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1 **Response of water-biochar interactions to physical and** 2 **biochemical aging**

3

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6

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13

14 **Abstract**

15 Biochar aging may affect the interactions of biochar with water and thus its performance as
16 soil amendment; yet the specific mechanisms underlying these effects are poorly understood.

17 By means of FTIR, N₂ adsorption, Hg intrusion porosimetry, thermogravimetric analysis, ¹³C

18 solid state nuclear magnetic resonance (NMR) and ¹H NMR relaxometry, we investigated

19 changes in the chemistry and structure of biochar as well as its interaction with water after

20 biochar aging, both physical (simulated by ball-milling) and biochemical (simulated by co-

21 composting). Three different porosities of biochar were examined: <5 nm, 1 μm and 10 μm

22 diameter sizes. Physical aging caused the disappearance of the porosity at 10 μm. With

23 biochemical aging, biochar underwent an enrichment of oxygenated functional groups either

24 as a result of surface functionalisation processes or by the deposition of fresh organic matter

25 layers on the surface and pores of biochar. ¹H NMR relaxometry revealed that the proportion

26 of water strongly interacting with biochar increased with both physical and biochemical aging.
27 Although biochemical aging significantly altered the composition of biochar surface and
28 modulates its interaction with water, ¹H NMR relaxometry proved that physical aging had a
29 relatively stronger influence on water mobility and dynamics in biochar, lowering both T₁ and
30 T₂ relaxation times in the initial contact times of biochar and water.

31

32 **Keywords**

33 Biochar; Aging; Co-composting; NMR Relaxometry; Water interactions; Porosity.

34

35 **Introduction**

36 In the last decades, the interest in the use of biochar as soil amendment has greatly increased.
37 Biochar is a carbonaceous material derived from the pyrolysis of biomass with great potential
38 for carbon sequestration while improving soil fertility [1,2]. During the pyrolysis process to
39 produce biochar, the biomass feedstock loses most of its labile organic matter leading to a
40 chemically stable and porous material with a considerably high degree of condensed aromatic
41 rings. Biochar has an estimated residence time of hundreds of years when applied to soils [3]
42 but during degradation suffers chemical and physical alterations, a process known as biochar
43 “aging” [4-6]. The characteristics of biochar, its interactions with plants, water and soils, and
44 its persistence within soils depend on the feedstock of biomass and on the temperature and
45 residence time of the pyrolysis process [7,8].

46 In recent years, the combination of compost and biochar has been proposed to obtain a fertile
47 mixture for soil amendment. The addition of biochar to compost improves the performance of
48 the composting process, increasing the temperature and duration of the thermophilic phase by
49 the enhancement of microbial activity and capturing potentially toxic metals and organic
50 compounds [9,10]. During co-composting, biochar undergoes surface modifications by the
51 addition of surface functional groups which increases its cationic exchange capacity (CEC) and

52 interaction with other chemical compounds present in soil, facilitating nutrient retention as
53 well as acting as a pH buffer [11]. Besides, the high porosity of biochar provides large specific
54 surface area which can greatly improve water holding capacity in soils or plant-growing media
55 [12], maintaining desired moisture and promoting the aforementioned nutrient retention.

56 Some biochar modifications during co-composting are produced by biochemical processes
57 driven by microbial decomposition of organic matter. As reported by Wang et al. (2020), this
58 can produce an enrichment of oxygenated functional groups on its surface. Besides, they
59 consider that biochar aging within composting piles and within soil after application should be
60 driven by similar biochemical reactions leading to similar aged biochars, but on a different
61 timescale considering co-composting process as a way to accelerate biochar aging [4,13]. Some
62 authors proposed that, during this biochemical aging taking place in biochar, a layer of fresh
63 organic matter is formed on the surface of biochar particles and pores, which creates a
64 chemically reactive and nutrient-rich material with beneficial properties for soil fertilisation
65 and plant growth [14,15]. To comprehend the mechanism concerning the benefits of aged
66 biochar and the effect on plant-biochar interactions modulated by water holding capacity and
67 nutrient release to the rhizosphere, the role of water interactions in the biochar particles must
68 be understood.

69 Physical fragmentation is another aging mechanism that may affect biochar porosity, particle
70 size and accessibility to inner porosity, which are key to water holding capacity and water
71 interactions in biochar. This physical aging (or disruption) is caused by soil weathering,
72 freeze/thaw temperature cycles and by tillage with agricultural machinery [4]. However, it
73 occurs during long time spans, thus for this study we used ball milling of biochar to reduce
74 particle size, which roughly led to a comparable effect as physical weathering (aging) of
75 biochar in the field. Several authors stated that water retention is mainly dependent on the
76 porosity and particle size of biochar [17,18], proposing different mechanisms where inter-
77 aggregate porosity (between particles), intra-aggregate porosity (structural pores), zeta

78 potential or poly-condensed carbon ring interaction by H-bonds play the main role in water
79 retention.

80 Thus, a number of studies of literature show that both biochemical and physical aging are key
81 parameters on the modulation of water holding capacity of biochar but their relative
82 importance is still unknown [19]. Most of these studies are based on biochars produced from
83 different feedstock materials or pyrolysis conditions, which also affect physical and chemical
84 properties of the final product and, thus, water retention [20]. Moreover, the information on
85 water interactions concerning biochar aged in composted piles or in soils, where the
86 interaction between water and functionalised surface of the material should change compared
87 to that of pristine biochar, mainly deals with quantification or macro-scale processes, while
88 processes at smaller scales are unaddressed [4]. In the present investigation, the effects of
89 physical and biochemical aging on the chemical properties of biochar and its interactions with
90 water were investigated. FTIR, porosimetry analysis, ^{13}C solid state nuclear magnetic
91 resonance (NMR) and thermogravimetric analysis (TGA) were used to examine the chemical
92 modification of biochar after physical aging (simulated by ball-milling) and during biochemical
93 aging (simulated by co-composting). This information was used in combination with 1D ^1H
94 NMR relaxometry and, for the first time, with 2D ^1H NMR relaxometry to study water dynamics
95 (i.e. molecular tumbling) in the different pores of biochar at the molecular scale.

96 There are several examples of ^1H NMR relaxometry (i.e. study of NMR relaxation) applications
97 in porous media in general such as wood, concrete, clay, etc [21-23]. Concerning
98 wood/lignocellulosic samples, the technique has already been used for some decades [24] but
99 it is gaining popularity in recent years due to the development of low-cost (and -maintenance)
100 low-field NMR spectrometers. These instruments allow to perform time domain (TD)-NMR
101 experiments to obtain NMR relaxation information but can also obtain 1D MRI profiles [25]
102 and diffusion information [26]. NMR relaxometry allows to study wood materials under
103 different conditions (non-invasively) to quantify water or organic molecules and to obtain

104 information regarding their local environment (i.e. pore size, affinity with molecules/surfaces
105 they are bonded to). The major part of this research focused on studying water adsorbed on
106 the wood's walls using 1D NMR relaxometry. For instance, Sharp et al. [27] studied wood's
107 moisture content (MC) and other related studies quantified bound water and free water
108 contents by spin-spin (T_2) NMR relaxation time measurements [28–32]. In addition, by means
109 of T_2 NMR measurements Araujo et al. (1994) focused on the separation of hydration and
110 solution water [33]. Recently, Cox et al. (2010) and Bonnet et al. (2017) have used 2D NMR
111 relaxometry experiments via spin lattice (T_1)- T_2 correlation [34, 35]. This better separate water
112 components detecting two types of bound water in wood cell-wall, which were not
113 differentiated in 1D experiments. Cox et al. also studied liquid water in the lumen, which was
114 identified as the peak with the highest T_1 and T_2 values and being close to the $T_1=T_2$ line. This
115 technique has also been used to study biomass recalcitrance in the presence of liquid water
116 [36]. Based on these previous works, the current study thus provides a characterization of
117 water-biochar interactions under aging simulated conditions, to optimize the use of biochar for
118 fertility enhancement and carbon sequestration under environmental conditions.

119

120 **Materials and methods**

121 Biochar, biochemical and physical aging, and sampling

122 Biochar produced from the pyrolysis of pine (*Pinus Halepensis*) prune using a low-tech Kon-tiki
123 oven with a high heating temperature (HTT) of 650-750 °C and a residence time of 3-3.5 h was
124 obtained from *Carbón Vivo, SCCL (Barcelona, Spain)*. The pyrolysis conditions (i.e. the absence
125 of oxygen) are assured by the fire curtains created on top of the material in the Kon-tiki oven
126 and quenching was carried out watering the oven from the top using approximately twice the
127 volume of water than the oven capacity. Biochemical aging of biochar was achieved co-
128 composting a mixture of prune, spent coffee grounds and biochar (1:1:1 v/v) in a 200 L
129 composter during 30 days under monitored temperature (Figure SI-3) and 40-60% humidity

130 conditions. A composite sample of about 500 g of the mixture was collected after 0, 9 and 30
131 days from five random points (\approx 100 g per point) within the composting pile and mixed
132 together to assure the homogenization of the sample. Biochar particles were separated by
133 hand from the composite samples using tweezers and selecting ≥ 2 mm diameter composted
134 particles. A portion of the samples were ground with a ball mill for 10 min at a frequency of 25
135 s^{-1} to simulate physical aging and for physicochemical characterization. Samples were labelled
136 as unaged biochar (BC), physically aged biochar (pa-BC), biochemically aged biochar (ba-BC),
137 and physically and biochemically aged biochar (pba-BC).

138

139 Physicochemical characterisation

140 Particle size was measured using a Mastersizer 3000 laser diffraction particle size analyser
141 (Malvern Panalytical). Fourier transformed infrared spectroscopy (FTIR) was performed in a
142 FTIR-8400 Shimadzu spectrometer [37]; samples were prepared by grinding 1 mg of biochar
143 materials (previously dried at 105 °C, 24 h) with 200 mg KBr and pressing into a pellet. Infrared
144 spectra were recorded in a wavenumber range of 450 – 4000 cm^{-1} . TGA was carried out in a
145 Setaram SETSYS 16/18 TGA-ATD analyser [38] under He and synthetic air atmospheres in a
146 temperature range of 25 – 900 °C and 10 $K \cdot min^{-1}$ heating ramp; 20 mg of the sample was
147 weighted in an alumina crucible for the measurement. Porosity was measured using two
148 different methods targeting micro and macro porosity using N_2 adsorption and Hg intrusion,
149 respectively. N_2 adsorption porosimetry was determined using a Quantachrome Autosorb AS-1
150 instrument [39]. Briefly, biochar samples were degasificated at 150 °C and biochemically aged
151 biochar samples at 105 °C (to avoid thermal decomposition of labile matter), both for 20 h in
152 vacuum conditions. Surface area and pore size distribution were obtained using Brunauer-
153 Emmett-Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively, using AS1-Win
154 software. Hg intrusion porosimetry was carried out with a AutoPore IV 9510 Micromeritics
155 equipment with a pore size resolution between 0.1 and 360 μm [40]. ^{13}C solid state NMR

156 measurements were performed using a cross-polarization sequence at the magic angle
157 spinning (CP-MAS) [41] in a 400 MHz Bruker Advance III spectrometer, using a 4 mm zirconia
158 rotor, 13 kHz spinning speed. A ramped ^1H -pulse from 100 to 50% of the full power was used
159 during a contact time of 1 ms to reduce Hartmann-Hahn mismatches and 500 ms recycle delay
160 between scans. A contact time of 1 ms is frequently used to obtain an efficient coupling
161 between protons and ^{13}C atoms in environmental samples rich in aromatic rings, such as
162 biochar, as a compromise for a good polarization for the different organic components [41,
163 42]. The obtained spectra were divided in six regions contributing to the total measured ^{13}C
164 intensity and corresponding to the carbon atoms in the following functional groups: alkyl (0-45
165 ppm), *N*-alkyl/mehoxyl (45-60 ppm), *O*-alkyl (60-90 ppm), anomeric (90-110 ppm), aryl (110-
166 140 ppm), heteroaromatic (140-160 ppm) and carbonyl/amide (160-220 ppm) [43,44].
167 FTIR, TGA-DSC and particle size analysis were performed on triplicate samples. For ^{13}C NMR
168 and porosimetry, to reduce experimental time and costs, analyses were performed on one
169 composite sample per treatment.

170

171 Measurements of water-biochar interactions using ^1H NMR relaxometry

172 Three different levels of water content were set up for all biochar samples. Firstly, dry samples
173 were wetted with an excess of deuterated water (D_2O) to increase the mobility of structural
174 hydrogen atoms and hence to increase their relaxation time signal without adding hydrogens
175 from water. This way, it is possible to evaluate the structural proton NMR signal from biochar
176 at the experiment conditions and its effect on the subsequent measurements with water
177 (H_2O). Secondly, samples were placed in different desiccators for 5 days in specific relative
178 humidity (RH) controlled by a saturated solution of salt; $\text{Mg}(\text{NO}_3)_2$ (RH=55%), NaCl (RH=75%)
179 and pure water (RH=100%), to prepare samples with adsorbed but not free water. Finally, all
180 samples were mixed with deionized water in a 1:4 mass ratio for liquid water analysis.

181 ^1H relaxometry measurements were carried out in a low field (0.5 Tesla) Bruker Minispec mq20
182 spectrometer. About 80 mg of sample was weighted for each sample and placed in 8 mm
183 diameter glass tube. Temperature was controlled by a BVT3000 temperature controller with
184 air flow of 1200 L h^{-1} at $30 \text{ }^\circ\text{C}$ for all measurements. Samples were maintained at these
185 conditions for 30 min before each measurement to ensure temperature control. Transverse
186 NMR relaxation times ($1\text{D } T_2$) were estimated using the Carr-Purcell-Meiboom-Gil (CPMG)
187 sequence [45,46], using the following test variables (i) for controlled % RH samples: 0.08 ms
188 echo time repeated 625 times, 1 s recycle delay and 96 scans and (ii) for samples with liquid
189 water: 0.5 ms echo time repeated 10000 times, 10 s recycle delay and 96 scans. The obtained
190 data was treated with CONTIN-based home-made method, as reported in previous work [47]
191 to obtain $1\text{D } T_2$ distributions.

192 Finally, 2D NMR correlation spectra of longitudinal (T_1) and transverse (T_2) relaxation times
193 were obtained using a coupled sequence of Inversion Recovery and the CPMG. For the
194 Inversion Recovery experiments, the delay was increased logarithmically in 48 steps from 0.01
195 to 3000 ms. The CPMG block utilised an echo time of 0.5 ms, among which 300 echoes were
196 recorded following a logarithmic series from 0.5 to 1000 ms. For this 2D sequence, 4 scans
197 were accumulated with a recycle delay of 5 s. T_1 - T_2 correlation spectra were calculated using
198 an in-house software, reproducing 2D -inverse Laplace transform (ILT) algorithm [48]. For
199 further information, refer to Bonnet et al. 2017 [35] and Rostom et al. 2019 [49].

200 In general, $1\text{D } T_2$ NMR relaxometry is used to distinguish bound and free water (being the main
201 advantage a short experimental time lasting few minutes) and $2\text{D } T_1T_2$ correlation NMR
202 relaxometry to improve resolution and obtain physical and chemical information on the
203 samples [50]. Concerning data interpretation, the area under each peak of either 1D or 2D
204 spectra is proportional to the amount of H atoms and thus water molecules. 1D spectra will
205 allow to quantify the amount of water in different environments. For 2D spectra, the T_1 and T_2
206 NMR values of each peak give unambiguous access to T_1 - T_2 ratios. This is characteristic of H

207 atoms mobility and confinement and greatly helps spectrum interpretation. Depending on the
208 value of these ratios, water can be identified as unconfined water, mobile free water, mobile
209 adsorbed water, and immobile water molecules bonded to solid macromolecules. Ratios lower
210 than one are physically not permitted [51].

211 For readers interested on this technique, let us briefly explain more about the influence of
212 water mobility and environment on the relaxation times T_1 and T_2 but cited references should
213 be consulted for detailed information. T_1 and T_2 NMR values depend on the local environment
214 of the measured hydrogen atoms (H). In this case this will correspond to water molecules and
215 their NMR relaxation values will depend on the size of the molecules they are bound to,
216 affinity with molecules interacting and pore size. T_2 NMR relaxation times decreases as pore
217 size is reduced (increase of surface-to-volume ratio) and/or when molecular tumbling (internal
218 mobility) decreases. They will also decrease if H atoms are in molecules with restricted
219 mobility due to viscosity, or the interactions being in macromolecules. For T_1 NMR relaxation
220 times, first they will decrease when molecular tumbling decreases (from liquid phase) but it
221 increases when molecular tumbling is low (in gel and solid like molecules) [49]. Here is where
222 we can see the importance of T_1 - T_2 ratios, which are characteristic of the mobility of H atoms
223 and will provide physical information of water. Values close to 1, 2–6, and over 10 have been
224 assigned to (i) unconfined water, (ii) mobile water at free or adsorbed state and (iii) bonded
225 immobile water molecule and solid macromolecules, respectively [35]. These values may vary
226 depending on the system studied but the trend in the increase of T_1 - T_2 should be valid for any
227 material.

228

229 **Results**

230 *Physicochemical properties of biochar*

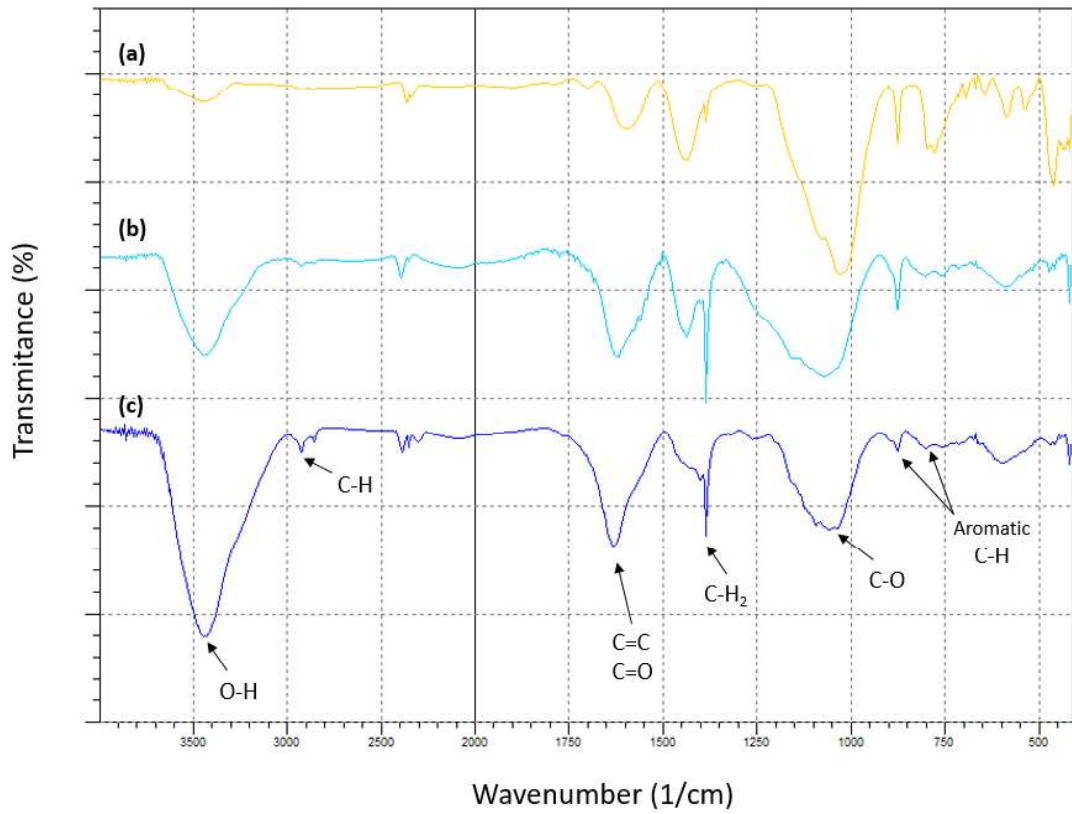
231 The FTIR spectrum of unaged biochar (BC) exhibits weak bands at 3400 cm^{-1} (mainly due to O-
232 H stretching) and at 2900 cm^{-1} (due to aliphatic C-H stretching). Relatively stronger bands were

233 found at 1600 cm^{-1} (attributed to C=C and C=O stretching of conjugated ketones and
234 quinones), at 1050 cm^{-1} (corresponding to C-O stretching likely from non-decomposed
235 lignocellulosic materials), and at 1400, 885 and 775 cm^{-1} (corresponding to C-H₂, aromatic C-H
236 and aromatic out-of-plane C-H stretching, respectively), characteristic of samples with a high
237 degree of C condensation (*Figure 1*). The absorption at 3400 cm^{-1} increases with the time of
238 biochemical aging (co-composting), indicating an increased presence of hydroxyl and carboxyl
239 groups. Similarly, the intensity of the signal at 2900 cm^{-1} increases with time of biochemical
240 aging, suggesting an increased contribution of signals from microbial lipids and/or persistent
241 vegetal lipids.

242 According to solid state NMR data (*Figures 2 and SI-1*), unaged biochar exhibits a high content
243 of aromatics (55.0% of the total C intensity measured) relative to other types of carbon. After
244 9- and 30 days of biochemical aging, the contribution of O-alkyl and alkyl groups increases
245 (from 5.5 to 11.0% and from 7.0 to 10.2%, respectively). The intensity of the aromatic carbon
246 signal is similar for unaged and biochemically aged biochar, indicating that the separation
247 process of biochar particles from the compost mixture, as referred in *Materials and Methods*,
248 is highly efficient.

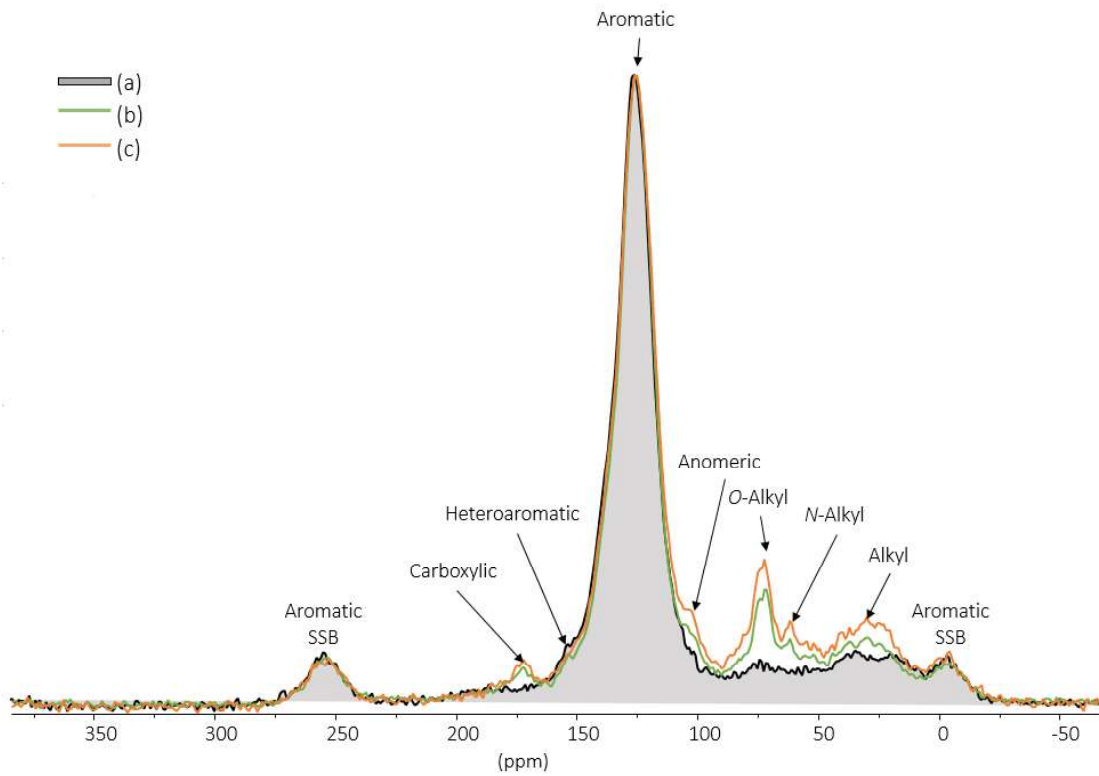
249 All samples exhibit an initial mass loss of 4% with heating below 110 °C corresponding to
250 adsorbed atmospheric humidity (*Figure 3*). In inert atmosphere, thermal decomposition of BC
251 starts at 350 °C, with a 6% mass loss below 680 °C and a 5% mass loss at temperatures above
252 680 °C. An additional mass loss of 11% is appreciated in ba-BC above 250 °C, corresponding to
253 the modification of biochar with a labile organic fraction or to surface functionalities during co-
254 composting. In the presence of air atmosphere, mass loss above 250 °C is similar, and ba-BC
255 underwent a 9% loss from oxidation. Both samples exhibit a high final residue of ~30%
256 corresponding to ash and remnants of high recalcitrance.

257



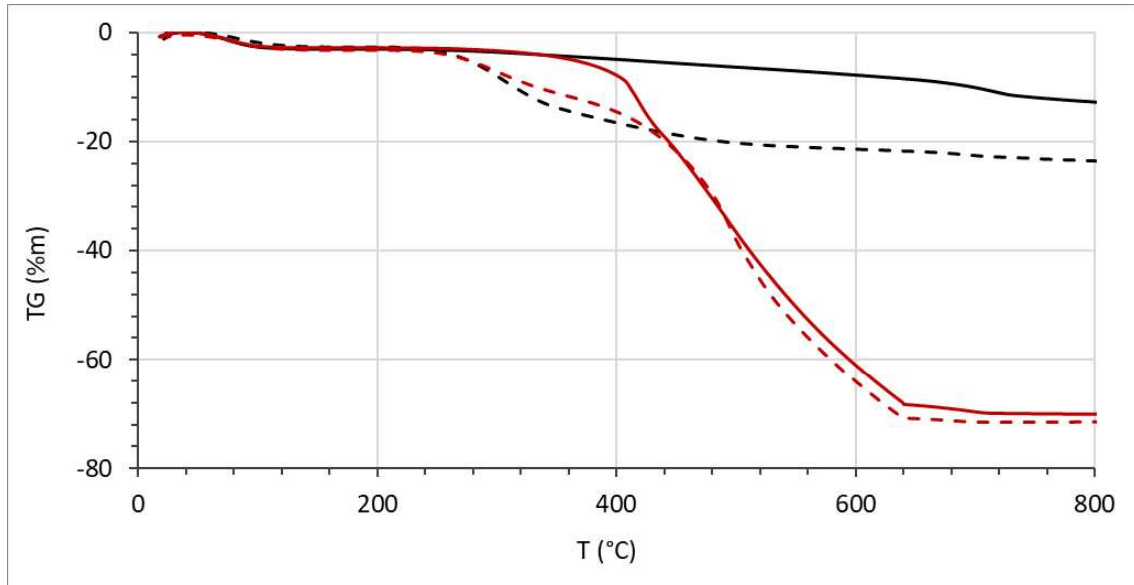
258

259 **Figure 1.** FTIR spectra of (a) BC and ba-BC after (b) 9 and (c) 30 days of co-composting.



260

261 **Figure 2.** ^{13}C -NMR spectra of (a) BC and ba-BC after (b) 9 and (c) 30 days co-composting. Spectral regions in which
262 carbon atoms resonate were assigned according to Knicker (2011) [52]. Note that two peaks correspond to the
263 spinning sidebands (SSB) of the aromatic one.
264



265
266 **Figure 3.** Thermogravimetric analysis of BC (solid line) and ba-BC (dashed line) in He (black) and in air (red).
267

268 BET surface area of biochar remains almost unaltered after the biochemical aging (obtained
269 from P/P_0 region between 0.05-0.30 of the adsorption isotherms, type I) but it increases by an
270 order of magnitude when physical aging is applied (*Table 1 and Figure 4a*). Consistently with
271 these results, micropore volume and pore area are also an order of magnitude higher in
272 physically aged samples which shows, in addition, a deep reduction in particle size.
273 Results of Hg intrusion porosimetry (*Table 1 and Figure 4b*) provide information about
274 macroporosity in the studied samples. Biochar before and after biochemical aging exhibits two
275 different macroporous characterized by approximately 1 and 10 μm pore diameter,
276 respectively. After physical aging, the porosity at 10 μm disappears, leading to a sharp porosity
277 distribution at $\sim 1 \mu\text{m}$. The total Hg intrusion volume and total area is higher in physically
278 unaged samples, because of the disappearance of the porosity at 10 μm after samples were
279 ball-milled. To avoid ambiguous and field-specific expressions in terms of pore size ranges,

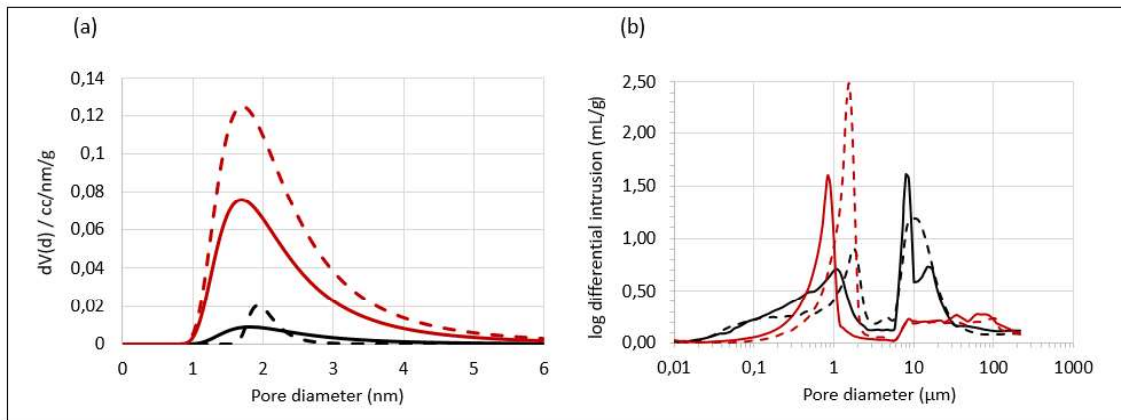
280 such as macro-, meso- and microporosity, the authors defined the ranges meaningful for this
 281 study as small, medium and large pore-size as as defined in *Table 2*.

282

283 **Table 1.** Particle size distribution, N₂ adsorption and Hg intrusion porosimetry results of unaged (BC), physically
 284 aged (pa-BC), biochemically aged (ba-BC) and physically and biochemically aged biochar (pba-BC).

	Particle size distribution	N ₂ adsorption porosimetry			Hg intrusion porosimetry	
	Mean (μm)	BET surface area (m ² g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Pore area (m ² g ⁻¹)	Total intrusion volume (mL g ⁻¹)	Total area (m ² g ⁻¹)
BC	2 x 10 ³	22.15	0.015	4.36	1.41	14.76
ba-BC	2 x 10 ³	20.50	0.011	2.91	1.35	13.39
pa-BC	7 / 75 *(bimodal distribution)	176.01	0.121	22.48	0.85	7.55
pba-BC	9	311.19	0.201	20.91	1.03	7.96

285



286

287 **Figure 4.** (a) BJH porosimetric analysis of N₂ adsorption isotherms and (b) Hg intrusion porosimetry analysis of BC
 288 (black solid line) and ba-BC (black dashed line), pa-BC (red solid line) and pba-BC (red dashed line).

289

290 **Table 2.** Definition of porosity ranges

Porosity range	Pore size
<i>Small-size pores</i>	1 – 5 nm
<i>Medium-size pores</i>	5 – 500 nm
<i>Large-size pores</i>	0.5 - 50 μm

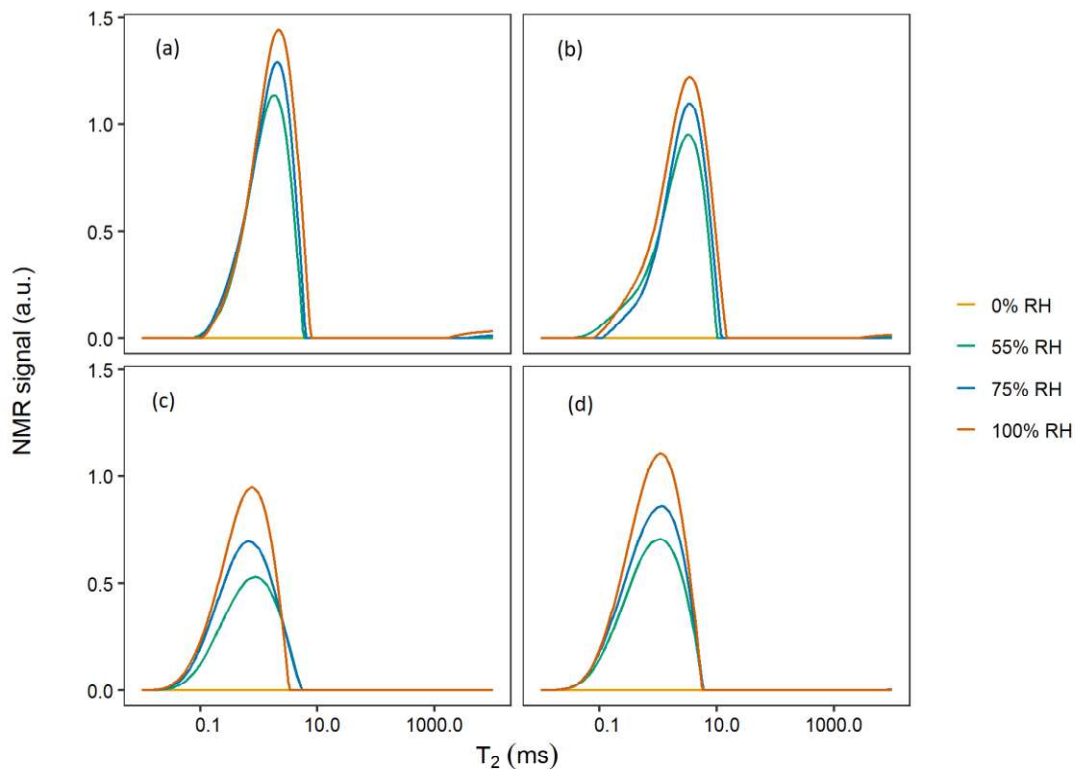
291

292 Biochar interactions with water

293 ^1H NMR relaxometry measurements were carried out to evaluate biochar-water interactions
294 using the T_1 and T_2 NMR observables, as it was previously described. Results were collected
295 from samples with adsorbed water from controlled RH atmospheres and from samples in
296 liquid water.

297 In samples with adsorbed water, the proton intensity of the peaks of T_2 NMR relaxation
298 distribution increases as expected with relative humidity, as there is more water adsorbed in
299 the sample (*Figure 5*). At this point it is important to remark that for all dry samples, in absence
300 of adsorbed water (0% RH), proton signal was not detectable, suggesting that structural
301 protons of biochar before and after aging are not visible with the parameters used in this
302 work. To verify this statement in presence of water (i.e., the actual conditions for the set of
303 studied samples) and check if water interactions could augment the mobility of structural
304 protons (increasing their T_2 NMR values and making them visible in the NMR experiments), dry
305 samples were wetted with D_2O to establish water-biochar interaction without providing
306 additional hydrogen atoms from water. No changes in NMR signal was either appreciated,
307 demonstrating that structural protons have no effects on the reported NMR results. The small
308 signal measured (*Supplementary Information, Figure SI-2*) is attributed to a minor replacement
309 of deuterium ions by hydrogen ions from atmospheric humidity.

310 The maxima of the broad and asymmetrical distribution of T_2 NMR relaxation times in
311 presence of adsorbed water in biochar before and after biochemical aging (BC and ba-BC)
312 appear at 3-4 ms whereas it is slightly shifted to lower times (around 1 ms) in physically aged
313 samples (pa-BC and pba-BC). These results allow us characterize the T_2 NMR relaxation times
314 of water interacting with biochar at $\text{RH} < 100\%$.



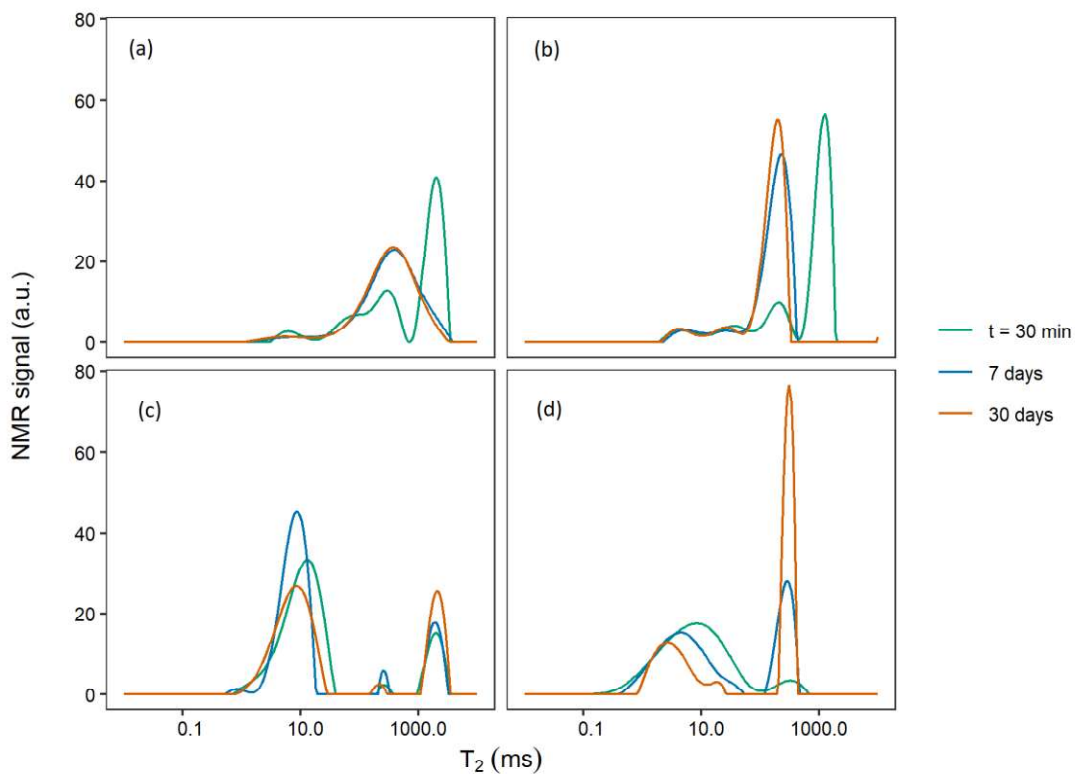
315

316 **Figure 5.** ^1H NMR relaxometry of (a) BC, (b) ba-BC, (c) pa-BC and (d) pba-BC at 0, 55, 75 and 100% of relative
 317 humidity.

318

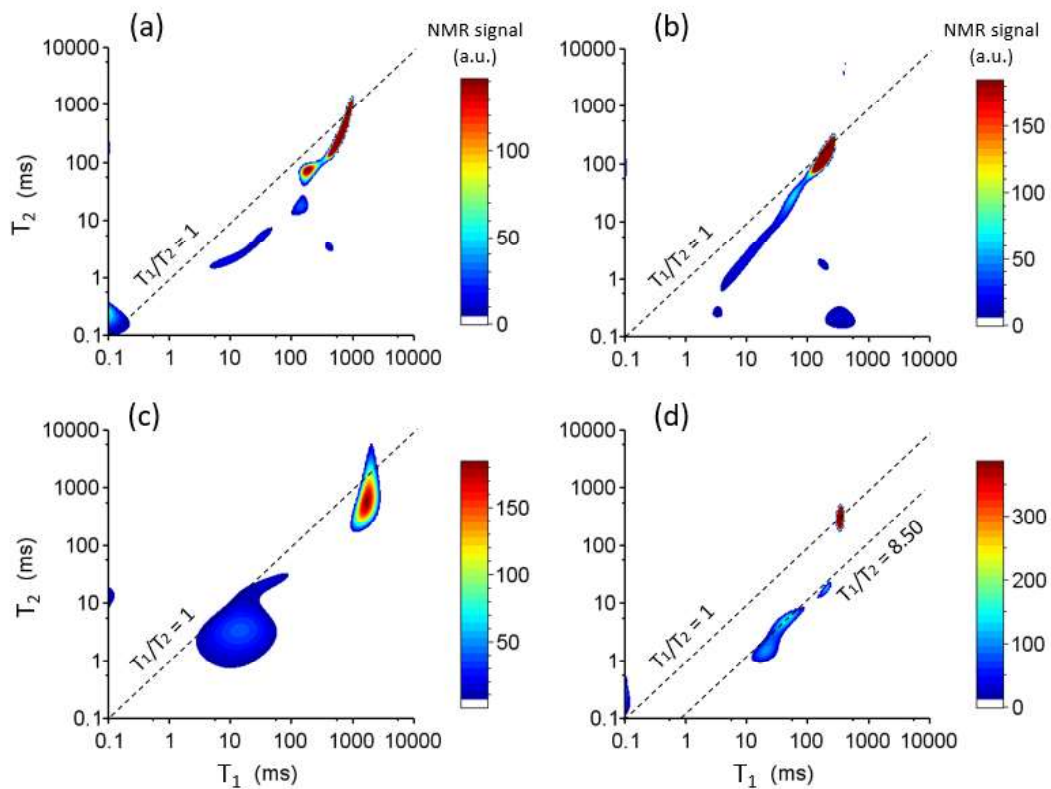
319 T_2 NMR relaxation time distributions of samples obtained with biochar and liquid water (using
 320 the same 1:4 mass ratio for all samples) are shown in *Figure 6*. After 30 minutes, the added
 321 water is able to distribute similarly in BC and ba-BC, whereas the effect of physical aging is
 322 evident in pa-BC and pba-BC, as the amount of water with short T_2 values (small pores) has
 323 greatly increased. In BC and ba-BC water protons show a complex behaviour, being possible to
 324 differentiate four different T_2 values with maxima at approximately 5, 50, 500 and 2000 ms.
 325 The main signal at 2000 ms is attributed to the relaxation time of water outside the sample
 326 [53], representing more than 50% of the total intensity at $t=30$ min. After 7 and 30 days this
 327 signal at 2000 ms disappears and its intensity is redistributed to the intermediate water signals
 328 characterized by a relaxation time at 500 ms for BC and at 200 ms for ba-BC, becoming the
 329 main signal for water in these samples. The faster T_2 relaxation times remain at 5-10 ms and
 330 around 50 ms and their intensity does not increase with time.

331 On the other hand, physically aged samples exhibit a small (~ 10% for pa-BC) or absent (pba-
 332 BC) contribution of water outside the sample (characterized by a relaxation time around 2000
 333 ms) after a short treatment time (e.g., t=30 min), indicating that most of the water interacts
 334 almost immediately with biochar. This rapid interaction is observed as the NMR value of water
 335 with the long T_2 decrease during the first 30 minutes and then stay constant over 30 days.
 336 Opposite to the behaviour described for BC and ba-BC, after 30 minutes of treatment the
 337 higher fraction of water signal relaxes at 10 ms and its intensity remains almost constant for
 338 physically aged samples. In addition, there is a decrease of T_2 NMR values for this peak (this is
 339 clearer for pba-BC but the same tendency is observed for pa-BC). Compared to physically
 340 unaged samples, another signal was found at 100-200 ms which follows different patterns for
 341 pa-BC and pba-BC. A low intensity and constant signal with time for pa-BC and a sharp increase
 342 with time for pba-BC.



343
 344 **Figure 6.** ^1H NMR relaxometry of (a) BC, (b) ba-BC, (c) pa-BC and (d) pba-BC with liquid water after 30 minutes, 7
 345 days, and 30 days.
 346

347 In T_1 - T_2 ^1H NMR relaxometry spectra of physically unaged samples (*Figures 7a and 7b*), most
 348 water signal is placed close to the $T_1=T_2$ line, indicating different degrees of confinement
 349 caused by the size of the pores (*Table 2*) [54]. The highest intensity signal, in the 100-1000 ms
 350 range and falling straight in the $T_1=T_2$ line, corresponds to water in larger size pores, while the
 351 signal exhibiting lower T_1 - T_2 ratios (10-100 and 1-10 ms) is placed slightly below the $T_1=T_2$ line
 352 indicating lower water dynamics. Three regions with different T_1 - T_2 ratios were observed in BC
 353 (1.68, 2.52 and 4.50) and ba-BC (1.30, 2.12 and 3.78), while two regions were differentiated in
 354 pa-BC (3.00 and 4.25) and pba-BC (1.12 and 8.50). For physically aged biochar samples (*Figures*
 355 *7c and 7d*), the region with high T_1 and T_2 values (100-1000 ms), which is close to the $T_1=T_2$ line,
 356 shows a higher T_1 - T_2 ratio for *Figure 7c* and the region with low relaxation time values (1-50
 357 ms) shows a higher T_1 - T_2 ratio (*Figure 7d*) in comparison to the other 3 spectra.
 358



359
 360 **Figure 7.** T_1 - T_2 ^1H NMR relaxometry correlation spectra of (a) BC, (b) ba-BC, (c) pa-BC and (d) pba-BC with liquid
 361 water.

362

363 **Discussion**

364 *Chemical and physical alteration of biochar during aging*

365 The properties of unaged biochar vary depending on the nature of the feedstock and pyrolysis
366 conditions of the process, in terms of chemical composition and stability, reactivity and porosity
367 [20]. Besides, it has been described that biochar undergoes several physicochemical changes in
368 contact with soil and during co-composting processes [11,54-56]. This aging process could be
369 related to biotic and/or abiotic processes. Abiotic aging could be mainly attributed to the
370 physical disruption of biochar coarse particles, exposing internal surfaces of the biochar skeleton
371 and thus changing its porosity and reactivity. Biotic aging is mediated by microbial communities
372 which could directly feed on biochar reactive surfaces edges [10] or use biochar pore space as
373 habitat [57].

374 In this study, two different factors of biochar aging were studied to understand the changes
375 undergoing in the material. On one hand, we considered the effect of 30-day co-composting
376 process of prune and coffee on wood biochar (biochemical or biotic aging) and, on the other
377 hand, we evaluated the physical disruption of the biochar particle (physical or abiotic aging) and
378 the combined effect of both processes.

379 According to the data obtained by FTIR analysis, pristine biochar spectrum exhibits bands
380 corresponding to stable carbon forms, characteristic of pyrolyzed organic matter with a clear
381 aromatic ring input and a series of bands in the 650-1800 cm^{-1} range that is attributed to non-
382 pyrolyzed lignocellulosic remains [58]. The presence of oxygenated functionalities is more
383 evident after 9 and 30-days co-composting process, where the spectrum exhibits a higher
384 signal corresponding to functional groups, indicating the presence of fresh organic matter or
385 minerals obtained in contact with compost and microbial activity [59]. This is consistent with
386 the bands attributed to aliphatic C-H stretching, suggesting the presence of plant lipids (i.e.,
387 suberines, cutines, surface wax) or microbial lipids (i.e., membrane phospholipids) which

388 appear after co-composting. These results are also in agreement with the data obtained by ¹³C
389 solid state NMR, where an increase in the signals of *O*-alkyl and alkyl groups is appreciated.
390 The continuous increase of signal during co-composting on the areas of *O*-alkyl and alkyl
391 groups (in comparison to aromatic signal) indicates a process of surface functionalisation or
392 strong adsorption of labile organic matter on biochar, rather than a physical mixture of biochar
393 and compost. However, direct functionalization of the aromatic rings cannot be assessed due
394 to the overlapping of the heteroaromatic peak with the large aromatic one. The combination
395 of both techniques shows that biochar undergoes surface functionalisation with acidic groups
396 in non-aromatic chains, coming from the interaction with compost and by microbial activity.
397 These results could also be explained by the presence of fresh organic matter coating on the
398 surface and within pores of biochar created during the co-composting process, as reported by
399 several authors [9,11,14]. This biochemical aging of biochar during co-composting is also
400 appreciated in thermogravimetric analysis. Mass loss difference in the 250-350 °C range
401 between both materials (in He and air atmospheres) indicates the presence of labile organic
402 compounds coming from functional groups generated in the co-composting process by the
403 interaction of biochar and compost, or from the decomposition of biochar by microbial
404 activity. Both samples exhibit rather high final residue of approximately 30% m/m
405 corresponding to ash and remnants of high recalcitrance.

406 Aging process also affects the physical properties of biochar, as seen in the results by
407 porosimetric analysis by Hg intrusion and N₂ adsorption. The porosity in the large pore-size
408 range (>0.5 μm) measured by Hg intrusion porosimetry described how physically unaged
409 samples exhibit two well defined porosity regimes at 1 and 10 μm pore diameter. After ball-
410 milling (simulating physical aging) the porosity at 10 μm is lost, leading to a single well-defined
411 porosity with a mean value of pore size distribution 1 μm. No reduction of pore size diameter
412 was appreciated after biochemical aging, which indicates that if a coating layer is formed on
413 the small size pore walls, it has no effect in the pore diameter at this scale. Regarding N₂

414 adsorption measurements, it is worth noting that all measured samples exhibit hysteresis
415 between N₂ adsorption and desorption isotherms in all the range of P/P₀ values. This is not a
416 type IV isotherm hysteresis caused by the capillarity in mesopores as it appears in the whole
417 P/P₀ range. This hysteresis is attributed to the entrapment of N₂ gas in the pores which is an
418 effect sometimes appreciated in carbon materials [60] and biochars [61]. In terms of BET
419 surface area results, there is an expected difference of an order of magnitude for physically
420 aged samples because of the reduction of particle size after the grinding process. Milled
421 samples (both after and before biochemical aging) exhibit porosity in the small size pore range
422 (1-5 nm), characteristic of this kind of carbon materials. In this sense, bulk samples are
423 characterized by a particle size distribution at 2 mm diameter size, whereas ground samples
424 exhibit a bimodal distribution with maxima at 7 and 75 μm after physically aging and a single
425 mean value of 9 μm for the biochemically aged.

426

427 *Water distribution and interactions with biochar as affected by aging*

428 ¹H NMR relaxometry measurements were carried out to obtain the T₂ NMR relaxation
429 distributions to estimate the distribution of water on different biochar porosities for unaged
430 and aged samples in contact with adsorbed and liquid water. This also allowed understanding
431 the effect of biochemical aging during co-composting process, which are reported to be
432 comparable to aging within the soil matrix [4]. Similarly, ball-milled samples were analysed and
433 compared to bulk samples to address the effect of physical aging, weathering, or physical
434 disruption that biochar undergoes with time after its application to soils.

435 Regarding the obtained results, it is important to note that there is not observable NMR signal
436 from protons coming from dry samples, demonstrating that structural hydrogen atoms from
437 biochar after and before aging have faster relaxation times than the spectrometer dead time.
438 To verify if structural hydrogen atoms could increase their relaxation times in presence of
439 water and, thus, contribute to the total measured intensities, dry samples were mixed with

440 deuterated water (D_2O) producing water-biochar interactions but without providing protons
441 from water. Results exhibited no increase in the signal (*Figure SI-2*), indicating that structural
442 hydrogen atoms of biochar do not provide relevant proton NMR signal for our experimental
443 condition and, thus, all incoming NMR signals for these samples will correspond only to
444 adsorbed water.

445 The relatively short transverse relaxation times obtained for biochar at $RH > 50\%$ is assigned to
446 water adsorbed to the surface of the particle (and pores), probably attached to remaining
447 functional groups and structural defects, describing strong interactions that do not allow fast
448 proton dynamics. However, as the amount of adsorbed water is relatively high (*Water*
449 *Retention Capacity (WRC) data showed in supplementary information, Table SI-1*) and similar
450 to what we can observe in wood samples (where the amount of functional groups is more
451 important) [35], thus other mechanisms could contribute to adsorption of water in biochar.

452 Relaxation time is shorter for ball-milled (simulating physical aging) samples (1 ms) than for
453 bulk samples (3-4 ms) probably because of a higher surface interaction due to the increase on
454 surface area or to the accessibility of water to smaller and inner pores after ball-milling.

455 T_2 NMR relaxation time results of liquid water in contact with physically unaged biochar before
456 and after biochemical aging (BC and ba-BC) (*Figure 6a and 6b*) indicate that after 30 minutes of
457 contact between water and the biochar, the liquid distributes similarly in both materials. In
458 these samples water shows a complex transverse relaxation behaviour with at least four quite
459 different relaxation times measured at around 2000, 500, 50 and 5 ms, respectively. The signal
460 at the largest T_2 time, e.g. 2000 ms, is attributed to the relaxation time of free water outside
461 the sample [62], indicating that after 30 minutes, more than 50% of the added water remains
462 without any interaction with the biochar. Results after 7 and 30 days show the progressive
463 disappearance of the signal at 2000 ms and an increment in the intensity at intermediate
464 relaxation times (500 ms for BC and 200 ms for ba-BC), indicating that water permeates into
465 the large pore size system with time. The intensities of the shorter T_2 NMR peaks (at 50 and 5

466 ms) remain constant with time, indicating that the small (and accessible) porosity regimes are
467 filled with a water fraction at the first stages of imbibition, remaining unaltered with the time.
468 It demonstrates that the number of small and accessible pores does not increase with the
469 exposure time. Each of these relaxation times correspond to water confined in a certain
470 porosity regime, which has also been defined as transmission like ($>50\ \mu\text{m}$), storage-like (50-5
471 μm) and residual-like ($<5\ \mu\text{m}$) pores in soil samples [63] and used as well for biochar studies
472 [18]. Following this classification, the intermediate T_2 signal measured at steady state could be
473 attributed to water in transmission and storage like pores where a relatively high mobility of
474 water is allowed. The shorter T_2 NMR values could be attributed to storage and residual-like
475 pores where water loses mobility because of a higher degree of confinement and, arguably,
476 due to the interactions with the surface of the pore walls. It is worth noting that the shortest
477 T_2 values are rather similar to that measured for adsorbed water (1-3 ms), which may be
478 understood as a shared contribution of small pore size and surface adsorption, which would
479 decrease the overall mobility of water molecules, provoking a faster transverse NMR
480 relaxation of water molecules (lower T_2 values) because of increasing dipolar interactions [17].
481 Water added to physically aged samples (*Figures 6c and 6d*) exhibit significantly shorter T_2
482 relaxation times after 30 minutes of treatment when they are compared with bulk samples. It
483 indicates that interaction of water with the biochar is strongly affected by the variation in the
484 particle size and pore structure caused by the ball-milling process. On the one hand, the
485 reduction in the particle size promotes a faster interaction of the added water with biochar,
486 showing a deep decrease or even the disappearance of free water (characterized by a
487 relaxation time T_2 around 2000 ms) in pba-BC after 30minutes. On the other hand, the water
488 fraction with restricted mobility, i.e., those characterized by a shorter relaxation time [62],
489 increases after ball-milling. This behaviour could be explained by the combination of different
490 factors, such as the increase in surface area and an improved access to the small size pores
491 volume as well as the reduction in the inter-aggregate space between biochar particles, that

492 increases the overall fraction of interacting water with shorter relaxation times. Nevertheless,
493 the interaction of water at the surface, in the small size pores or at the inter-aggregate space
494 appears to be different, which can be the cause of the observed differences on water mobility
495 and hence, in the corresponding NMR relaxation time [35]. In pa-BC, however, there is a T_2
496 signal at 2000 ms which is attributed to an excess of water that remains outside the sample
497 after all the inter-aggregate spaces of the system were saturated, which could increase
498 because of particle sedimentation over time.

499 T_1 - T_2 spectra at steady state for physically unaged samples (BC and ba-BC) show three different
500 regions. The strongest signal, at long T_1 and T_2 values, corresponds to free water with high
501 mobility which falls straight in the $T_1=T_2$ line, presumably water that permeated in the large
502 pore size system of the material. The two regions at lower T_1 - T_2 ratios would correspond to
503 water in a higher surface-to-volume ratio system, this is, smaller porosity regime. As they
504 appear slightly below the $T_1=T_2$ line, lower dynamics (molecular tumbling) could be assumed by
505 a certain degree of adsorption or interactions with the material reactive surfaces. In T_1 - T_2
506 spectra at steady state of ball-milled samples (pa-BC and pba-BC) the high-mobility free water,
507 with the most intense peak in the 100-1000 ms range it is clearly differentiated from water
508 placed in the smaller porosity regime [50]. After biochemical aging, T_1 - T_2 ratios for the three
509 different regions are similar to that of BC sample, indicating the higher degree of chemical
510 functionalisation originated from the composting process is not increasing water adsorption. In
511 addition, after physical aging we do not see an increase of T_1 - T_2 ratio for the water in the
512 smaller porosity (which is likely to be the water that interacts strongly with biochar) but we see
513 an increase of the T_1 - T_2 ratio for the water in the larger porosity. However, it seems that this
514 effect should be important as for the pba-BC sample we can see an important increase on the
515 T_1 - T_2 for the water in smaller porosities (from about 4 to 8).

516 The capacity of biochar to retain water in their structure is crucial to understand the mobility
517 and availability of nutrients for plants. The water placed in the inter-aggregate space and in

518 large size pores (*i.e.* transmission-like) can move and permeate easily between biochar and soil
519 being easily available for the roots of the plant. As a counterpart, water in this state can also
520 be more easily lost by evaporation or diffusion. Actually, we can see that some of this water
521 transfer from the inter-aggregate state to a more mobile state over the 30 days but the
522 amount is relatively low, showing the capability of aged biochar to keep water for long periods
523 of time. In addition, water in medium size pores (*i.e.* storage-like) exhibit stronger interactions
524 and is longer retained, providing an attractive water/nutrient “pool” for plants and
525 microorganisms. Finally, water in small size pores (*i.e.* residual-like) appears to be strongly
526 bonded to the material and would require certain negative pressure by root suction to be
527 available [63]. To allow the assignment of each of the T_2 signals to a specific porosity regime
528 further studies are needed with deep analysis in ^1H NMR relaxometry and porosimetry
529 techniques.

530

531 **Conclusions**

532 This study indicates that a surface modification in chemical composition of biochar takes place
533 during co-composting process, with an enrichment of oxygen functionalities. The mobility and
534 plant availability of soil cations such as nutrients and contaminants will be dependent of water
535 mobility throughout the soil matrix and its and its porosity, making biochar/water interactions
536 a key issue in the understanding of the role of this material as soil amendment. ^1H NMR
537 relaxometry results indicate that water interacts in a more intimate manner with biochar,
538 exhibiting shorter T_2 NMR relaxation times and slightly higher T_1 - T_2 ratios, after the
539 biochemical aging process, probably due to a higher wettability and stronger interactions with
540 the functionalised surface. Particle size reduction has a clear effect in the interaction with
541 water, making stronger and faster interactions when particle size is reduced as proved by ^1H
542 NMR relaxometry. Water placed in the inter-aggregate porosity is the main contributor to
543 lower T_2 times. Physical and biochemical aging of biochar is therefore critical to understand the

544 enhancement on the agronomic performance of biochar with time when used as amendment
545 in soils, not only because of the enrichment in nutrients, but also because of water dynamics
546 and retention capacity in biochar particles.

547

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561

562 **Credit Author Statement**

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564 Conceptualization, Data curation, Methodology, Writing-review & editing, Validation.
565 Giuseppe Picca: Investigation. Juan López-Valentín: Methodology, Reviewing. César Plaza:
566 Reviewing, Validation. Marco Panettieri: Supervision, Conceptualization, Funding acquisition,
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568

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