

Environmental fate and efficiency of bispyribac-sodium in rice soils under conventional and alternative production systems affected by fresh and aged biochar amendment

Antonio López-Piñeiro¹, Carmen Martín-Franco¹, Jaime Terrón-Sánchez², Luis Andrés Vicente¹, Damián Fernández-Rodríguez², Ángel Albarrán², José Manuel Rato Nunes³, David Peña^{4}*

¹ Área de Edafología y Química Agrícola, Facultad de Ciencias – IACYS, Universidad de Extremadura, Avda de Elvas s/n, 06071 - Badajoz, Spain.

² Área de Producción Vegetal, Escuela de Ingenierías Agrarias – IACYS, Universidad de Extremadura, Ctra de Cáceres, 06071 - Badajoz, Spain.

³ Instituto Politécnico de Portalegre, Escola Superior Agraria de Elvas, Elvas, Portugal.

⁴ Área de Edafología y Química Agrícola, Escuela de Ingenierías Agrarias– IACYS, Universidad de Extremadura, Ctra de Cáceres, 06071 - Badajoz, Spain.

* Corresponding author:

David Peña Abades

Área de Edafología y Química Agrícola

Escuela de Ingenierías Agrarias

Universidad de Extremadura

Ctra de Cáceres, 06071 - Badajoz, Spain

Telephone: +34 924286243

E-mail: davidpa@unex.es

23 **Abstract**

24 Irrigation and tillage practice alternatives to conventional flooding production, with or
25 without organic amendments, are attracting great interest to adapt rice cultivation to climate
26 change. However, they can alter the behaviour of pesticides and their efficiency against
27 weeds. A two-year field experiment was conducted to investigate how the environmental fate
28 and the weed control efficiency (WCE) of bispyribac-sodium (BS) were influenced by
29 biochar produced from holm oak prunings (BHO) testing both the fresh and the aged effects.
30 The treatments were: flooding irrigation and tillage (FT), sprinkler irrigation and tillage (ST),
31 sprinkler irrigation and no-tillage (SNT), and the corresponding homologues with BHO
32 addition (FT-BHO, ST-BHO, and SNT-BHO, respectively). Fresh BHO amendment decreased
33 the sorption of BS onto the soil in all treatments, while, after aging, it also decreased sorption
34 in FT-BHO (1.3-fold) but increased it in SNT-BHO and ST-BHO (1.1-fold). BHO addition
35 reduced BS persistence under non-flooding and flooding incubation conditions, except for FT
36 under the former condition for which $t_{1/2}$ increased ≈ 1.5 -fold in both years. The addition of
37 BHO led to a decrease in BS leaching from 58.3% and 44.6% and from 70.4% and 58.1% in
38 ST and FT to 50.1% and 38.3% and 63.6% and 50.3% in the homologue amended soils for the
39 fresh and aged years, respectively. While fresh BHO addition decreased the WCE of BS in
40 SNT-BHO, ST-BHO, and FT-BHO on average by a factor of 1.5, with aged BHO there was
41 only such a decrease (by a factor of 1.4) in FT-BHO. The use of BHO could be effective for
42 reducing water contamination by BS in flooding or sprinkler irrigation rice farming as long as
43 conventional tillage is used. But it may also contribute to greatly reducing the herbicide's
44 efficiency, although with time to allow aging, this reduction would only persist under
45 conventional flooding production.

46 *Keywords:* Herbicide efficacy; Bispyribac-sodium; Leaching; Persistence; Sorption; Sprinkler
47 irrigation.

48 **1. Introduction**

49 The lack of sustainability of conventional rice (*Oryza sativa* L.) cultivation under flooding is
50 increasingly being aggravated by a growing demand for water. The adverse impact of climate
51 change on the hydrological cycle is also reducing water resources. This is particularly notable
52 in Mediterranean countries where there currently can be no guarantee of the water supply for
53 this crucial crop. This is leading to a continual fall in the area devoted to rice farming in
54 major producing nations such as Spain (MAPA, 2019), the rice producing country ranked
55 second of the European Union at 30% of total EU output. Therefore, in order to adapt rice
56 cultivation to climate change, alternative irrigation and tillage practices to replace
57 conventional flooding production are attracting great interest to ensure the crop's
58 sustainability by enhancing water productivity, especially in water-stressed regions such as
59 Mediterranean countries where the volume of water consumed under conventional rice
60 production is more than reported for various nations in Asia by a factor of 2.3 (Sánchez-
61 Llerena et al., 2016; Arunrat et al., 2020).

62 Growing rice aerobically using irrigation by sprinkler in Mediterranean rice agro-ecosystems
63 under both direct seeding (no-tillage) and tillage practices has been widely perceived as a
64 promising agricultural practice to achieve sustainability since it could help reduce water
65 requirements, minimize greenhouse gas emissions, and decrease the levels of As in the grain
66 (Sánchez-Llerena et al., 2016; Fangueiro et al., 2017; Spanu et al. 2021). However, the
67 potential water-deficit stress may reduce the yield by 10-50% compared with an anaerobic
68 system (e.g., Peng et al., 2006). Sánchez-Llerena et al. (2016) describe up to 50% reduction in
69 rice production under aerobic conditions. Although this was only the case for soils whose
70 levels of total organic carbon (TOC) were below 15.0 g kg⁻¹, such figures can be very
71 common for soils used for agriculture in mediterranean environments (Muñoz et al., 2007).
72 Therefore, in regions with limited availability of water resources and soils low in organic

73 matter, the application of organic amendments for rice cropping under aerobic conditions
74 could be beneficial to avoid reduced yields, ensuring the crop's sustainability with a
75 decreasing water footprint.

76 Biochar is one of the principal organic amendments used worldwide due to its potential to
77 minimize greenhouse gas emissions and enhance crop productivity. These beneficial effects
78 have been confirmed in rice cultivation (Sun et al., 2016; Thammasom et al., 2016; Yang et
79 al., 2019; Li et al., 2021), being the result of improvement in the soil's biological and
80 chemical properties (Méndez et al., 2013; Oleszczuk et al., 2014). Furthermore, biochar may
81 have an impact on the soil's hydrological properties such as infiltration and water-holding
82 capacity (Wong et al., 2018; Haque et al., 2021). Although biochar can be derived from a
83 great variety of organic materials, that derived from holm oak (BHO) can be extensively
84 produced in large areas of several Mediterranean countries (e.g. Spain, Portugal) at a
85 reasonable price. Furthermore, due to its high TOC content, BHO is characterized by having a
86 greater capacity to retain water and pollutants such as pesticides than biochars based on other
87 organic materials (Takaya et al., 2016).

88 Although the application of biochar to agricultural soils could affect the environmental fate of
89 pesticides and consequently their efficacy against the target weeds (Kookana et al., 2010;
90 Gámiz et al., 2021), distinct tendencies have been widely observed depending on the
91 characteristics of not only the amendments or soils but also of the pesticides themselves
92 (Cabrera et al., 2011; Siedt et al., 2021). Thus, in a soil treated with 1% of hardwood biochar
93 fomesafen sorption was 13.3 times greater, but the increase with biochar based on rice straw
94 was 10.8-fold (Khorram et al., 2018). Cabrera et al. (2014) reported aminocyclopyrachlor
95 sorption being on average lower by a factor of 1.8 in a macadamia nut shell biochar amended
96 soil, while amendment with wood chip pellet biochar led to a 25-fold increase. Si et al. (2011)
97 reported increased isoproturon sorption and persistence in various soils after charcoal

98 amendment, with both being greatest in the soils whose cation exchange capacity and pH
99 were lowest in value. Li et al. (2021) reported the increase in atrazine sorption after
100 application of biochar derived from tall fescue being greatest in the soil with the lowest
101 organic matter content. García-Jaramillo et al. (2020) found that while azimsulfuron sorption
102 increased by a factor of 1.2 in an acidic paddy soil amended with biochar obtained from olive
103 mill waste compost, penoxsulam sorption decreased by a factor of 1.3 in the same amended
104 soil. Abdel Ghani et al. (2018) reported that while fenamiphos persistence increased by a
105 factor of 6.7 in a sandy soil poor in organic matter amended with date palm and eucalyptus
106 biochar, cadusafos persistence was unaffected in the same amended soil. Gámiz et al. (2017)
107 found that while amendments with biochars from two hardwoods pyrolysed at 700 °C
108 inhibited the phytotoxicity of clomazone, there was no such effect when the herbicide used
109 was bispyribac-sodium in the same amended soils. Furthermore, once biochar is incorporated
110 into a soil, its physicochemical properties may be altered by weathering processes, which
111 could modify the fate, environmental impact, and efficacy of applied pesticides (e.g. Gámiz et
112 al., 2019).

113 Weed infestation is considered to be the major concern worldwide restricting rice yields,
114 regardless of whether conventional or alternative rice production practices are applied (Sing et
115 al., 2018; Ghosh et al., 2021). Therefore, weed management by the appropriate use of
116 pesticides that ensures adequate efficacy is required to obtain profitable rice production, and
117 hence help guarantee the crop's sustainability. In this sense, acetolactate synthase (ALS)
118 inhibiting herbicides such as bispyribac-sodium (BS) (sodium 2,6-bis[(4,6-
119 dimethoxypyrimidin-2-yl)oxy]benzoate) is recognized as being one of the most effective post-
120 emergence herbicides (Mascanzoni et al., 2018). It is extensively used in rice cropping for
121 control of a wide range of weeds (sedges, grasses, and broadleaf weeds). However, BS may
122 negatively impact not only non-target soil microorganisms (Kumar et al., 2020) but also
123 aquatic organisms including macroinvertebrates (Stenert et al., 2018) and freshwater fish

124 (Pradhan et al., 2020). Furthermore, the high water solubility of this compound (64 g L^{-1}) and
125 its moderate-to-high persistence in soils increase its potential risk for water resource
126 contamination. For instance, Vieira et al. (2016) detected high levels ($3.5 \mu\text{g L}^{-1}$) of BS in
127 water samples of regions associated with irrigated rice production.

128 Despite the increasingly common use of biochars as organic amendment to enhance the
129 agronomic and environmental sustainability of rice cultivation (Asadi et al., 2021), and that
130 BS has a great potential risk for contaminating water resources, to the best of our knowledge,
131 only three works (Gámiz et al., 2017; Sharma et al., 2020; Kaur et al., 2022) have as yet been
132 conducted to assess how such amendments can affect the herbicide's behaviour. In these
133 studies, the biochars were applied under laboratory conditions, and no aging effects were
134 evaluated. In particular, we found no published research focused on how BS's fate and its
135 effectiveness in controlling weeds may be affected by biochar amendment when, in field
136 experiments, it is added to soils under different management regimes of irrigation and tillage.
137 Therefore, the objective of the present work was to assess, in a two-year field experiment,
138 how the sorption-desorption, leaching, dissipation, and efficacy of BS was influenced by fresh
139 BHO applied to rice soils under conventional and alternative production systems. Since
140 weathering and aging processes could greatly modify the original BHO properties, which in
141 turn could influence BS's environmental fate and availability to weeds, the effects of BHO
142 aging under natural field conditions were also examined.

143 **2. Material and Methods**

144 ***2.1. The herbicide***

145 BS analytical standard (98.3% purity) was procured from Dr Ehrenstorfer, GmbH (Germany).
146 Its properties are described in BPDB (2019). BS assays were performed by high-performance
147 liquid chromatography (HPLC) using a Waters 600E chromatograph coupled to a Waters 996

148 diode-array detector. The conditions used are presented in detail in Text S1 of the
149 Supplementary Material (SM).

150 **2.2. The biochar**

151 The commercial amendment (BHO) employed in the field experiment was purchased from
152 Carylevere Co., Ltd (Zahinos, Spain). It was produced from prunings of holm oak by
153 pyrolysis at 550°C (48 h). Prior to assay and application, the BHO underwent milling to a 2-
154 mm sieving size. BHO properties of carbon (TC), hydrogen (TH), nitrogen (TN), ash, oxygen,
155 water-soluble organic carbon (WSOC) contents, and specific surface area (SSA), Fourier-
156 transform infrared (FTIR) spectra, porosity, pH, and electrical conductivity were measured as
157 detailed previously by López-Piñeiro et al. (2022) and presented briefly in Text S2 of SM.
158 The properties of aged BHO were determined after harvest in the second year of the
159 experiment. For this, BHO particles were separated from samples of soil down to 20-cm depth
160 corresponding to the FT-BHO, ST-BHO, and SNT-BHO treatments. Suspensions of these
161 BHO samples were prepared in distilled water at a 1:10 w/v dosage, and then shaken to
162 eliminate any particles of soil. In accordance with Koide et al. (2011), the BHO was rinsed
163 four times using distilled water before assay. Table 1, which is adapted from López-Piñeiro et
164 al. (2022) presents a selection of the aged and fresh BHO characteristics. Additionally, the
165 FTIR characterization is presented in Fig. S1 (SM) and briefly discussed in Text S3 of SM.

166 **2.3. Design of the experiments, sampling, and assay**

167 A two-year (2018-2019) field trial was conducted in a rice paddy located in the province of
168 Badajoz (38°55'N; 6°57'W; SW Spain), with climate classified as Mediterranean semi-arid
169 (mean yearly temperature 16.2 °C and rainfall 460 mm). This experimental area had been
170 managed for 14 years as conventional rice (*O. sativa* L.) cropping by flooding irrigation and
171 tillage. The soil (0-20 cm) is loam textured (clay 20.8%, silt 28.9%, and sand 50.3%). The

172 experimental design involved a total of 18 plots (six treatments with three replicates), with
173 each plot measuring 10 m × 18 m (180 m²). The applied treatments were: conventional
174 flooding irrigation and tillage (FT), sprinkler irrigation and tillage (ST), sprinkler irrigation
175 and no-tillage (SNT), and the corresponding homologues with only first-year BHO addition
176 (FT-BHO, ST-BHO, and SNT-BHO treatments, respectively). The BHO application rate (28
177 Mg ha⁻¹) was applied by spreading onto the surface of the soil of the FT-BHO, ST-BHO, and
178 SNT-BHO treatments in April 2018, and then it was incorporated into the soil by a rotary hoe.
179 After rice harvest (September 2018 and 2019), four subsamples of topsoil (0-20 cm) were
180 collected for each of the plots to make a composite sample which was used to determine BS
181 sorption-desorption, leaching, and dissipation. The data obtained in the year one and year two
182 following BHO administration were used for evaluating its effects both “fresh” as well as
183 “aged”, respectively. Selected soil properties (WSOC, TC, and TN contents, EC, and pH) of
184 the unamended and BHO-amended soils are presented in Table S1 of the SM. Please refer to
185 López-Piñeiro et al. (2022) for more details.

186 ***2.4. Experiments of adsorption and desorption***

187 Isotherms of BS adsorption-desorption for the soil samples of unamended and BHO-amended
188 treatments were determined in triplicate in accordance with López-Piñeiro et al. (2016) using
189 the batch equilibration method. Briefly, soil samples (5 g) were treated by mechanical shaking
190 at 20±1°C for 24 h with 10 mL of solutions of BS in 0.01M CaCl₂ at initial concentrations
191 (C_i) of 0.5, 2.5, 5, 10, and 20 µM, which cover the field application rates frequently used by
192 farmers in the region of the study (0.1-0.5 kg ha⁻¹). BS adsorption-desorption data were fitted
193 to the Freundlich equation ($C_s = K_f C_e^{n_f}$). Detailed information on these experiments is
194 presented in SM (Text S4).

195 ***2.5. Studies of the dissipation of the herbicide***

196 For the dissipation of BS, soil samples from treatments with and without BHO addition were
197 analysed under two incubation conditions (flooded and non-flooded). BS was spiked to give
198 an application rate of $1.63 \mu\text{g g}^{-1}$. For each treatment, triplicate soil samples were removed at
199 selected intervals after BS application (up to maximum of 49 days) for its residual extraction.
200 The BS was extracted with 10 mL of a 60:40 (v/v) distilled water/methanol mixture, and an
201 HPLC analysis was made of its supernatant residues. Measurements for the original and
202 BHO-amended soils were fitted to a first-order kinetics equation in order to calculate the
203 respective half-lives ($t_{1/2}$). The activity of dehydrogenase (DHA) for the two conditions of
204 incubation was also determined employing INT as substrate in accordance with García et al.
205 (1993). Additional details of these studies are given in Text S5 of SM.

206 ***2.6. Studies of the leaching***

207 To determine the leaching of BS, triplicates of air-dried soils from non-amended as well as
208 BHO-amended treatments were introduced by packing into 5-cm inner diameter \times 30-cm
209 length PVC columns. They were then oversaturated using 0.01 M CaCl_2 , allowing 24 h for the
210 excess to drain. BS was then added at a rate of 0.5 kg a.i./ha onto the top of the soil columns.
211 Each column was eluted each day by adding 50 mL 0.01M calcium chloride solution, with
212 each leachate being assayed using high-performance liquid chromatography. Terminated the
213 period of monitoring, all columns were sectioned into each of the 5-cm depths to determine
214 the BS remaining. BS extraction was as for the studies of dissipation described above. Further
215 details of these leaching experiments are provided in SM (Text S6).

216 ***2.7. Bioassays***

217 For the aged and fresh years, a laboratory bioassay was conducted to assess how the
218 phytotoxicity of BS is influenced by the addition of BHO to soils that had been subjected to
219 distinct tillage and irrigation managements. Triplicates of air-dried soils (50 g) were put into

220 pots of 30 cm². The soils under non-flooding irrigation (SNT, ST, SNT-BHO and ST-BHO)
221 were incubated at 80% field capacity, and those under flooding irrigation (FT and FT-BHO) at
222 1:1.25 w/v soil-to-water ratio. For incubation, the pots were randomly placed inside a growth
223 chamber and kept under conditions of 25 °C and 12-h daylight for 14 days. Then, for each
224 treatment, the weeds were removed by hand, and 10 pre-germinated seeds of *Echinochloa*
225 *crus-galli* L. (one of the main weeds causing critical rice yield losses) were put onto the soil
226 surface of each pot. After 10 days, BS was applied to one set of pots at the recommended
227 dosage of 100 g ha⁻¹, leaving as controls another set without herbicide. In order to simulate
228 field BS application for treatments under flooding irrigation, the excess of water was carefully
229 removed from the corresponding pots until two days after its application. After 14 days of BS
230 application, the weights of *E. crus-galli* L. were measured to determine the weed control
231 efficacy (WCE) in all treatments, which was calculated as $WCE = (DWC - DWT) / DWC$,
232 where DWC and DWT are the dry weights of weeds in the control and in the BS treated pots,
233 respectively (Mohammed et al., 2016).

234 **2.8. Statistical analyses**

235 Statistical analyses (Pearson's correlation, ANOVA, Duncan's test) were done with the use of
236 IBM's SPSS (vn. 22) software package. A *p*-value >0.05 was considered to indicate statistical
237 non-significance.

238 **3. Results and Discussion**

239 **3.1. Sorption-desorption studies**

240 Figure S2 shows sorption–desorption isotherms of BS for fresh and aged years. For both
241 years, all sorption isotherms from original and BHO amended soils were appropriately
242 described by the Freundlich model ($R^2=0.972-0.998$; Table 2). These results agree with Kaur
243 et al. (2022) who indicated that the Freundlich model was the most satisfactory to describe the

244 adsorption behaviour of BS in unamended and rice-straw biochar amended soils. Moreover,
245 the values of n_f (<1) indicate that BS sorption was greatly dependent on its initial
246 concentration in the solution. However, C-shaped BS adsorption isotherms ($n_f \approx 1$) were
247 reported by Kaur et al. (2022) for a sandy loam soil with and without addition of rice straw
248 biochar, which may be attributable to the different properties of the soils and biochar used.
249 The treatments significantly ($p < 0.001$) affected the BS sorption, with differences between the
250 effects in the fresh and aged years as shown by the significant treatment \times year interaction
251 ($p < 0.001$; Table 2). For the soils without BHO amendment, the BS K_f values varied from
252 0.494 to 1.09 and from 0.583 to 0.929 in the first and second year, respectively (Table 2),
253 which are of the same order of magnitude as those found by Singh and Singh (2015) who
254 reported values ranging from 0.37 to 0.87 for Indian soils with lower TOC content (3.0-6.3 g
255 kg^{-1}) and values of pH of 5.2-7.9. Our K_f values are lower than those reported by Gómez et al.
256 (2019) who found values ranging from 0.634 to 1.531, also in rice soils from Spain although
257 with lower pH values (4.9-6.1) and slightly higher TOC contents (10.2-15.1 g kg^{-1}). However,
258 Gámiz et al. (2017) found, in an agricultural soil also from Spain with TOC of 13 g kg^{-1} but
259 pH of 7.9, a lower value of K_f (0.2) than in our study. Furthermore, the BS sorption in our
260 study was much lower than that found by Chirukuri and Atmakuru (2015) who reported K_f
261 values of 3.4 and 5.6 for soils from the United States and 3.9 and 4.8 for soils from the
262 Netherlands (with 39 and 33, and 34 and 44 g kg^{-1} TOC, and pH values of 6.5 and 6.3, and 5.4
263 and 5.2, respectively). This indicates that there should be expected a much greater potential
264 for water resource contamination by BS (and consequently less safety in its use) when this
265 compound is applied to Mediterranean fields with edaphic characteristics such as those in this
266 study in comparison with other soils which have characteristics of more acidic pH values
267 and/or very high values of TOC content.

268 For both years, the BS sorption was significantly greater in FT than in SNT and ST treatments
269 ($p < 0.05$). The greatest differences were found in the first year. Thus, whereas in the first year

270 the FT K_f values were 1.9 and 2.2 times as great as in ST and SNT, respectively, in the second
271 year they were greater than in ST and SNT by a factor of 1.6 (see Table 2). This is in
272 agreement with López-Piñeiro et al. (2016) who, also for rice soils from Spain, concluded that
273 in the short-to-medium term an increase in the values of soil pH resulting from the flooding to
274 non-flooding irrigation transition under no-tillage and tillage management resulted in reduced
275 BS sorption by 2.4 times. Indeed, when only our original soils were included in a correlation
276 analysis, K_f showed a significant negative correlation with respect to pH ($r = -0.958$,
277 $p < 0.01$). In accordance with Hyun et al. (2003) and Kaur et al. (2022) our results appear to
278 corroborate that the observed pH values in SNT and ST management (pH>6.3) can lead to
279 decreasing the proportion of neutral BS molecules which could be readily adsorbed onto the
280 negatively charged surface of soil colloids. In addition, the presence of greater WSOC in SNT
281 and ST than in FT treatments may also have resulted in lower BS sorption due to the
282 competition between WSOC and BS molecules for occupying available sorption sites
283 (Cabrera et al., 2014). The BHO application influenced BS sorption significantly ($p < 0.05$) in
284 flooded and non-flooded treatments for both years. However, compared with the respective
285 original soils, in the fresh case, BHO application decreased the BS K_f values in SNT-BHO,
286 ST-BHO, and FT-BHO 1.1-, 1.2-, and 1.6-fold. In the aged case, these values also decreased
287 in FT-BHO by a factor of 1.3 but slightly increased in SNT-BHO and ST-BHO (by a factor of
288 1.1; Table 2), indicative of BHO amendment's impact on BS sorption in soils managed under
289 different irrigation and tillage practices also being time dependent. In part, an explanation for
290 these findings may lie in the increases observed in the pH values of the BHO-amended with
291 respect to the corresponding original soils. Indeed, K_f was significantly (negatively) correlated
292 with soil pH ($r = -0.831$; $p < 0.01$), confirming the key role it plays in BS sorption as previously
293 reported by Chirukuri and Atmakaruru (2015) for instance. Thus, according to different
294 authors (Kah and Brown, 2006; Gómez et al., 2019), increasing pH after addition of organic
295 amendments such as BHO could lead to an increase in the ratio of the BS anion form which

296 may be less easily adsorbed than the protonated fraction. However, the slight increase in the
297 BS K_f values observed in non-flooded BHO-amended soils (SNT-BHO and ST-BHO)
298 compared with the corresponding original soils (SNT and ST) in the aged year cannot be
299 attributed to their different pH since both pH and K_f had the greatest values in BHO-amended
300 soils (Table S1 and Table 2). This could well be ascribed to the additional sorption sites
301 promoted by the significantly ($p<0.05$) greater SSA (Table1) observed in aged than in fresh
302 BHO (Martin et al., 2012; Gámiz et al., 2019). Greater increases (by factors of 2.5 and 1.9) in
303 BS sorption were found by Gámiz et al. (2017) when two biochars produced from hardwood
304 at a pyrolysis temperature similar (500°C) to the BHO applied for this study were used as
305 amendment, although this was a laboratory experiment in which the initial soil, with a very
306 low K_f value (0.2), was amended with a dose of biochars approximately twice that of the
307 present study, and aging effects were not measured. Similar findings were observed by Kaur
308 et al. (2022) who found a significant positive correlation between BS sorption capacity and
309 SSA, although in a study in which only a fresh biochar effect was measured.

310 Similar to sorption, BS desorption was significantly ($p<0.001$) affected by which treatment
311 was applied, as well as the effects in the two years (fresh and aged) being different as shown
312 in the significance of the treatment \times year interaction (Table 2; $p<0.001$). In the case of soils
313 without BHO amendment, D values were lower in ST and SNT than in FT by factors of 2.0
314 and 1.3 and 1.4 and 1.7 for the first and second years of the experiment, respectively (Table
315 2). After BHO field addition, the values of D were significantly ($p<0.05$) reduced in flooded
316 and non-flooded treatments in both years, although this effect was more evident in the former.
317 A decrease in desorption after rice straw biochar addition was also found for fomesafen
318 (Khorram et al., 2018) and imazapyr and imazapic (Yavari et al., 2016), suggesting that the
319 bond between BS and unamended soils is less robust than between BS and biochar particles
320 (Ogura et al., 2021). Moreover, similarly to the original soils, BS desorption was significantly
321 greater in TF-BHO than in NTS-BHO and TS-BHO for the fresh (by factors of 2.3 and 1.7)

322 and aged (by factors of 1.5 and 1.4) years (Table 2), confirming that in unamended and BHO-
323 amended soils the sorbed BS may be more weakly retained in those under flooding than under
324 non-flooding, irrespective of the tillage practices implemented. The order of BS desorption
325 may be explained by the soil organic matter (TOC and WSOC) (Tables S1 and Table 2).
326 Indeed, D was significantly and negatively correlated with TOC ($r=-0.497$; $p<0.05$) and
327 WSOC ($r=-0.333$; $p<0.05$). These results agree with previous reports of lower reversibility of
328 BS (Gómez et al., 2019) and another anionic herbicide (MCPA) (López-Piñero et al., 2014)
329 with increasing TOC and WSOC in rice and olive grove soils, respectively, both amended
330 with olive mill waste. However, greater reversibility of terbuthylazine and diuron (Cabrera et
331 al., 2007) and metribuzine (López-Piñero et al., 2013) was also found in olive mill waste
332 amended soils than in unamended soils, which was attributed to the greater WSOC in the
333 former, coherent with the desorption capacity of pesticides applied to soils being influenced
334 not just by the most reactive and mobile source of soil carbon but also by the pesticides'
335 diversity of chemical structures. Compared with the fresh year, a marked increase in sorption
336 reversibility was observed in the soils after BHO aging (Table 2), which could be due to the
337 significant differences ($p<0.05$) found between the micropore volume to total pore volume
338 ratios of the fresh and aged BHO (Table S2) (Khorram et al., 2018). Also, this increase in BS
339 desorption because of the aging effect may be attributable to blockage in adsorption sites by
340 minerals, acids, and oxides in soils (Ogura et al., 2021), which would have been more
341 significant under flooding conditions. Our results suggest that, besides a decline in the risk of
342 water resource contamination as a consequence of the increased sorption capacity in non-
343 flooded BHO treatments, a better bioavailability and weed control effectiveness of BS could
344 also be expected in both non-flooded and flooded BHO treatments with aging time.

345 **3.2. Dissipation studies**

346 The BS dissipation curves and DHA for unamended and BHO-amended soils are shown in
347 Fig. 1. For the fresh and aged years, the data fit first-order kinetics for non-flooded ($R^2>0.870$)
348 and flooded ($R^2>0.855$) conditions (Table 3). In each of the two years, the DHA values
349 measured for the whole incubation period (DHAT) were lower under non-flooded than under
350 flooded conditions of incubation, especially in the soils under flooding irrigation, with DHAT
351 values in these treatments being up to factors of 3.0 (year fresh) and 3.1 (year aged) lower
352 under non-flooded conditions of incubation (see Table 3). Gómez et al. (2019) also found
353 lower values of DHAT under non-flooded than flooded conditions of incubation, although
354 using olive mill waste as amendment of organic type in rice-cropping soils following the
355 application of BS. BHO application with statistical significance ($p<0.05$) increased DHAT
356 values in all treatments and under both incubation conditions, an effect which is attributable to
357 the greater organic matter content of the BHO-amended soils. Indeed, significant positive
358 correlations were found between DHAT and TOC under flooding ($r=0.403$, $p<0.05$) and non-
359 flooding ($r=0.541$, $p<0.01$) incubation conditions. These results are consistent with a previous
360 meta-analysis by Liao et al (2022) who observed DHA increases when biochar produced at
361 low temperature is applied, suggesting that TOC is one of the dominant factors influencing
362 biochar effects on soil enzyme activities.

363 The BS dissipation was significantly ($p<0.001$) treatment affected. The differences before
364 with respect to after BHO aging are shown by the significance ($p<0.001$) of the interaction
365 treatment \times year (Table 3). As was to be expected according to the K_f values, overall a
366 significant increase in the BS persistence was observed for the unamended and BHO-
367 amended treatments of the aged compared with the corresponding fresh-year soils, with $t_{1/2}$
368 values up to 1.5 times greater for treatments without BHO amendment in both experimental
369 incubation conditions and up to 1.4 and 1.3 times greater for treatments with BHO
370 amendment under non-flooded and flooded conditions of incubation, respectively (Tables 2
371 and 3).

372 For soils without BHO amendment, the $t_{1/2}$ values varied from 31.9 to 86.4 d and from 34.4 to
373 129 d under non-flooded and flooded conditions of incubation, respectively (Table 3). These
374 are of the same order as those found by López-Piñero et al. (2016) under flooded (45.4 to
375 131.8 d) but slightly greater than those under non-flooded (31.0 to 51.5 d) experimental
376 conditions. However, the values of the present work are much greater than those reported by
377 Gámiz et al. (2017) of 21 d for a non-flooded type of condition, although this was for a soil of
378 much lower capacity for sorption ($K_f=0.21$) which might have the result of greater
379 biodegradation availability of the compound, and with the samples being moistened to 30% of
380 field capacity. Except for the FT treatment, the BS persistence for soils without BHO
381 amendment was significantly ($p<0.05$) lower in the soils under non-flooded than under
382 flooded experimental conditions in the two years of the study, with $t_{1/2}$ values increasing up to
383 1.4- and 1.9-fold for year one and the year two of the study, respectively (see Table 3). Kalsi
384 and Kur (2019) and Sharma et al. (2020) also found lesser persistence of BS under non-
385 flooded than under flooded conditions of incubation as a consequence of a poorer ability of
386 the anaerobic microbial community to dissipate BS, showing soil moisture to be a major
387 factor influencing herbicide persistence because of its being essential for microbial activity.
388 Furthermore, despite BS sorption being significantly greater in the treatment under flooding
389 (FT) than in those under sprinkler irrigation (SNT and ST), the BS dissipation rate was
390 significantly ($p<0.05$) greater in FT than in SNT and ST in both years of the study, with $t_{1/2}$
391 values increasing up to 1.9-fold in SNT and ST under non-flooded, and up to 2.3- and 2.7-fold
392 in SNT and ST, respectively, under flooded incubation conditions (Table 3). When only
393 original soils were included in a correlation analysis, $t_{1/2}$ showed a significant positive
394 correlation with pH for non-flooded ($r=0.736$, $p<0.01$) and flooded ($r=0.685$, $p<0.01$)
395 incubation conditions, indicating that BS dissipation rates decreased in response to increased
396 pH of the soil that resulted from the conventional flooding to alternative sprinkler irrigation
397 regime transition irrespective of whether or not tillage was applied. This is consistent with

398 Chirukuri and Atmakuru (2015) and Kalsi and Kaur (2019) who reported that BS was less
399 stable and more available for dissipation with decreasing soil pH due to diminished hydrolysis
400 of this compound at the higher pH values. In addition, Chirukuri and Atmakuru (2015) found
401 that TOC had a positive influence on BS dissipation rates, although their study used 21
402 unamended soils from different locations with a wider range of TOC values (3.5-44 g kg⁻¹)
403 than in our work (9.3-10.7 g kg⁻¹).

404 As was observed for the original soils, the BS persistence for soils with BHO amendment was
405 also significantly ($p<0.05$) lower in the non-flooded than the flooded experimental conditions
406 soils in the two years (fresh and aged), although only for the treatments under non-flooding
407 irrigation (SNT-BHO and ST-BHO). Thus while for these treatments the $t_{1/2}$ values increased
408 by factors of 1.7 and 1.8 for the treatment under flooding irrigation (FT-BHO) they decreased
409 by factors of 1.6 and 1.8 for the fresh and residual years, respectively (Table 3). This decrease
410 may be explained by the DHAT values which resulted to be factors of 3.0 (fresh) and 2.8
411 (aged) greater in FT-BHO under flooded than under non-flooded conditions, respectively
412 (Table 3). Indeed, $t_{1/2}$ was negatively correlated significantly with DHAT for non-flooded
413 ($r=-0.539$, $p<0.01$) and flooded ($r=-0.620$, $p<0.01$) experimental incubation conditions. The
414 field BHO application significantly ($p<0.05$) decreased BS persistence in all treatments and
415 under both incubation conditions, except for FT-BHO under non-flooded conditions in which,
416 relative to FT, the $t_{1/2}$ values increased from 31.9 to 48.4 d and from 49.4 to 66.3 d for the
417 fresh and aged years, respectively (Table 3). This increase may be explained by the expected
418 lesser availability of BS for dissipation with increasing soil pH from 5.5 to 6.4 (fresh year)
419 and from 5.6 to 6.5 (aged year) (Table S1), coupled with the poorer ability of soil microbial
420 communities to degrade this compound due to their lack of adaptation to aerobic conditions
421 after 14 years under flooding irrigation management (Sharma et al. 2020). The observed
422 decrease in BS persistence after BHO amendment was more evident in the aged year, in
423 which the $t_{1/2}$ values were 1.2, 1.6, and 1.3 times lower in SNT-BHO, ST-BHO, and FT-BHO,

424 as well as lower by factors of 1.3 and 1.8 in ST-BHO and SNT-BHO than in corresponding
425 unamended soils, for flooded conditions of incubation and non-flooded conditions,
426 respectively (see Table 3). In accordance with Khorram et al. (2016), the observed
427 enhancement in BS dissipation after BHO application may be attributed to microbial
428 stimulation as a result of the high organic matter content present in this amendment. Indeed,
429 $t_{1/2}$ was significantly negatively correlated with TOC for non-flooded ($r=-0.471$, $p<0.01$) and
430 flooded ($r=-0.420$, $p<0.01$) incubation conditions. Significant decrease in BS persistence after
431 rice straw biochar application has been reported by Sharma et al. (2020) under flooded and
432 non-flooded conditions, although unlike our work this was in a laboratory study with soils not
433 under different management regimes of tillage and irrigation and without measuring any
434 aging effect. However, Gámiz et al. (2017) found longer persistence of BS in a soil that had
435 been amended using two types of biochars produced from hardwood, although that study was
436 conducted only under a non-flooded condition in which the biochars were pyrolysed at a
437 higher temperature (700°C) than the BHO in our study (550°C), which could mean opposite
438 effects on soil enzymes activities (Liao et al., 2022), thereby affecting the herbicides
439 dissipation. Likewise, other studies found increases in persistence of different pesticides (e.g.
440 MCPA, carbofuran and dimethyl disulphide) in soils amended with different biochars
441 (Khorram et al., 2016; Han et al., 2017). Besides differences in the soils' physicochemical
442 properties due to the different management regimes, these contradictory results also highlight
443 how important are the particular characteristics of the pesticides and biochar when their
444 behaviour is analysed in amended soils (Sharma et al. 2020).

445 **3.3. Leaching studies**

446 Figure 2 shows the BS breakthrough curves. Table 4 lists the proportions of BS first leached
447 and then extracted from the columns of soil once terminated the leaching study. Total BS
448 leaching was affected significantly ($p<0.001$) by the treatment, and there were differences

449 between the two years (fresh and aged) as shown in the significance ($p < 0.05$) of the
450 interaction treatment \times year (see Table 4). In soils without BHO amendment, the amount of
451 BS leached ranged from 44.6% to 58.3% (year 2018) and from 58.1% to 70.4% (year 2019)
452 of the total of the compound initially applied (Table 4), which are somewhat greater values
453 than those reported (40.2-55.3%) by Gómez et al. (2019) also in rice soils. Greater
454 percentages of leached BS (76.3-87.1%) were found, however, by Kaur et al. (2021), although
455 in alkaline soils (pH=8.0-8.8) with very little organic matter content (TOC=1.4-3.6 g kg⁻¹).
456 The total of BS leached was greater in SNT and ST than in FT by factors of 1.3 and 1.3 and
457 1.1 and 1.2, for the first and the second year of the experiment, respectively, suggesting that
458 the soil property changes following the implementation of alternative rice production under
459 non-flooding irrigation could enhance the leaching of BS, especially under tillage
460 management. These results are consistent with those reported by Gómez et al. (2019) who,
461 also for rice soils from Spain, reported a greater amount of BS leached in SNT and ST than in
462 FT management, which was attributed to the lower BS sorption capacity and much greater
463 persistence observed in the treatments under non-flooding irrigation. Thus, in the present
464 study (fresh year), the values of K_f in FT were 2.2 and 1.9 times greater (Table 2), and the
465 values of $t_{1/2}$ 2.2 and 2.5 times lower (Table 3) than in SNT and ST, respectively.

466 Despite the significant decrease in BS sorption capability observed in all treatments with
467 BHO amendment in the fresh year and in the FT-BHO treatment in the aged year (Table 2),
468 except for the SNT treatment, the field BHO amendment was followed by a decline in BS
469 leaching from 58.3% and 44.6% and from 70.4% and 58.1% in ST and FT, to 50.1% and
470 38.3% and 63.6% and 50.3% in the homologue amended soils for the fresh and aged years,
471 respectively (Table 4; Fig. 2). This may be attributable to the lesser persistence observed in
472 the ST-BHO and FT-BHO relative to the homologue non-amended treatments (see Table 3
473 and Table 4). In fact, the proportion of BS leached was positively correlated with $t_{1/2}$ values
474 under non-flooding ($r = 0.475$, $p < 0.01$) and flooding ($r = 0.827$, $p < 0.01$) incubation conditions.

475 These results agree with Gómez et al. (2019) who, also for rice soils, attributed the significant
476 decrease observed in BS leaching of amended compared with unamended soils to a lower
477 persistence, although that study used olive mill waste instead of BHO as organic amendment.
478 However, despite the significant decrease in BS persistence also observed in SNT-BHO
479 compared with SNT, no significant differences ($p>0.05$) between these cases were observed
480 for the amount corresponding to BS leached in the two years (fresh and aged; see Table 4). An
481 explanation may be the greater content of WSOC found for the treatments under no-tillage
482 which could act as co-transporter for BS (Peña et al., 2015), and this could have
483 counterbalanced the favourable effect of the decreased persistence on the reduction of BS
484 leaching. Indeed, a significant positive correlation ($r=0.444$, $p<0.01$) was found between the
485 percentage of BS leached and WSOC. Therefore, although the transition from a flooding to a
486 non-flooding irrigation regime could enhance the risk of water contamination by BS, our
487 results suggest the fresh or aged BHO may reduce this effect in both irrigation systems,
488 particularly under tillage practices. Similar findings were observed by Kaur et al. (2022), who
489 indicated that the application of rice-straw biochars might be an effective management
490 practice in controlling the leaching potential of BS. In addition, for a range of different
491 herbicides, biochar has been shown to have a great potential to reduce the leaching capacity of
492 these compounds (e.g., Trigo et al. 2016; Mendes et al. 2018). However, López-Piñeiro et al.
493 (2022) reported that, after BHO aging, the capacity of this amendment to mitigate clomazone
494 leaching decreased, especially under flooding management and conventional tillage,
495 highlighting how the behaviour of applied pesticides in soils with BHO amendment strongly
496 depends on properties specific to the compound selected.

497 At termination of the trial concerning leaching, no significant differences ($p>0.05$) were found
498 between managements or years in the total amount of BS remaining in the soil columns (Table
499 4). Nonetheless, except for the treatment with flooding irrigation, the amounts of BS
500 recovered were on average 1.9 and 1.6 times lower in the treatments with BHO amendment

501 (SNT-BHO and ST-BHO) than the homologue unamended soils for the fresh and aged years,
502 respectively. This is coherent with the results of the dissipation study, with the smaller amount
503 of BS recovered in BHO-amended soils being attributable to its lower persistence. Indeed,
504 there was a significant positive correlation of the BS recovered with the $t_{1/2}$ values ($r=0.704$,
505 $p<0.01$).

506 **3.4. Weed control efficacy**

507 The weed control efficacy (WCE) of BS for unamended and BHO-amended soils is shown in
508 Fig. 3. The WCE was significantly ($p<0.001$) affected by treatment, there being differences
509 between the two years of BHO aging. This is shown in the significance ($p<0.001$) of the
510 interaction treatment \times year (see Table S3). In soils without BHO amendment, and for both
511 years, the efficacy of BS against *E. crus-galli* L. was greater in the treatments under non-
512 flooding than under flooding types of irrigation, regardless of which tillage system had been
513 used, although this effect was only significant ($p<0.05$) in the first year of the study with
514 WCE values decreasing from 80.4% (SNT) and 83.8% (ST) to 56.4% (FT) (Fig. 3). When
515 only original soils were included in the correlation analysis, WCE showed a significant
516 negative correlation with K_f values ($r=-0.925$, $p<0.01$), indicating that a decrease in the
517 sorption capacity of BS resulting from the transition from flooding to sprinkler irrigation, as
518 was discussed above in the sorption-desorption section, could enhance the weed control
519 effectiveness of this compound.

520 The BHO application significantly ($p<0.05$) influenced the WCE of BS in flooded and non-
521 flooded treatments for both years. However, compared with the corresponding original soils,
522 in the fresh year the application of BHO decreased WCE BS values in SNT-BHO, ST-BHO,
523 and FT-BHO 1.6-, 1.2-, and 1.7-fold, in the aged case these values also decreased in FT-BHO
524 by a factor of 1.4 but increased, although without significance ($p>0.05$), in SNT-BHO and ST-
525 BHO (by factors of 1.2 and 1.1, respectively; Fig. 3), indicating that the impact of BHO

526 amendment on the effectiveness of BS in soils managed under distinct tillage and irrigation
527 practices was time dependent due to the aging process. These results may in part be attributed
528 to the significantly ($p<0.05$) lower percentage of BS desorption observed in all BHO-
529 amended soils compared with unamended soils, especially in the fresh year (Table 2), which
530 could have lessened its availability to control *E. crus-galli* L. Therefore, as suggested by
531 Mendes et al. (2019), it is extremely relevant to gain a better understanding of how biochar
532 application affects herbicide sorption–desorption to determine these chemicals' weed control
533 efficacy. Moreover, the findings might also have their explanation in the observed lower BS
534 persistence for the BHO-amended soils compared with their corresponding original soils
535 (Table 3). Indeed, WCE was significantly positively correlated with $t_{1/2}$ values ($r=0.625$,
536 $p<0.01$). These results agree with Kalsi and Kaur (2019) who indicated that dissipation is one
537 of the fundamental processes which determine the effect of herbicides on the environment as
538 well as their weed control efficacy. However, the increases in the effectiveness of BS
539 observed in non-flooded BHO-amended soils (SNT-BHO and ST-BHO) compared with the
540 corresponding original soils (SNT and ST) in the aged year cannot be attributed to differences
541 in their persistence, since the greatest values in WCE (Fig. 3) and lowest in $t_{1/2}$ (Table 3)
542 corresponded to those BHO-amended soils. This could well be ascribed to the observed much
543 lesser desorption of BS in the fresh than in the aged amended soils, given that D increases
544 from 5.92% and 7.97% to 21.1% and 22.3% for SNT-BHO and ST-BHO, respectively (Table
545 2), which may lead to an increase in the herbicide's bioavailability. Our results contrast with
546 those of Gámiz et al. (2017) who found no differences in BS efficacy against *Eruca vesicaria*
547 plants in unamended and amended soils with two different biochars, although that study was
548 conducted only under non-flooding conditions in which the aging effect was not measured,
549 and using compounds pyrolysed at a higher temperature (700°C) with SSA values, on
550 average, 15 times greater than the BHO amendment used in the present work.

551 **4. Conclusions**

552 The use of BHO as amendment in conventional and alternative rice production systems
553 modified the environmental fate and efficacy of BS against weeds in a form that was
554 dependent on the irrigation and tillage regimes implemented as well as on BHO that has aged.
555 Consequent from the soil property (pH, TOC, WSOC) and BHO (SSA, pore-size distribution)
556 changes, BS sorption together with its reversibility decreased for all the BHO-amended soils
557 although, after the amendment's aging, while this effect on reversibility was maintained, that
558 corresponding to sorption was present only in soils managed under conventional flooding
559 management. As a consequence of microbial stimulation resulting from the high organic
560 matter content present in the BHO, both the fresh and the aged amendments decreased BS
561 persistence in the soil, whether under flooding or sprinkler irrigation. Despite the transition to
562 sprinkler irrigation leading to more BS being leached, the lower persistence of this herbicide
563 in fresh and aged BHO-amended soils reduced BS leaching, although only in soils under
564 conventional tillage irrespective of the irrigation regime implemented. Further research,
565 including the formation of possible metabolites in dissipation and leaching studies, is required
566 for a better understanding of how the environmental fate of BS is influenced by alternative
567 production systems using BHO amendment. Additionally, BS's weed control efficiency was
568 enhanced as a consequence of the transition from flooding to sprinkler irrigation, reflecting
569 the decrease in its sorption capacity and greater persistence. Also as a consequence of the
570 changes in the sorption-desorption and dissipation processes, BHO reduced BS's efficiency in
571 all the amended soils, although after aging this effect only persisted in soils subjected to
572 conventional flooding irrigation. Therefore, although alternative rice production systems
573 using sprinkler irrigation might increase the risk of water contamination by BS, amendment
574 with BHO can be an effective strategy to mitigate this risk under both flooding and sprinkler
575 irrigation but only with conventional tillage. However, BHO amendment might also greatly
576 reduce BS's weed control efficiency in soils under regardless of whether the system is

577 sprinkler irrigation or flooding, although after a time of aging this effect would only persist
578 for conventional flooding rice production.

579 **Acknowledgements**

580 This work was supported by Grant GR21038 and IB16075 funded by the Extremadura
581 Regional Government, Grant RTI2018-095461-B-I00 funded by MCIN/AEI/
582 10.13039/501100011033 and by “ERDF A way of making Europe”. Jaime Terrón Sánchez
583 and Carmen Martín are recipients of a grant from the Extremadura Regional Government’s
584 Consejería de Economía, Comercio e Innovación co-financing ESF A way of making Europe
585 (PD18025; PD18026). Luis Vicente and Damian Fernández are recipients of a grant-in-aid
586 promoting the hiring of research support staff, awarded by the Extremadura Regional
587 Government’s SEXPE co-financing ESF Investing in your future (TE-0042-18; TE-0055-19).

588 **References**

- 589 Abdel Ghani, S.B., Al-Rehiayani, S., El Agamy, M., Lucini, L., 2018. Effects of biochar
590 amendment on sorption, dissipation, and uptake of fenamiphos and cadusafos nematicides in
591 sandy soil. *Pest Manag. Sci.* 74 (11), 2652-2659. <https://doi.org/10.1002/ps.5075>
- 592 Arunrat, N., Pumijumnong, N., Sereenonchai, S., Chareonwong, U., Wang, C., 2020.
593 Assessment of climate change impact on rice yield and water footprint of large-scale and
594 individual farming in Thailand. *Sci. Total Environ.* 726, 137864.
595 <https://doi.org/10.1016/j.scitotenv.2020.137864>.
- 596 Asadi, H., Ghorbani, M., Rezaei-Rashti, M., Abrishamkesh, S., Amirahmadi, E., Chengrong,
597 C., Gorji, M., 2021. Application of Rice Husk Biochar for Achieving Sustainable Agriculture
598 and Environment. *Rice Sci.* 28 (4), 325-343. <https://doi.org/10.1016/j.rsci.2021.05.004>.
- 599 Cabrera, A., Cox, L., Velarde, P., Koskinen, W.C., Cornejo, J., 2007. Fate of diuron and
600 terbuthylazine in soils amended with two-phase olive oil mill waste. *J. Agr. Food Chem.* 55
601 (12), 4828-4834. <https://doi.org/10.1021/jf070525b>.
- 602 Cabrera, A., Cox, L., Spokas, K.A., Celis, R., Hermosín, M.C., Cornejo, J., Koskinen, W.C.,
603 2011. Comparative sorption and leaching study of the herbicides fluometuron and 4-chloro-2-
604 methylphenoxyacetic acid (MCPA) in a soil amended with biochars and other sorbents. *J.*
605 *Agr. Food Chem.* 59 (23), 12550-12560. <https://doi.org/10.1021/jf202713q>.
- 606 Cabrera, A., Cox, L., Spokas, K., Hermosín, M.C., Cornejo, J., Koskinen, W.C., 2014.
607 Influence of biochar amendments on the sorption-desorption of aminocyclopyrachlor,
608 bentazone and pyraclostrobin pesticides to an agricultural soil. *Sci. Total Environ.* 470-471,
609 438-443. <https://doi.org/10.1016/j.scitotenv.2013.09.080>.

- 610 Chirukuri, R., Atmakuru, R., 2015. Sorption characteristics and persistence of herbicide
611 bispyribac sodium in different global soils. *Chemosphere* 138, 16430, pp. 932-939.
612 <https://doi.org/10.1016/j.chemosphere.2014.12.029>
- 613 Fangueiro, D., Becerra, D., Albarrán, Á., Peña, D., Sanchez-Llerena, J., Rato-Nunes, J.M.,
614 López-Piñeiro, A., 2017. Effect of tillage and water management on GHG emissions from
615 Mediterranean rice growing ecosystems. *Atmos. Environ.* 150, 303-312.
616 <https://doi.org/10.1016/j.atmosenv.2016.11.020>.
- 617 Gámiz, B., Velarde, P., Spokas, K.A., Hermosín, M.C., Cox, L., 2017. Biochar Soil Additions
618 Affect Herbicide Fate: Importance of Application Timing and Feedstock Species. *J. Agr. Food*
619 *Chem.* 65 (15), 3109-3117. <https://doi.org/10.1021/acs.jafc.7b00458>
- 620 Gámiz, B., Velarde, P., Spokas, K.A., Celis, R., Cox, L., 2019. Changes in sorption and
621 bioavailability of herbicides in soil amended with fresh and aged biochar. *Geoderma* 337,
622 341-349. <https://doi.org/10.1016/j.geoderma.2018.09.033>.
- 623 Gámiz, B., López-Cabeza, R., Velarde, P., Spokas, K.A., Cox, L., 2021. Biochar changes the
624 bioavailability and bioefficacy of the allelochemical coumarin in agricultural soils. *Pest*
625 *Manag. Sci.* 77 (2), 834-843. <https://doi.org/10.1002/ps.6086>.
- 626 García, C., Hernandez, T., Costa, C., Ceccanti, B., Masciandaro, G., Ciardi, C., 1993. A study
627 of biochemical parameters of composted and fresh municipal wastes. *Bioresour. Technol.* 44
628 (1), 17-23. [https://doi.org/10.1016/0960-8524\(93\)90202-M](https://doi.org/10.1016/0960-8524(93)90202-M)
- 629 García-Jaramillo, M., Trippe, K.M., Helmus, R., Knicker, H.E., Cox, L., Hermosín, M.C.,
630 Parsons, J.R., Kalbitz, K., 2020. An examination of the role of biochar and biochar water-
631 extractable substances on the sorption of ionizable herbicides in rice paddy soils. *Sci. Total*
632 *Environ.* 706, 135682. <https://doi.org/10.1016/j.scitotenv.2019.135682>
- 633 Ghosh, D., Chethan, C.R., Chander, S., Kumar, B., Dubey, R.P., Bisen, H.S., Parey, S.K.,
634 Singh, P.K., 2021. Conservational Tillage and Weed Management Practices Enhance Farmers
635 Income and System Productivity of Rice–Wheat Cropping System in Central India. *Agr. Res.*
636 10 (3), 398-406. <https://doi.org/10.1007/s40003-020-00508-w>.
- 637 Gómez, S., Fernández, D., Peña, D., Albarrán, Á., López-Piñeiro, A., 2019. Behaviour of
638 bispyribac-sodium in aerobic and anaerobic rice-growing conditions with and without olive-
639 mill waste amendment. *Soil Till. Res.* 194, 104333. <https://doi.org/10.1016/j.still.2019.104333>.
- 640 Han, D., Yan, D., Cao, A., Fang, W., Liu, P., Li, Y., Ouyang, C., Wang, Q., 2017. Degradation
641 of dimethyl disulphide in soil with or without biochar amendment. *Pest Manag. Sci.* 73 (9),
642 1830-1836. <https://doi.org/10.1002/ps.4545>
- 643 Haque, A.N.A., Uddin, M.K., Sulaiman, M.F., Amin, A.M., Hossain, M., Aziz, A.A.,
644 Mosharrof, M., 2021. Impact of organic amendment with alternate wetting and drying
645 irrigation on rice yield, water use efficiency and physicochemical properties of soil.
646 *Agronomy*, 11 (8), 1529. <https://doi.org/10.3390/agronomy11081529>.
- 647 Hyun, S., Lee, L.S., Rao, P.S.C., 2003. Significance of anion exchange in pentachlorophenol
648 sorption by variable-charge soils. *J. Environ. Qual.* 32 (3), 966-976.
649 <https://doi.org/10.2134/jeq2003.9660>.
- 650 Kah, M., Brown, C.D., 2006. Adsorption of ionisable pesticides in soils. *Rev. Environ.*
651 *Contam. T.* 188, 149-217. https://doi.org/10.1007/978-0-387-32964-2_5.

- 652 Kalsi, N.K., Kaur, P., 2019. Dissipation of bispyribac sodium in aridisols: Impact of soil type,
653 moisture and temperature. *Ecotox. Environ. Safe.* 170, 375-382.
654 <https://doi.org/10.1016/j.ecoenv.2018.12.005>.
- 655 Kaur, P., Kaur, H., Kaur Kalsi, N., Bhullar, M.S., 2021. Evaluation of leaching potential of
656 penoxsulam and bispyribac sodium in Punjab soils under laboratory conditions. *Int. J.*
657 *Environ. An. Ch.* <https://doi.org/10.1080/03067319.2021.1970148>.
- 658 Kaur, P., Sharma, N., Kaur, K., 2022. Influence of pyrolysis temperature on rice straw biochar
659 properties and their effect on dynamic changes in bispyribac-sodium adsorption and leaching
660 behaviour. *Pedosphere.* 32 'in press'.
- 661 Khorram, M. S., Zhang, Q., Lin, D., Zheng, Y., Fang, H., Yu, Y., 2016. Biochar: A review of
662 its impact on pesticide behavior in soil environments and its potential applications. *J. Environ.*
663 *Sci-China* 44, 269-279. <https://doi.org/10.1016/j.jes.2015.12.027>.
- 664 Khorram, M.S., Sarmah, A.K., Yu, Y., 2018. The effects of biochar properties on fomesafen
665 adsorption-desorption capacity of biochar-amended soil. *Water Air Soil Poll.* 229 (3), 60, 1-
666 13. <https://doi.org/10.1007/s11270-017-3603-2>
- 667 Koide, R.T., Petprakob, K., Peoples, M., 2011. Quantitative analysis of biochar in field soil.
668 *Soil Biol. Biochem.* 43 (7), 1563-1568. <https://doi.org/10.1016/j.soilbio.2011.04.006>
- 669 Kookana, R.S., 2010. The role of biochar in modifying the environmental fate, bioavailability,
670 and efficacy of pesticides in soils: A review. *Aust. J. Soil Res.* 48 (6-7), 627-637.
671 <https://doi.org/10.1071/SR10007>.
- 672 Kumar, U., Behera, S., Saha, S., Das, D., Guru, P.K., Kaviraj, M., Munda, S., Adak, T.,
673 Nayak, A.K., 2020. Non-target effect of bispyribac sodium on soil microbial community in
674 paddy soil. *Ecotox. Environ. Safe.* 189, 110019.
675 <https://doi.org/10.1016/j.ecoenv.2019.110019>.
- 676 Li, S., Ma, Q., Zhou, C., Yu, W., Shangguan, Z., 2021. Applying biochar under topsoil
677 facilitates soil carbon sequestration: A case study in a dryland agricultural system on the
678 Loess Plateau. *Geoderma* 403, 115186. <https://doi.org/10.1016/j.geoderma.2021.115186>.
- 679 Liao, X., Kang, H., Haidar, G., Wang, W., Malghani, S., 2022. The impact of biochar on the
680 activities of soil nutrients acquisition enzymes is potentially controlled by the pyrolysis
681 temperature: A meta-analysis. *Geoderma* 411, 115692.
682 <https://doi.org/10.1016/j.geoderma.2021.115692>.
- 683 López-Piñeiro, A., Peña, D., Albarrán, A., Becerra, D., Sánchez-Llerena, J., 2013. Sorption,
684 leaching and persistence of metribuzin in Mediterranean soils amended with olive mill waste
685 of different degrees of organic matter maturity. *J. Environ. Manage.* 122, 76-84.
686 <https://doi.org/10.1016/j.jenvman.2013.03.006>.
- 687 López-Piñeiro, A., Peña, D., Albarrán, T., Sánchez-Llerena, J., Becerra, D., 2014. Long-term
688 effects of olive mill waste amendment on the leaching of herbicides through undisturbed soil
689 columns and mobility under field conditions. *Soil Till. Res.* 144, 195-204.
690 <https://doi.org/10.1016/j.still.2014.08.001>
- 691 López-Piñeiro, A., Sánchez-Llerena, J., Peña, D., Albarrán, Á., Ramírez, M., 2016. Transition
692 from flooding to sprinkler irrigation in Mediterranean rice growing ecosystems: Effect on
693 behaviour of bispyribac sodium. *Agr. Ecosyst. Environ.* 223, 99-107.
694 <https://doi.org/10.1016/j.agee.2016.03.003>

695 López-Piñeiro, A., Sánchez-Terrón, J., Martín-Franco, C., Peña, D., Vicente, L.A., Gómez, S.,
696 Fernández-Rodríguez, D., Albarrán, Á., 2022. Impacts of fresh and aged holm-oak biochar on
697 clomazone behaviour in rice cropping soils after transition to sprinkler irrigation. *Geoderma*,
698 413, 115768. <https://doi.org/10.1016/j.geoderma.2022.115768>.

699 MAPA (Ministerio de Agricultura, Pesca y Alimentación), 2019. Cultivos herbáceos e
700 industriales: el arroz. [https://www.mapa.gob.es/es/agricultura/temas/producciones-](https://www.mapa.gob.es/es/agricultura/temas/producciones-agricolas/cultivos-herbaceos/arroz/)
701 [agricolas/cultivos-herbaceos/arroz/](https://www.mapa.gob.es/es/agricultura/temas/producciones-agricolas/cultivos-herbaceos/arroz/) (accessed 4 february 2022).

702 Martin, S.M., Kookana, R.S., Van Zwieten, L., Krull, E., 2012. Marked changes in herbicide
703 sorption-desorption upon ageing of biochars in soil. *J. Hazard. Mater.* 231-232, 70-78.
704 <https://doi.org/10.1016/j.jhazmat.2012.06.040>

705 Mascanzoni, E., Perego, A., Marchi, N., Scarabel, L., Panozzo, S., Ferrero, A., Acutis, M.,
706 Sattin, M., 2018. Epidemiology and agronomic predictors of herbicide resistance in rice at a
707 large scale. *Agron. Sustain. Dev.* 38 (6), 68. <https://doi.org/10.1007/s13593-018-0548-9>.

708 Mendes, K.F., Hall, K.E., Takeshita, V., Rossi, M.L., Tornisielo, V.L., 2018. Animal bonechar
709 increases sorption and decreases leaching potential of aminocyclopyrachlor and mesotrione in
710 a tropical soil. *Geoderma* 316, 11-18. <https://doi.org/10.1016/j.geoderma.2017.12.017>.

711 Mendes, K.F., Olivatto, G.P., de Sousa, R.N., Junqueira, L.V., Tornisielo, V.L., 2019. Natural
712 biochar effect on sorption–desorption and mobility of diclosulam and pendimethalin in soil.
713 *Geoderma* 347, 118-125. <https://doi.org/10.1016/j.geoderma.2019.03.038>.

714 Méndez, A., Terradillos, M., Gascó, G., 2013. Physicochemical and agronomic properties of
715 biochar from sewage sludge pyrolysed at different temperatures. *J. Anal. Appl. Pyrol.* 102,
716 124-130. <https://doi.org/10.1016/j.jaap.2013.03.006>.

717 Mohammed, U., Aimrun, W., Amin, M.S.M., Khalina, A., Zubairu, U.B., 2016. Influence of
718 soil cover on moisture content and weed suppression under system of rice intensification
719 (SRI). *Paddy Water Environ.* 14 (1), 159-167. <https://doi.org/10.1007/s10333-015-0487-x>.

720 Muñoz, A., López-Piñeiro, A., Ramírez, M., 2007. Soil quality attributes of conservation
721 management regimes in a semi-arid region of south western Spain. *Soil Till. Res.* 95 (1-2),
722 255-265. <https://doi.org/10.1016/j.still.2007.01.009>.

723 Oleszczuk, P., Joško, I., Futa, B., Pasiieczna-Patkowska, S., Pałys, E., Kraska, P., 2014. Effect
724 of pesticides on microorganisms, enzymatic activity and plant in biochar-amended soil.
725 *Geoderma* 214-215, 10-18. <https://doi.org/10.1016/j.geoderma.2013.10.010>.

726 Ogura, A.P., Lima, J.Z., Marques, J.P., Massaro Sousa, L., Rodrigues, V.G.S., Espíndola,
727 E.L.G., 2021. A review of pesticides sorption in biochar from maize, rice, and wheat residues:
728 Current status and challenges for soil application. *J. Environ. Manage.* 300, 113753.
729 <https://doi.org/10.1016/j.jenvman.2021.113753>.

730 Peng, S., Bouman, B., Visperas, R.M., Castañeda, A., Nie, L., Park, H.-K., 2006. Comparison
731 between aerobic and flooded rice in the tropics: Agronomic performance in an eight-season
732 experiment. *Field Crop. Res.* 96 (2-3), 252-259. <https://doi.org/10.1016/j.fcr.2005.07.007>.

733 Peña, D., López-Piñeiro, A., Albarrán, Á., Becerra, D., Sánchez-Llerena, J., 2015.
734 Environmental fate of the herbicide MCPA in agricultural soils amended with fresh and aged
735 de-oiled two-phase olive mill waste. *Environ. Sci. Pollut. R.* 22 (18), 13915-13925.
736 <https://doi.org/10.1007/s11356-015-4622-4>.

- 737 Pradhan, D., Singh, R.K., Verma, S.K., 2020. Genotoxic Potential Assessment of the
738 Herbicide Bispyribac-Sodium in a Fresh Water Fish *Clarias batrachus* (Linn.). *B. Environ.*
739 *Contam. Tox.* 105 (5), 715-720. <https://doi.org/10.1007/s00128-020-03003-8>.
- 740 Sánchez-Llerena, J., López-Piñeiro, A., Albarrán, Á., Peña, D., Becerra, D., Rato-Nunes, J.M.,
741 2016. Short and long-term effects of different irrigation and tillage systems on soil properties
742 and rice productivity under Mediterranean conditions. *Eur. J. Agron.* 77, 101-110.
743 <https://doi.org/10.1016/j.eja.2016.04.005>.
- 744 Sharma, N., Kaur, P., Jain, D., Bhullar, M.S., 2020. In-vitro evaluation of rice straw biochars'
745 effect on bispyribac-sodium dissipation and microbial activity in soil. *Ecotox. Environ. Safe.*
746 191, 110204. <https://doi.org/10.1016/j.ecoenv.2020.110204>.
- 747 Si, Y., Wang, M., Tian, C., Zhou, J., Zhou, D., 2011. Effect of charcoal amendment on
748 adsorption, leaching and degradation of isoproturon in soils. *J. Contam. Hydrol.* 123 (1-2),
749 75-81. <https://doi.org/10.1016/j.jconhyd.2010.12.008>
- 750 Siedt, M., Schäffer, A., Smith, K.E.C., Nabel, M., Roß-Nickoll, M., van Dongen, J.T., 2021.
751 Comparing straw, compost, and biochar regarding their suitability as agricultural soil
752 amendments to affect soil structure, nutrient leaching, microbial communities, and the fate of
753 pesticides. *Sci. Total Environ.* 751, 141607. <https://doi.org/10.1016/j.scitotenv.2020.141607>
- 754 Singh, M., Bhullar, M.S., Gill, G., 2018. Integrated weed management in dry-seeded rice
755 using stale seedbeds and post sowing herbicides. *Field Crop. Res.* 224, 182-191.
756 <https://doi.org/10.1016/j.fcr.2018.03.002>.
- 757 Singh, N., Singh, S.B., 2015. Adsorption and leaching behaviour of bispyribac-sodium in
758 soils. *B. Environ. Contam. Tox.* 94 (1), 125-128. <https://doi.org/10.1007/s00128-014-1420-5>.
- 759 Spanu, A., Langasco, I., Serra, M., Deroma, M.A., Spano, N., Barracu, F., Pilo, M.I., Sanna,
760 G., 2021. Sprinkler irrigation in the production of safe rice by soils heavily polluted by
761 arsenic and cadmium. *Chemosphere* 277, 130351.
762 <https://doi.org/10.1016/j.chemosphere.2021.130351>.
- 763 Stenert C, De Mello ICMF, Pires MM, Knauth DS, Katayama N and Maltchik L, 2018.
764 Responses of macroinvertebrate communities to pesticide application in irrigated rice fields.
765 *Environ. Monit. Assess.* 190:74. <https://doi.org/10.1007/s10661-017-6425-1>.
- 766 Sun, H., Zhang, H., Min, J., Feng, Y., Shi, W., 2016. Controlled-release fertilizer, floating
767 duckweed, and biochar affect ammonia volatilization and nitrous oxide emission from rice
768 paddy fields irrigated with nitrogen-rich wastewater. *Paddy Water Environ.* 14 (1), 105-111.
769 <https://doi.org/10.1007/s10333-015-0482-2>.
- 770 Takaya, C.A., Fletcher, L.A., Singh, S., Anyikude, K.U., Ross, A.B., 2016. Phosphate and
771 ammonium sorption capacity of biochar and hydrochar from different wastes. *Chemosphere*
772 145, 518-527. <https://doi.org/10.1016/j.chemosphere.2015.11.052>.
- 773 Thammasom, N., Vityakon, P., Lawongsa, P., Saenjan, P., 2016. Biochar and rice straw have
774 different effects on soil productivity, greenhouse gas emission and carbon sequestration in
775 Northeast Thailand paddy soil. *Agriculture and Natural Resources* 50 (3), 192-198.
776 <https://doi.org/10.1016/j.anres.2016.01.003>.
- 777 Trigo, C., Cox, L., Spokas, K., 2016. Influence of pyrolysis temperature and hardwood species
778 on resulting biochar properties and their effect on azimsulfuron sorption as compared to other
779 sorbents. *Sci Total Environ* 566, 1454-1464. <https://doi.org/10.1016/j.scito tenv.2016.06.027>

- 780 Vieira, D.C., Noldin, J.A., Deschamps, F.C., Resgalla, C., 2016. Ecological risk analysis of
781 pesticides used on irrigated rice crops in southern Brazil. *Chemosphere* 162, 48-54.
782 <https://doi.org/10.1016/j.chemosphere.2016.07.046>.
- 783 Wong, J.T.F., Chen, Z., Wong, A.Y.Y., Ng, C.W.W., Wong, M.H., 2018. Effects of biochar on
784 hydraulic conductivity of compacted kaolin clay. *Environ. Pollut.* 234, 468-472.
785 <https://doi.org/10.1016/j.envpol.2017.11.079>.
- 786 Yang, S., Xiao, Y., Sun, X., Ding, J., Jiang, Z., Xu, J., 2019. Biochar improved rice yield and
787 mitigated CH₄ and N₂O emissions from paddy field under controlled irrigation in the Taihu
788 Lake Region of China. *Atmos. Environ.* 200, 69-77.
789 <https://doi.org/10.1016/j.atmosenv.2018.12.003>.
- 790 Yavari, S., Malakahmad, A., Sapari, N.B., 2015. Biochar efficiency in pesticides sorption as a
791 function of production variables-a review. *Environ. Sci. Pollut. R.* 22 (18), 13824-13841.
792 <https://doi.org/10.1007/s11356-015-5114-2>.
- 793

794 **Table 1**
 795 Selected properties of the fresh and aged biochar.

	Fresh	Aged SNT-BHO	Aged ST-BHO	Aged FT-BHO
TC (%)	77.1c	74.1a	74.0a	75.2b
TH (%)	3.61c	3.22b	3.22b	3.18a
TN (%)	0.470a	0.690c	0.690c	0.520b
TO* (%)	18.8a	22.0c	22.1c	21.1b
Ash (%)	9.94a	10.9a	13.8b	15.7c
H/C (molar ratio)	0.562c	0.521b	0.522b	0.507a
O/C (molar ratio)	0.183a	0.223c	0.224c	0.210b
pH	9.08d	6.78c	6.21a	6.38b
EC (dS m ⁻¹)	3.54d	0.603c	0.373a	0.457b
WSOC (mg kg ⁻¹)	368c	273b	261ab	258a
SSA (m ² g ⁻¹)	17.4a	20.0b	52.7c	67.1d

796 The data for total carbon (TC), total hydrogen (TH), total nitrogen (TN), total oxygen (TO),
 797 electrical conductivity (EC), water-soluble organic carbon (WSOC), and specific surface are
 798 (SSA) are mean values. *TO calculated assuming < 1% of S without ash content. Values with
 799 the same letter within a row are not significantly different at the p< 0.05 level of probability
 800

801 **Table 2**
 802 Effect of different management regimes on bispyribac-sodium sorption–desorption
 803 parameters.

		n_f	K_f	R^2 sor	% D [†]	R^2 des
2018						
	SNT	0.848aA	0.494aA	0.982	30.6cA	0.988
	SNT-BHO	0.910abA	0.456aA	0.972	5.92aA	0.949
	ST	0.909abA	0.562bA	0.984	20.9bA	0.999
	ST-BHO	0.917abA	0.453aA	0.995	7.97aA	0.991
	FT	0.929bA	1.09dB	0.991	41.1dA	0.990
	FT-BHO	0.916abA	0.672cA	0.983	13.6abA	0.904
2019						
	SNT	0.865abA	0.598aB	0.996	25.8bA	0.915
	SNT-BHO	0.832aA	0.649bB	0.998	21.1aB	0.974
	ST	0.892bcA	0.583aB	0.997	30.5cA	0.786
	ST-BHO	0.869abA	0.652bB	0.995	22.3aB	0.885
	FT	0.889bcA	0.929dA	0.997	43.5dA	0.996
	FT-BHO	0.933cA	0.708cA	0.998	31.4cB	0.966
Y	F-values	2.69NS	80.4***	-	59.4***	-
M	F-values	9.16*	356***	-	54.8***	-
Y x M	F-values	3.44*	46.7***	-	14.1***	-

804 ANOVA factors are: Y, year; M, management regime; Y × M, interaction
 805 year × management regime; F-values indicate the significance levels * $p < 0.05$,
 806 ** $p < 0.01$, and *** $p < 0.001$, respectively, and NS: not significant. Different
 807 letters indicate significant differences ($p < 0.05$) between management regimes
 808 in the same year (lower case letters) and between years within the same
 809 management regime (upper case letters).

810 [†]The percentage of D was calculated after three cycles of desorption.

811

812 **Table 3**
 813 Effect of different management regimes on dehydrogenase activity and bispyribac-sodium
 814 dissipation parameters.

		$t_{1/2\ 80\%}$ (days)	$R^2_{80\%}$	$t_{1/2\ 1:1.25}$ (days)	$R^2_{1:1.25}$	DHAT _{80%} ($\mu\text{g INTF g}^{-1}\text{ h}^{-1}$)	DHAT _{1:1.25}} ($\mu\text{g INTF g}^{-1}\text{ h}^{-1}$)
2018							
	SNT	60.6dA	0.871	75.0cA	0.950	6.35bA	6.61bA
	SNT-BHO	38.1bA	0.940	63.8bA	0.931	7.35cA	9.91cA
	ST	59.5dA	0.934	86.6dA	0.855	4.49aA	5.00aA
	ST-BHO	49.8cA	0.935	76.9cA	0.769	6.12bA	6.59bA
	FT	31.9aA	0.961	34.4aA	0.955	6.05bA	10.5cA
	FT-BHO	48.4cA	0.944	31.3aA	0.899	10.1dA	30.2dA
2019							
	SNT	86.4cB	0.954	105dB	0.945	7.62bA	10.6bA
	SNT-BHO	48.6aB	0.992	85.9cB	0.931	12.3dB	16.8cB
	ST	67.7bB	0.992	129eB	0.955	4.96aB	7.50aB
	ST-BHO	50.4aA	0.982	79.9cA	0.897	7.49bA	10.8bB
	FT	49.4aB	0.979	46.6bB	0.914	9.86cB	30.2dA
	FT-BHO	66.3bB	0.967	36.4aB	0.959	12.0dA	33.6cB
Y	F-values	492***	-	142***	-	386***	2404***
M	F-values	252***	-	187***	-	188***	1315***
Y x M	F-values	35.5***	-	14.5***	-	58.8***	673***

815 Half-lives: $t_{1/2\ 80\%}$ in soils at 80% field water capacity; $t_{1/2\ 1:1.25}$ in soils with 1:1.25 (w/v)
 816 (soil/water) moisture content. DHAT, total dehydrogenase activity considering all the
 817 incubation times in soils conditioned to 80% field capacity and 1:1.25 (w/v) (soil/water)
 818 moisture content. The data presented are mean values. ANOVA factors are: Y, year; M,
 819 management regime; Y x M, interaction year x management regime; F-values indicate the
 820 significance levels * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$, respectively, and NS: not
 821 significant. Different letters indicate significant differences ($p < 0.05$) between management
 822 regimes in the same year (lowercase letters) and between years within the same management
 823 regime (uppercase letters).
 824

825 **Table 4**

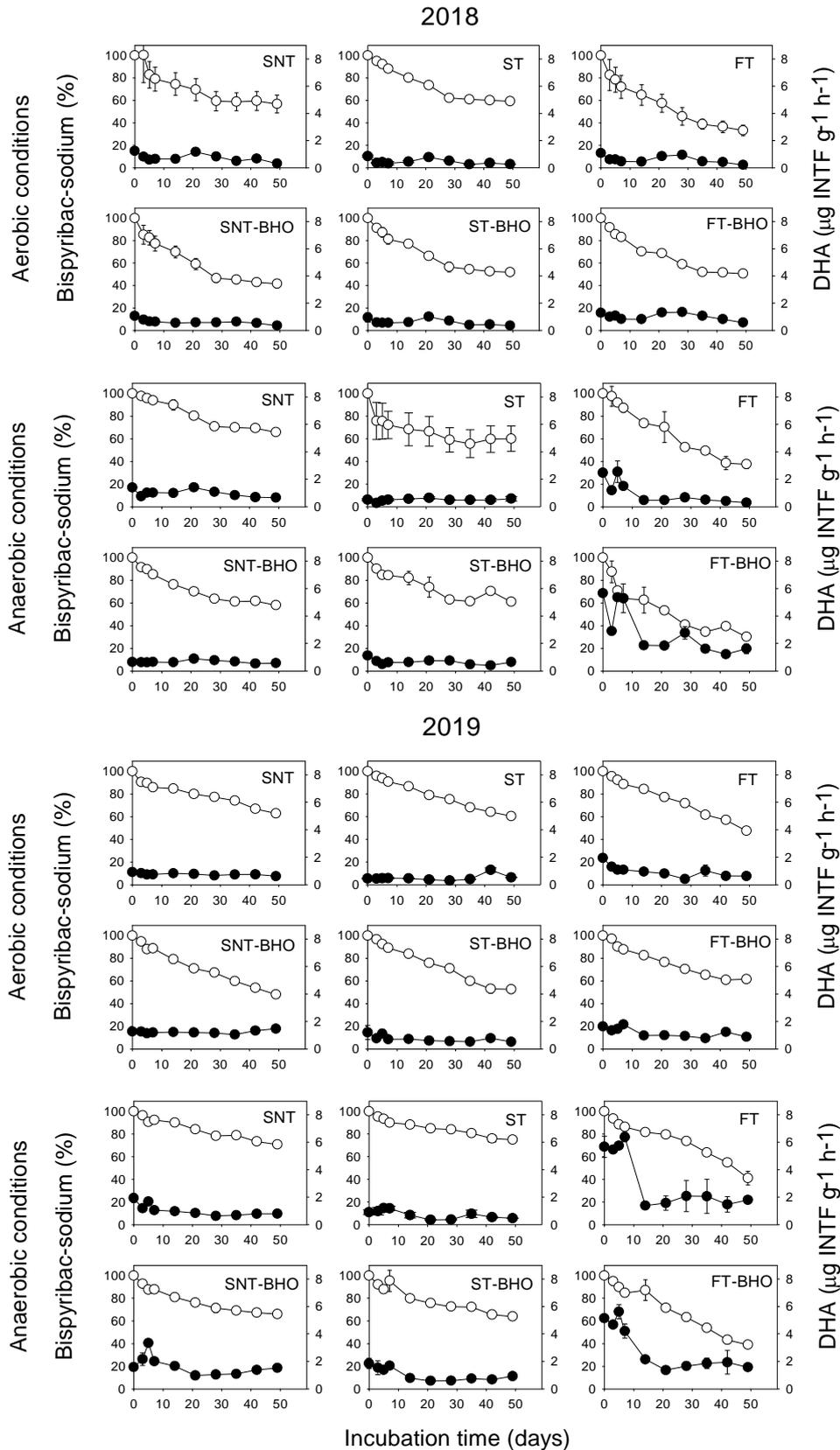
826 Effect of different management regimes on bispyribac-sodium leaching parameters.

		Initial Pore volume [†]	Max. Concentration leached (μ M)	Total leached (%)	Total extracted (%)	Not recovered (%)
2018						
	SNT	0.768bB	1.35cA	57.4dA	5.60aA	37.0aA
	SNT-BHO	0.417aA	0.699abA	54.4dA	2.81aA	42.8aB
	ST	1.16cB	1.03bcA	58.3dA	7.42aA	34.3aB
	ST-BHO	0.770bA	0.967abcA	50.1cA	4.01aA	45.9bB
	FT	1.14cB	0.837abA	44.6bA	1.46aA	53.9cB
	FT-BHO	0.744bB	0.571aA	38.3aA	2.51aA	59.2cB
2019						
	SNT	0.357aA	0.991aA	62.2cA	12.6aA	25.2aA
	SNT-BHO	0.675bB	1.09aA	62.1cB	7.24aA	30.6aA
	ST	0.690bA	1.05aA	70.4dB	7.64aA	22.0aA
	ST-BHO	0.667bA	0.998aA	63.6cB	4.99aA	31.4aA
	FT	0.657bA	0.955aA	58.1bB	4.92aA	37.0abA
	FT-BHO	0.343aA	0.850aA	50.3aB	6.13aA	43.5bA
Y	F-values	523***	0.778NS	251***	0.969NS	55.1***
M	F-values	162***	3.80*	85.9***	1.17NS	18.6***
Y x M	F-values	103***	1.33NS	4.64*	1.20NS	1.37NS

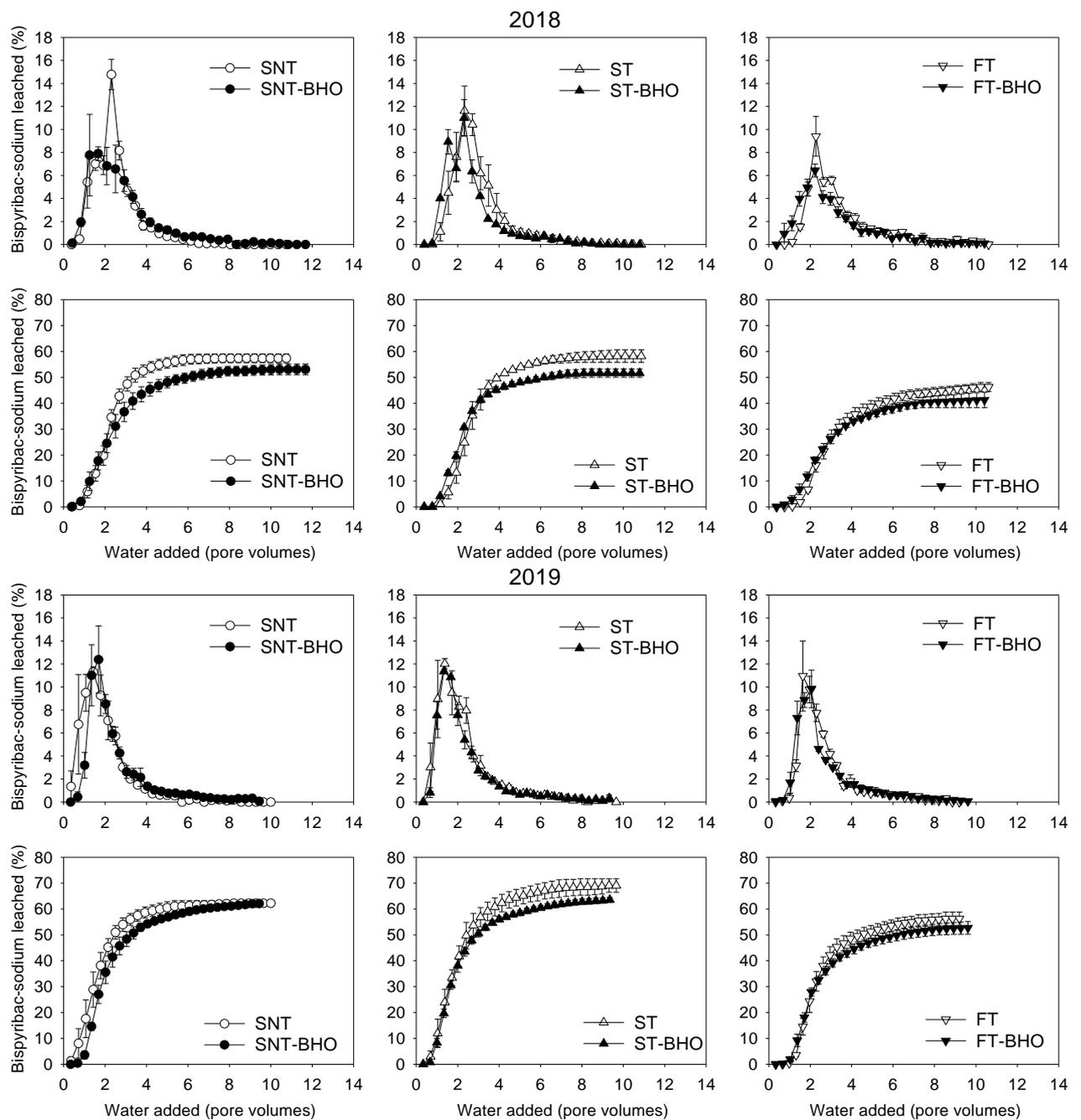
827 The ANOVA factors are: Y, year; M, management regime; Y \times M, interaction year \times
828 management regime; F-values indicate the significance levels * p < 0.05, ** p < 0.01, and
829 *** p < 0.001, respectively, and NS: not significant. Different letters indicate significant
830 differences (p < 0.05) between management regimes in the same year (lowercase letters) and
831 between years within the same management regime (uppercase letters).

832 [†]Pore volume for initiation of the herbicide's leaching.

833

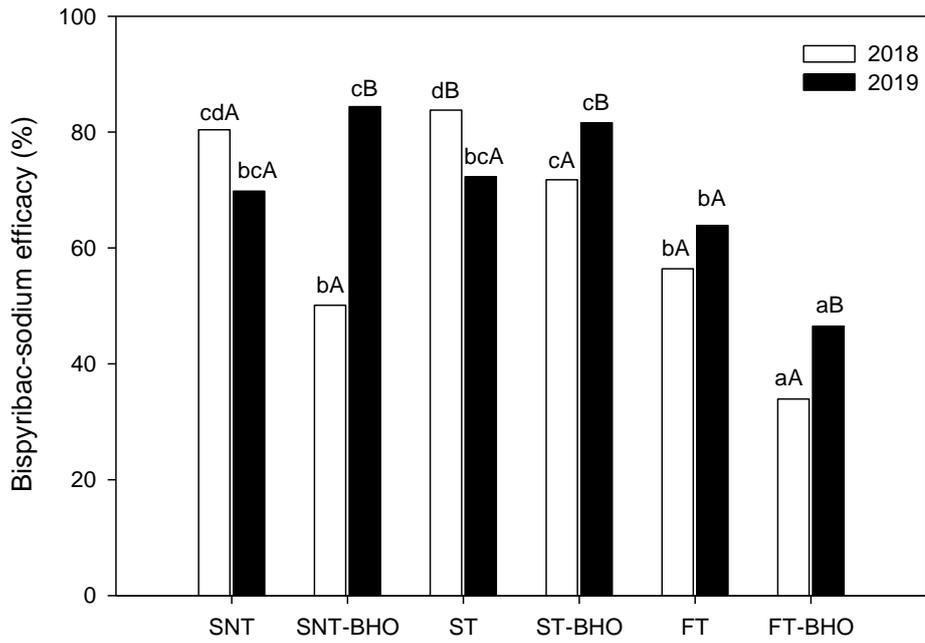


834
 835 **Fig. 1.** Effect of different management regimes on dehydrogenase activity (●) and bispyribac-
 836 sodium dissipation (○). Vertical bars representing one standard error of the mean were smaller
 837 than the symbols in most cases. Treatments are: no-tillage and sprinkler irrigation without
 838 (SNT) or with biochar application (SNT-BHO); conventional tillage and sprinkler irrigation
 839 without (ST) or with biochar application (ST-BHO); continuous flooding irrigation and tillage
 840 without (FT) or with biochar application (FT-BHO).



841
842
843
844
845
846
847
848

Fig. 2. Effect of different management regimes on the relative (above) and cumulative (below) breakthrough curves of bispyribac-sodium. Vertical bars represent one standard error of the mean. Treatments are: no-tillage and sprinkler irrigation without (SNT) or with biochar application (SNT-BHO); conventional tillage and sprinkler irrigation without (ST) or with biochar application (ST-BHO); continuous flooding irrigation and tillage without (FT) or with biochar application (FT-BHO).



849 **Fig. 3.** Effect of different management regimes on bispyribac-sodium efficiency against
 850 *Echinochloa crus-galli* L. Beauv. Treatments are: sprinkler irrigation and no-tillage without
 851 (SNT) or with biochar application (SNT-BHO); sprinkler irrigation and conventional tillage
 852 without (ST) or with biochar application (ST-BHO); traditional flooding irrigation and tillage
 853 without (FT) or with biochar application (FT-BHO).
 854
 855
 856