. Such an interpretation was already proposed for simple
591 organic acids by Evanko and Dzombak (1998), who suggested that enhanced sorption with increasing number
592 of carboxyl groups of acids was due to changes in the acidity of compound rather than to multiple bonding,
593 and was supported by the results of Janot et al. (2012). The interpretation is also supported by our results
594 showing that a lengthening of aliphatic chains of a molecule within a $-\text{CH}_2$ series, which is expected to
595 decrease the molecule acidity due to donor inductive effect, decreases the affinity for the surface of alumina.
596 Regarding the NCAs with $\text{O/C} < 0.2$ and the PACs, the bell shape of the curves reporting affinity of
597 molecules in CO_2 -series for alumina surface vs. number of carboxyl groups indicate that different mechanisms
598 are responsible for the sorption of molecules of lowest O/C ratios and highest O/C ratios, respectively. For the
599 latter molecules, acidity is the key parameter controlling the degree of sorption (same types of $n_{\text{C-I}}$ inverse
600 correlation as those observed for the aliphatics), and surface ligand exchange is the mechanism driving the
601 sorption. For the former compounds, the positive $n_{\text{C-I}}$ correlation observed rules out acidity as a parameter
602 governing sorption. The existence of this correlation for compounds having many hydrophobic moieties (e.g.
603 aromatic structures) and few oxygenated functional groups provides strong evidence that their degree of
604 hydrophobicity determines their affinity for the surface of the oxide. A possible explanation is as follows. As
605 evidenced by the impact of molecule acidity on the degree of sorption of a FA molecule onto alumina, - either
606 for aliphatics, NCAs and PACs-, the supramolecular structure of FA appears to be not preserved during
607 sorption, allowing : (i) the sorption of the most highly acidic FA compounds to be sorbed via surface ligand
608 exchange involving their hydrophilic moieties and (ii) the release into solution of PACs with very low O/C
609 and their subsequent sorption via interaction between their hydrophobic moieties and those of the strongly
610 sorbed PACs (which form a first sorption layer onto alumina). Another possible interpretation is that the
611 electric fields induced by the surface charge of alumina influence the dielectric constant of water (Booth,
612 1951). Water at the surface of alumina would thus have a lower apparent dielectric constant, which favors the
613 adsorption of hydrophobic molecules. Molecular-scale evidence that the degree of hydrophobicity governs the

614 degree of sorption of poorly-oxygenated PACs and NCAs onto a metallic oxide has been published recently
615 for a peat humic acid (Galindo and Del Nero, 2015) but has never been so far demonstrated for fulvic acids.
616 The molecular-scale results presented here for the sorption of PPH are useful for rationalizing the contrasting
617 results of spectroscopic studies published on the sorption of bulk FAs at the surfaces of metallic (hydr)oxides
618 and clays, respectively. Ghosh et al. (2009) studied by spectroscopy techniques the fractionation behavior of
619 HS on minerals with different surface properties. They reported that aliphatic fractions of HS are more prone
620 to sorption at the surface of clay minerals than the highly aromatic fractions, while carboxylic functional
621 groups play a significant role in the sorption of HA on goethite. Spectroscopic studies have long reported
622 preferential sorption of aromatic structures bearing oxygenated functionalities of HS at the surface of metallic
623 (hydr)oxides (Meier et al., 1999; Zhou et al., 2001; Kaiser, 2003; Claret et al., 2008). For example, Kaiser
624 showed for HS-solution-goethite systems a preferential removal from solution of aromatic and carboxyl C,
625 whereas alkyl-C accumulated in the solution. Claret et al. (2008) reported a preferential sorption at the surface
626 of alumina of the hydrophobic fractions of FA and/or of the FA compounds showing high contents in aromatic
627 moieties and functional groups, as compared to aliphatic fractions. In the present study, on the one hand, we
628 provide molecular-scale evidence that most of the acidic, aliphatic compounds of a FA display a greater
629 affinity for the kaolinite surface than PACs because the most effective mechanism of sorption of FA
630 molecules at such a clay surface is a weak sorption via H-bonds at the aluminol / silanol sites on the doubly
631 coordinated oxygens located on the basal planes of the clay. On the other hand, the present molecular-scale
632 study also confirms unequivocally that clear relationships exist between molecular parameters such as acidity
633 or hydrophobicity of a molecule and its degree of sorption in a metallic oxide–solution system. The sorptive
634 fractionation of FAs in such systems, in contrast to clay systems, is due to a competition between protons and
635 metallic centers at the surface of the mineral for coordination of FA molecules, and to the subsequent sorption
636 of poorly-oxygenated PACs by hydrophobic forces involving hydrophobic moieties in the first layer of sorbed
637 FA molecules on the oxide surface.

638

639 **5. CONCLUSION**

640

641 The results of the present study on the fractionation behavior of a soil FA onto alumina and kaolinite provide
642 valuable molecular-scale insights on the relationships existing between the chemical characteristics of the

643 molecules and their distribution between aqueous and mineral phases, as well as on the distinct mechanisms
644 involved in the fractionation of a FA during its sorption onto minerals of different surface properties. A main
645 finding is that the molecular-scale fractionation of FA in kaolinite suspensions is highly contrasting with that
646 observed here for alumina or with those reported in previously published studies for aluminum oxide (Galindo
647 and Del Nero, 2014; Galindo and Del Nero, 2015). Such a finding highlights that the key parameter
648 controlling the sorptive fractionation trends of FAs is the nature, i.e. oxides vs. clays, and the surface
649 properties of sorbing minerals.

650

651 The data presented here confirm previous work by our team (Galindo and Del Nero, 2014) indicating that
652 acidity of FA molecules is a main parameter determining the relative degree of sorption onto Al-oxides of FA
653 molecules, with the highly acidic molecules bearing oxygenated functionalities being sorbed preferentially via
654 surface ligand exchange involving the high-affinity aluminol surface sites. Our study also reveals that degree
655 of hydrophobicity of PACs and NCAs of low O/C ratio is another key molecular parameter influencing the
656 degree of sorption of these FA compounds, which are able to interact with hydrophobic domains of organic
657 molecules (probably mainly PACs) strongly retained at the Al oxide surface within a first layer of
658 specifically-sorbed organic molecules. The present study establishes that, whatever the FA composition and in
659 a range of acidic pH values, surface ligand exchange and hydrophobic interactions are the main (cooperative)
660 mechanisms leading to the preferential retention on metal oxides of most of PACs, of NCAs with high O/C
661 ratios (>0.5) and of highly-oxygenated aliphatic compounds ($O/C > 0.7$), whereas hydrogenated and less
662 oxygenated NCAs and aliphatics are left in the solution.

663

664 The first molecular-scale description presented here of the fractionation of a FA in a clay mineral-solution
665 system reveals that, unlike for metallic oxides, molecular acidity has no substantial effect on the degree of
666 sorption of a FA molecule onto a clay, and that surface ligand exchange is not the mechanism driving the
667 sorptive fractionation of FA in such systems. Instead, the main mechanism of sorption is hydrogen bonding of
668 FA molecules at the low affinity sites (aluminol or silanol) present on the basal planes of the clay, as
669 evidenced here by the weak sorptive fractionation existing amongst members of $-CO_2$ homologous series of
670 aliphatics or NCAs during their sorption onto kaolinite at low pH. In contrast, at slightly acidic pH (5), a
671 fractionation occurs to a certain extent between molecules within a same class of FA compounds (for

672 aliphatics as well as NCAs), due to a decreasing with pH of the degree of sorption of highly acidic molecules
673 bearing oxygenated functionalities. Such a fractionation is explained by the fact that dissolved Al has the
674 ability to compete successfully for the coordination of such reactive organic molecules against a weak
675 sorption process such as H-bonding. Finally, the predominance of a weak and poorly-selective mechanism of
676 sorption of FA molecules like H-bonding indirectly accounts for a very low degree of sorption of PACs or of
677 low O/C NCAs onto kaolinite. Absence of preferential and specific sorption at surface of kaolinite of aromatic
678 structures activated by oxygenated functionalities prevents the formation of a first layer of strongly-sorbed
679 molecules exhibiting hydrophobic domains which would be available for further sorption of FA compounds
680 via hydrophobic interactions.

681

682 The results of the present molecular scale studies have several implications on our knowledge of storage of
683 natural organic matter in soils as well as on the cycle of metals. It is to be expected that clayey soils trap lesser
684 amounts of condensed aromatics than metal oxide-rich soils and may retain non-selectively most of FA
685 compounds of the types of aliphatics or not-condensed aromatics at acidic pH, via weak sorption mechanisms.
686 In turn, solutions percolating through clayey soils, if being slightly acidic, would contain a multiplicity of the
687 FA organic acids bearing multiple oxygenated functionalities, owing to the high ability of these FA molecules
688 for binding dissolved metals and their only weak sorption at clay surfaces. Such a feature would promote the
689 transport of metal pollutants with soil solutions. Consequently, (long term) metal sorption capacities of clayey
690 soils are expected to be rather low compared to that of soils rich in Al oxi-hydroxides.

691

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695

696 **REFERENCES**

697

- 698 Aiken G. R., McKnight D. M., Wershaw R. L. and MacCarthy P. (1985) *Humic substances in soil,*
699 *sediment, and water: geochemistry, isolation and characterization.*, Wiley.
- 700 Booth F. (1951) The Dielectric Constant of Water and the Saturation Effect. *J. Chem. Phys.* **19**,
701 391–394.

- 702 Brown T. L. and Rice J. A. (2000) Effect of Experimental Parameters on the ESI FT-ICR Mass
703 Spectrum of Fulvic Acid. *Anal. Chem.* **72**, 384–390.
- 704 Bryan N. D., Abrahamsen L., Evans N., Warwick P., Buckau G., Weng L. and Van Riemsdijk W. H.
705 (2012) The effects of humic substances on the transport of radionuclides: Recent
706 improvements in the prediction of behaviour and the understanding of mechanisms. *Appl.*
707 *Geochem.* **27**, 378–389.
- 708 Claret F., Schäfer T., Brevet J. and Reiller P. E. (2008) Fractionation of Suwannee river fulvic acid
709 and aldrich humic acid on α -Al₂O₃: Spectroscopic evidence. *Environ. Sci. Technol.* **42**,
710 8809–8815.
- 711 D’Andrilli J., Chanton J. P., Glaser P. H. and Cooper W. T. (2010) Characterization of dissolved
712 organic matter in northern peatland soil porewaters by ultra high resolution mass
713 spectrometry. *Org. Geochem.* **41**, 791–799.
- 714 D’Andrilli J., Cooper W. T., Foreman C. M. and Marshall A. G. (2015) An ultrahigh-resolution mass
715 spectrometry index to estimate natural organic matter lability: FTICRMS organic matter
716 molecular lability index. *Rapid Commun. Mass Spectrom.* **29**, 2385–2401.
- 717 Del Nero M., Galindo C., Barillon R., Halter E. and Madé B. (2010) Surface reactivity of α -Al₂O₃
718 and mechanisms of phosphate sorption: In situ ATR-FTIR spectroscopy and ζ potential
719 studies. *J. Colloid Interface Sci.* **342**, 437–444.
- 720 Dobbs J. C., Susetyo W., Knight F. E., Castles M. A., Carreira L. A. and Azarraga L. V. (1989)
721 Characterization of metal binding sites in fulvic acids by lanthanide ion probe spectroscopy.
722 *Anal. Chem.* **61**, 483–488.
- 723 Engebretson R. R. and von Wandruszka R. (1994) Micro-organization in dissolved humic acids.
724 *Environ. Sci. Technol.* **28**, 1934–1941.
- 725 Evanko C. R. and Dzombak D. A. (1998) Influence of structural features on sorption of NOM-
726 analogue organic acids to goethite. *Environ. Sci. Technol.* **32**, 2846–2855.
- 727 Fairhurst A. J. and Warwick P. (1998) The influence of humic acid on europium-mineral interactions.
728 *Colloids Surf. Physicochem. Eng. Asp.* **145**, 229–234.
- 729 Feng X., Simpson A. J. and Simpson M. J. (2005) Chemical and mineralogical controls on humic
730 acid sorption to clay mineral surfaces. *Org. Geochem.* **36**, 1553–1566.
- 731 Filius J. D., Meeussen J. C., Lumsdon D. G., Hiemstra T. and van Riemsdijk W. H. (2003) Modeling
732 the binding of fulvic acid by goethite: the speciation of adsorbed FA molecules. *Geochim.*
733 *Cosmochim. Acta* **67**, 1463–1474.
- 734 Fu H., Quan X., Chen S., Zhao H. and Zhao Y. (2005) Interaction of humic substances and
735 hematite: FTIR study. *J. Environ. Sci.* **17**, 43–47.
- 736 Galindo C. and Del Nero M. (2015) Chemical fractionation of a terrestrial humic acid upon sorption
737 on alumina by high resolution mass spectrometry. *RSC Adv* **5**, 73058–73067.
- 738 Galindo C. and Del Nero M. (2014) Molecular Level Description of the Sorptive Fractionation of a
739 Fulvic Acid on Aluminum Oxide Using Electrospray Ionization Fourier Transform Mass
740 Spectrometry. *Environ. Sci. Technol.* **48**, 7401–7408.
- 741 Ghosh S., Wang Z.-Y., Kang S., Bhowmik P. C. and Xing B. S. (2009) Sorption and fractionation of
742 a peat derived humic acid by kaolinite, montmorillonite, and goethite. *Pedosphere* **19**, 21–30.

- 743 Gu B., Schmitt J., Chen Z., Liang L. and McCarthy J. F. (1995) Adsorption and desorption of natural
744 organic matter on iron oxide: mechanisms and models. *Environ. Sci. Technol.* **28**, 38–46.
- 745 Hertkorn N., Frommberger M., Witt M., Koch B. P., Schmitt-Kopplin P. and Perdue E. M. (2008)
746 Natural Organic Matter and the Event Horizon of Mass Spectrometry. *Anal. Chem.* **80**,
747 8908–8919.
- 748 Hur J. and Schlautman M. A. (2004) Effects of pH and phosphate on the adsorptive fractionation of
749 purified Aldrich humic acid on kaolinite and hematite. *J. Colloid Interface Sci.* **277**, 264–270.
- 750 Janot N., Reiller P. E. and Benedetti M. F. (2013) Modelling Eu(III) speciation in a Eu(III)/PAHA/ α -
751 Al₂O₃ ternary system. *Colloids Surf. Physicochem. Eng. Asp.* **435**, 9–15.
- 752 Janot N., Reiller P. E., Zheng X., Croué J.-P. and Benedetti M. F. (2012) Characterization of humic
753 acid reactivity modifications due to adsorption onto α -Al₂O₃. *Water Res.* **46**, 731–740.
- 754 Kaiser K. (2003) Sorption of natural organic matter fractions to goethite (α -FeOOH): effect of
755 chemical composition as revealed by liquid-state ¹³C NMR and wet-chemical analysis. *Org.*
756 *Geochem.* **34**, 1569–1579.
- 757 Kim S., Kramer R. W. and Hatcher P. G. (2003) Graphical Method for Analysis of Ultrahigh-
758 Resolution Broadband Mass Spectra of Natural Organic Matter, the Van Krevelen Diagram.
759 *Anal. Chem.* **75**, 5336–5344.
- 760 Koch B. P. and Dittmar T. (2006) From mass to structure: an aromaticity index for high-resolution
761 mass data of natural organic matter. *Rapid Commun. Mass Spectrom.* **20**, 926–932.
- 762 Kujawinski E. B., Freitas M. A., Zang X., Hatcher P. G., Green-Church K. B. and Jones R. B. (2002)
763 The application of electrospray ionization mass spectrometry (ESI MS) to the structural
764 characterization of natural organic matter. *Org. Geochem.* **33**, 171–180.
- 765 Kujawinski E. B., Hatcher P. G. and Freitas M. A. (2002) High-Resolution Fourier Transform Ion
766 Cyclotron Resonance Mass Spectrometry of Humic and Fulvic Acids: Improvements and
767 Comparisons. *Anal. Chem.* **74**, 413–419.
- 768 Kummert R. and Stumm W. (1980) The surface complexation of organic acids on hydrous γ -Al₂O₃.
769 *J. Colloid Interface Sci.* **75**, 373–385.
- 770 Leenheer J. A., Rostad C. E., Gates P. M., Furlong E. T. and Ferrer I. (2001) Molecular Resolution
771 and Fragmentation of Fulvic Acid by Electrospray Ionization/Multistage Tandem Mass
772 Spectrometry. *Anal. Chem.* **73**, 1461–1471.
- 773 Loffredo E. and Senesi N. (2006) Fate of anthropogenic organic pollutants in soils with emphasis on
774 adsorption/desorption processes of endocrine disruptor compounds. *Pure Appl. Chem.* **78**.
- 775 Meier M., Namjesnik-Dejanovic K., Maurice P. A., Chin Y.-P. and Aiken G. R. (1999) Fractionation
776 of aquatic natural organic matter upon sorption to goethite and kaolinite. *Chem. Geol.* **157**,
777 275–284.
- 778 Milne C. J., Kinniburgh D. G., Van Riemsdijk W. H. and Tipping E. (2003) Generic NICA-Donnan
779 model parameters for metal-ion binding by humic substances. *Environ. Sci. Technol.* **37**,
780 958–971.
- 781 Ochs M., Cosovic B. and Stumm W. (1994) Coordinative and hydrophobic interaction of humic
782 substances with hydrophilic Al₂O₃ and hydrophobic mercury surfaces. *Geochim.*
783 *Cosmochim. Acta* **58**, 639–650.
- 784 Piccolo A. (2001) The supramolecular structure of humic substances. *Soil Sci.* **166**, 810–832.

- 785 Piccolo A., Conte P. and Cozzolino A. (2001) Chromatographic and spectrophotometric properties
786 of dissolved humic substances compared with macromolecular polymers. *Soil Sci.* **166**, 174–
787 185.
- 788 Piccolo A., Spiteller M. and Nebbioso A. (2010) Effects of sample properties and mass
789 spectroscopic parameters on electrospray ionization mass spectra of size-fractions from a
790 soil humic acid. *Anal. Bioanal. Chem.* **397**, 3071–3078.
- 791 Plancque G., Amekraz B., Moulin V., Toulhoat P. and Moulin C. (2001) Molecular structure of fulvic
792 acids by electrospray with quadrupole time-of-flight mass spectrometry. *Rapid Commun.*
793 *Mass Spectrom.* **15**, 827–835.
- 794 Pruettt R. J. and Webb H. L. (1993) Sampling and analysis of KGa-1 B well-crystallized kaolin
795 source clay. *Clays Clay Miner.* **41**, 514–19.
- 796 Rebhun M., De Smedt F. and Rwetabula J. (1996) Dissolved humic substances for remediation of
797 sites contaminated by organic pollutants. Binding-desorption model predictions. *Water Res.*
798 **30**, 2027–2038.
- 799 Reemtsma T. (2009) Determination of molecular formulas of natural organic matter molecules by
800 (ultra-) high-resolution mass spectrometry. *J. Chromatogr. A* **1216**, 3687–3701.
- 801 Reemtsma T., These A., Springer A. and Linscheid M. (2008) Differences in the molecular
802 composition of fulvic acid size fractions detected by size-exclusion chromatography–on line
803 Fourier transform ion cyclotron resonance (FTICR–) mass spectrometry. *Water Res.* **42**, 63–
804 72.
- 805 Reiller P., Amekraz B. and Moulin C. (2006) Sorption of Aldrich humic acid onto hematite: Insights
806 into fractionation phenomena by electrospray ionization with quadrupole time-of-flight mass
807 spectrometry. *Environ. Sci. Technol.* **40**, 2235–2241.
- 808 Rice J. A. and MacCarthy P. (1991) Statistical evaluation of the elemental composition of humic
809 substances. *Org. Geochem.* **17**, 635–648.
- 810 Ritchie J. D. and Perdue E. M. (2003) Proton-binding study of standard and reference fulvic acids,
811 humic acids, and natural organic matter. *Geochim. Cosmochim. Acta* **67**, 85–96.
- 812 Schlautman M. A. and Morgan J. J. (1994) Adsorption of aquatic humic substances on colloidal-size
813 aluminum oxide particles: Influence of solution chemistry. *Geochim. Cosmochim. Acta* **58**,
814 4293–4303.
- 815 Sparks D. L., Page A. L., Helmke P. A., Loeppert R. H. and Swift R. S. (1996) Organic Matter
816 Characterization. In *SSSA Book Series* Soil Science Society of America, American Society
817 of Agronomy.
- 818 Stenson A. C., Landing W. M., Marshall A. G. and Cooper W. T. (2002) Ionization and
819 Fragmentation of Humic Substances in Electrospray Ionization Fourier Transform-Ion
820 Cyclotron Resonance Mass Spectrometry. *Anal. Chem.* **74**, 4397–4409.
- 821 Stenson A. C., Marshall A. G. and Cooper W. T. (2003) Exact Masses and Chemical Formulas of
822 Individual Suwannee River Fulvic Acids from Ultrahigh Resolution Electrospray Ionization
823 Fourier Transform Ion Cyclotron Resonance Mass Spectra. *Anal. Chem.* **75**, 1275–1284.
- 824 Sutton R. and Sposito G. (2005) Molecular Structure in Soil Humic Substances: The New View.
825 *Environ. Sci. Technol.* **39**, 9009–9015.

- 826 Sverjensky D. A. and Sahai N. (1996) Thoretical prediction of single-site surface-protonation
827 equilibrium constants for oxides and silicates in water. *Geochim. Cosmochim. Acta* **60**,
828 3773–3797.
- 829 Swift R. S. (1989) Molecular weight, size, shape, and charge characteristics of humic substances:
830 Some basic considerations. In *Humic Substances II: In Search of Structure* Wiley,
831 Chichester, UK. pp. 449–466.
- 832 Tipping E. (2002) *Cation binding by humic substances.*, Cambridge University Press, Cambridge,
833 U.K.
- 834 Wang K. and Xing B. (2005) Structural and sorption characteristics of adsorbed humic acid on clay
835 minerals. *J. Environ. Qual.* **34**, 342–349.
- 836 Wershaw R. (1993) Model for humus in soils and sediments. *Environ. Sci. Technol.* **27**, 814–816.
- 837 Wieland E. and Stumm W. (1992) Dissolution kinetics of kaolinite in acidic aqueous solutions at
838 25°C. *Geochim. Cosmochim. Acta* **56**, 3339–3355.
- 839 Yang S., Sheng G., Montavon G., Guo Z., Tan X., Grambow B. and Wang X. (2013) Investigation of
840 Eu(III) immobilization on γ -Al₂O₃ surfaces by combining batch technique and EXAFS
841 analyses: Role of contact time and humic acid. *Geochim. Cosmochim. Acta* **121**, 84–104.
- 842 Zhou Q., Maurice P. A. and Cabaniss S. E. (2001) Size fractionation upon adsorption of fulvic acid
843 on goethite: equilibrium and kinetic studies. *Geochim. Cosmochim. Acta* **65**, 803–812.
- 844