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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_c /kg (cobalthexammine
92 method) and its specific surface area was 19 m²/g (BET method). The biochar was further
93 acid-rinsed with HNO₃ 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⁻¹ at a resolution of 1 cm⁻¹.

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⁻¹, H-bonded O–H stretching vibrations of
103 hydroxyl groups from alcohols, phenols, and organic acids; 2850 to 2950 cm⁻¹, C–H
104 stretching of alkyl structures; 1580 to 1590 cm⁻¹, COO⁻ asymmetric stretching; 1460 cm⁻¹, C–
105 H deformation of CH₃ group; 1280–1270 cm⁻¹, O–H stretching of phenolic compounds; and

106 1000–1100 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% 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 LnOH^{2+} and 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 μm 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_d values increase with pH and log K_d 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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