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Biochar physico-chemical properties as affected by environmental exposure

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Biochar physico-chemical properties as affected by environmental exposure

Q5 Giovambattista Sorrenti ^{a,*}, Caroline A. Masiello ^b, Brandon Dugan ^c, Moreno Toselli ^a

ABSTRACT

^a Department of Agricultural Sciences, University of Bologna, viale G. Fanin 44, 40127 Bologna, Italy

^b Departments of Earth Science, BioSciences, and Chemistry, Rice University, Houston, TX 77005, USA

Q6 ^c Department of Earth Science, Rice University, Houston, TX 77005, USA

94 HIGHLIGHTS

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GRAPHICAL ABSTRACT



19 face at% of O, S, N, Na, AI, Ca, Mn and Fe.
20 Oxidation included the development of

O-containing functional groups down
 to 75 nm.



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To best use biochar as a sustainable soil management and carbon (C) sequestration technique, we must understand the effect of environmental exposure on its physical and chemical properties because they likely vary with time. These properties play an important role in biochar's environmental behavior and delivery of ecosys- 46 tem services. We measured biochar before amendment and four years after amendment to a commercial nectar- 47 ine orchard at rates of 5, 15 and 30 t ha⁻¹. We combined two pycnometry techniques to measure skeletal (ρ_s) and 48 envelope (ρ_e) density and to estimate the total pore volume of biochar particles. We also examined imbibition, 49 which can provide information about soil hydraulic conductivity. Finally, we investigated the chemical properties, surface, inner layers atomic composition and C1s bonding state of biochar fragments through X-ray photo- 51 electron spectroscopy (XPS). Ageing increased biochar skeletal density and reduced the water imbibition rate 52 within fragments as a consequence of partial pore clogging. However, porosity and the volume of water stored 53 in particles remained unchanged. Exposure reduced biochar pH, EC, and total C, but enhanced total N, nitrate- 54 N, and ammonium-N. X-ray photoelectron spectroscopy analyses showed an increase of O, Si, N, Na, Al, Ca, 55 Mn, and Fe surface (0-5 nm) atomic composition (at%) and a reduction of C and K in aged particles, confirming 56 the interactions of biochar with soil inorganic and organic phases. Oxidation of aged biochar fragments occurred 57 mainly in the particle surface, and progressively decreased down to 75 nm. Biochar surface chemistry changes 58 included the development of carbonyl and carboxylate functional groups, again mainly on the particle surface. 59 However, changes were noticeable down to 75 nm, while no significant changes were measured in the deepest 60

* Corresponding author.

E-mail addresses: g.sorrenti@unibo.it (G. Sorrenti), masiello@rice.edu (C.A. Masiello), dugan@rice.edu (B. Dugan), moreno.toselli@unibo.it (M. Toselli).

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layer, up to 110 nm. Results show unequivocal shifts in biochar physical and chemical properties/characteristics 61 over short (~years) timescales. 62

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1. Introduction

76Biochar is the solid residue of biomass pyrolysis intentionally added 77 to soil to sequester carbon (C) (Woolf et al., 2010), to ameliorate soil 78properties (Spokas et al., 2012) and to improve crop performance (Verheijen et al., 2010). Many biochar-induced ecosystem services, in-79 cluding improving soil water properties and ions retention, are due to 80 81its high (~75%) porosity which indicates the fraction of the total fragment volume not filled by solid (Brewer et al., 2014). Interconnected 82 biochar pores are arranged in complex structures (Nguyen et al., 83 2010) and range from <1 nm (Sun et al., 2012; Keiluweit et al., 2010;) 84 to pores on the order of 0.01 mm in size, reflecting the cellular arrange-85 ment of the pyrolyzed feedstocks (Bird et al., 2008; Wildman and 86 Derbyshire, 1991) Pore surface area and reactivity control biochar sorp-07 tive capacities and modulate its interactions with minerals, water, mi-88 crobes, fungal hyphae and plant roots (Downie et al., 2009; Thies and 89 90 Rillig, 2009; Chen et al., 2008; Warnock et al., 2007; Hockaday et al., 2006; Pietikäinen et al., 2000). Recent findings suggest that pores 08 >50 nm (nm) are responsible for most of the biochar porosity (Brewer 92et al., 2014). This result has been validated using mercury porosimetry 93 by Baltrenas et al. (2015) who estimated that up to 90% of either birch 9495or pine-derived biochar pore volume consisted of pores larger than 500 nm in diameter while pores <500 nm took <1.5% of the total pore 96 volume. Similarly, Laine and Yunes (1992) report than activated char-09 98 coal micropore surface area is larger than macropore surface area, but 99 macropore volumes can be more than double than micropore volume. Macropores affect hydraulic conductivity (Masiello et al., 2015; Barnes 100et al., 2014; Brockhoff et al., 2010; Oguntunde et al., 2008) and other hy-101 drologic processes (e.g. infiltration, erosiveness, wettability, water re-102tention, nutrient leaching) (Baronti et al., 2014; Bruun et al., 2014; 103104 Novak et al., 2012; Major et al., 2009). These properties impact microbial habitats (Lehmann et al., 2011), offering shelters for mycorrhizal 105 fungi (Warnock et al., 2007). 106

Biochar physico-chemical properties may change after environmen-107 tal exposure, challenging our ability to predict its long-term ecosystem 108 109 services. Changes result from shifts in temperature, water content, tillage, fertilization and interactions with the soil matrix (Joseph et al., 110 2010). Density and porosity of biochar can be altered through the trap-111 ping of minerals, roots, OM or microbes (Jaafar et al., 2014; Warnock 112 et al., 2007), shifting biochar sorption capacity, soil hydraulic conductiv-113 114 ity and water retention. (Masiello et al., 2015; Baronti et al., 2014).

Several studies report changes of biochar properties as a consequence of ageing (LeCroy et al., 2013; Lin et al., 2012; Jones et al.,
2012; Joseph et al., 2010; Zimmerman, 2010; Cheng et al., 2008) However, most of these findings come from environmental exposures <-
6 months or weathering induced through chemical and/or physical
treatments (Yao et al., 2010).

Similarly, some studies suggest that oxidation is a surface process;
 others report oxidation throughout particles (Cheng et al., 2006). It
 seems reasonable to assume that chemical changes start at the surface,
 but no information exists about the progression of the oxidation front.

We evaluated porosity shifts induced by 4 years of environmental 125exposure by comparing fresh (never applied to the field) and field-126 applied biochar from the same biochar batch. We combined two 127pycnometry techniques to determine skeletal (ρ_s) and envelope (ρ_e) 128densities which allow estimation of porosity of biochar particles 129(Brewer et al., 2014). We also evaluated hydrologic implications of bio-130char ageing by an imbibition assay. Finally, we measured chemical prop-131 erties, surface, inner layers elemental composition and C1s bonding 132133 state of biochar through X-ray photoelectron spectroscopy (XPS). We hypothesized that i) environmental exposure generates physical- 134 chemical changes of biochar fragments, ii) chemical changes are not 135 limited to the top exposed surface iii) the extent of the changes may 136 be rate-dependent and iv) ageing alter biochar-water interactions. 137

2. Materials and methods

138 139

2.1. Experimental site and biochar characteristics

A four-year experiment was carried out using a commercial nectar- 140 ine (*Prunus persica* L., Batsch) orchard (Big Top/GF677) planted in 1997 141 with a density of 519 trees ha⁻¹ (3.5×5.5 m) located in the southeast- 142 ern Italian Po Valley (Tebano, Ravenna, 44° 29' N, 11° 78'E, 58 m a.s.l.) 143 on a sandy-loam Inceptisol soil with pH = 8.08, organic matter 144 (OM) = 10.6 g kg⁻¹, cation exchange capacity (CEC) = 13.0 meq 145 100 g⁻¹, and total N, available P, exchangeable K, Na, Ca, and Mg of 146 800, 8, 97, 37, 2347, and 109 mg kg⁻¹. 147

The area has a temperate sub-continental climate with cold winters 148 and warm, humid summers ($T_{average} = 13.6$ °C; $T_{highest} = 40.5$ °C, 149 $T_{lowest} = -4.1$ °C). Annual precipitation ranged between 650 and 150 910 mm. Alleys were maintained with native grass species while tree 151 rows were herbicided with glufosinate ammonium (DL- 152 phosphinothricin). Trees were managed by pruning, thinning, fertilization, irrigation, and control of pest and disease according to regional 154 guidelines (ICM, 2009). From May to August trees were drip-irrigated 155 and yearly fertilized with 0.25 kg N tree⁻¹ (130 kg N ha⁻¹) as urea at 156 petal fall.

The biochar we used was produced in a commercial slow-pyrolysis 158 unit (Romagna Carbone snc, Bagnacavallo (RA), Italy) using cylindrical, 159 vertical charcoal kiln of 8.14 m³ (2.40 m diameter and 1.80 m height). 160 We used non-contaminated chipped hardwood (peach and grapevine 161 at the same rate (v v⁻¹) pruning wood) slowly pyrolyzed with continuous (150 min) heating from ambient temperature (heating rate of 10–163 15 °C min⁻¹), reaching the highest T of ~550 °C with a 30 min peak temperature hold time (Table S1). Charred fragments were allowed to cool 165 to ambient conditions in the absence of O₂.

2.1.1. Experimental design

In November 2009 we distributed biochar at the rates of 5, 15, and 168 30 t fresh weight (fw) ha⁻¹ according to a randomized experimental 169 block design, with 5 replicates of 5 trees each, arranged in 4 consecutive 170 tree rows, leaving 10 unamended meters between consecutive plots. 171 Treatments were randomly distributed in each row with at least one 172 replicate per biochar rate in each row. Biochar was distributed on a 173 35 m² area per experimental plot (2 m wide along the herbicided 174 strip) and mixed into the first 20-cm soil depth (A horizon) by a disc 175 harrow. Control samples of biochar (never field-applied, termed here "fresh") were hermetically stored in plastic bags four years. 177

2.1.2. Biochar recovery

We randomly recovered (Nov-13) ~50 biochar fragments of different sizes from each replicate. To accomplish this we removed the first 180 3–5 cm depth of the soil layer and carefully collected fragments from 181 the soil by forceps, avoiding manual contact or any physical damage to 182 the particles. We sealed the particles in polyethylene bags and 183 transported them to the laboratory in a portable refrigerator. A com-184 posed biochar sample of ~2.5 kg (never field-applied, termed here 185 "fresh") from the same biochar batch (from a unique and homogenized 186 heap of ~2 t) was stored in hermetically closed plastic bags of ~250 g ea. 187 and maintained four years at room temperature, in a dry and dark place. 188

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After four years, a random subset of these stored fresh biochar frag ments (~100 pieces) were isolated by forceps, transferred in several
 test tubes, then analyzed as the soil-recovered biochar fragments.

192 Particles were dried at 50 °C for 72 h, sieved to 1 mm and the surface 193 of individual fragments (keeping each piece by forceps under a magni-

fying lens) was cleaned with a soft brush and rinsed twice with deion-

1977 Fing tends water (DI-H₂O) to remove adhering soil. Fragments were not 1978 relation to the standard st

196 physically damaged during handling and drying.

197 2.2. Biochar physical changes as affected by the environmental exposure

198 2.2.1. Skeletal density (ρ_s)

Skeletal density (ρ_s) is the mass of a particle divided by its volume and was determined by helium (He) pycnomentry. We measured the ρ_s of ~0.1 g dry biochar mass per replicate (samples composed of about 5–6 fragments, with each piece smaller than 1 cm³) using an AccuPyc 1340 (Micromeritics, Norcross, GA) fitted with a 1 cm³ chamber (Brewer et al., 2014).

205 2.2.2. Envelope density (ρ_e)

Envelope density (ρ_e) is the mass of a dry biochar sample divided by 206 207the volume of its non-wetting exterior measured if an "envelope" were placed around each individual particle (Brewer et al., 2014). We mea-208sured ρ_e of biochar samples that were ~0.215 g (dry mass) per replicate 209(samples composed of about 8-9 fragments, with each piece smaller 210than 1 cm³) using a Geopyc 1360 Envelope Density Analyzer 211(Micromeritics, Norcross, GA). Fragments were placed in a bed of 212 DryFlo® granular medium (density of ~0.4 g cm⁻³). Consolidation 213 was achieved by continuous rotation and vibration of the cylindrical 214 chamber as the piston was gradually pushed into the chamber until 215the stated 22 N force was reached (Brewer et al., 2014). 216

217 2.2.3. Porosity

Q10 Porosity (ϕ) is a function of ρ_e and ρ_s :

$$\varphi = \frac{v_e - v_s}{v_e} = 1 - \frac{m/\rho_s}{m/\rho_s} = 1 - \frac{\rho_e}{\rho_s} = 1 - \frac{\rho_e}{\rho_s}$$

220

 v_e and v_s = envelope and skeletal volume and m = mass.

221 2.3. Imbibition assay

We compared aged biochar recovered from the 30 t ha⁻¹ plots with 222fresh biochar particles. Samples were treated as described earlier and 223three pairs of fragments with similar weight (± 0.04 mg) and shape 224225were selected, rinsed (DI-H₂O), and oven-dried at 75 °C for 48 h. The 226last washing step was repeated 3 times to reduce sample hydrophobicity. Fragments were individually transferred into 75 mL glass tubes filled 227with DI-H₂O and carefully placed on the water surface, allowing the 228fragments to float. Tubes were unsealed, never disturbed, and main-229230tained at room temperature, allowing natural water infiltration. We recorded the sinking of each fragment until particles reached the bottom 231of the tubes. The amount of absorbed water in sunken fragments was 232233determined by massing before and after drying at 105 °C (96 h).

234 2.4. Biochar chemistry changes following environmental exposure

235 2.4.1. pH and electrical conductivity (EC)

Oven-dried (105 °C) samples were added to DI-H₂O at a mass ratio
 of 1:20 and shaken 90 min at 120 rpm (Rajkovich et al., 2012). pH and
 EC were measured on the filtered surnatant under continuous stirring
 by a pH-meter (BasiC 20, Crison, Barcelona, Spain) and a conductometer
 (CDM210 Conductivity Meter, Radiometer Analytical, Copenhagen, DK).

2.4.2. Total C, N and H content

We sampled 3 mg of ground biochar for total N and H and 0.1 mg for 242 C determination by catalytic combustion (ECS 4010, Costech Analytical 243 Technologies Inc.; Valencia, CA). 244

2.4.3. KCl extractable NO_3^-N and NH_4^+-N 245

We extracted intact oven-dried biochar fragments using a 2 M KCl 246 solution at a ratio of 1:20 (w w⁻¹). Samples were shaken for 90 min 247 at 100 rpm by an orbital shaker and the filtered (Whatman 42) 248 surnatant was analyzed by a continuous flow autoanalyzer (AA-3, 249 Bran + Luebbe, Norderstadt, Germany). 250

2.4.4. Biochar surface atomic composition

We analyzed three fragments per replicate by XPS for relative C, O, 252 Si, N, Na, Al, Mg, P, K, Ca, Mn, and Fe atomic composition (at%) in the 253 top 5 nm (Fig. 1) using a PHI Quantera XPS with a focused monochro-254 matic Al K α X-ray source for excitation at 1486.6 eV and 49.2 W. We 255 performed high-resolution, low-intensity scans to focus on the C bond-256 ing environments with 40 scans. XPS spectra were analyzed using a 257 nonlinear, least-squares curve-fitting program with a Gaussian - 258 Lorentzian mixed function to optimize the spectra using MultiPak data 259 analysis software (MultiPak V7.0.1, Ulvac-Phi, Inc.). 260

2.4.5. Biochar inner layer at%

We compared fresh and aged (from 30 t ha^{-1} plots) biochar frag- 262 ments (4 replicates) for relative C, O, Si, N, and Al at% at four depths 263 (S1 = 0-5 nm, L2 = 5-10 nm, L3 = 15-20 nm and L4 = 30-35 nm; 264 Fig. 1). 265

Three additional fragments of fresh and aged biochars were used to 266 determine the relative C, O, Si, N, and Al at% at additional depths (S1 = 267 0-5 nm, L5 = 35-40 nm, L6 = 70-75 nm and L7 = 105-110 nm; Fig. 1). 268

We calibrated the XPS assessing the etching depth by using a stan-269 dard 100 nm tick of SiO₂ as a reference. The relative etching rate for C-270 containing compounds was extrapolated by a computer simulation 271 (based on the exact etching rate for SiO₂) as compared with a spread-272 sheet provided by the manufacturer. 273

We deconvoluted the C1s region bonding state into component 274 functional groups. The -C-C/-C-H/-C = C bonds exhibit the same bind-275 ing energy (284.74 eV) and thus were considered together, while -C-O, 276 -C = O and -COOH were targeted at 285.95, 287.18 and 288.56 eV. 277

3. Statistical analyses

Data were evaluated according to a randomized block design with 5 279 replicates. Data of XPS analyses at different fragment depths were eval-280 uated as a factorial randomized block design with 2 factors: biochar age 281 (2 levels) and layer (4 levels). When ANOVA showed statistical effects 282 ($p \le 0.05$), means were separated by Student-Newman-Keuls Test; 283 when interaction between factors was significant, 2 times standard 284 error of means was used as the minimum difference between two statistically different means (Saville and Rowarth, 2008). Data of the imbibition assay were submitted to repeated measures analysis of variance 287 using PROC MIXED (Littell et al., 1998) in SAS 9.0 (SAS Institute Inc. Cary, NC, USA), with the fragment weight as covariant and a compound 289 symmetry covariance structure. 290

4. Results and discussion

4.1. Biochar physical properties as affected by environmental exposure 292

4.1.1. Density and porosity

Field exposure induced the most significant physical changes in bio- 294 char ρ_s and ρ_e , which increased by 160 and 15 mg cm⁻³, respectively 295 (Fig. 2). 296

This increase in ρ_s may be due to biochar particle breakage and me- 297 chanical stresses (e.g. freeze-thaw cycles) as recently evidenced by 298

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Fig. 1. The biochar profiles scanned by X-ray photoelectron spectroscopy (XPS). Magnification obtained by a Zeiss SteREO Discovery.V20 microscope. *Depths are not strictly to scale.

Spokas et al. (2014) who reported cracks and fractures (physical disin-299 tegration) on biochar surfaces induced by water and soil exposure. This 300 breakage may increase pore connectivity by i) connecting previously 301 isolated pores and ii) opening externally connected pores which may 302 303 represent entry points for denser minerals that may fill or partially fill previously empty spaces. Similarly, capillary forces may also drive the 304 soil solution into biochar pores since plant-derived biochars have a 305 306 high concentration of macropores (>50 nm) (Downie et al., 2009), which are much larger than a water molecule (0.28 nm). Flowing 307 308 water can carry small particles in suspension (including small biochar fragments) into biochar micropores; these particles may accumulate 309 and/or clog in the pore channels (Joseph et al., 2010). Charred and 310 non-charred compounds may remain physically blocked or chemically 311 312 attracted within particles, altering pore connectivity (Jaafar et al., 2014; Joseph et al., 2010). 313

Recent studies support the rationale that soil particles (e.g. colloidal, 314 dissolved, soluble inorganic salts and/or aluminosilicates) can fill ex- 315 posed cavities of soil-exposed biochar fragments (Spokas, 2013; Q12 Spokas et al., 2014). Q13

Our microscopic images (Fig. 3) support the idea that interactions 318 with minerals and/or microbes change the biochar's physical properties 319 (Jaafar et al., 2014; Brodowski et al., 2006; Liang et al., 2006; Warnock 320 et al., 2007; Hockaday et al., 2006) In our images minerals partially fill 321 biochar fractures, starting from the particle's outer edges. Newly inaccessible volumes may be occupied by a combination of trapped water 323 and/or air, leading to porosities that vary with water exposure history. 324

4.1.2. Ageing reduced the rate of water imbibition

Biochar pores have been classified as surface-site pores (α -type) and 326 bulk-site pores (β -types) (Clarkson et al., 1998). As biochar become 327



Fig. 2. Effect of environmental exposure (4 years in field conditions) on density (skeletal and envelope) and porosity of biochar fragments (avg. \pm SE n = 5) applied at different rates as compared with fresh biochar. ns and * = effect of biochar ageing and rate not significant or significant at $p \le 0.05$. Bars with the same letter are not statistically different ($p \le 0.05$) according to the Student-Newman-Keuls (SNK) test.

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Fig. 3. Magnification of biochar fragments recovered from a nectarine orchard after 4 years of environmental exposure. Minerals and soil particles are adhering and/or are physically trapped over the entire particle surface. Pores appear partially or totally blocked by soil particles, likely reducing accessibility. Color magnifications were obtained by an Olympus SXZ16 microscope coupled with an Olympus digital camera whereas the others were obtained by a Zeiss SteREO Discovery.V20 microscope.

328 water-filled, diffusional processes allow the transition of water between the α -type and β -type pores. However, physical (pore size) and/or 329 chemical (solid-liquid interactions) factors may interfere with water 330 movement within biochar particles (Clarkson et al., 1998; Conte et al., 331 3322013). When biochar pores totally or partially clog, water flow into 333 and out of particles becomes physically hampered, hence water infiltration rate likely changes. In our biochar imbibition assay, fresh biochar 334sank faster than aged particles. Fresh biochar samples started to sink 335 after 156 h and completely settled between 162 and 168 h while aged 336 samples started sinking between 168 and 180 h, settling slowly up to 337 268 h, then accelerated until reaching the bottom of the tubes near 338 276 h (Fig. 4). The ratio of water:biochar (w w^{-1}) of the sunken frag-339 ments was unaffected by ageing and values were 4.98 (± 0.30) and 340 5.16 (± 0.35) for fresh and aged fragments, respectively. These results 341 342 suggest that pore openings are becoming partially clogged, but not filled 343 with solid materials.

However, as mentioned above, chemical factors may also interfere in 344 the biochar-water relationship. This, in turn, refers to the development 345 of H bonds between the water-derived O and H atoms of the biochar aromatic systems (Clarkson et al., 1998). The last interaction was elucidat-447 ed by Conte et al. (2013), who suggested that water molecules may be bound to the solid carbonaceous material through non-conventional H bonds. As ageing induces the development of O- and H-containing functional groups onto the biochar surface, as a consequence of surface oxidation (Zimmerman, 2010), the last biochar-water mechanism results promoted in aged biochar with implications on the water mobility.

It seems also reasonable to hypothesize a similar reverse sense (pore 355 drainage), with aged biochar fragments retaining water longer. In this 356 case, and assuming water-saturated particles, the partial blocking of 357 biochar pores may allow biochar-amended soils to hold water longer 358 between rainfall events. 359



Fig. 4. Sinking dynamics of fresh vs. aged (4 years in field conditions at the rate of 30 t ha⁻¹) biochar fragments (n = 3). ns, * and *** = effect not significant or significant at $p \le 0.05$ and $p \le 0.001$, respectively.

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360 4.2. Biochar chemistry changes as affected by the environmental exposure

4.2.1. pH, EC, total elemental C, N, H, extractable NO_3^-N and NH_4^+-N 361 362 concentration

Ageing decreased biochar pH and increased EC (Table 1). 363

The weathering-induced carboxylic acids functional groups lead to a 364 decrease of basic sites on the biochar surface (Qian and Chen, 2014; Yao 014 et al., 2010; Cheng and Lehmann, 2009), explaining the significant re-015 367 duction of pH (~2 units) in aged biochar. This suggests that biochar lim-368 ing potential is be limited to few years after its application. Hence, 369 biochar-induced benefits in nutrient availability in acid soils may be more pronounced in the first seasons following application. Similarly, 370 the undesirable further pH increase in alkaline soils due to biochar ap-371 372 plication may be transient.

Total C concentration was reduced by $14.5\% (\pm 0.18)$ by ageing, irre-373 spective of the application rate (Table 1). The last response is partly due 374 to mineralization of the labile C-fraction associated with biochar 375 (Norwood et al., 2013). This mineralization may occur through the 376 loss of volatile organic compounds generated during pyrolysis and con-377 densed during cooling (Rajkovich et al., 2012) which are more reactive 378 than the aromatic fractions (Joseph et al., 2010). This leads to an initial 379 evolution of biochar-derived CO₂ in soils after its application (few 380 381 months), partly attributed to biochar surface oxidation (Bruun et al., 382 2008; Steiner et al., 2008).

Finally, a fraction of biochar-derived C was likely lost through 383 leaching of dissolved organic C (DOC). Mukherjee and Zimmerman 384 (2013), for instance, measured a significantly higher DOC in the soil 385 386 leachate amended with two different biochars obtained at two pyrolysis temperatures. The additional rate of DOC in the leachate was unambig-387 uously biochar-derived, as shown by the increase in the aromaticity of 388 389 the DOC measured in the biochar-amended soil leachate (Barnes et al., 2014). 390

391 However, the 14% reduction of total C concentration in biochar fragments after 4 years soil incubation appear higher compared to mean av-392 erages reported in literature (Lehmann et al., 2009; Kuzyakov et al., 393 2014). To this regard, it must be mentioned that at the time of soil appli-394 395 cation, biochar was freshly produced thereby its content of water-396 soluble C-containing compounds was abundant, likely promoted also by the relatively low max T° (550 °C) reached during pyrolysis. In addi-397 tion, a dilution effect induced by the attachment of organo-mineral 398 complexes on the aged biochar surfaces is also reasonable, consistent 399 400 with the increase of both the Norg and Nmin fractions measured on the aged fragments. This last mechanism was recently proposed by 401 Kammann et al. (2015) to explain NO₃–N capture on/in the porous bio-402 403 char structure, encompassing with the development of acid and basic functional groups (as we also observed in our study) as well as the de-404 405 velopment of unconventional H-bonding.

Total N concentration increased in aged biochars by 3.8 fold, irre-406 spective of application rate. Such increase was more pronounced 407 when biochar was applied at 5 t ha^{-1} (4.0 fold) and 30 t ha^{-1} (4.2 408 fold) (Table 1). The most significant contribution to the total N increase 409 410 was due to the organic N forms, which were 56% of the total N, on aver-411 age. Similarly, Joseph et al. (2010) reported an increase in the N content

8.08b

158.2b

of two different biochars mainly associated with proteins, amino acids, 412 NH₄⁺ and N–C compounds. 413

Likewise, extractable inorganic N increased in aged biochar, and 414 NO_3^- and NH_4^+ concentrations were significantly higher in aged than 415 in fresh biochar, confirming the potential of charred biomasses in N re- 416 tention and reduction in N-containing GHGs emission in soils (Spokas 417 et al., 2012). However, recent evidences suggest that standard analytical 418 methods (as adopted in our study) could not detect all biochar-bound 419 nutrients, in particular nitrate-N, which may then remain frequently 420 underestimated (Kammann et al., 2015). However, although the abso- 421 lute total value we measured may be underestimated, the nitrate-N ex- 422 tracted from aged biochar (78.3 mg kg⁻¹) was 14 times higher than 423 fresh biochar (5.5 mg kg $^{-1}$), and unlikely the total nitrate-N content 424 of fresh biochar, would result higher than aged particles. Besides, 425 Kammann et al. (2015) report that the non-detectable NO₃-N remains 426 non-exchangeable and captured onto biochar particles, thereby we con- 427 clude that such portion is not available to plants. 428

4.2.2. Biochar C and N behave differently as it ages in soil

Consistent with the total biochar C content (Table 1), XPS analyses 430 showed that environmental exposure significantly reduced biochar C 431 at% (Tables 2, 3 and Fig. 5). 432

429

Independent of the application rate, 4 years of field exposure re- 433 duced surface (0–5 nm) biochar relative C at% up to 35.5% compared 434 to unexposed fragments (Fig. 5). The most intense reduction in biochar 435 C at% occurred in the top 5 nm layer either in fresh (-13%) and aged 436 biochars (-19.4%) (Table 2) as a response to the natural oxidation. Bio- 437 char C depletion was less intense in inner layers and no effects were ob- 438 served in layers deeper than 35 nm in fresh particles. Depletion of C 439 occurred up to 70 nm depth in aged fragments (Table 3). Within aged 440 particles, biochar C at% vs depth could be fit by a positive regression 441 model according to an exponential trend with a coefficient of determi- 442 nation (\mathbb{R}^2) equal to 0.93 ($y = 44.025e^{0.1167x}$). These responses suggest 443 that exposure in croplands strongly alters biochar C surface composition 444 and that C depletion starts from the top exposed layer and proceed to- 445 ward the interior, as a consequence of both biotic and abiotic oxidation. 446 In our experiment after 4 years biochar's relative C content was reduced 447 by ~15% compared to its initial values. This relative reduction in C con- 448 tent could be due to loss of biochar C, or it could simply be the result of 449 increased contents of other atoms relative to C (Tables 2, 3), as men- 450 tioned above. Regardless, the amount of labile C lost compared to stable 451 C stored in soils with biochar is still considered comparatively negligible 452 and should not affect the C sequestration potential of biochar on a long- 453 term basis (Joseph et al., 2010). 454

As expected, relative N at% was unaffected within layers of fresh par- 455 ticles (Tables 2 and 3). Total N concentration (Table 1) and N at% 456 (Tables 2, 3 and Fig. 5) was statistically higher in aged fragments, show- 457 ing the opposite trend compared to C. In aged fragments, biochar N at% 458 was statistically higher mostly in the top surface (Fig. 5, Tables 2 and 3), 459 up to 40 nm depth (Table 3). Ageing and depth significantly interacted 460 with atomic N composition and it decreased progressively within aged 461 fragments as the depth increased up to 75 nm depth (L6), while no dif- 462 ferences were recorded between the deepest (L6 and L7) layers 463

83.4 a

342.7 a

0.97a

t1.1 t Q1	Table 1 pH, electrical conductivity (EC), total C, H, N concentration and KCl extractable NO ₃ -N and NH ₄ -N of different rates of aged as compared with fresh biochar fragments.											
t1.3	Biochar	pН	EC	С	Н	Ν	NO_3^-N	$\frac{\rm NH_4^+ - \rm N}{\rm mg \ kg^{-2}}$				
t1.4			μS	$\overline{{ m g}100{ m g}^{-1}}$	$g 100 g^{-1}$	$g 100 g^{-1}$	$mg kg^{-1}$					
t1.5	Fresh	9.97a	903.5a	77.6a	1.41	0.23c	5.51 b	132.3 b				
t1.6	Aged 5 t ha ⁻¹	7.81b	129.8b	66.7b	1.48	0.92a	82.5 a	248.8 a				
t1.7	Aged 15 t ha ⁻¹	8.09b	144.8b	66.3b	1.40	0.73b	69.2 a	230.9 a				

66.1b

Aged 30 t hat1.8 t1.9 Significance

ns, *, ** and *** = effect not significant or significant at p < 0.05, p < 0.01 and p < 0.001, respectively. In the same column, means followed by the same letter are not statistically different (p < 0.001, respectively. t1.10 0.05, SNK Test). t1.11

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1.21

ns

t2.1 Table 2

t2.2 Elemental composition (atomic concentration - at%) of aged (4-year in field conditions at 30 t ha⁻¹) biochar surface (S1) and 3 depths (L2, L3 and L4) compared with fresh biochar t2.3 t **O2** as determined by XPS.

t2.5	Ageing	С	Ν				0	Al	Si
t2.6			S1 (0–5 nm)	L2 (6–10 nm)	L3 (15–20 nm)	L4 (30-35 nm)			
t2.7	Fresh	91.6	1.2	0.89	0.85	0.76	6.7	0.29	0.47
t2.8	Aged	55.3	3.15	1.40	1.15	1.13	32.7	3.73	6.50
t2.9	Significance ***			2SEN	***	***	***		
t2.10	DEPTH								
t2.11	S1	68.74					24.1	1.53	3.47
t2.12	L2	74.03					19.0	2.15	3.69
t2.13	L3	75.01					18.2	2.25	3.49
t2.14	L4	76					17.6	2.12	3.31
t2.15	Significance	ns					ns	ns	ns
t2.16 t2.17	Interaction Ageing *Depth	ns			**		ns	ns	ns

ns, ** and *** = effect not significant or significant at p < 0.01 and p < 0.001, respectively. t2.18 Interaction between biochar and layer significant at p < 0.01. Values differing by ≥ 2 SEM +2.10 are statistically differen. t2.20

464 (Table 3). This evidence suggests that mechanisms for N retention in 465 aged biochar occur mainly in the exposed top surface, but are not only limited to this. Furthermore, the C/N ratio of the biochar fragments dra-466 matically decreases as biochar ages, with potential implications for pro-467 cesses that are C/N-influenced (e.g. microbial activity). 468

4.2.3. Environmental exposure alters biochar surface K, Ca, Mn and Fe ratio 469 Ageing significantly affected the biochar surface relative at% of K, Ca, 470 Mn and Fe with no effects induced by the application rate (Fig. 5). No 471 472differences were detected for Mg and P at%. Surface relative K at% of 473aged biochar was reduced compared to fresh biochar up to 29.3 fold for the 30 t ha^{-1} application rate (Fig. 5). On the contrary, surface at% 474 of Ca, Mn, and Fe were higher in aged fragments, with no effects induced 475by the application rate (Fig. 5). The most abundant increase was mea-476 sured for Ca which increased by 90 fold while Mn at% recorded a limited 477478increase, although significant. It is worth mentioning that these changes are expressed as relative at%, which estimate the relative atomic abun-479dance ratio among scanned elements instead of giving the absolute con-480 centration. Biochar surface ageing-induced effects can be ascribed either 481 to physical or chemical mechanisms. The surface of the weathered bio-482 char particles was finely coated with soil and organic residues which ap-483 peared to adhere and/or be trapped in pores and fractures, partially 484 explaining the higher concentration for most of the elements found on 485 the biochar surface. Chemical mechanisms involved the high reactive 486 487 charge density of the biochar surface (Van Zwieten et al., 2010), which

has adsorption sites where cations, clay, and organic matter may be 488 ionically or covalently bound, confirming the interaction of biochar 489 with minerals and organic compounds in soils. This may also contribute 490 to explaining the higher values of O at% recorded in aged fragments 491 (Fig. 5). The potential of biochar to retain minerals directly on its surface 492 (Glaser et al., 2002) increases the ability of biochar to retain nutrients in 493 soils. Various combinations of Al, Si, C, Fe, and Ti, and trace amounts of 494 Ca, Mg, Mn, K, Na, P, and S were found at the external surfaces of aged 495 greenwaste biochar particles (Joseph et al., 2010). However, the lack 496 of change in the P and Mg atomic surface composition found in this 497 study indicates that this process is biochar-type and soil dependent. Dif- 498 ferent processes (dissolution, hydrolysis, carbonation, decarbonation, 499 hydration, redox reactions) and several mechanisms (H-bonding, 500 cation-bridging, covalent bonding and hydrophobic types of interac- 501 tions) are involved in biochar weathering processes as a consequence 502 of its interactions with OM, water, adsorption of dissolved organic 503 (e.g. root exudates) and inorganic compounds and oxidation (Joseph 504 et al., 2010). In particular, the significant decrease of K at% in aged bio- 505 char surfaces we observed (87% in average relative to the fresh parti- 506 cles) may be due to the dissolution of soluble salts and organic 507 compounds (i.e. biopolymers and low molecular weight compounds) 508 associated with charred particles which is among the first reactions 509 upon biochar addition to soil (Joseph et al., 2010; Shinogi et al., 2003). 510 This is also confirmed by the reduced EC that we measured in aged par- 511 ticles. The dissolution process may induce a rapid increase in the avail- 512 ability of water soluble cations in the soil layer, where biochar is 513 incorporated, thus when high rates are applied, biochar may represent 514 a consistent source of K, enough to fulfill plant requirement (according 515 to the application rate, biochar type and crop) for the first 2–3 seasons 516 after its incorporation. However, results from a column experiment 517 showed that weathering reduced not only the content of K but also S, 518 Ca, and P (Yao et al., 2010), suggesting that mineral release from charred 519 materials is controlled by biochar characteristics and the environment. 520

4.2.4. Ageing promotes biochar oxidation, Al and Si at%

Although chemically induced biochar degradation starts before in- 522 corporation in soil as a result of the oxidation of exposed C rings with 523 a high density of π -electrons (Contescu et al., 1998) and free radicals Q16 (Montes-Morán et al., 2004), only once in soil does biochar experience 525 significant chemical weathering. In our experiment, ageing increased 526 values of biochar O, Al, and Si at% (Fig. 5, Table 2). Ageing and depth 527 did not interact in atomic O, Al, and Si composition and values of biochar 528 O, Al, and Si at%, were comparable among layers (Tables 2 and 3). Nev- 529 ertheless, depth affected atomic O composition, which was reduced as 530 the depth increased (Table 3). Independently of the layer, values of O, 531 Al, and Si always increased in aged biochar by 3, 5, and 18 fold, respec- 532 tively (Table 3). Environmental exposure promoted fragment's 533

t3.1 Table 3

Atomic concentration (at%) of aged (4-year in field conditions at 30 t ha⁻¹) biochar surface (S1) and 3 depths (L5, L6 and L7) compared with fresh biochar as determined by XPS. t3.2

t3.3 t3.4 t3.5	Ageing	с				Ν		0	Al	Si		
		S1 (0–5 nm)	L5 (35–40 nm)	L6 (70–75 nm)	L7 (105–110 nm)	S1 (0–5 nm)	L5 (35–40 nm)	L6 (70–75 nm)	L7 (105–110 nm)			
t3.6	Fresh	79.0	90.2	91.0	91.2	1.02	0.82	0.76	0.80	10.3	0.64	0.33
t3.7	Aged	50.4	52.8	65.5	69.2	3.81	2.14	1.18	1.13	30.1	3.51	5.93
t3.8	Significance		2SE	M = 4.82	M = 0.81		***	***	***			
t3.9	DEPTH											
t3.10	S1									28.0a	1.69	3.16
t3.11	L5									21.2b	2.33	3.51
t3.12	L6									16.4c	2.03	2.89
t3.13	L7									15.3c	2.23	2.98
t3.14	Significance									***	ns	ns
t3.15	Interaction			*				*		ns	ns	ns
t3.16	Ageing*depth											

ns, * and *** = effect not significant or significant at p < 0.05 and p < 0.001, respectively. In the same column, means followed by the same letter are not statistically different (p < 0.05, SNK t3.17 t3.18 Test). Interaction between biochar and depth significant at p < 0.05. Values differing by ≥ 2 SEM are statistically different. t3.19

Estimated depth layers: S1 (0-5 nm), L5 (35-40 nm), L6 (70-75 nm), L7 (105-110 nm).

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Fig. 5. Atomic percentage surface elemental composition (XPS) of aged (4 years) biochar applied at different rates as compared with fresh biochar. ns, *, ** and **** = effect of biochar ageing and rate not significant and significant at $p \le 0.05$, $p \le 0.01$ and $p \le 0.001$, respectively. Within each element, bars with the same letter are not statistically different ($p \le 0.05$), according to the Student-Newman-Keuls (SNK) test.

oxidation (Tables 2 and 3) and, independent of the age, oxidation 534started from the top exposed surface and was progressively reduced 535as depth increased down to 75 nm (Table 3), likely as a result of both bi-536otic and abiotic processes, although some research suggests that biotic 537538processes dominate (Zimmerman, 2010; Cheng et al., 2006). The O:C ratio of our biochar surface shifted from <0.074 to >0.58 after 4 years 539 in field conditions as a consequence of the depletion of C and increase 540of O content. This may have consequences for biochar stability in soil, 541since the increase of the O:C ratio has been cited as a fundamental attri-542543bute in controlling the resistance to microbial mineralization (Harvey et al., 2012; Spokas et al., 2010;), although it may also simply reflect 544the increased O present in soil minerals and/or dissolved organic matter 545that have attached to the biochar. 546

547 4.2.5. Oxidation affects biochar C functional groups

Our results show that biochar C functional groups were affected by 548the interaction between ageing and depth (Table 4). The relative at% 549of the C functional groups always increased by ageing in the top 3 layers 550(S1 + L5 + L6 layers, equal to 0-75 nm depth) (Table 4), except for the 551 -C-C/-C-H/-C = C bonds, where only in the top surface an opposite 552trend was recorded (Table 4). No differences were measured in the 553deepest layer (105-110 nm) between fresh and aged biochars 554(Table 4). The overall development of C functional groups (-C = 0, -555556C–O, –COOH) on the aged biochar surface as a consequence of the natural oxidation which involves the increase in O and H composition 557(Cheng et al., 2008; Yao et al., 2010; Jones et al., 2012; Lin et al., 2012; 558LeCroy et al., 2013; Qian and Chen, 2014) This oxidation is attributed 559to both biotic and abiotic processes, although some data suggest that bi-560561otic processes dominate (Cheng et al., 2006; Zimmerman, 2010). The increased oxidation of C in the uppermost surface layers of the aged 562biochar confirms that oxidation and/or adsorption of soil OM occurred 563(Joseph et al., 2010). Nevertheless, different functional groups can be 564

formed on aged biochar through oxidation such as lactonic, o- 565 quinone-like structures and ether-type oxygen (Boem, 2001). In our Q17 case, the -C-C/-C-H/C = C bonding state was always the major compo- 567 nent of both fresh and aged biochar, although after 4 years the relative 568 composition of these C bonds significantly decreased only in the top 569 surface. 570

The most significant changes in the C1s bonding state were evident 571 on the top surface (0–5 nm), where the relative concentration of -C = 572 O, -C-O and, to a lesser extent, -COOH, were significantly higher in 573 aged biochar. It is possible that carboxyl functional groups were less de-574 veloped relative to other oxidized C forms because carboxyl groups may 575 be partially decarboxylated through hydrolysis reactions occurring in 576 solution (Yan et al., 1996). 577

4.3. Agronomical and ecological implications 578

Our findings suggest that biochar's effects on soil hydrology may 579 change with time, raising a number of points. It seems reasonable to as- 580 sume that different soil textures and mineralogies interact differently 581 with various biochars; thus biochar and ecosystem-specific patterns of 582 exterior pore blockage may be expected (Barnes et al., 2014). Further- 583 more, shifts in soil hydrology pose several implications for water- 584 mediated processes as well as for the erosive fate of applied particles. 585 For instance, soil leaching patterns may be different in aged biochar- 586 mixed soils compared to the immediate response of biochar addition. 587 Likewise, the influence of biochar on water retention may change as 588 biochar ages, in particular in easily drained soils and especially if a dra- 589 matic reduction occurs in the number of pores between 0.01 and 590 0.1 mm. This pore-size range in biochar is fundamental to increased 591 plant available water since larger pores weakly retain water under grav- 592 ity (Jury et al., 1991) and smaller pores do not provide water in a plant- 593 accessible form (Masiello et al., 2015). 594

t4.1 Table 4

8

t4.2 C1s bonding state and relative atomic percentage of aged (4-year in field conditions at 30 t ha⁻¹) biochar surface (S1) and 3 depths (L5, L3 and L7) compared with the fresh biochar as t Q3 determined by XPS.

t4.4	Ageing	Binding	sinding energy (eV) (avg \pm std dev)														
t4.5		-C-C/-CH/-C = C			-C-0			-C = 0				-соон					
t4.6		284.79	284.76	284.75	284.75	286.14	285.96	285.91	285.85	287.53	286.91	287.16	287.19	288.76	288.87	288.61	288.73
4.7		± 0.05	± 0.06	± 0.04	± 0.05	± 0.46	± 0.29	± 0.21	± 0.12	± 0.5	\pm 1.28	± 0.61	± 0.22	± 0.39	± 0.32	± 0.45	± 0.35
t4.8		S1	L5	L6	L7	S1	L5	L6	L7	S1	L5	L6	L7	S1	L5	L6	L7
t4.9	Fresh	75.5	67.2	65.8	65.2	13.2	23.9	24.7	25.2	5.1	5.1	5.6	5.6	6.1	3.8	3.9	4.0
4.10	Aged	51.9	79.8	78.9	73.7	27.4	15.4	16.4	18.8	12.5	3.0	3.1	4.7	8.15	1.7	1.5	2.8
4.11	Significance	2SEM =	2SEM = 8.79				2SEM = 7.35			2SEM = 1.77				2SEM = 1.29			
4.12	Interaction ageing*depth	**				*				***				*			

t4.13 *, ** and *** = Interaction between ageing and depth significant at p < 0.05, p < 0.01 and p < 0.001, respectively. Values differing by ≥ 2 SEM are statistically different. t4.14 Estimated depth layers: S1 (0–5 nm), L5 (35–40 nm), L6 (70–75 nm), L7 (105–110 nm).

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Water infiltration shifts the functional density of biochar as water
fills internal pores previously occupied by air. Once partially waterfilled, the functional density of biochar particles exceeds that of water
and the particles sink. The sinking process seems to be altered by field
ageing, with mineral blockages of pore throats slowing the rate of
water infiltration.

Similarly, it seems reasonable to hypothesize that it takes longer for
 aged fragments to dry out. This lag in particle infill time may suggest im plications also for the erosion rate of biochar particles.

604 The porous structure of biochar provides suitable habitat for a range 605of microbial communities (Hockaday et al., 2006; Warnock et al., 2007; Downie et al., 2009; Thies and Rillig, 2009), and fungi can grow from Q18 607 within the pores out into the soil (Lehmann et al., 2011). Pore connec-608 tivity has been suggested to modulate the availability of biocharassociated labile organic compounds to microbial enzymes (Barnes 609 et al., 2014). Easier access to these sites in recently added biochar 610 could partially explain the initial high mineralization rates observed 611 after biochar addition (Cross and Sohi, 2011). Our findings suggest po-612 tential shifts in microbial colonization patterns as biochar ages in soil. 613 Due to ageing, the attachment of soil particles, changes in pore connec-614 tivity and pore clogging of biochar particles may alter habitat suitability 615 and microbial activity (Lehmann et al., 2011; Thies and Rillig, 2009) re-019 617 ducing microbes colonization. However, fractures on the weathering 618 particles may offer new opportunities for microbial colonization. Furthermore, minerals covering the external surface of biochar fragments 619 interfere with its reactive surface, limiting its sorption capacity 620 (Joseph et al., 2010) but at the same time the greater surface reactivity 621 622 due to oxidation may promote physical protection of biochars and, thus, its long-term stability (Brodowski et al., 2006). 623

The development of O-containing C functional groups of aged biochar increases the reactivity of the biochar surface, leading to an enhancement of chemical sites able to retain nutrients and other organic compounds on this surface. This process is also responsible for the evolution of negative charges, raising the biochar CEC over time (Zimmerman, 2010).

These processes occurred mostly on the O-exposed biochar surface, 630 leading to an enhancement of chemical sites able to retain nutrients 631 632 and other organic compounds on this surface, consistent with the ion sorption pattern of our aged biochar. Oxidized biochar particles may 633 then be bound to soil minerals. Mineral attachment has been indicated 634 as one of the possible mechanisms for the slowing of biochar decompo-635 sition and oxidation (Brodowski et al., 2006; Nguyen et al., 2008), acting 020 as a control on the stabilization process of charred particles. 637

638 Supplementary data to this article can be found online at http://dx. 639 doi.org/10.1016/j.scitotenv.2016.03.245.

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