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1 **Characterization of metal binding sites onto biochar using**  
2 **rare earth elements as a fingerprint**

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14 **Abstract**

15 The ability of biochar to immobilize metals relies on the amount of functional groups at its  
16 surface but the contribution of each functional groups (e.g. carboxylic, phenolic) to metal  
17 bonding is poorly known. Using a new approach based on previous works on rare earth  
18 element (REE) interactions with humic substances, we aim at elucidating the relative  
19 contribution of these binding sites to metal sorption under various conditions (i.e. pH and  
20 ionic strengths, IS). Using batch experiments, REE sorption onto biochar was analyzed from  
21 pH 3 to 9 and IS  $10^{-1}$  mol/L to  $10^{-3}$  mol/L. Rare earth element patterns show a Middle REE  
22 (MREE) downward concavity at acidic pH and low ionic strength. These patterns are in good  
23 agreement with existing datasets quantifying REE binding with humic substances. Indeed, the  
24 MREE downward concavity displayed by REE-biochar complexation pattern compares well  
25 with REE patterns with various organic compounds. This similarity in the REE complexation  
26 pattern shapes suggests that carboxylic groups are the main binding sites of REE in biochar.  
27 Overall, our results indicate that the strength of the metal bonding with biochar increases  
28 when pH and IS increase, suggesting that biochar is more efficient for long-term metal  
29 immobilization at near neutral pH and high ionic strength.

30

31

## 32 **1. Introduction**

33 Biochar, the carbon-rich product of biomass pyrolysis, has sparked a broad interest  
34 due to its attractive potential for improving soil fertility, carbon sequestration and soil  
35 remediation (Beesley et al., 2011; Houben et al., 2013a; Lehmann and Joseph, 2009). Surface  
36 functional groups play an important role in the application of biochar as a functional material,  
37 especially for the immobilization of toxic metals (Chen et al., 2015; Liu et al., 2015). For  
38 example, using biochars produced at 400 and 700 °C from rice straw and cattle manure, Qian  
39 and Chen (2013) found that aluminum (Al) binding onto biochar was predominantly due to  
40 complexation of Al with the hydroxyl and carboxyl group at the surface of biochar particles.  
41 Similarly, the sorption of copper (Cu) and lead (Pb) was found to be directly correlated with  
42 the amount of oxygen-containing carboxyl, hydroxyl, and phenolic functional groups at the  
43 surface of biochars produced at various temperatures (200 – 800°C) from cottonseed hulls  
44 (Uchimiya et al., 2011). Understanding biochar surface reactivity is therefore a prerequisite  
45 to its application in soils. Spectroscopic approaches including Fourier transform infrared  
46 spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy have been frequently  
47 employed to characterize the functional groups of biochar (Brewer et al., 2011; Keiluweit et  
48 al., 2010; Zhao et al., 2013). However, these techniques do not allow determining to what  
49 extent each functional group contributes to metal binding under various conditions. Previous  
50 research on humic substances has shown that metal binding to carboxylic and phenolic sites  
51 was strongly dependent on pH and ionic strength in the aqueous phase (Guo et al., 2008;  
52 Ravat et al., 2000; Tipping, 2002). Characterization of humic substances has also revealed  
53 that carboxylic groups generally exhibit low metal affinity sites, while phenolic groups host  
54 high affinity sites (Benedetti et al., 1995; Kinniburgh et al., 1999). Unraveling the relative  
55 contribution of carboxylic and phenolic groups to metal binding by biochar under various pH  
56 and ionic strengths is therefore crucial to gain insight into the strength of association between

57 metal and biochar and to predict metal interaction with biochar over a wide range of  
58 conditions.

59 An emergent approach for characterizing the surface reactivity of organic substances  
60 consists in analyzing the pattern of rare earth element (REE) sorption by these compounds  
61 (Pédrot et al., 2010). Rare earth elements are a group of seventeen elements presenting very  
62 similar and coherent chemical properties (Connelly et al., 2005). In this contribution, we will  
63 consider the fifteen lanthanides as REEs. Due to the unique properties of REEs, their partition  
64 coefficients ( $K_d$ ; commonly used in estimating the potential sorption of dissolved metals by a  
65 solid phase) between humic substances and aqueous solution are highly sensitive to the  
66 heterogeneity of binding sites (i.e. the nature of the functional group involved) (Marsac et al.,  
67 2010; Sonke and Salters, 2006). As a result, specific  $K_d$  patterns arise depending on the  
68 nature of the major binding sites at the surface of humic substances. For example, log  $K_d$   
69 pattern exhibits a medium REE (MREE) downward concavity when REE binding occurs at  
70 carboxylic sites (Pourret et al., 2007). On the other hand, REE binding to phenolic groups  
71 results in a log  $K_d$  pattern exhibiting a regular increase from light REEs (LREEs) to heavy  
72 REEs (HREEs) (Davranche et al., 2015; Marsac et al., 2010). More specifically, studies have  
73 revealed that LREEs are mainly bound by weak carboxylic sites at pHs ranging between 3 and  
74 6, while HREEs are preferentially bound to strong multidentate sites at pH = 3 and to  
75 phenolic groups at pH = 6 (Marsac et al., 2011). These findings have raised the possibility to  
76 use REEs as a tool to determine which of the carboxylic, phenolic or chelate functional  
77 groups are implicated in the binding of cations to humic substances under various  
78 environmental conditions (Davranche et al., 2015; Marsac et al., 2011).

79 In the current study, a new approach based on previous works on REE interactions  
80 with humic substances, was developed to provide new insight into the nature of the sorption  
81 sites responsible for metal binding to biochar under various pH and ionic strengths.

82

## 83 2. Material and methods

84

### 85 2.1. Biochar characteristics

86 Biochar was obtained from VT Green (France) who uses an industrial pyrolysis reactor  
87 (Biogreen®, ETIA, France) and sewage sludge as feedstock. Operating conditions include a  
88 residence time in the reactor of 10 min and an end temperature of pyrolysis of 500 °C. The  
89 biochar was then rinsed with MilliQ water and ground to 0.05 mm particle size. The pH of the  
90 obtained biochar was 8.2 (biochar:water ratio of 1:10; w/v). Its electrical conductivity at 20°C  
91 was 0.009 mS/cm and its cation exchange capacity was 4.6 mmol<sub>c</sub> /kg (cobalthexammine  
92 method) and its specific surface area was 19 m<sup>2</sup>/g (BET method). The biochar was further  
93 acid-rinsed with HNO<sub>3</sub> at pH 2 to remove ash and avoid masking metal sorption by  
94 precipitation phenomenon and by metal complexation with inorganic ligands like carbonate  
95 (Houben and Sonnet, 2015). The PZC value of the studied biochar is 7.81, which is consistent  
96 with previous studies that evidenced an average value of 8.1 and a range from 6.2 to 9.6 (Lu  
97 et al., 2013). The biochar surface functional groups were measured with FTIR: 0.7 mg of  
98 biochar was gently mixed with 100 mg of KBr and the mixture were pressed into a pellet.  
99 FTIR spectrum of the biochar was recorded using a Nicolet iS10 spectrophotometer (Thermo  
100 Fisher Scientific), scanning from 4000 to 400 cm<sup>-1</sup> at a resolution of 1 cm<sup>-1</sup>.

101 The following FTIR broad-band assignment was used to characterize the biochar (Jindo et al.,  
102 2014; Keiluweit et al., 2010): 3400 to 3410 cm<sup>-1</sup>, H-bonded O–H stretching vibrations of  
103 hydroxyl groups from alcohols, phenols, and organic acids; 2850 to 2950 cm<sup>-1</sup>, C–H  
104 stretching of alkyl structures; 1580 to 1590 cm<sup>-1</sup>, COO<sup>-</sup> asymmetric stretching; 1460 cm<sup>-1</sup>, C–  
105 H deformation of CH<sub>3</sub> group; 1280–1270 cm<sup>-1</sup>, O–H stretching of phenolic compounds; and

106 1000–1100  $\text{cm}^{-1}$ , bending of Si–O stretching. The sewage sludge-derived biochar from this  
107 study have comparable properties to those from previous studies (Lu et al., 2012).

108

## 109 **2.2. Experimental setup description**

110 All chemicals used in this study were of analytical grade, and all the experimental solutions  
111 used were prepared with doubly deionized water (MilliQ system, Millipore). REEs–biochar  
112 complexes were prepared in glassware containers previously soaked in 10%  $\text{HNO}_3$  for 48 h at  
113 60 °C, then rinsed with MilliQ water for 24 h at 60 °C to remove all possible REE  
114 contamination sources. Synthetic REE solutions were prepared from nitrate REE standards  
115 (10 mg/L, Accu Trace Reference Standard).

116 Batch experiments were performed to study the pH and ionic strength effect on REE sorption  
117 by biochar as performed for humic acid (HA) by Pourret et al. (2007). REE (50  $\mu\text{g/L}$  of each  
118 REE) and biochar (20 mg/L) were added together in solution, at various ionic strength (0.001  
119 mol/L to 0.1 mol/L, adjusted by NaCl) and pH (from 3 to 9, adjusted by HCl and NaOH).  
120 Prior to addition of biochar, the pH of the solution was adjusted to near 4. The initial  
121 hydroxide and carbonate concentrations were considered negligible and concentrations of  
122  $\text{LnOH}^{2+}$  and  $\text{LnCO}_3^{2-}$  were therefore also considered negligible. The pH was measured with a  
123 Mettler Toledo EL 20 pH-meter equipped with a LE407 electrode having an accuracy of 0.01  
124 pH units. Solutions were agitated at 120 rpm for 48 h (equilibrium time determined from  
125 preliminary kinetic experiments) at room temperature (20 +/- 2°C) to allow equilibrium and  
126 REES fractionation between aqueous solution and biochar suspension. Solution aliquots of 10  
127 mL were sampled at the beginning of the experiment and at equilibrium state (i.e., after 48 h).  
128 REEs sorbed by biochar were separated from the remaining dissolved REE by filtration  
129 through 0.2  $\mu\text{m}$  acetate cellulose filters.

130 To check possible sorption of inorganic REE species onto the membrane of the filter or onto  
131 tube walls, inorganic REE solutions of known REE concentration were filtered for each  
132 experimental conditions and monitored. More than 99% of the REEs present in the solution  
133 were recovered in the filtrates. It thus demonstrates that no REE were retained onto the  
134 membranes or on the walls of the tubes used.

135 Sorption behavior was quantified by using the apparent partition coefficient (i.e.,  $K_d$ ), defined  
136 as the ratio between REE concentration associated with the biochar and REE concentration in  
137 the aqueous solution when the system is at equilibrium, following the equation below:

$$138 K_d = (\mu\text{g REE sorbed} / \text{g biochar}) / (\mu\text{g/mL REE in solution}) \quad (1)$$

139

140 Rare earth element concentrations in the filtered samples were determined by Inductively  
141 Coupled Plasma Mass Spectrometry (ICP-MS; Thermo Fisher Scientific XSERIES2).  
142 Quantification was carried out by external calibration (REE multi elemental standard solution  
143 from Accu Trace Reference, USA) and using indium (2.5  $\mu\text{g/L}$ ) as an internal standard. The  
144 instrumental accuracy was assessed by analyzing the SPS-SW2 certified reference material  
145 for measurement of elements in surface water (SpectraPur standards, Oslo, Norway). The  
146 analyses of real samples were carried out provided that the bias of measured concentration  
147 was <5% compared to the certified values.

148

### 149 **2.3. Modeling**

150 Humic ion-binding Model VI (Tipping, 1998) was introduced into PHREEQC version 3.1.5  
151 (Parkhurst and Appelo, 2013) for the whole REEs group (Marsac et al., 2011). This coupling  
152 allows the REE–HA binding description to be improved (Marsac et al., 2011). Indeed, HAs  
153 are described as 80 different sites that are expected to participate in the cation-HA binding. To  
154 simplify the REE speciation on the HA surface, these 80 sites can be gathered in several

155 groups based on two main characteristics: the chemical nature of the ligands (i.e. carboxylic  
156 groups: CG, phenolic groups: PG and carboxy-phenolic groups: CPG) and their denticity (i.e.  
157 mono-, bi- and tridentate sites) (Marsac et al., 2011; Tipping, 1998). Modeling parameters are  
158 given in Table 1.

159

### 160 **3. Results and discussion**

#### 161 **3.1. pH drives the REE sorption on biochar**

162 The effect of pH on REE sorption was investigated in an initial pH range between 3 and 9.  
163 Results are shown for the first REE (i.e., La) in Figure 1. pH appears to be the parameter  
164 which most strongly modified surface reactivity of biochars (Lee et al., 2010). The proportion  
165 of REEs removed from solution increases with increasing pH. The removal capacity is  
166 minimal at acidic pH (i.e. below pH 5) and increases along with the increase of pH.  
167 Irrespective of the ionic strength, Figure 1 showed a regular increase of La concentration  
168 sorbed to the biochar surface with pH. This general feature is well expressed for all REEs and  
169 follows general trend of metal sorbed to biochars (Chen et al., 2011; Liu and Zhang, 2009).  
170 The REE sorption increase with increasing pH likely results from deprotonation of the biochar  
171 surface functional group (e.g., carboxylic) (Harvey et al., 2011; Lu et al., 2012) making them  
172 available for REE sorption.

173 Moreover, as displayed on Figure 2, log K<sub>d</sub> values increase with pH and log K<sub>d</sub> REE patterns  
174 highlighted a HREE enrichment (i.e., La/Sm<1 and Gd/Yb<1), especially for acidic pH and  
175 higher ionic strength. These patterns are in good agreement with the few existing datasets  
176 quantifying the binding of REEs with humic substances (Marsac et al., 2010). In particular,  
177 the HREE enrichment displayed by REE-biochar complexation pattern determined in this  
178 study compares well with results from REE sorption on carboxylic sites hosted by humic acid  
179 (HA), fulvic acid (FA) and acetic acid (e.g., Davranche et al., 2015).

180

### 181 **3.2. Ionic strength effect on REE fractionation**

182 Ionic strength also appeared to have a general effect on the sorption of REEs onto biochar.  
183 Log  $K_d$  increases with decreasing ionic strength (Figure 2). However, if we look in details,  
184 some exception arises. Indeed, experiments performed at ionic strength of  $10^{-3}$  mol/L and pH  
185 4 and 5 show smaller  $K_d$  than that performed at pH 4.5 and ionic strength of  $10^{-2}$  mol/L. In  
186 addition, experiment performed at pH 9 and ionic strength of  $10^{-1}$  mol/L shows larger  $K_d$  than  
187 those performed under ionic strength of  $10^{-2}$  mol/L. Moreover, fractionation between LREEs  
188 and HREEs increases with increasing ionic strength (Figure 3). As shown in Figure 3, log  
189  $K_d(\text{Gd/Yb})$  and log  $K_d(\text{La/Sm})$  values vary by ca. 0.15 and 0.2 log units, reflecting  
190 fractionation of the REE patterns.

191 Previous studies on organic matter have shown that HREE enrichment patterns is a general  
192 feature of simple organic compounds possessing carboxylic functional groups (Marsac et al.,  
193 2010). Such carboxylic functional groups can be regarded as weak sites. They displayed log  
194  $K_d(\text{Gd/Yb}) < 1$  and log  $K_d(\text{La/Sm}) < 1$ . A similar comparative approach may provide  
195 information about the nature of strong sites that occur at high ionic strength; high affinity sites  
196 are generally thought to comprise phenolic, hydroxylic and/or multidentate carboxylic  
197 functions (Uchimiya, 2014) displaying log  $K_d(\text{Gd/Yb}) < 1$  and log  $K_d(\text{La/Sm}) < 1$ , illustrating  
198 a lanthanide contraction effect. Thus, at low ionic strength (i.e.,  $10^{-3}$  mol/L; Figures 2a and 3),  
199 as log  $K_d(\text{Gd/Yb})$  is closed to 1, REEs are interpreted to be mainly sorbed by weak carboxylic  
200 groups. At high ionic strength (i.e.,  $10^{-1}$  mol/L; Figure 2c and 3), as log  $K_d(\text{Gd/Yb})$  decreased  
201 below 1, they are interpreted to be mainly bound to strong multidentate carboxylic and  
202 phenolic ones (Figure 5). Moreover, ionic strength dependence can be used to differentiate  
203 inner-sphere (ionic strength independent) and outer-sphere (ionic strength dependent) sorption  
204 mechanisms (Uchimiya, 2014). An inner sphere complex is a stable molecular entity resulting

205 from the ionic or covalent bonding of a metal ion with a surface functional group. In the  
206 outer-sphere mechanism at least one water molecule remains between the surface functional  
207 group and sorbed ion (Stumm and Morgan, 1996). Our results reveal thus that the strength of  
208 REE bonding with biochar increases with increasing ionic strength. These findings have  
209 implications for the use of biochar as a REE immobilizing agent as they indicate that REE  
210 immobilization by biochar is expected to be more efficient at high than at low ionic strength  
211 at acidic pH whereas at more alkaline pH opposite behavior happened as already observed for  
212 other metals (Hadjittofi et al., 2014; Uchimiya, 2014; Vithanage et al., 2015). For example,  
213 for La at pH 8, ionic strength increase from 0.001 mol/L to 0.1 mol/L results in removal  
214 decrease from 60% to 30% whereas at pH 5, the same ionic strength increase results in  
215 removal increase from 10% to 20%. It can be thus inferred that REE binding to biochar was  
216 not weak and potentially reversible.

217

### 218 **3.3. Rare earth elements as a fingerprint**

219 As previously discussed, REE patterns highlight a shift from LREEs to HREEs with  
220 increasing ionic strength and pH (Figures 2 and 3). This suggests that (i) at low ionic strength  
221 and acidic pH, REEs are mainly sorbed by carboxylic groups, (ii) at high ionic strength and  
222 alkaline pH, REEs are mainly sorbed by carboxy-phenolic groups. Moreover, when cations  
223 are bound to biochars, changes may occur in the surface reactivity of the biochars themselves  
224 such as (i) the formation of multidentate complexes and (ii) the decrease of the net surface  
225 charge (Uchimiya, 2014).

226 Previous studies investigating REE binding to humic acids (i.e. considered in this study as  
227 analogous material to biochar) reported two kinds of REE-HA patterns depending on the  
228 occurring metal loading. (i) At high metal loading, MREE downward concavity patterns are  
229 observed (Pourret et al., 2007; Yamamoto et al., 2005). (ii) At much lower metal loading,

230 patterns displaying a lanthanide contraction effect are highlighted (Sonke and Salters, 2006;  
231 Stern et al., 2007). The combined effect of metal loading and HA surface heterogeneity  
232 (Davranche et al., 2015) is expressed by stronger but less abundant surface sites (i.e., carboxy-  
233 phenolic groups) at lower metal loading, and weaker but more abundant surface sites (i.e.,  
234 carboxylic groups) at higher metal loading. Comparison of experimental log  $K_d$  REE-biochar  
235 patterns with the pattern for the stability constants (log  $K$ ) of 101 REE organic ligands (Byrne  
236 and Li, 1995) highlight that biochar surface is in the same range as these 101 organic ligands  
237 and can thus be considered as a group of discrete sites (Figure 4). The major sites identified  
238 on the biochar surface are the carboxylic and carboxy-phenolic groups (as also highlighted by  
239 FTIR), which can form monodentate or multidentate complexes (Uchimiya, 2014). Using this  
240 simplified representation, biochar binding properties can be compared with the binding  
241 properties of model organic ligands as already shown in literature (Davranche et al., 2015;  
242 Marsac et al., 2011; Marsac et al., 2010). Indeed, The REE patterns corresponding to the  
243 binding of REE with acetate (carboxylic group model ligand) exhibit a MREE downward  
244 concavity, whereas NTA (chelate group model ligand) exhibit a lanthanide contraction effect  
245 corresponding to both REE-HA patterns obtained at high and low metal loading, respectively.  
246 Moreover, as illustrated by the compilation of organic ligands (Byrne and Li, 1995) and  
247 infrared spectroscopy results (Gangloff et al., 2014), when the ligand is stronger (i.e., strong  
248 aromatic functional groups such as carboxy-phenolic and phenolic groups), HREEs are more  
249 strongly bound to the ligand compared to LREEs, as observed on the REE-biochar binding  
250 experiments presented in the present study. Moreover, as already proposed by Pourret and  
251 Martinez (2009), literature compilation of Log  $K$ (La/Sm) organic ligand constants (Byrne and  
252 Li, 1995; Martinez et al., 2014; Pourret et al., 2007; Sonke and Salters, 2006) as plotted  
253 against Log  $K$ (Gd/Yb) (Figure 4) evidenced that calculated log  $K_d$  values in this study are in  
254 the range of natural carboxylic acids, further illustrating the major role of carboxylic groups.

255 To confirm this hypothesis and to gain access to the REE speciation on each biochar site  
256 types, the same modeling approach as already performed for humic substances was used  
257 (Marsac et al., 2011). Modeling can account for changes in pH and ionic strength as already  
258 proposed by Alam et al. (2017) for cadmium and selenium. Considering biochar as analogous  
259 to humic substances, further allows to dissociate binding parameter of carboxylic and  
260 carboxy-phenolic sites. Such modeling also allows accessing the REE distribution onto each  
261 binding group (Figure 5; Table 2). At low ionic strength (i.e.  $10^{-3}$  mol/L) and pH 3, REEs are  
262 mostly bound to carboxylic groups (33% for La) whereas at higher ionic strength and pH 3,  
263 LREEs are bound to carboxylic groups (21%) and HREEs are bound to carboxylic (13% for  
264 Lu) and carboxy-phenolic (10 % for Lu) groups. At pH of 5 and irrespective of the ionic  
265 strength, LREEs are mostly bound to carboxylic (from 83% at  $10^{-3}$  mol/L to 57% at  $10^{-1}$   
266 mol/L for La) whereas HREEs are bound to carboxylic (from 38% at  $10^{-3}$  mol/L to 28% at  $10^{-1}$   
267 mol/L for Lu) and carboxy-phenolic (from 50% at  $10^{-3}$  mol/L to 38% at  $10^{-1}$  mol/L for Lu)  
268 groups. At a near neutral pH, LREEs are bound to carboxylic groups (from 85% at  $10^{-3}$  mol/L  
269 to 71% at  $10^{-1}$  mol/L for La) and carboxy-phenolic groups (from 14% at  $10^{-3}$  mol/L to 19% at  
270  $10^{-1}$  mol/L for La) and HREEs via carboxy-phenolic (from 55% at  $10^{-3}$  mol/L to 54% at  $10^{-1}$   
271 mol/L for Lu), carboxylic (from 28% at  $10^{-3}$  mol/L to 18% at  $10^{-1}$  mol/L for Lu) and phenolic  
272 (from 18% at  $10^{-3}$  mol/L to 25% at  $10^{-1}$  mol/L for Lu) groups (Figure 5; Table 2). As already  
273 discussed, modeling further indicates that REE immobilization by biochar is expected to be  
274 more efficient at high than at low ionic strength at acidic pH whereas at more alkaline pH  
275 opposite behavior happened as already observed for other metals (Hadjittofi et al., 2014;  
276 Uchimiya, 2014; Vithanage et al., 2015). It must be noted that modeling considering HA  
277 overestimates sorption of REE at pH 7 but overall is a good representation of experimental  
278 results. Eventually, the denticity of the complex is dependent on the metal loading. The  
279 number of groups coordinated to REEs increased with decreasing loading (Marsac et al.,

280 2011; Marsac et al., 2015). The binding of REEs to blocked phenolic and carboxylic sites of  
281 HA suggests that REE binding to stronger sites can be assumed to be the chelator  
282 (Kautenburger et al., 2014). They consist in a combination of phenolic and carboxylic groups  
283 (Kautenburger et al., 2014). EXAFS results considering ytterbium complexation with HA  
284 synthesized at low and high metal loadings, show that at low metal loading, REEs are bound  
285 to HA through bi-ligand complexes without any chelation effect. In these conditions, REE act  
286 as a cation bridge between two organic molecules. At the opposite, at high metal loading,  
287 REEs are bound to HA via multi-carboxylic ligands (Marsac et al., 2015). This modelling  
288 approach is a considerable advance in the sense that such modeling considering HA surfaces  
289 as analogous of biochar surfaces account for changes in pH, ionic strength, and metal-to-  
290 sorbent ratio.

291

### 292 **3.4. Implications for the use of biochar as a sorbent for metals**

293 An increasing number of studies consider biochar as a potential sorbent to remove and  
294 immobilize metals in water and soil, respectively (Ahmad et al., 2014). However, little is  
295 known concerning the stability, and therefore the longevity, of the immobilizing processes  
296 when environmental parameters change (Houben et al., 2013b). Like any other organic  
297 matter, biochar can possess functional groups, namely carboxyl and phenolic groups  
298 (Uchimiya et al., 2011), which host low and high metal affinity sites, respectively. Here, our  
299 results showed that, despite a decrease in the amount of metal sorbed onto biochar, increasing  
300 ionic strength favors metal sorption on high affinity sites, as indicated by the higher relative  
301 contribution of carboxy-phenolic and phenolic groups. Moreover, our data demonstrated that  
302 rising pH from acidic to near neutral values increases both the amount of sorbed metal and the  
303 relative contribution of carboxy-phenolic and phenolic groups to metal sorption. These  
304 findings have great implications for the use of biochar as a sorbent or an immobilizing agent

305 for metals in water and soil because they reveal that environmental conditions affect not only  
306 the amount of sorbed metal onto biochar but also the metal-biochar binding strengths and  
307 stabilities. Overall, the strength of the binding of metals with biochar increases when pH and  
308 ionic strength increase, indicating that biochar is more efficient for long-term metal  
309 immobilization at near neutral pH and high ionic strength. Eventually, considering surface  
310 complexation modeling of biochar comparable to humic substances is a promising direction  
311 even if some other alternative may be considered (Alam et al., 2017).

312

#### 313 **4. Conclusions**

314 The efficiency of biochar to sorb metals is critically dependent on the type of metal-binding  
315 sites at the surface of biochar particles. Although techniques such as FTIR provide a  
316 preliminary biochar characterization by quantifying these sites, they give no information  
317 about the change in surface reactivity of biochar once added to water or soil. Using a new  
318 approach based on previous works on REE interactions with humic substances, this study is,  
319 to our knowledge, the first attempting to elucidate the relative contribution of these binding  
320 sites to metal sorption onto biochar under various conditions (i.e. various pH and ionic  
321 strengths). Our findings indicate that environmental conditions affect not only the amount of  
322 sorbed metal onto biochar but also the metal-biochar binding strengths and stabilities. In  
323 particular, the strength of the metal binding with biochar increases when pH and ionic  
324 strength increase, which has a great implication for the use of biochar as a metal sorbent in the  
325 long run. More generally, our study highlights the great potential of REEs as a fingerprint for  
326 the characterization of metal binding sites onto sorbing matrixes, including biochar.

327

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330 Lakhal for help during analytical procedures, to VT Green and ETIA for providing the  
331 biochar samples.

332 **Table and figure captions**

333 **Figure 1** Proportion of La sorbed to biochar as a function of pH for various ionic strength  
334 conditions.

335 **Figure 2** REE patterns for log Kd (REE sorbed onto biochar) for increasing pH values as a  
336 function of ionic strength (a)  $10^{-3}$  mol/L, (b)  $10^{-2}$  mol/L and (c)  $10^{-1}$  mol/L.

337 **Figure 3** Log Kd(Gd/Yb) versus Log Kd(La/Sm) highlighting change among REE  
338 fractionation as a function of ionic strength.

339 **Figure 4** Literature compilation of REE constants with (a) low molecular weight organic  
340 acids (Byrne and Li, 1995), (b) biochars from this study (c) *Bacillus subtilis* bacteria  
341 (Martinez et al., 2014), (d) Aldrich humic acid (AHA), (e) Suwannee River fulvic acid  
342 (SRFA) and Leonardite humic acid (LHA) (Sonke and Salters, 2006).

343  
344 **Figure 5** REE patterns of modelled log Kd (REE-humic acid) at (a) pH 5 and  $IS$   $10^{-3}$  mol/L  
345 and (b) pH 7 and  $IS$   $10^{-3}$  mol/L, (c) pH 5 and  $IS$   $10^{-2}$  mol/L, (d) pH 7 and  $IS$   $10^{-2}$  mol/L, (e)  
346 pH 5 and  $IS$   $10^{-1}$  mol/L and (f) pH 7 and  $IS$   $10^{-1}$  mol/L, illustrating evolution of REE  
347 fractionation. Modelling was performed using PHREEQC-Model VI considering  
348 experimental condition and HA acting as biochar.

349

350 **Table 1** Model VI parameters for humic acid (Tipping, 1998).

351

352 **Table 2** Proportions of REE sorbed by carboxylic groups (CG), phenolic groups (PG),  
353 carboxy-phenolic groups (CPG) and total (TOT) for various experimental conditions obtained  
354 by modeling using PHREEQC-Model VI.

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