Postprint of: Journal of Agricultural and Food Chemistry 65(15): 3109-3117 (2017)

Biochar soil additions impacts herbicide fate: Importance of application timing and feedstock species

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ABSTRACT

Biochar (BC), solid biomass subjected to pyrolysis, can alter the fate of pesticides in soil. We investigated the effect of soil amendment with several biochars on the efficacy of two herbicides, clomazone (CMZ) and bispyribac sodium (BYP). To this aim, we evaluated CMZ and BYP sorption, persistence and leaching in biochar amended soil. Sorption of CMZ and BYP was greater in soil amended with BC produced at high temperature (700 ºC). Significant sorption of the neutral CMZ herbicide also occurred in amended soil with BC prepared at low temperature (350 and 500 ºC). For both herbicides, desorption possessed higher hysteretic behavior in soil amended with BC made at 700 ºC (pyrolysis temperature). Dissipation of CMZ was enhanced after addition of BCs to soil, but no correlation between persistence and sorption was observed. Persistence of BYP was up to 3 times greater when BC made at 700 ºC was added to soil. All BCs suppressed the leaching of CMZ and BYP as compared to the unamended soil. Amendment with 700 ºC BC inhibited the action of CMZ against weeds but not when 350 and 500 ºC BC´s were added to soil. BYP activity was similar than that exhibited by unamended soil after the addition of 700 ºC BC. From these results, biochar amendments can be a successful strategy to reduce the environmental impact of CMZ and BYP in soil. However, the phytotoxicity of soil-applied herbicides will depend on BC sorption characteristics, the pesticide chemical properties, as well as the pesticide application timing (e.g., pre- or post-emergence). According to our results, proper biochar screening with intended pesticides in light of the application mode (pre- or post- emergence) is required prior to use in order to ensure adequate efficacy.

***Keywords*: bispyribac sodium; clomazone; degradation; efficacy; leaching; soil amendments; sorption; weed control.**

INTRODUCTION

Biochar (BC) is the C-rich product resulting of the pyrolysis of organic residues such as wood, animal wastes, crop residues and biosolids.[1] A number of reviews and studies have highlighted the potential benefits of utilizing biochar as a soil amendment due to its apparent beneficial properties. Biochar application to soil has attracted great attention mainly for being a means for carbon sequestration to mitigate climate change.[2,3] Additionally, BC has been promoted as an additive for soil conditioning, fertilization impacts, bolstering buffering capacity and resulting in lower greenhouse gas (GHG) emissions, which make biochar a promising tool for restoring soil agronomic productivity.[4] Other concomitant benefits of BC use are associated with soil properties, such as its ability to decrease the soil bulk density[5] and increase the soil water holding capacity.[6] In this regard, BC is an heterogeneous material and, depending on the pyrolysis conditions and the biomass parent materials, different soil properties can be modified.[4] Since BC owns a wide range of chemical structures, there is a growing interest in designing biochar that has properties tailored to improve specific soil conditions.[6]

Lately, research focused on BC use to mitigate contamination problems from pesticide use has been progressively increasing.[7] This attention is based on the fact that BC can possess a strong affinity to sorb organic compounds. BC sorption capacity is determined by their surface area, microposority, and surface chemistry,[8] which are strongly influenced by pyrolysis conditions, aromatic carbon content, and feedstock species.[9] Overall, high temperatures of pyrolysis (HTT) (> 500 ºC) result in more graphitized (aromatic) material, with higher SSA and reduced abundance of surface functional groups. By contrast, lower temperatures of pyrolysis (< 400 ºC) produce biochars with low specific surface area (SSA) and more surface functionality that implies partitioning and specific interactions with functional groups on biochar surface.[10] Furthermore, it is well-known that desorption is affected by the extent of pesticide sorption on biochar, controlling their bioavailability in soils.[8] In general, higher pyrolysis temperatures leads to greater hysteretic desorption processes.[11–13] Also, several published studies dealing with the impact of biochar on pesticides degradation and leaching have pointed out longer persistence and reduced mobility of pesticides through the soil profile upon biochar amendment as compared to the unamended soil. These results are attributed to the high pesticide sorption capacity of biochar compared to the original soils.[13–17]

The question of whether or not biochar application can reduce the efficacy of soil-applied pesticides still needs more investigation.[18] Some authors have found lower bioefficacy of herbicides after the addition of biochar to soil due to the enhancement in sorption, which reduces the amount of pesticides in the soil solution.[19–21] Consequently, this behavior may affect pest management control and implies a need for additional pesticide amounts which could generate new environmental risks. [18]

We hypothesized in this work that the efficiency governing plant growth of the two highly mobile herbicides clomazone (CMZ) and bispyribac sodium (BYP) with different mode of action and application regime[22] could be suppressed due to biochar application. Hence, the objective was to examine the effect of six biochar additions to soil made from two different wood species and prepared at three different temperatures (350, 500 and 700 ºC) to test at laboratory scale: i) the sorption–desorption behavior of the herbicides clomazone and bispyribac sodium in soils amended with biochar, ii) the influence of biochar addition on the dissipation and leaching of CMZ and BYP, and iii) how the bioefficacy of these herbicides is affected by the presence of the biochars in soil.

MATERIALS AND METHODS

Herbicides, biochars and soil. The herbicides clomazone (CMZ) and bispyribac sodium (BYP) (analytical standard grade, purity > 99%) were purchased from Sigma-Aldrich (Spain). Chemical structures of the herbicides are shown in Fig. 1. Clomazone is a systemic, selective soil-applied isoxazolidinone acting as a pre-emergence herbicide inhibiting the synthesis of carotenoid plant pigments (Fig.1). It has a water solubility of 1.102 mg L^{-1} at 20 ºC and organic carbon-water partition coefficient, Koc, of 300.[22] BYP is a pyrimidinyl carboxy compound with a water solubility of 64 g L^{-1} at 25 ºC, (20ºC, pH=7), pK_a 3.35 [22] and Koc = 114 (Fig. 1). [23] It is a systemic, selective, post-emergent herbicide which inhibits plants amino acid synthesis. BYP is considered highly mobile and very toxic to aquatic organisms and hazardous to the environment.[22]

The soil was collected from an experimental farm of IRNAS (Coria del Río, Sevilla, Spain), by sampling the first 0-20 cm of soil, then mixed, air-dried and sieved (2 mm mesh) and finally stored at 4ºC. This was a clay loam soil with 24% sand, 47% silt, and 30% clay, organic carbon (OC) of 1.3% and pH of 7.87.

Six biochars were derived from two types of hardwoods [*Carya tomentosa* (ρ=0.83 g cc^{-1}; hickory) and *Carya illinoinensis* (ρ=0.77 g cc^{-1}; pecan)] and obtained at three different pyrolysis temperatures (350, 500 and 700 ºC), under a very restricting oxygen atmosphere with subsequent purge of N_2 for 2 h. Nomenclature and selected properties of these biochars are compiled in the Table 1. Further characterization can also be found in Trigo et al.[24] All soil treatments with the biochars were performed at 2% (w:w). Soil was immediately amended before being used in sorption and degradation experiments.

Sorption experiments. Sorption-desorption isotherms of both pesticides in unamended and BC-amended soil were obtained by the batch equilibration method. Duplicate 2.5 g of soil, either unamended or amended with the various types of BC (2% w:w), were treated separately with 8 mL of herbicide aqueous solutions with initial concentration ranging between 0.5 and 5 mg L^{-1}. The pH of all biochar amended soils ranged between 8.2 and 8.5. Samples were equilibrated by shaking at 20±2 °C in a rotating (end-over-end) shaker at 30 cycles/min during 24 h. Then, the suspensions were centrifuged (7000 x *g*) for 15 min and 4 mL of the supernatant were removed and filtered (0.45 µm) prior to chemical analysis.

Pesticide analysis. Equilibrium concentration (C_e) of CMZ and BYP was measured by high-performance liquid chromatography (HPLC) on a C-18 column (Kinetex C-18; Waters 600E chromatograph coupled to a 996 diode-array detector). The mobile phase was 35:65 (v/v) methanol/water for CMZ and 45:55 (v/v) acetonitrile /water adjusted to pH 2.0 with phosphoric acid (H_3PO_4) for BYP with a 1 mL min^{-1} flow and 25 µL injection volume. The UV absorbance was monitored at 230 nm and 213 nm for CMZ and BYP, respectively. The amount of CMZ and BYP adsorbed, C_s (mg kg^{-1}), was calculated from the difference between the initial (C_i) and equilibrium solution concentrations (C_e). Controls without soil were also performed to document possible herbicide losses. Subsequently, desorption was determined by successive dilution from the highest initial concentration point in sorption (C_i= 5 mg L^{-1}), replacing the 4 mL of supernatant removed with 4 mL of deionized water. The soil suspensions were remixed, allowing equilibration for additional 24 h at 20 ± 2°C. After that, the sample tubes were centrifuged and the herbicide concentration in the supernatant was determined by HPLC. This desorption procedure was repeated three times. Sorption-desorption isotherms were fitted to the Freundlich equation:

$$C_s = K_f C e^{N_f}$$

and sorption coefficients K_f and N_f calculated from its linearized form.

Thermodynamic index of irreversibility (TII) [25] was used to quantify irreversibility in the desorption using the expression:

$$TII = 1-(N_{fd}/N_f)$$

where N_f and N_{fd} are the Freundlich constants obtained from the sorption and desorption isotherm, respectively. TII ranges from 0 to 1, where TII= 0 denotes completely reversible sorption and TII= 1 indicates irreversible sorption.

Dissipation study. Laboratory incubations were conducted to evaluate the effect of biochar addition on the dissipation of CMZ and BYP under aerobic conditions. The BCs were selected according to the sorption capacity observed in the sorption-desorption experiment. The soil was amended at a rate of 2 g/100 $g_{mixture}$ with the six biochars for CMZ dissipation. However, for BYP only H700 and P700 were used. After soil was amended, 100 g of unamended or amended soil with BC´s were placed in screw glass bottles and treated either with an aqueous solution of CMZ or BYP to give a final concentration of 1 mg kg^{-1} dry soil. Moisture contents were adjusted to 30% of soil water-holding capacity and maintained at a constant level throughout the experiment by adding distilled water as necessary. Samples were incubated in darkness at 20 ± 2 °C for 69 days. At appropriate time intervals, aliquots of 3 g of soil (triplicate) were weighed into 50 mL centrifuge tubes with a sterilized spatula and immediately frozen. Extraction was performed with 8 mL of methanol for CMZ or a mixture 45:55 (v/v) CH_3CN /diluted H_3PO_4 (pH=2) for BYP and then placed on a shaker for 12 h. Extracts were analyzed by HPLC to determine the total amount of herbicide in the soil samples. Recoveries for both herbicides were >90% in spike recovery tests (data not shown).

Following the analyses of the various time points, degradation curves were fitted to the linearized first-order kinetics:

$$\ln (C / C_0) = -k\ t$$

where C (mg kg^{-1}) and C_0 (mg kg^{-1}) are the concentration of each herbicide in the soil at time t (d) and t = 0, respectively, and k (d^{-1}) is the first-order dissipation constant. A lag-phase was considered as the interval of time from the beginning of the incubation experiment (t = 0) up to that point at which the herbicides decreased to 95% of their initial concentration [$C <= (0.95C_o)$; t = x]. In those cases where a lag-phase was observed, the data points during this period were not used for the curve fitting. The time required to reduce the 50% of the initial concentration of the herbicides, DT_{50}, was calculated from the fitted dissipation constant (0.693 / k), whereas if a lag–phase occurred DT_{50} was corrected by adding the corresponding time (t = x).

Leaching experiments. Triplicate glass columns (3.1 cm i.d. x 30 cm) were hand-packed with 160 g of unamended soil to a height of 20 cm soil in each column. To assess the effect of amending the soil with BC, 40 g of soil amended with BC at 2 % (w/w), was also placed at the top of the column full-filled the upper 5 cm-soil. The BCs used in this experiment were the same than those used in the incubation experiment for each herbicide. Glass wool was placed at the bottom of the column to avoid soil losses, and 10 g of sand (sea sand; Sigma-Aldrich) was added at the bottom and top of all soil columns to improve water flow dynamics and distribution. The columns were saturated by adding 100 mL of distilled water. After 24 h drainage, CMZ and BYP aqueous solutions were applied to the top of soil columns in amount equivalent to a dose of 1 kg ha^{-1} (0.075 mg a.i. per column). Columns were sequentially leached by adding 10 mL of distilled water twice a day to the top of the columns, and leachates were collected during 30 and 20 days for CMZ and BYP, respectively. Leachates were filtered and analyzed by HPLC. At the end of the leaching experiment, the residual amounts of herbicides in soil columns were also measured by extracting 40 g of unamended or amended soil taken from different depths of the columns (0-5, 5-10, 10-15, and 15-20 cm). Soil was extracted in the same fashion as in the incubation experiment.

Bioassays. A bioassay was conducted to ascertain whether CMZ and BYP phytotoxicity was affected by the presence of BC in soil. Bioassays were performed in 20 cm^2-pots (triplicate) with 40 g of unamended soil, approximately 2.5 cm height. For BC-amended soil, the upper 20 g of soil (i.e., about 1.25 cm) were also mixed with all BCs tested in this work at a rate of 2 % (w/w). Pots were randomly distributed, saturated with distilled water and allowed to gravity grain overnight. After which, 12 *Eruca vesicaria* seeds were planted on soil surface. Immediately after planting, CMZ was applied in the recommended pre-emergence rate of 0.1 kg ha^{-1}, whereas BYP was applied one week after planting, simulating post-emergence control at the same rate of 0.1 kg ha^{-1}. Control pots of unamended soil without herbicides were also prepared. The pots were watered daily with 10 mL of distilled water. After 2 weeks of CMZ application or one week after BYP was applied, *Eruca vesicaria* plants (shoots and leaves) were cut and weighed to determine herbicide efficacy in all treatments together with a visual evaluation of plant appearance.

Data analysis. Statistical analysis was performed using IBM SPSS Statistics (Version 22). Standard error was used to assess variability among triplicate samples of the same treatment. Biomass weight in bioassay was compared using an ANOVA followed by a post-hoc Tukey´s test to establish if statistically significant differences existed between treatments. An analysis of covariance (ANCOVA) was performed to compare pairwise the slopes of the regression lines (k) of the first-order dissipation data. Differences between results were considered statistically significant at $p < 0.05$.

RESULTS AND DISCUSSION

Sorption-desorption of herbicides in biochar amended soils. Sorption-desorption isotherms of CMZ and BYP on unamended soil and soil amended with BC´s are shown in Fig. 2. The coefficients of the Freundlich equation are compiled in Table S1 and S2 for CMZ and BYP, respectively. Overall, CMZ and BYP sorption was initially concentration-dependent, since the majority of all N_f coefficients calculated were < 1 (Table S1 and S2). In addition, there was a gradual loss of linearity of the isotherm for both herbicides, but particularly noticeable for CMZ, when increasing the pyrolysis temperature of the BC. This effect can be related to a progressive pore filling from *partitioning* to *adsorption* mechanism, which has been previously observed for organic compounds in carbonaceous materials. [26–28]

The lowest sorption was observed for CMZ in unamended soil, which has been attributed to its high water solubility, [29] resulting in a K_{oc} of 88. This value is in the low range observed for a variety of soil types (60-573 L kg^{-1}). [30] Following biochar addition, differences in CMZ sorption can be ascribed to BC properties. Despite the variable fitting of isotherms to Freundlich equation with R^2 ranging from 0.88 to 0.98 (Table S1), soil addition of the BCs consistently increased sorption of CMZ (Fig. 2). Additionally, CMZ sorption was not affected by feedstock species (i.e. pecan or hickory). Variation in sorption was dependent on the temperature of BC production, following the increasing trend: 700> 350 > 500 > control soil (Fig. 2). Higher sorption of CMZ on H700- and P700-amended soil was expected since H700 and P700 were the BC´s that presented higher SSA values, 230 and 281 m^2/g, respectively (Table 1). SSA has been typically correlated to the sorption capability of BCs[7,31]. This result is also in agreement with studies reporting higher sorption of organic compounds on soils amended with BCs prepared at high temperature of pyrolysis.[7,32] However, in our study higher production temperature did not always imply greater CMZ sorption, given that both, P350-and H350-amended soils, performed better than P500- and H500-amended soils. Two plausible explanations can be inferred. First, the presence of more amorphous organic matter within the carbonaceous matrix in BCs prepared at 350 than at 500 °C. [9] Second, a further abundance of surface functional groups, according to their higher O/C ratios could favor specific chemical interactions, as reported for others ionizable or polar organic compounds.[33–35]

With regard to BYP, the herbicide was poorly sorbed in unamended soil, with K_f of 0.21(Table S2) and Koc of 16 L kg^{-1} , which is consistent with data previously reported for soils of low OC content (~ 1%) [36,37] and the herbicide's anionic character. [38] A very small increase in sorption was observed after amendment with BCs prepared at 350 and 500 ºC as compared to the unamended soil, whereas a greater increase occurred in P700- and H700-amended soils (Fig. 2). In general, there is a positive correlation between pesticide sorption and BC pyrolysis temperature. [24,31,39] This fact has been linked to a graphitization of carbon promoting the development of aromaticity and microposority in BC as temperature increases. Nevertheless, repulsion between anions and the negatively charged BC particles cannot be ruled out, since BYP is an ionizable compound with pK_a of 3.35 and is mainly present as anionic species at the pH of the sorption experiments (8.2-8.5). Contrasting with CMZ, repulsion could be more important in soils amended with BC prepared at low temperature, according to their O/C molar ratios.[9] The wood species greatly affected BYP sorption, since it was remarkable higher in soil amended with P700 than in soil amended with H700 (Fig. 2C and 2D), with K_f values of 9.46 and 2.47, respectively (Table S2). Slightly greater SSA and higher dissolved organic carbon (DOC) content of P700 (Table 1), which can provide additional sorption sites[40] could account for the higher observed sorption. Although the exact mechanism was not investigated further.

Desorption of CMZ was more hysteretic for BC amended soils as compared to unamended soil, except for P500-amended soil. Hysteresis was more significant for P700- and H700-amended soils, achieving TII values of 0.83 and 0.77 (Fig. 2 and Table S1). These results indicated that CMZ difficulties to be desorbed can be mainly related to the extent of sorption [41]. Thus, some degradation of CMZ after 4 days-desorption experiment cannot be ruled out as a possible cause of hysteresis. [42]

Similarly to CMZ, BYP desorption was very limited (Fig. 2 and Table S2). The upward slopes observed for BYP in BC-amended soil at 700 ºC during desorption (i.e., desorption branch) could indicate experimental artifacts during the desorption measurements, such as insufficient time to reach equilibrium,[41] or some degradation as it has been pointed out for CMZ. The latter could be unlikely for BYP, contrasting with CMZ, since a lag-phase of at least 7 days was observed in the dissipation curves in BC-amended soil as it will be explained below. Consequently, TII might not be truly representative of mechanistic steps (Table S2). Nevertheless, the relative flattening observed in the desorption isotherms of P700- and H700-amended soils also suggest hysteresis of BYP in these cases, supporting irreversible binding of the molecules to the BC´s surfaces. Causes of irreversibility can be associated to the non-linear form of the isotherms which implies rate limited desorption.[14] Irreversibility in sorption of organic compounds can involve sorption intraparticle diffusion, pore deformation during sorption, or entrapment into micropores.[43,44]

Dissipation of herbicides in the soil amended with biochars. Figure 3 shows the dissipation curves of CMZ and BYP in unamended soil and BC-amended soils. For

BYP, we only used P700 and H700 to amend the soil since they were the BCs which significantly sorbed this herbicide. The first-order dissipation constants and TD_{50} of CMZ and BYP are also given in Table 2. It is worth mentioning that there is a lag-phase in the dissipation of the herbicides for all treatment except for CMZ in P700-and H700-amended soils. This could be attributed to microorganism metabolism or adaptation of microorganisms to degrade the compounds.[45]

Clomazone dissipation occurred faster in unamended soil compared to all amended soils ($p < 0.05$) (Fig. 3A and 3B). The experimental data for all treatments fit first-order kinetics with $R^2 > 0.843$ (Table 2). The calculated DT_{50} of this herbicide in unamended soil was 29 days, which is lower than that reported by Mervosh et al.[46] (49-58 days) or Tomco et al. [47] (47 days) in soils under aerobic conditions. The addition of BCs to soil at 2 % (w:w) rendered DT_{50} values for CMZ ranging between 65 and 107 days (Table 2), a 2.2 to 3.7x increases. In general, BC is considered to reduce the bioavailability of pesticides while increasing their persistence in soil. This has been associated to its capability of sorbing organic compounds and is directly affected by the extent and reversibility of the sorption process.[8,15,17,48,49] According to our results BC markedly extended soil persistence of CMZ ($p < 0.05$), even though no significant differences between the BC-amended soils in TD_{50} values were found ($p > 0.05$), with the exception of H350 and H500-amended soils (Table 2). Therefore, the dissipation rate of the herbicide in BC-amended soils did not follow the same trend than that observed in the sorption experiment. Longer persistence in P700 and H700-amended soil would have been expected given that they were the treatments which exhibited higher sorption towards CMZ. Plausible explanation for this fact could be changes in sorption mechanisms during the incubation experiment. [48,50] The amount of CMZ in soil solution through all the experiment could have decreased as the herbicide was being degraded. This phenomenon could be intensified according to the hysteresis observed for CMZ (Fig. 2), reducing its dissipation rate. Moreover, bearing in mind that the main degradation pathway of CMZ is biodegradation,[51] BCs could induce alterations on microbial biomass, enzyme activities and/or soil microbial community changing its dissipation in soil.[16,19,52] However, these secondary effects were not examined in this study.

The dissipation of BYP was similar than that observed for CMZ in unamended soil, with calculated TD_{50} 21 days and fitting to the first-order kinetics with $R^2 > 0.923$ (Table 2). This value is higher than those reported by Chirukuri and Atmakuru[36] in several types of soil, with TD_{50} values ranging between 5 and 16 days, but lower than 31 and 51 days obtained by López-Piñero et al. [37] Among others, discrepancies can be attributed to different moisture content at which the experiments were conducted. Likewise, López-Piñero et al.[37] also observed that the pH and total organic carbon are the factors which had more impact on BYP dissipation. Disparate behavior was established for BYP after amending soil with H700 and P700. When compared to unamended soil, slightly longer persistence was obtained in H700-amended soil (TD_{50}= 33 days) ($p > 0.05$) whereas amendment with P700 led to a greater persistence of the herbicide, following the order: P700- > H700- > unamended soil (Fig. 3C). The scarce effect upon amendment soil with H700 on BYP dissipation suggests that the small increase in sorption in this case was not great enough to alter its dissipation and that concomitant factors, similarly than those explained above for CMZ, can take place. On the contrary, sorption seemed to be remarkable for BYP in P700-amended soil (Fig. 2 and Table S2) which is in agreement with the idea that sorption protects the herbicide from biodegradation, as it has been suggested for other pesticides in BC-amended soils. [8,17]

Leaching of herbicides in the soil amended with biochars. The fact that BCs enhanced adsorption and decreased desorption of CMZ and BYP should alter their soil mobility. In order to assess the influence of biochar on the mobility of CMZ and BYP in soil, leaching experiments were conducted, as shown in Table 3 and Fig. 4.

Clomazone was only detected in leachates for unamended soil, approximately 59% of the applied herbicide (Table 3). In contrast, CMZ was not detected in leachates for amended soil with BCs at a rate of 2%, despite the increase in persistence of CMZ in BC amended soils (Fig. 3). Likely, the enhanced soil sorption capacity in the first upper 5 cm where BCs were added resulted in no observed CMZ leaching (Table 3). Generally, increasing sorption of pesticides by biochar additions has reduced observed movement of these compounds through the soil profile.[13,17,24,53] To estimate the extent of the downward soil migration of CMZ, soil columns were extracted by depth intervals to determine the remaining amount of CMZ at the end of the leaching experiment (Fig. 4 and Table 3). The lowest amount of CMZ extracted (20 %) from soil columns corresponded to unamended soil ($p < 0.05$), as it was expected according to the percentage leached (Table 3). Also, CMZ was homogenously distributed through the control soil column. In amended soils, CMZ was primarily located in first 5 cm of soil. The highest amounts of CMZ were extracted from the 0-5 cm fraction of P700-amended soil column (66% of applied CMZ), verifying that sorption reduced the leaching of pesticides. However, we had poor total mass balance for the column experiments (40-60% not accounted for) that could be explained by strong (irreversible) sorption or the potential degradation during the experiment. For unamended soil, degradation may have predominated over irreversible sorption in accordance, due to the low sorption and rapid dissipation rates observed. On the other hand, a combination of both processes could occur in BC-amended soil columns; however, given the lack of transport of CMZ through the column reduces the potential of degradation to take place throughout the column.

Greater BYP leaching losses was shown by unamended soil, where up to 49 % of BYP applied to the columns appeared in the leached water (Table 3). This is in line with the 51% of BYP transported by López-Piñero[37] in an experiment using soil columns packed with soil under conventional tillage. However, this contrasted with the >95% leaching of BYP observed by Singh and Singh[54] in an alkaline soil with very low organic matter content, similar than the soil used in this study. The amendment with H700 reduced BYP leaching (12%) compared to unamended soil, while the herbicide was not detected in the leachates of soil columns amended with P700. This is analogous to what occurred with CMZ (Table 3). This behavior ratified that sorption reduces leaching of pesticides,[13,17] since there is a positive relationship between both processes (Fig. 2 and Table 3). After the extraction of the soil columns, BYP was only extracted in columns amended with H700 and P700, representing 23% and 63%, respectively, of the applied amounts (Table 3). Furthermore, in P700-amended soil, BYP residues were only present in the first 5 cm soil, which indicated greater immobilization capacity of P700, than H700- and unamended treatments (Table 3). Also longer persistence of the herbicide was evidenced in concordance with the soil incubation data (Fig. 3). Lower amounts of BYP in H700-amended soil verified lower sorption and more rapid dissipation of the herbicide in H700 amended soil.

Bioefficacy of herbicides in biochar amended soils. The herbicidal activity of CMZ in all treatments is summarized in Fig. S1. The phytotoxicity of CMZ results from the inhibition of the synthesis of chlorophyll and carotenoids, resulting in foliage lacking of pigmentation. [51] the visual evaluation of plant symptoms of *Eruca vesicaria* clearly revealed two different behaviors. One of them, corresponded with pots containing plants where the leaves were decolored, which are the case of unamended soil and BC-amended soil with H350, H700, P350 and P500 (Fig. S1). Conversely, P700- and H700-amended soils were similar in appearance as the control, with the majority of *Eruca vesicaria* leaves displaying normal green coloration. However, a few plants also possessed white coloration as in the control (Fig. S1). These data are also supported by the results from the above-ground biomass after 14 days from CMZ application date (Fig. 5A). Control and BC 700C treatments possessed similar biomass weights ($p > 0.05$), corresponding with visually green-colored plants. On the other hand, for the rest of treatments, plants behaved similar to unamended soil, without no significant differences in biomass ($p < 0.05$) across this grouping (Fig. 5A). These results indicate that the BCs made at lower temperature were ineffective in preventing CMZ phytotoxicity. Most likely, the low solution concentrations of CMZ in the soil pots amended with P700 and H700 together with the difficulties to be desorbed reduced herbicide efficacy of CMZ in controlling *Eruca vesicaria* in the high temperature biochar treatments.

The addition of BYP in *Eruca vesicaria* growth is shown in Figure S2. The visual evaluation of the plants after 7 days following BYP application revealed withered leaves with amendment of H700 and P700 biochars (Fig. S2). To corroborate the efficacy of the herbicide, the above-ground biomass was also weighted and the results are shown in Fig. 5B. Addition of P700- and H700 to soil resulted in similar amounts of biomass ($p > 0.05$) as compared to unamended soil, but markedly different respect to the control ($p < 0.05$). These results suggested that, most likely, BYP sorption mechanisms occur slowly and, since the herbicide was applied post-emergence, its efficacy is not greatly affected as for the pre-emergence application. Hence, from our results it is inferred that pre- or post-emergence application timings is an important factor when evaluating the effect of BC amendment on herbicide efficacy.

The findings from this work clearly demonstrated that amending soils with biochar prepared from hardwood species at different temperatures had different effects on the soil fate of studied herbicides depending on both BC and herbicides characteristics. The larger surface area of biochars made at 700 ºC increased sorption capacities for CMZ and BYP. Additionally, this sortion also involves greater hysteresis during desorption. Furthermore, sorption-desorption behavior of CMZ and BYP in BC-amended soil had direct impact on their degradation, leaching and efficacy. In every case, addition of BC resulted in longer persistence of CMZ, without a direct correlation between sorption and persistence, which can be attributed to changes in sorption and/or other effects generated by the presence of BC in soil. However, BYP persistence was directly related to sorption in BC-amended soils. Leaching experiments supplied direct evidence of the effectiveness of biochar reduces the instant leaching of both herbicides. Greater sorption, persistence and immobilizing capacity only reduced the phytotoxicity of CMZ in soils amended with the biochars obtained at 700ºC. Based on our adsorption–desorption data and previous studies,[20] it appears that weed and pest control requirements would be best served by biochars possessing low SSAs. Our results emphasize the need for proper screening of BC and herbicide characteristics before application can maximize adequate pest control. This data suggests that lower pyrolysis temperature biochars (350-500 C) could be the better route for minimizing environmental impacts of applied pesticides, while optimizing efficacy.

ABBREVIATIONS USED

BYP, bispyribac sodium; CMZ, clomazone; BC, biochar; DOC, dissolved organic carbon; K_{oc}, organic carbon-water partition coefficient; P350, P500, P700 pecan wood biochars prepared at 350, 500 and 700 ºC; H350, H500 and H700 hickory wood biochars HPLC, high performance liquid cromathography; SSA, specific surface area; TII, Thermodynamic index of irreversibility.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information Available:

Figure S1. Effect of CMZ on *Eruca vesicaria* in unamended soil and BC-amended soil at a rate of 2% (w:w) after 14 days of herbicide application;

Figure S2. Effect of BYP on *Eruca vesicaria* in unamended soil and BC-amended soil at a rate of 2% (w:w) after 7 days of herbicide application;

Table S1. Freundlich coefficients for clomazone (CMZ) sorption isotherms on BC-amended soil;

Table S2. Freundlich coefficients for bispyribac sodium (BYP) sorption-desorption isotherms on BC-amended soil.

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Funding

This work has been financed by the Spanish Ministry of Economy and Competitiveness (MINECO Project AGL2013-48446-C3-1-R and AGL2016-77821-R), EU FACCE-JPI (Designchar4food Project) and Junta de Andalucía (P011-AGR-7400 and Research Group AGR-264), co-financed with European FEDER funds. The use of trade, firm, or corporation names in this manuscript is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the United States Department of Agriculture-Agricultural Research Service, or the Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC) of any product or service to the exclusion of others that may be suitable.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank I. Avilés and I. González for their laboratory assistance.

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FIGURE CAPTIONS

Figure 1. Chemical structures of clomazone and bispyribac sodium.

Figure 2. Sorption-desorption isotherms for clomazone (A and B) and bispyribac sodium(C and D) in unamended soil and amended soil with BC´s at 2 %. Solid and empty symbols correspond with sorption and desorption branch, respectively.

Figure 3. CMZ (A and B) and BYP (C) dissipation curves in unamended and BC-amended soil. In the dissipation curves, symbols represent experimental data and lines are the fittings to single first-order dissipation kinetics. Error bars correspond to standard errors of triplicate measurements

Figure 4. CMZ extracted from different depths of the soil columns at the end of the leaching experiment.

Figure 5. Biomass of *Eruca vesicaria* plants with different treatments: control (no herbicide), unamended soil and BC-amended soil at a rate of 2% (w:w) after 14 days of herbicide application for CMZ or 7 days for BYP. Different letter on the bars indicate statistically significant differences between the treatments ($p < 0.05$).

Table 1. Selected Properties and Nomenclature of the Biochars Used in this Work.[a]

Feedstock	Temperature (ºC)	Nomenclature	pH[b]	SSA (m^2/g)	%C	%H	% O[c]	DOC (mg/L)[d]
Pecan	350	P350	6.78	0.6	70.18	5.05	24.54	17.9
Pecan	500	P500	9.70	7.5	81.56	3.53	14.51	8.6
Pecan	700	P700	10.42	280.9	83.69	1.50	14.61	10.8
Hickory	350	H350	6.55	0.8	69.40	3.91	26.45	25.3
Hickory	500	H500	9.38	14.4	75.99	2.88	20.74	6.9
Hickory	700	H700	10.44	229.7	81.07	1.09	17.76	4.6

[a] From Trigo et al. 2016

[b] Determined in a 1:10 (w/v) biochar/ water suspension

[c] Calculated assuming less than 1 % of S and without ash content.

[d] Determined in a 1:2 (w/v) biochar/ 0.01 M $CaCl_2$ slurry

Table 2. First-order Dissipation Constants and TD_{50} for CMZ and BYP in Unamended and BC-amended soil. Different Letters in Each Column for Each Herbicide Indicate Significant Differences in Numbers ($p < 0.05$).

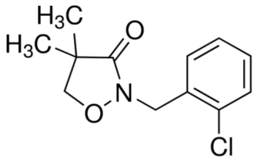
Treatment	Lag phase[a] (days)	k [b] (days^{-1})	R^2	TD_{50}[c] (days)
		Clomazone		
Unamended Soil	7	0.032 ± 0.002[d] a	0.982	29
P350-amended soil	20	0.009 ± 0.002 b,c	0.892	97
P500-amended soil	7	0.012 ± 0.001 b,c	0.954	77
P700-amended soil	-	0.008 ± 0.001 b,c	0.843	99
H350-amended soil	20	0.008 ± 0.001 c	0.939	107
H500-amended soil	7	0.012 ± 0.001 b	0.992	65
H700-amended soil	-	0.010 ± 0.001 b,c	0.907	67
		Bispyribac sodium		
Unamended Soil	7	0.047 ± 0.005 a	0.951	21
P700-amended soil	7	0.009 ± 0.001 b	0.923	84
H700-amended soil	14	0.035 ± 0.001 a	0.999	33

[a] lag phase is the period from the start of the incubation experiment to the time point at which the pesticides decrease to 95%.
[b] calculated excluding the lag-phase
[c] Time for the 50% dissipation plus the lag phase when necessary
[d] value ± standard error.

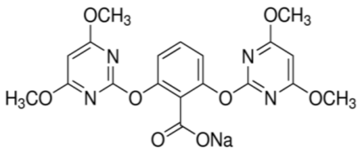
Table 3. Percentage of CMZ and BYP Leached, Extracted and Note Recovered Different Letters in Each Column for Each Herbicide Indicate Significant Differences in Numbers ($p < 0.05$).

Treatment	Leached (%)	Extracted (%)	Not recovered (%)
Clomazone			
Unamended Soil	59 ± 1[a] a	20 ± 5	21
P350-amended soil	n.d.[b]	64 ± 4	36
P500-amended soil	n.d.	49 ± 8	51
P700-amended soil	n.d.	66 ± 2	34
H350-amended soil	n.d.	64 ± 6	36
H500-amended soil	n.d.	46 ± 8	54
H700-amended soil	n.d.	52 ± 1	48
Bispyribac sodium			
Unamended Soil	49 ± 1 a	n.d.	51
H700-amended soil	12 ± 2 b	23 ± 2	65
P700-amended soil	n.d.	64 ± 5	36

[a] value ± standard error.
[b] not detected



Clomazone



Bispyribac sodium

Figure 1. Chemical structures of clomazone and bispyribac sodium.

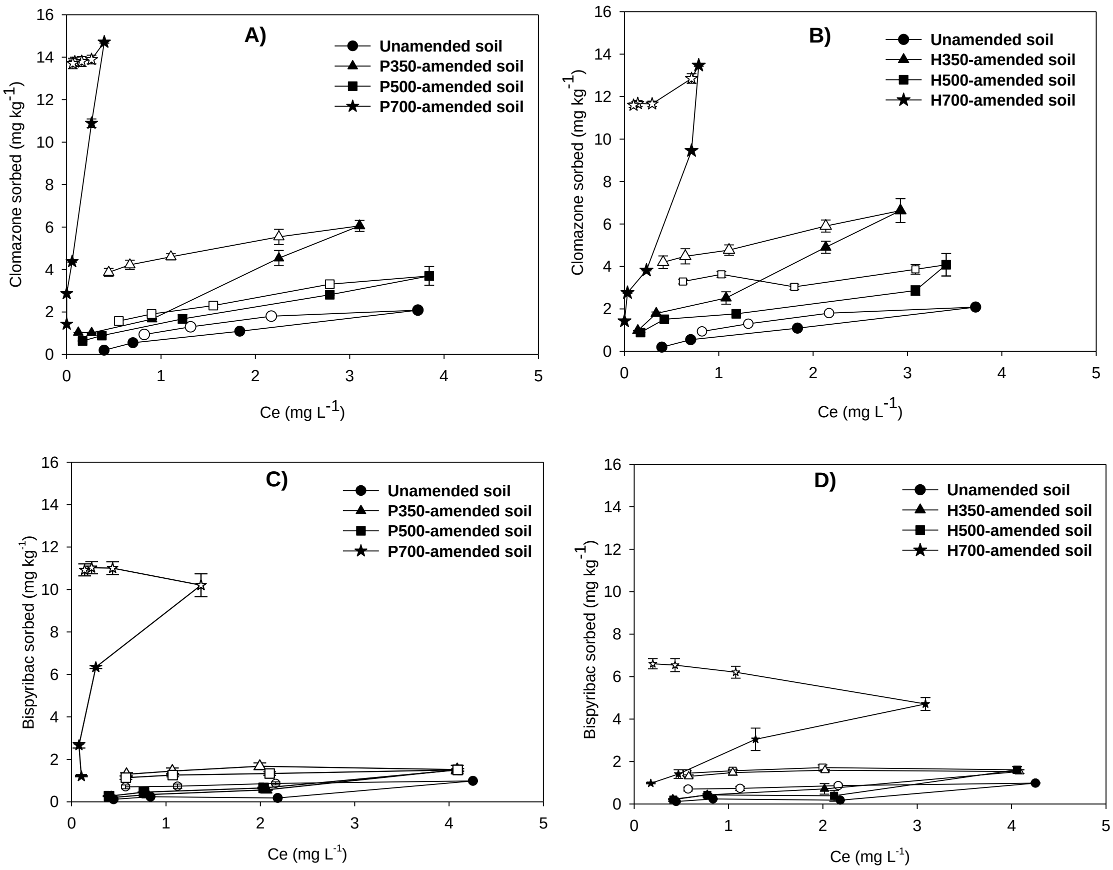
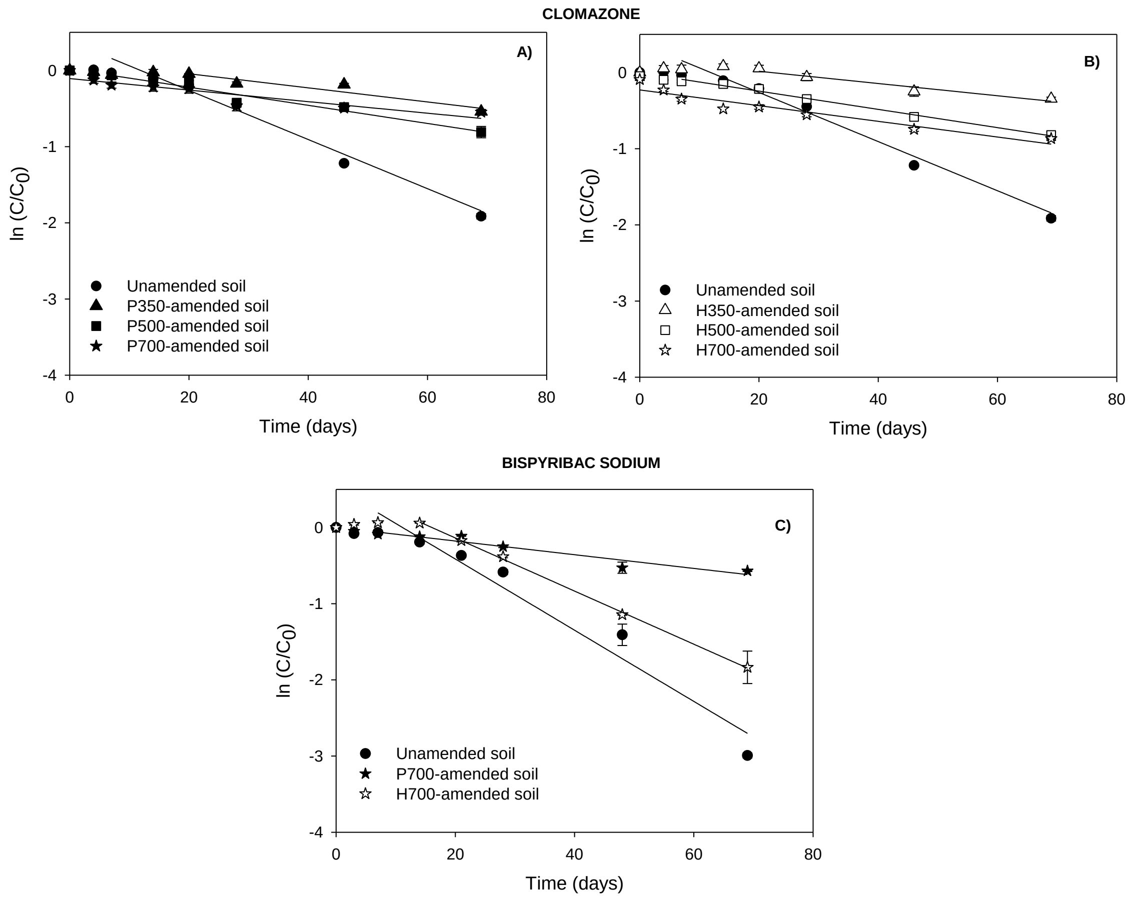


Figure 2. Sorption-desorption isotherms for clomazone (A and B) and bispyribac sodium(C and D) in unamended soil and amended soil with BC´s at 2 %. Solid and empty symbols correspond with sorption and desorption branch, respectively.



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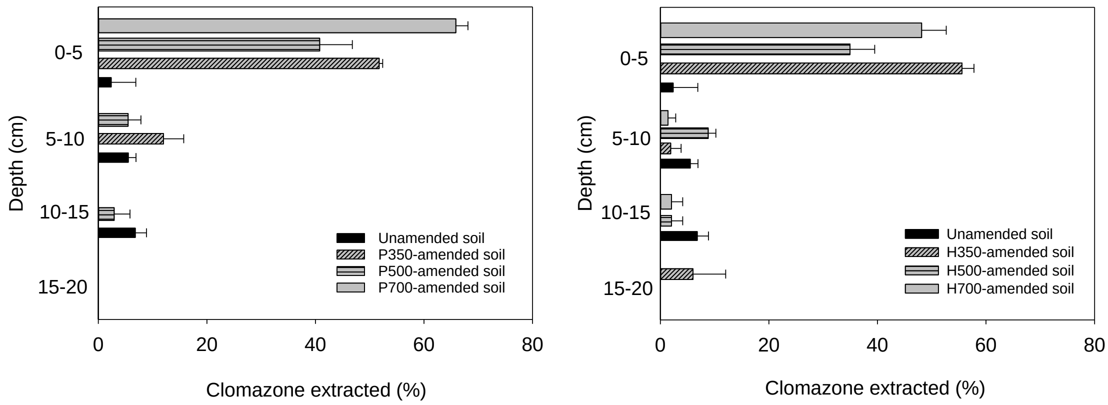
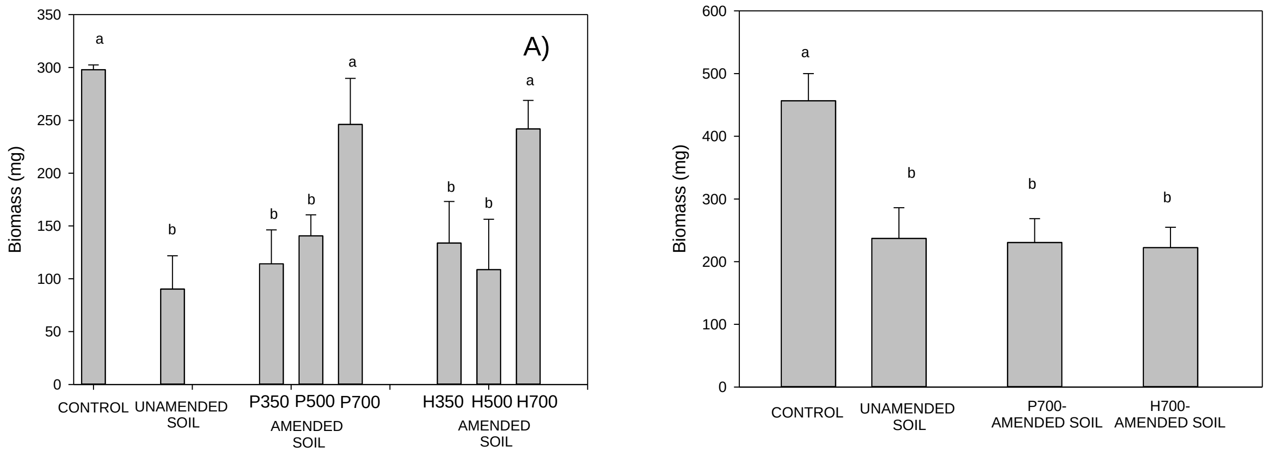


Figure 4. CMZ extracted from different depths of the soil columns at the end of the leaching experiment.



B)

Figure 5. Biomass of *Eruca vesicaria* plants with different treatments: control (no herbicide), unamended soil and BC-amended soil at a rate of 2% (w:w) after 14 days of herbicide application for CMZ (A) or 7 days for BYP (B). Different letter on the bars indicate statistically significant differences between the treatments ($p < 0.05$).

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