Potential of fluorescent tracers to appraise biochar amendment strategies for pesticide mitigation - insights from comparative sorption

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1 **Potential of fluorescent tracers to appraise biochar amendment strategies for pesticide**
2 **mitigation – insights from comparative sorption**

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8

9 **Abstract**: Mitigation of pesticides dispersion in soil and water is required to protect ecosystem
10 health and the anthropic uses of water bodies. Biochar amendments have been suggested to reduce
11 pesticide dispersion due to their high sorption potentials. Nevertheless, appraisals at different scales
12 have been limited by the costs of pesticide analyses. The aim of this study was to evaluate the
13 potential of two fluorescent tracers, uranine (UR) and sulforhodamine B (SRB) for use as pesticide
14 proxies in the context of biochar amendments used for mitigation purposes. Therefore, we compared
15 the sorption processes of both fluorescent tracers and those of three pesticides, glyphosate, 2,4-D
16 and difenoconazole for soils, three wood biochars (pine, oak & beech/charm blend) and soil/biochar
17 mixtures representing agricultural usages. The results showed that the sorption of glyphosate by soil
18 was unaffected by amendment with the tested pine, oak and wood blend biochars. In contrast, the
19 sorption coefficients of UR, SRB, 2,4-D and difenoconazole were significantly increased with these
20 biochar amendments. SRB, in particular, exhibited sorption behavior similar to that of the
21 hydrophobic fungicide difenoconazole. This indicate promise for the use of SRB as a proxy for
22 hydrophobic pesticides, in testing biochar amendments.

23 **Keywords:** *Biochar; Fluorescent dyes; Pesticides; Best management practices; Sorption; Pollution;*
24 *Water quality*

25

26 **Introduction**

27

28 Dispersion of pesticides applied on fields to protect the crops from pests and weeds threatens the
29 health of nearby ecosystems and the human use of water bodies (Tang et al., 2012). Contamination
30 of groundwater, freshwater and terrestrial ecosystems by pesticides is a worldwide phenomenon
31 (Sharma et al., 2019; Tang et al., 2021). To limit the risks to humans and the ecosystems, best
32 management practices (BMPs) are encouraged in agricultural policies (Dosskey et al., 2010;
33 Martinho, 2019; Reichenberger et al., 2007). The use of traditional BMPs for pesticide mitigation is
34 currently being criticized due to maintenance costs and to the high ecological value of these

vegetated buffer zones as corridors and shelters for biodiversity (Dollinger et al., 2015a; Dosskey, 2001; Leenhardt et al., 2022). Amendment of crop soils with treated organic wastes provides an alternative strategy for mitigating pesticide dispersion, and it has additional benefits for crop production (plant nutrition, soil quality), climate change mitigation and waste disposal (Briceño et al., 2007; Houot et al., 2014).

Biochar has been praised among a range of possible amendments due to the high sorption affinity of many pesticides for this material (Liu et al., 2018; Safaei Khorram et al., 2016; Yavari et al., 2015), and its utility in crop production and carbon sequestration (Ding et al., 2017; Lévesque et al., 2022; Siedt et al., 2021). Biochars are carbon-rich materials obtained by the pyrolysis of organic materials under oxygen-limited atmospheres. Depending on the feedstock, pyrolysis temperature and duration, biochars can develop contrasting physico-chemical properties (specific surface area, porosity, surface functional groups, pH, CEC etc.) that modulate their efficiencies for pesticide retention (Dai et al., 2019; Khorram et al., 2018; Liu et al., 2018; Yavari et al., 2015). Biochar ageing after amendment might modify these properties and the sorption affinities of pesticides for these materials (Martin et al., 2012).

The literature contains many studies of pesticide sorption on fresh biochar. However, field scale appraisals of biochar amendment strategies that integrate the long term effects of ageing on pesticide release are lacking (Ding et al., 2017; Safaei Khorram et al., 2016). These evaluations are particularly limited by the high cost of pesticide analyses. Therefore, the use of fluorescent tracers as proxies for pesticides to upscale the evaluation of this mitigation strategy could be a cost-effective alternative.

Fluorescent dyes such as uranine (UR) and sulforhodamine B (SRB) were historically used as hydrological tracers to characterize surface and subsurface water flows (Flury and Wai, 2003). In the past decade, research on their sorption, photolytic and degradation properties showed that they could be used as proxies for pesticides when evaluating mitigation strategies such as constructed wetlands, ponds or engineered ditches (Bork et al., 2020; Dollinger et al., 2017; Fernández-Pascual et al., 2019; Lange et al., 2011; Ulrich et al., 2019). Behavior similar to those of moderately hydrophobic herbicides was observed in the aforementioned infrastructures (Durst et al., 2013; Lange et al., 2011; Maillard et al., 2016; Ulrich et al., 2019). To use the fluorescent tracers as proxies for pesticides while studying their dispersion in soils and amended soils, the sorption coefficients of the tracers and targeted pesticides must be similar (Bork et al., 2020; Dollinger et al., 2017). Indeed, sorption is the prime process regulating the dispersion of organic contaminants (Wauchope et al., 2002).

67 Few studies have investigated the dependence of linear adsorption coefficients (Kd) on soil
68 properties and compared the Kd values to those for a range of herbicides. Those studies reported
69 that the range of soil Kd values for UR were equivalent to those of moderately hydrophobic
70 herbicides (metolachlor, diuron and isoproturon). Kd was, likewise, positively correlated with the
71 organic carbon (OC) content and negatively correlated with the pH of the soil (Bork et al., 2020;
72 Dollinger et al., 2017; Sabatini, 2000). In contrast, the Kd values for SRB with soil and sediments are
73 high, comparable to those of glyphosate, and positively correlated with the clay content and
74 negatively correlated with OC content (Bork et al., 2020; Dollinger et al., 2017). For materials rich in
75 organic matter such as litters, the Kd values of both tracers (UR and SRB) are high and similar to
76 those of hydrophobic herbicides but different from those of glyphosate. To our knowledge, there are
77 no data for sorption of fluorescent tracers on biochar.

78 The study was designed to determine whether the fluorescent tracers SRB and UR could be used as
79 proxies for pesticides in designing optimal biochar amendment strategies to improve agricultural
80 water quality. Therefore, we hypothesized that similar sorption coefficients for the tracers and the
81 tested pesticides with soils, biochars and soil/biochar mixtures would result in similar dispersion
82 behaviours at the field scale.

83 Three pesticides that are extensively used worldwide for a wide range of crops including cereals,
84 orchards and vineyards, were selected for this study. These pesticides are: glyphosate, a hydrophilic
85 broad-spectrum postemergence herbicide; 2,4-D, a hydrophilic selective postemergence herbicide;
86 and difenoconazole, a hydrophobic systemic fungicide. In addition to their extensive usage and their
87 threats to human and ecosystem health (PPDB, 2022), these molecules were selected for their
88 contrasting hydrophobicities and water solubilities in order to cover a range of potential behaviours.

89

90

91 **2. Material and Methods**

92

93 **2.1. Chemicals**

94 The main physico-chemical properties of the tracers and pesticides used herein are displayed in Table
95 1. UR is hydrophobic and exhibits high aqueous solubility. It is negatively charged above pH 8.7. In
96 contrast, SRB is more hydrophilic and its solubility is greater than that of UR. SRB is a zwitterion at
97 environmental pH ranges. Both SRB and UR were supplied by FluotechniK (Cavaillon, France).

98   Glyphosate has a very high aqueous solubility and is a zwitterion at pH 10.2. 2,4-D also has a very

99   high aqueous solubility but is negatively charged at environmental pHs. Difenoconazole has low

100   aqueous solubility and is uncharged at environmental pHs. Nonlabelled glyphosate, 2,4-D and

101   difenoconazole were supplied by Merck (France) and 14C-labelled pesticides were supplied by

102   ISOBIO (Fleurus, Belgium).

103   Sodium azide and calcium chloride were supplied by Merck. All chemicals used were analytical grade.

104   *Table 1 could be inserted here*

105

106   **2.2. Origin of the soils, biochars and activated carbon**

107   *2.2.1 Provenance of the biochars*

108   The studied biochars were derived from oak wood (OB), pine wood (PB), and a blend of oak, beech

109   and charm wood named Gyé Biochar (GB). They were supplied by the Carbonex Company (Gyé-sur-

110   Seine, France). Pyrolyses were performed at a temperature of 456 °C for 14 hours. To compare these

111   biochars to a universal sorbent medium commonly used for water treatment, we included an

112   activated carbon (AquaSorbTM 2000) derived from pyrolyzed mine coal.

113

114   *2.2.2 Soil sampling*

115   Two soils were sampled in a vineyard area located in Roujan, in the south of France (Molénat et al.,

116   2018). Both are calcareous loamy soils classified as gleyic cambisol (IUSS Working Group WRB, 2014).

117   The main difference between the two soils lies in their organic matter contents (Table 2).

118   *Table 2 could be inserted here*

119

120   **2.3. Characterization of the soils and biochars**

121   *2.3.1 Determination of physico-chemical properties*

122   The values of pH, CEC, CHN and OC of the biochars and the activated carbon are presented in Table 2

123   and were performed by the US 49 laboratory of Cirad (Montpellier, France). The physico-chemical

124   properties of the soils reported in Table 2 were determined at the LAS laboratory of INRAE (Arras,

125   France). The specific surface areas of both soils and the biochars were determined by the European

126 Membranes Institute (IEMM) (Montpellier, France) with the BET method and a Micromeritics-

127 Analyser ASAP 202.

128

129 ### 2.3.2 Determination of surface functional groups with mid-infrared spectroscopy

130 To determine the superficial chemical compositions of the solid matrices and especially the

131 functional groups, all solid materials were analysed by Fourier Transform Infrared Spectrometry

132 (FTIR) with a MIRS Thermo Nicolet 6700 (Thermo Fischer Scientific, Madison, WI, USA). The matrices

133 were ground and sieved at 200 μm. They were dried at 40 °C just before the analyses performed with

134 a diffuse reflectance cell over the range 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

135

136 ## 2.4. Determination of sorption coefficients

137 ### 2.4.1 Adsorption isotherms

138 Adsorption isotherms were generated for each of the raw materials (biochars, activated carbon and

139 soils) and the selected molecules (glyphosate, 2,4-D & difenoconazole). The adsorption batch

140 procedure was designed while following OECD guideline n°106 (OECD, 2000). 14C-labelled

141 glyphosate, 2,4-D and difenoconazole were used for the experiments. The concentrations of the

142 difenoconazole and 2,4-D solutions were 5, 10, 50, 100 and 1000 μg/L and they were 20, 100, 200,

143 500 and 1000 μg/L for the glyphosate solutions. A solution containing 100% labelled pesticide was

144 used for the three lowest concentrations and a solution of 50% labelled/nonlabelled pesticide was

145 used for the two highest concentrations to optimize quantification via liquid scintillation (LSC). The

146 concentrations of the SRB solutions were 50, 75, 100, 500 and 1000 μg/L, and those of UR were 25,

147 37.5, 50, 250, and 500 μg/L. The background electrolyte comprised of 0.01 M $CaCl_2$ plus 200 mg/L

148 NaN_3 except for the glyphosate study for which the background electrolyte contained only NaN_3 to

149 avoid an artificial increase in sorption via cation bridging (Dollinger et al., 2015b). The solid-to-liquid

150 ratios for all materials were 1:10 (g/mL). The solid matrices and the pesticide or fluorescent dye

151 solutions were equilibrated in glass tubes for 24h at a shaking speed of 150 rpm. The tubes were

152 then centrifuged at 3000 rpm (1770 g) for 10 min and the supernatant was sampled and analysed.

153 The experiments were all conducted in triplicate.

154 SRB and UR contents were analysed with a BMG Labtech-CLARIOstar fluorescent spectrophotometer

155 based on the method described by Lange et al. (2011). The excitation/emission wavelengths were

156 474/560 ± 10 nm for UR and 545/590 ± 10 nm for SRB. Labelled pesticides were analysed with a

157 Tricarb liquid scintillation counter of Perkin Elmer.

158 The linear adsorption coefficients Kd were calculated with Equation (1) and the Freundlich Kf and n

159 coefficients were calculated with Equation 2 (Wauchope et al., 2002).

160 $C_s = K_d * C_{aq}$ (Equation 1)

161 $C_s = K_f * C_{aq}^n$ (Equation 2)

162 where C_{aq} is the concentration in the aqueous phase at equilibrium (µg/L), Kd is the linear

163 adsorption coefficient (L/kg), Kf ($µg^{(1-n)} L^n kg^{-1}$) and n (-) are the Freundlich coefficients and Cs the

164 concentration in the solid material (µg/kg).

165

166 *2.4.2. Adsorption coefficients of the soil-biochar mixtures*

167 Adsorption coefficients (Kd) were also determined for soil/biochar mixtures representing the

168 agricultural amendments. The oak and pine biochars were mixed with soil S1 and S2 at rates of 1 and

169 5%, respectively. These 8 mixtures were prepared directly in glass tubes to control the masses of

170 both components (soil and biochar). For glyphosate, 2,4-D and difenoconazole, 10 mL of a 100 µg/L

171 solution containing 50:50% 14C-labelled/nonlabelled pesticide solutions was equilibrated with 1 g of

172 the mixture for 24 h at a shaking speed of 150 rpm. The tubes were then centrifuged at 3000 rpm

173 (1770 g) for 10 min and the supernatant was sampled and analysed. The experiments were all

174 conducted in triplicate. For SRB and UR, the experimental conditions were equivalent but the

175 concentration of SRB was 500 µg/L and that of UR was 250 µg/L.

176

177 **2.5. Statistical analyses**

178 Kruskal-Wallis tests were performed with R software (R Core Team, 2021) to evaluate the effects of

179 biochar amendments in the soils (with factors being the type of soil, type and proportion of biochar

180 amendment) on the adsorption of a given molecule. We also performed Kruskal-Wallis tests to

181 evaluate the contrasts between the sorption coefficients of the five molecules for a given

182 soil/biochar mixture (factor was the type of molecule). Pairwise Wilcoxon rank sum tests were then

183 computed to analyse the differences between the factors.

184

185

3. Results and discussion

3.1. Contrasts in reactive properties of the sorbent materials

The three biochars used as amendments in this study exhibited similar physico-chemical properties (Table 2). The pine biochar had a slightly lower pH and higher carbon content and C/N ratio than the other two biochars. The oak derived-biochar had the lowest specific surface area. Unlike the biochars, the activated carbon had an extremely high specific surface area. The soils were both loamy soil with high pH and they differed mainly in their OC contents, which was low for S1 and high for S2.

Figure 1 could be inserted here

The FTIR studies of the surface functional groups (Fig. 1) revealed that there were no marked differences among the 3 biochars. While the absorbance intensities differed slightly for all spectral bands of the biochars, there were no differences in the peak shapes and positions. The FTIR spectra indicated the presence of many functional groups on the surfaces of the biochars, including OH, CH_2, C=O, C=C, C-O and COO^- most of which originated from hydrophobic organic molecules (Table 3). The surface chemistries of the biochars contrasted greatly with that of the activated carbon, for which absolutely no peaks were detected (Fig. 1). The spectra of the biochars and soil differed mainly in the bands at 3700-3500 cm^{-1}, 2520-2500 cm^{-1} and 900-400 cm^{-1} associated to the mineral fraction (Table 3). Peaks in the 1820-1760 and 1700-1540 cm^{-1} ranges were observed for the soils but not for the biochars. These bands corresponded to hydrophilic organic molecules (Table 3).

Table 3 could be inserted here

The grain sizes of the feedstocks and the pyrolysis procedures were the same for the three types of wood, which explains the great similarities of the 3 biochars. Woody feedstocks usually provide biochars with high OC content and those of OB, PB and GB (80-82%) were in the high range of values reported in the literature and varied from 39 to 95% (Ding et al., 2017; Lévesque et al., 2022). The specific surface areas were extremely low (0.06-0.6 m²/g) compared to values reported in the literature, which varied from 20 to 300 m²/g (Ding et al., 2017; Lévesque et al., 2022). This could be due to the grain sizes of the feedstocks (whole wood logs), which did not allow good heat conduction, and the relatively low pyrolysis temperatures (456°C). The specific surface areas of the biochars were 4 to 5 orders of magnitude lower than that of the activated carbon, while the other properties, except the CEC, were equivalent (Table 2). The specific surface area of the activated carbon was consistent with values reported in the literature (Wang et al., 2022).

7

217 The relatively low pyrolysis temperature used to prepare the biochars likely led to the great diversity
218 of the surface functional groups (Lévesque et al., 2022). For activated carbons, the presence and
219 nature of the surface functional groups depend on the feedstock and the activation process
220 (Bhatnagar et al., 2013; Rivera-Utrilla et al., 2011; Wang et al., 2022). The lack of detectable
221 functional groups on the surface of the activated carbon (Fig. 1) was likely due both to the feedstock
222 used (mine coal) and to the thermal activation.

223

224 **3.2. Sorption mechanisms of fluorescent tracers and pesticides for the raw sorbent materials**

225 The adsorption coefficients of the fluorescent tracers and pesticides on the raw sorbent materials are
226 presented in Table 4. The linear and Freundlich models (Equations 1 and 2) exhibited equivalent fits
227 to the experimental data. Moreover, the range of n values indicated a weak dependency of the
228 sorption equilibrium on the concentrations of the contaminants, especially for the soils and biochars.
229 Therefore, we compared sorption affinities over the range of materials and contaminants with the Kd
230 coefficients.

231 For UR, SRB, difenoconazole and 2,4-D the linear adsorption coefficients (Kd) were lowest for the
232 soils, intermediate and with approximately for the three biochars, and 1 to 3 orders of magnitude
233 higher for the activated carbon (Table 4). The Kd values of the biochars were relatively low for 2,4-D,
234 moderate for UR and high for SRB and difenoconazole. Glyphosate stood out from this trend with
235 extremely low Kd values for the biochars and high values for the soils and activated carbon.

236 *Table 4 could be inserted here*

237 The Kd values for the biochars showed a significant disparity due to the heterogeneity of the biochar
238 pellets. In addition, the extreme range of sorption affinities among the materials and molecules
239 made accurate measurement of the sorption coefficients challenging. On the one hand, the very
240 strong adsorption of the tracers and difenoconazole on the activated carbon resulted in equilibrium
241 concentrations close to the detection limit, which explains the poor fit of the experimental data. In
242 contrast, the very low level for adsorption of glyphosate on the biochars resulted in very limited
243 reductions of the initial aqueous concentrations and consequently generated uncertainty in the
244 experimental data. Increasing the solid/liquid ratio to increase the gap between the initial and
245 equilibrium aqueous concentrations was complicated because, due to their porous textures, the
246 biochars tend to absorb liquids.

247 The extremely low Kd values for glyphosate adsorption on the biochars and high Kd values

248 adsorption on the soils were consistent with the physico-chemical properties of the molecules (Table

249 1). Indeed, glyphosate is composed almost exclusively of hydrophilic groups (phosphonate, carboxylic

250 and amine), while the other molecules also contain hydrophobic groups (such as phenol/benzene

251 rings). Hydrophobic interactions are unlikely to occur for glyphosate, and anion attraction is limited

252 by the pH range of the studied materials. Given the very low specific surface areas of the biochars,

253 pore filling is likely to be a minor effect, which may explain the high Kd for activated carbon

254 (Dissanayake Herath et al., 2019) (Tables 2 and 4). Possible interactions between glyphosate and the

255 biochars are therefore limited, which explains the low Kd values (Dai et al., 2019; Ding et al., 2017).

256 Those values were consistent with those reported in the literature (Hall et al., 2018). In soils,

257 glyphosate adsorption is driven by interactions with the mineral fractions, cation bridging and

258 partitioning into the clay layers and iron/aluminium oxides (Dollinger et al., 2015b).

259 For the other molecules, PB exhibited the highest Kd values among the three biochars, which was

260 explained by its higher OC content and, most important, its lower pH. Hydrophobic interactions and

261 hydrogen bonds likely drive the interactions of these molecules with the studied biochars. This is in

262 accordance with sorption affinities, which increase in the order 2,4-D<UR<SRB≈difenoconazole. Pore

263 filling is likely a minor mechanism for these biochars given the low specific surface areas, but that

264 along with hydrophobic interactions, could explain the very high Kd seen for activated carbon. There

265 are only limited literature data for these pesticides and biochars that are not surface-activated with

266 metal ions. For UR, difenoconazole and 2,4-D, the Kd of soil S1 with a low OC content was 3 to 6

267 times lower than that of soil S2, confirming the role of the soil OC in sorption of these molecules

268 (Bork et al., 2020; Dollinger et al., 2017; Werner et al., 2013). The Kd values for SRB differ only slightly

269 for the 2 soils. The higher OC content in S2 negatively affects the Kd for SRB, but is compensated by

270 the higher clay content that drives sorption of this molecule on the soils (Bork et al., 2020; Dollinger

271 et al., 2017).

272

273 **3.3. Comparative efficiencies of biochar soil-amendments for pesticides and the fluorescent tracers**

274 The adsorption coefficients of the tracers and pesticides were compared for soil/biochar mixtures

275 relevant to agricultural systems. The proportions of biochar in the mixtures were 1 and 5%,

276 respectively. This corresponded to amendment rates of 13 to 65 t/ha for surface incorporation in

277 crop soils (down to 10 cm) and an average soil density of 1.3 g/cm^3. Figure 2 presents the Kd values

278 of the mixtures normalized with the soil Kd values.

279 *Figure 2 could be inserted here*

280   The sorption coefficients of both tracers, 2,4-D and difenoconazole were significantly affected by the

281   biochar amendments (0.008< P-value <0.001). The effects of the biochar amendments were

282   contrasted for the soils, the molecules and the amendment rates (Fig. 2). However, consistent with

283   their equivalent Kd values (Table 2), the biochar type (OB or PB) did not affect the sorption

284   coefficients of those molecules in the mixture of equivalent amendment rates. Unlike the other

285   pesticides, biochar amendment with OB and PB did not significantly affect glyphosate sorption on soil

286   S1 (P-value=0.4) (Fig. 2).

287   Amendment with 1% OB or PB only slightly modified UR and SRB sorption, but it doubled 2,4-D and

288   difenoconazole sorption. Amendment with 5% OB or PB had a limited impact on UR sorption,

289   doubled the level of SRB sorption and increased the sorption coefficients of 2,4-D and

290   difenoconazole by 3 to 6 times in S1 and by 2 to 4 times in S2. The increases in Kd values for SRB, 2,4-

291   D and difenoconazole with increased biochar amendment rates were less marked for soil S2, which

292   had a high OC content, than for soil S1. The trends for sorption level increases with increasing

293   biochar contents were comparable for SRB, 2,4-D and difenoconazole.

294   Neither the type nor the content of the biochar influenced glyphosate sorption (Fig. 2), which was

295   consistent with the very low affinities of this herbicide for the three biochars (Table 4). The behaviour

296   of glyphosate differed from those of UR and SRB. These tracers do not appear to be suitable proxies

297   for glyphosate in this specific context. However, given the negligible impact of biochar amendment

298   on its sorption level, there is limited interest in further appraise of the efficiency of those biochar

299   amendments to mitigate the dispersion of glyphosate in the environment.

300   SRB seems able to react to discrepancies in sorption behaviour related to the soil type and biochar

301   amendment rate, as observed for a range of pesticides, and especially with hydrophobic pesticides

302   such as difenoconazole. However, the absolute Kd values increased in the order 2,4-

303   D<<SRB<difenoconazole. SRB can be a useful probe with which to compare the retention efficiency

304   of different amendment strategies for a range of pesticides but precise values for pesticide retention

305   might require a preliminary comparison of the Kd values.

306

307

308   **Conclusion**

309   This study was undertaken to evaluate the use of fluorescent tracers, UR and SRB, as proxies for

310   pesticides to evaluate biochar amendment strategies designed to mitigate pesticide dispersion at the

311   field scale. This evaluation was based on the hypothesis that similar coefficients for the sorption of

312   the tracers and the pesticides on soils, biochars and soil/biochar mixtures would result in similar

313 dispersion behaviours at the field scale. The results showed that, unlike activated carbon, the

314 biochars were not efficient sorbents for all types of pesticides. Over the range of tested pesticides,

315 the sorption affinities for the tested woody biochars increased with increasing pesticide

316 hydrophobicity. The sorption levels of the hydrophilic herbicide glyphosate was unaffected by

317 biochar amendment, in contrast with the tracers UR and SRB. Neither tracer is therefore a good

318 proxy for glyphosate in this context. However, given its very low affinity for biochars, amendment

319 strategies are unlikely to reduce glyphosate dispersion in crop fields. In contrasts, the sorption levels

320 of SRB, difenoconazole, 2,4-D and, to a lesser extent, UR, were significantly increased by the biochar

321 amendments. These tracers could potentially become suitable surrogates to test the efficiencies of

322 biochar amendments to mitigate dispersion of hydrophobic pesticide.

323 The three woody biochars tested in this study had very similar physico-chemical properties. They all

324 had particularly low specific surface areas and high organic carbon contents compared to the range

325 of biochar properties described in the literature. Extending these comparative sorption studies to

326 biochars with a wider range of properties would help provide greater insight into the potential of

327 these tracers for use as pesticide proxiesin this specific context. In addition, the range of tested

328 pesticides should be extended to include neutral to moderately hydrophobic molecules.

329

334

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Statements & Declarations

Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Seynabou Sene, Jeanne Dollinger, Manon Lagacherie and Sandrine Negro. The first draft of the manuscript was written by Seynabou Sene and Jeanne Dollinger and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding

The study was funded by the Carbonex Company in the framework of a research and development project.

Ethical Approval

Not applicable

Consent to Participate

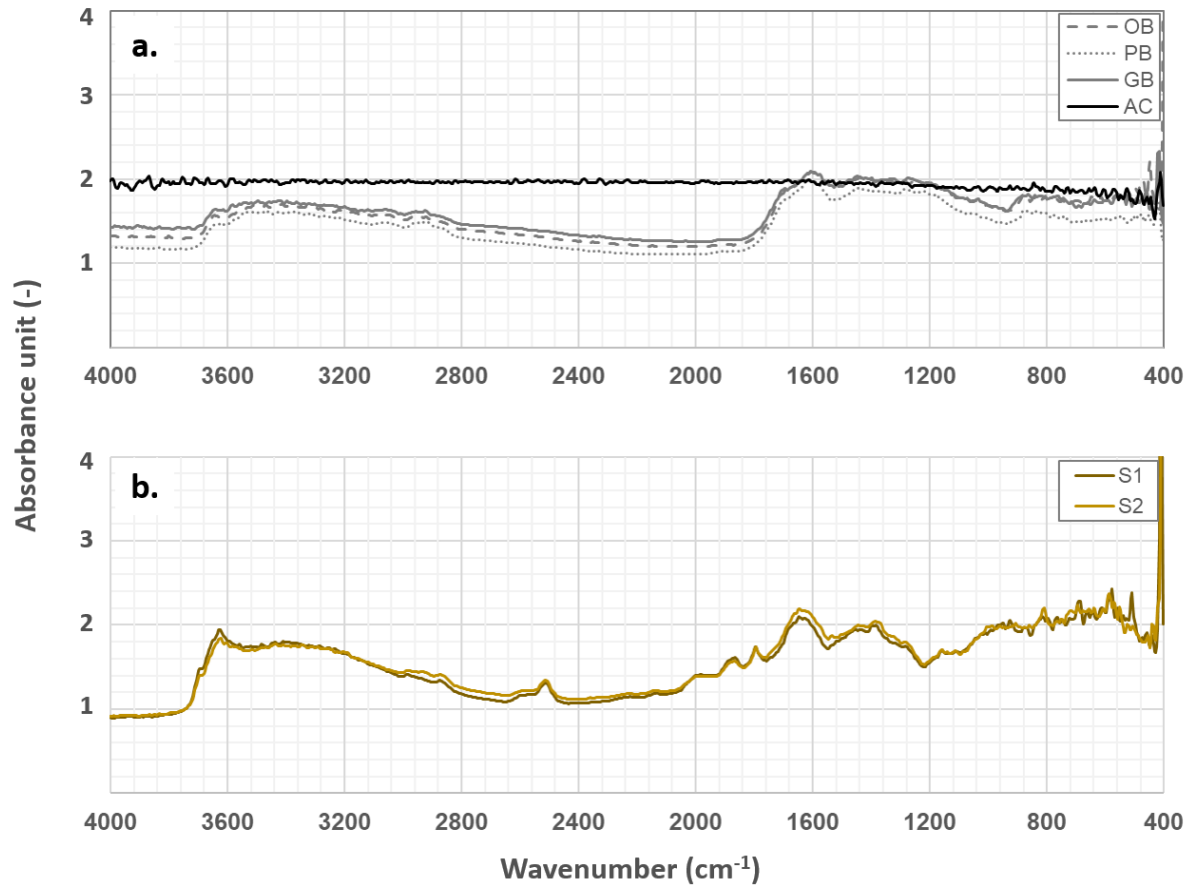Not applicable

Consent to Publish

Not applicable

Figure 1: FTIR spectra of the raw materials (activated carbon, biochars and soils). *a.) FTIR spectra for the activated carbon (AC), the oak biochar (OB), the pine biochar (PB) and the Gyé biochar (GB). b.) FTIR spectra for soil 1 (S1) with low organic matter content and soil 2 (S2) with high organic matter content.*
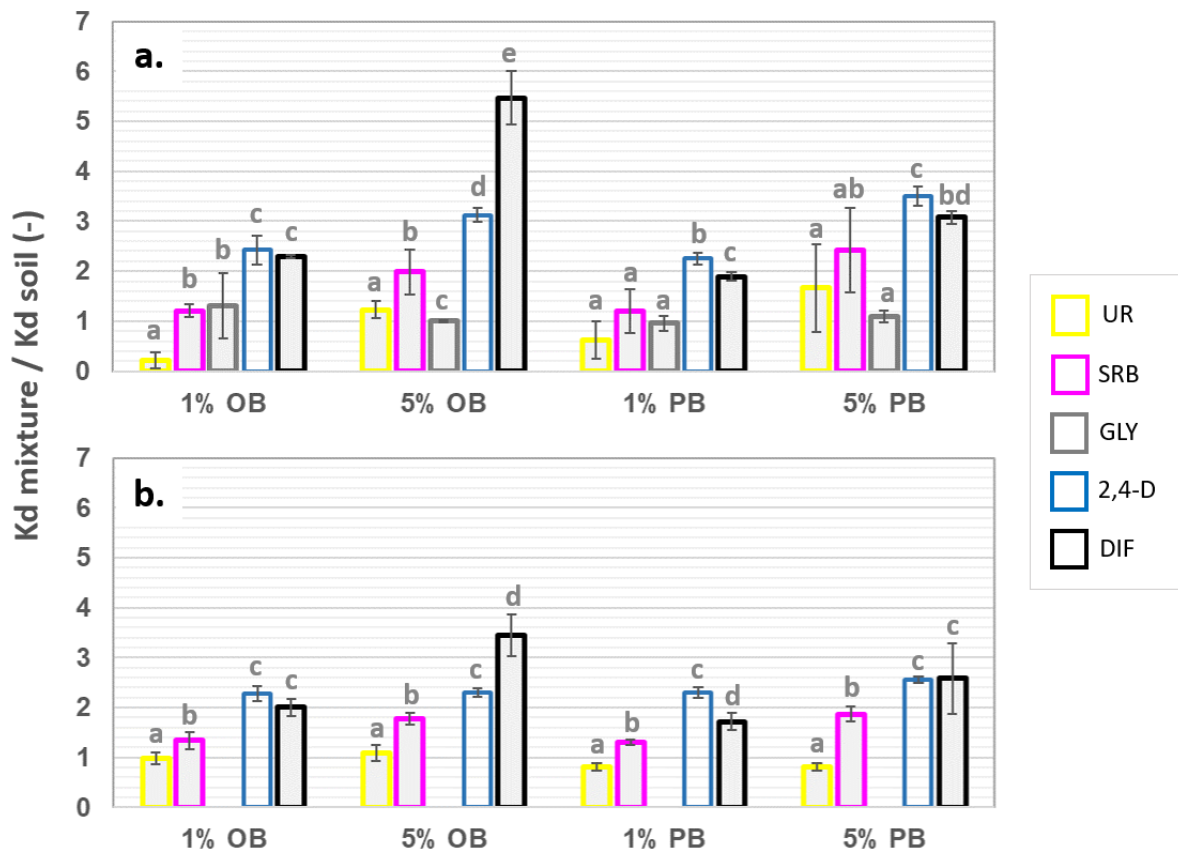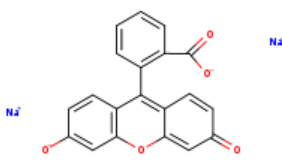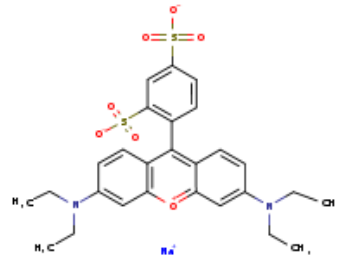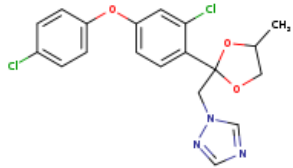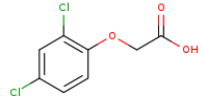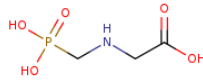
***Figure 2: Modification of the adsorption coefficient Kd following the addition of 1 and 5% oak (OB) or pine (PB) biochar in soil**. a.) Kd values for the soil/biochar mixtures normalized with Kd for soil S1, which has a low organic matter content. b.) Kd values for the soil/biochar mixtures normalized with Kd for soil S2, which has a high organic matter content. The error bars represent the standard deviation of the three replicates. Please note that given the very low and similar Kd of glyphosate for the biochars (<0.5 L/kg) and the minimal effect of OB and PB addition in S1 (a.), the values were not determined for S2. Pairwise Wilcoxon rank sum tests were used to evaluate the significant differences (P-value≤0.1) among the molecules in a given mixture, as displayed by the letters a, b, c, d and e.*

Tables

Table 1: Physico-chemical properties of the tracers and pesticides

	Uranine	Sulforhodamine B	Difenoconazole	2,4-D	Glyphosate
Structure[a]					
Molecular Formula[a]	$C_{20}H_{10}Na_2O_5$	$C_{27}H_{30}N_2O_7S_2.Na$	$C_{19}H_{17}Cl_2N_3O_3$	$C_8H_6Cl_2O_3$	$C_3H_8NO_5P$
Molecular Mass (g/mol)[a]	376.3	580.7	406.3	221.0	169.1
Aqueous solubility (mg/L)	25 000[b]	70 000[b]	15[c]	24 300[c]	10 500[c]
Log Kow	3.9[d]	1.3[d]	4.4[c]	-0.8[c]	-3.2[c]
pKa	8.7 – 9.3[d]	1.1 – 2.2[d]	1.1[c]	3.4[c]	2.2 – 5.5 – 10.2[c]

a: ChemID plus; b: Sabatini (2000); c: FOOTPRINT PPDB (2022) ; d: Dollinger et al. (2017)

Table 2: Physico-chemical properties of the materials (biochars, activated carbon and soils)

Material	pH $_{H2O}$	CEC	Organic Carbon (OC)	C/N	Specific Surface Area (SSA)	Sand	Silt	Clay
	-	cmole/kg	%	-	m²/g	%	%	%
OB	8.46	9.80	79.81	348.51	0.06	NR	NR	NR
PB	7.27	6.30	81.33	956.77	0.26	NR	NR	NR
GB	8.97	6.00	80.76	416.31	0.60	NR	NR	NR
AC	7.66	1.10	82.07	506.63	1095.59	NR	NR	NR
S1	8.48	11.62	0.82	10.07	21.63	40.10	37.90	22.00
S2	8.27	16.62	3.04	12.38	19.33	34.50	41.40	24.10

OB: Oak biochar; PB: Pine biochar; GB: Gyé biochar; AC: Activated carbon; S1: Soil 1; S2: Soil 2.

Table 3: Peak assignments for the FTIR spectra

Spectral band (cm^{-1})	Functional group	Putative origin	References
3700-3550	OH (*stretching*)	Phyllosilicate minerals	Parolo et al., 2017; Simkovic et al., 2008
3500-3200	OH (*vibration/stretching*)	Phenols, humic substances, lignin	Cox et al., 2000; Parolo et al., 2017; Wen et al., 2018
3000-2800	CH$_2$ (*stretching vibration*)	Fats, wax, lipids, humic substances	Cocozza et al., 2003; Niemeyer et al., 1992; Verchot et al., 2011; Wen et al., 2018
2520-2500	CO$_3^{2-}$ (*vibration*)	Minerals	Parolo et al., 2017;
1920-1840	C=O (*stretching*)	Carboxilic acids	Wen et al., 2018;
1820-1760	C=O (*stretching*)	Hydrophylic SOM	Simkovic et al., 2008; Verchot et al., 2011
1700-1540	C=O / COO- / C=C	Aromatic organic matter	Ellerbrock and Kaiser, 2005; Simkovic et al., 2008; Wen et al., 2018
1300-1200	C–O stretching or OH deformations	alcohols, ethers, phenols, carboxylic acids and esters	Parolo et al., 2017; Verchot et al., 2011
900-400	Si-O (*stretching*)	Minerals	Parolo et al., 2017; Xiao et al., 2020

Table 4: Adsorption coefficients of the raw materials

Molecule	Material	Linear model		Freundlich model		
		Kd	R²	Kf	n	R²
		L/kg	-	$\mu g^{(1-n)} L^n kg^{-1}$	-	-
Uranine	OB	9.04	0.99	28.62	0.77	0.99
	PB	12.11	0.98	59.70	0.67	0.98
	GB	9.69	0.97	45.38	0.69	0.97
	AC	11372.17	0.60	7639.22	0.80	0.70
	S1	0.45	0.99	0.05	1.36	1.00
	S2	2.84	0.99	2.46	1.03	0.94
Sulforhodamine B	OB	716.97	0.96	706.72	0.96	0.97
	PB	919.60	0.79	799.69	0.82	0.57
	GB	851.73	0.99	1027.06	0.89	0.95
	AC	20160.32	0.44	31703.12	1.57	0.44
	S1	10.40	0.99	19.92	0.90	0.99
	S2	13.71	0.97	36.77	0.83	0.99
Difenoconazole	OB	674.75	0.90	1239.29	0.92	0.96
	PB	1391.09	0.95	1393.05	1.09	0.96
	GB	320.63	1.00	663.83	0.84	0.97
	AC	5861.87	0.79	6189.77	1.41	0.93
	S1	11.99	1.00	14.12	0.98	0.99
	S2	41.75	1.00	71.67	0.92	0.97
2,4-D	OB	1.09	0.99	1.90	0.94	0.99
	PB	2.29	0.99	3.61	0.95	0.99
	GB	1.02	1.00	1.68	0.94	1.00
	AC	7409.98	0.80	6185.54	1.44	0.82
	S1	0.15	0.99	0.36	0.87	1.00
	S2	0.43	1.00	1.53	0.82	0.99
Glyphosate	OB	<0.50	-	nd	nd	-
	PB	<0.50	-	nd	nd	-
	GB	<0.50	-	nd	nd	-
	AC	*94.00**	-	nd	nd	-
	S1	24.01	1.00	26.20	0.95	0.99
	S2	22.07	1.00	27.38	0.94	1.00

OB: Oak biochar; PB: Pine biochar; GB: Gyé biochar; AC: Activated carbon; S1: Soil 1; S2: Soil 2. Please note that the Kd value for glyphosate and activate carbon was taken from the literature (Dissanayake Herath et al., 2019)*. Freundlich isotherms for glyphosate adsorption on the biochars could not be derived from the experimental data due to the very low adsorption levels.*