**Dynamic Effect of Fresh and Aged Biochar on the Behavior of the Herbicide
Mesotrione in Soils**

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ABSTRACT

In this study, we assessed the sorption, dissipation, and leaching of the herbicide mesotrione in soil amended with fresh and field-aged biochars, when added to the soil. The aging process was performed by burying the fresh biochar at 10 cm depth in three soils located in different points across the USA [Wisconsin (ABC_WI), Idaho (ABC_ID) and South Carolina (ABC_SC)] for six months. ABC_ID and ABC_SC slightly increased the sorption of mesotrione in soils, whereas ABC_WI removed greater amounts of herbicide from the solution. This was attributed to differences in water-soluble components and metal content of this aged biochar. Consequently, the persistence of the herbicide in the amended soils with fresh biochar and ABC_ID and ABC_SC were similar to that in unamended soils, while ABC_WI slightly increased mesotrione half-life. Differences between treatments were detected in leaching studies although no direct relationship with the dissipation batch studies was observed. Mesotrione leaching could not be detected in soil columns amended with ABC_WI and was high for the rest of treatments. The outcomes from this work demonstrate that temporal variability of biochar sorption capacities due to soil exposure can occur altering the mesotrione's behavior in biochar amended soils.

KEYWORDS: biodegradation; bound residues; desorption; leaching; organic amendments; soil weathering

INTRODUCTION

The solid material resulting after the thermochemical transformation of biomass in anaerobic environment (pyrolysis) when used as a soil amendment is called biochar (BC).¹ One of the main benefits for the potential use of biochar is related to its ability for mitigating climate change as a consequence of its carbon sequestration ability,² due to its slower microbial decomposition as compared to the raw biomass.³ BC is considered a multifunctional material with different environmental and agronomic benefits.⁴ Among others, it affects nutrient availability and can improve some physicochemical properties of soils, including pH, cation exchange capacity, and bulk density.⁵ Thereby, BC has the potential to be an important soil management tool in the context of sustainable agriculture and land reclamation.

The presence of pesticide residues in soil is still a matter of concern because of their undesirable effects on the environment and human health.⁶ Due to the peculiarity of its surface, biochar is able to remove organic compounds, such as pesticides, from water and soils.⁷ The key governing the sorption capacity of the material is the initial feedstock and pyrolysis conditions, resulting in a vast heterogeneous and complex structure needed to be customized. Usually, the effects of the amendment of soil with BC regarding the behavior of pesticides in soils have been evaluated when BC is freshly applied to soil,^{5,8} being the properties of newly produced biochar well documented. Nevertheless, less and inconsistent knowledge exists dealing with the long-term BC changes after soil incorporation¹ relative to sorption pesticide behavior.⁹ The reactions between biochar and soil constituents, such as dissolved organic and inorganic matter, microorganisms, fauna, and plant roots, can affect the stability of biochars,¹⁰ changing the surface properties of the carbonaceous material,¹¹ and subsequently, affecting the interactions BC-pesticides. As residence time in soils increases, physical and chemical changes occur by abiotic and

biotic reactions.¹¹ With time, more heterogeneous biochar particles are formed, which become covered by a plaque of mineral and organic compounds.^{12,13} These alterations modify the stability of the BC and challenges our ability to predict their long-term ecosystem services.^{9,11,14}

Several studies have pointed out lower sorption of pesticides after the aging of biochar in soil due to blockage of limited number of the sorption sites on BC surfaces,¹⁵ hypothesized by dissolved organic carbon.^{16,17} Conversely, field-aging can increase the surface area and porosity of the material through physical disintegration resulting in greater sorption of pesticides.¹⁸ Also, as with fresh biochar, the initial pyrolysis conditions has been reported to influence sorption capacity of aged biochar.¹⁹ More recently, we found that three highly persistent ionizable pesticides had a completely different sorption behavior over time on aged BC, affecting their bioavailability in soil.⁹ All these results bring to light the difficulties to standardize BC production to maximize its utilization as sorbent amendment.^{2,20,21} Therefore, the field-aging of biochar merits further investigations to predict the long-term behavior of pesticides in soil.

Mesotrione [2-(4-mesyl-2-nitrobenzoyl)-1,3-cyclohexanedione] (Figure 1) is a pre- and early post-emergence triketone herbicide widely used for controlling some grass and broad-leaved weeds mainly in maize crops. It is a synthetic leptospermone analog developed to mimic the effects of this natural herbicide.²² This work aims to get insight into the behavior of this new generation herbicide, since little is known about its fate in BC amended soils. Furthermore, no research has been conducted on the assessment on how aging of this BC material affects sorption, dissipation and leaching of mesotrione in soils. We hypothesized that the aging of a fresh BC during 6 months in three different soils located across the USA will affect the dynamics of mesotrione in soil. Hence, the specific objectives of this work were: i) to evaluate the evolution of the properties of one

BC after aging for 6 months in three different locations and ii) to assess the sorption, dissipation and leaching of mesotrione in soil after the addition of the fresh BC and its corresponding aged samples. The information provided should be helpful to elucidate the changes of BC sorption capacities in soil over time and to predict its long-term behavior particularly affecting the dynamic in soils of new generation and low persistent herbicides such as mesotrione.

MATERIALS AND METHODS

Herbicide. Mesotrione (99.6 %) was supplied by Sigma-Aldrich. It has a molecular weight of 339.3 g/mol and a water solubility of 1500 mg/L at 20°C, vapor pressure of 5.70×10^{-3} Pa at 25 °C and *pKa* of 3.12.²³ A stock solution of 200 mg/L in methanol of mesotrione was used to perform laboratory experiments and in external calibration curves. The degradation product of mesotrione 2-amino-4-methylsulfonylbenzoic acid (AMBA) was also purchased from Sigma Aldrich (97% chemical purity). The chemical structure of mesotrione is shown in Figure 1.

Soil. A sandy loam soil (82% sand, 3 % silt, and 15% clay) was collected from the CSIC experimental station in Seville (Spain) (37°16' 54" N, 6°3' 54" W). Soil contained 0.65 % organic carbon (OC) and 1.9% of CaCO₃. The pH was 8.2, measured in a 1/2.5 (w/v) soil:deionized water slurry. The soil was free of previous mesotrione treatments.

Amendments. The fresh biochar (BCF) was prepared from oak wood by slow pyrolysis in a Missouri-type concrete kiln at 550 °C (maximum pyrolysis temperature). Some of this BC were initially placed into multiple mesh bags (Mesh Cord Bags, Vaultz®, Idea Stream Consumer Products LLC, Cleveland, OH; 1.5 mm openings; total of 9 bags). Triplicate BC filled bags were buried at 10 cm at each of three locations during the growing season (April-October), along with a temperature logger (Onset HOBO, Part

Number: UA-001-08) to record average soil temperature during the field exposure time (Figure S1). The three locations were (1) a silt loam soil located in Columbia County, Wisconsin (ABC_WI), (2) a sandy loam in Florence, SC (ABC_SC) and (3) a silt loam in Kimberly, ID (ABC_ID) for 6 months (~April to October; Figure S1). Soil chemical properties are listed in Table S1. These soils were selected for being located in different places with different physicochemical properties which is expected to modify differently the surfaces of the aged biochars (Table S1).

Once the mesh bags were retrieved the data from the temperature logger was downloaded and then the bags were washed with deionized water from a laboratory faucet to remove the visible soil particles present on the samples. Then, the biochars were taken out from the bags and oven dried at 105 °C. Prior to the biochars being ground (<2 mm) and homogenized, the mass loss or gain from each BC bag was calculated (Table S1). The ABC_WI was unique from the standpoint there was an observed increase in mass, where the other two locations possessed an overall small mass loss ($p < 0.05$; Table S1). Further evaluation into the causes of these differences were not conducted.

Biochars samples were characterized through different techniques. The elemental analysis of the samples was conducted by using a combustion elemental analyzer (LECO, Model CHN 932). Physisorption of CO₂ was used to determine the surface area of the BC samples with an ASAP Micromeritics Model 2420. Zeta potential values for BC samples were obtained at the pH of the suspensions of 1 mg/mL and measured with a Zetasizer Nano ZS equipment (Malvern Instrument). Fourier-transform infrared (FTIR) spectra were recorded on a Jasco FT/IR 6300 spectrometer (Jasco Europe s.r.l.) equipped with deuterated triglycine (DTGS) and Mercury-cadmium-telluride (MCT) detectors, using the spectral range of 4000–500 cm⁻¹; for the analysis, pellets of samples prepared at 1% (w/w) in KBr were prepared. Finally, the pH was measured in a 1:2.5 (w:v)

biochar:deionized water slurry. An additional analysis of the dissolved organic carbon (DOC) of the BC samples was performed by fluorescence spectroscopy. For this, 0.5 g of each of BC was shaken at room temperature with 10 mL of a CaCl_2 solution (0.01 M) to mimic the ionic strength of soil pore water. After 15 minutes, the suspensions were centrifuged, and the supernatants were removed and filtered through 0.45 μm filters to measure the carbon content by a total organic carbon analyzer (Shimadzu TOC-5050A). In order to avoid interferences by concentration effects, prior to fluorescence measurements, samples were diluted to obtain an absorbance value at 254 nm of <1 .²⁴ The samples were analyzed in a spectrophotometer (F-2500 FL- Spectrophotometer HITACHI) recording the spectra from 300 to 480 nm under excitation at 254 nm.

Sorption of mesotrione on biochar samples, unamended soil and soil amended with biochar. The sorption of mesotrione was determined both on the biochars samples and on unamended soil and on soil amended with the fresh and aged biochars at a rate of 2% (w/w). This rate is equivalent to a dose of 13 t/ha for the first 5 cm of soil and bulk density of soil of 1.3 g/cm³, being in the range of amount at which biochar can provide agronomical benefit. The methodology used was the batch equilibration technique at a single initial concentration of mesotrione. Triplicate BC samples (40 mg) or unamended and BC-amended soils (4 g) were placed in Pyrex® glass tubes and were treated with 8 mL of an aqueous solution of the herbicide of 1 mg/L (C_i). Samples were shaken for 24 h at 20 ± 2 °C in a rotating (end-over-end) shaker. Then, the suspensions were centrifuged (15 min at 8000 rpm) and 4 mL of the supernatant was removed and filtered (0.45 μm pore size GHP membrane disk filters) prior to analysis by high-performance liquid chromatography (HPLC). Previously, 24h-contact time was tested to be enough for reaching the equilibrium, and that no measurable degradation occurred during this period. Furthermore, there was no sorption on Pyrex® tubes, syringes or syringe filters of control

samples (data not shown). The amount of mesotrione sorbed C_s (mg/kg), was calculated as the difference between that concentration initially present in solution (C_i) and that remaining after equilibration with the sorbents (C_e).

A desorption experiment was additionally performed. For this purpose, 40 mg of BC samples in triplicate were equilibrated in Pyrex® glass tubes with 8 mL of an aqueous solution of mesotrione with initial concentration of 1 mg L⁻¹. Samples were shaken for 24 h at 20 ± 2 °C, suspensions centrifuged for 15 min, and 6 mL of the supernatant removed and filtered prior to analysis by HPLC. The 6 mL of supernatant removed were replaced by 6 mL of the extractant, consisting of 40/60 (v/v) MeOH/H₃PO₄ (pH=2). Samples were resuspended and shaken for 24 h at 20 ± 2 °C, centrifuged, filtered and analyzed by HPLC. In this way, the amount of pesticide initially sorbed was directly determined from their desorbed amounts determined during the desorption step.

Soil incubation experiment. Laboratory incubation experiments were conducted to assess the dissipation of mesotrione in unamended soil and in soil amended with the fresh and aged biochars at a rate of 2% (w/w). Simultaneously, the extent of the herbicide sorption during the experiment was also measured following a methodology proposed in Gámiz et al.^{25,26} In duplicate, mesotrione was spiked to 200 g of unamended soil or soil amended with the BC samples, previously placed in glass jars (250 mL) closed with screw caps, to reach a final application rate of 1 mg/kg dry soil. This is approximately 10 times of the recommended dose, incremented to ensure a reliable quantification of the herbicide. The moisture content was adjusted close to the water holding capacity of the soils (~30%) and kept at a constant level by adding Milli-Q ultrapure water when necessary by gravimetric weighing. Soil samples were incubated under aerobic conditions at 25 ± 2 °C in darkness to avoid photodegradation for 11 days. At different times after the herbicide application, aliquots of 3 g of soil were taken and immediately frozen. Mesotrione

residues in soil samples were extracted with 8 mL of 40/60 (v/v) denatured MeOH/H₃PO₄ (pH=2) after 24 h shaking and centrifugation at 8000 rpm for 10 minutes. The supernatant was filtered using GHP filters (0.45 µm) and analyzed by HPLC to determine the total amount of herbicide in the soil samples. Preliminary tests showed that the recovery rate of mesotrione for this extraction procedure was > 95% for a dose of 2 mg/kg.

The fraction of mesotrione sorbed during the incubation experiment was determined at different times after herbicide application (0, 1, 4, and 7 days). By means of this methodology, it is possible to ascertain whether or not the addition of fresh or aged biochar to soil produces changes in the readily bioavailable fraction of mesotrione during its dissipation in soil, for instance, if greater sorption implies the enhancement of mesotrione persistence. For this aim, 5 g of unamended soil and soil amended with fresh an aged biochars were directly weighed from the incubation jars in Macrosep®Advance Centrifugal tubes (Pall Corporation) containing a polyethersulfone membrane of 0.45 µm. The tubes were centrifuged at 10000 rpm for 10 min and the supernatant obtained were immediately analyzed by HPLC to determine the aqueous concentration of mesotrione (Ce) in unamended and amended soils, Amounts of herbicide sorbed (%Ads) were calculated from the difference between the residues extracted from 3 g soil with 8 mL of 40/60 (v/v) MeOH/H₃PO₄ (pH=2), which corresponded with the total amount of mesotrione present in soil at each selected time, and its concentration in the aqueous phase determined with this procedure.⁹

Leaching experiment. The movement of mesotrione through soil profile was simulated using glass columns of 30 cm length and 3.1 cm internal diameter filled with 160 g of unamended soil to a height of 20 cm soil. The bottom of the columns was also filled with glass wool and 10 g of sea sand to avoid soil losses. The amendment of the soil consisted of mixing the upper 5 cm of soil (40 g) with each BC (fresh or aged) at a

rate of 2% (w/w). Finally, 10 g of sea sand were also placed on the top column to favor the homogeneous distribution of the compound and water during the application. The experiment was conducted in triplicate. The columns were saturated with 100 mL of deionized water and allowed to drain for 24h. The resulting pore volume (V_p) was 51 ± 1 mL across all treatments, calculated as the difference between the amount of water applied and the amount of water recovered in leachates in this saturation step. For the leaching experiment, mesotrione was applied to the top of the columns at a rate of 1 kg/ha (0.075 mg per column), as in the incubation experiment, this dose was increased to get reliable measurement. Fifteen mL of deionized water was daily added to the columns, up to a total volume of 255 mL, which is approximately 300 L/m², amount similar to the average annual precipitation in the area from which the soil was sampled. The amount leached every day was 15 mL since the columns were saturated to keep the flow constant along the experiment. Leachates were collected, and the concentration of mesotrione in the leachates was determined by HPLC. The remained amount of mesotrione in soil columns at the end of the leaching experiment were extracted from different depths (0-5, 5-10, 10-15, and 15-20 cm) with 100 mL of solvent as described in the soil dissipation experiment.

Data treatment and modeling. Sorption of mesotrione on BC samples and on unamended and amended soils was evaluated by the percentage of mesotrione sorbed at single initial concentration as % Ads = $[(C_i - C_e)/C_i] \times 100$. Distribution coefficients, K_d (L kg⁻¹), were calculated as $K_d = C_s/C_e$.

Dissipation data were fitted to two different kinetics models, sigmoidal and first-order kinetics, following these expressions:

a) First-order kinetic equation:

$$C = C_0 e^{-k \cdot t} \quad (1)$$

where C (mg/kg) is the mesotrione concentration in soil at time t (days), C_0 (mg/kg) is the herbicide concentration in soil extracted at time zero, and k (days⁻¹) is the single first-order dissipation rate.

b) Sigmoidal four parameters equation:

$$C = C_{\infty} + \frac{a}{1 + e^{-\left(\frac{t-t_0}{b}\right)}} \quad (2)$$

where C (mg kg⁻¹) is the mesotrione concentration in soil at time t (days), C_{∞} (mg/kg) is the herbicide concentration in soil at $t = \infty$, i.e. the amount not degraded, and a , b and t_0 are constants that define the sigmoidal curve.²⁵

Calculations of the DT_{50} . The time required to reduce to 50% of the initial concentration of the herbicides, DT_{50} , was calculated according to the equation (1) or (2). For the first-order model, the half-lives (DT_{50}) were calculated as $DT_{50} = 0.693/k$ and the sigmoidal model DT_{50} was calculated according to $DT_{50} = t_0 - b \cdot \ln[2a/(C_{ini} - 2C_0) - 1]$, where $C_{ini} = C_0 + a/(1 + e^{t_0/b})$. The goodness of the models was compared using the chi-square (χ^2) test.

The fitting of the curves and the statistical analyses were performed with Sigma Plot 13.0 software. Treatment effects were determined by analysis of variance (ANOVA) and t-tests. A p value < 0.05 indicated statistical significance.

Herbicide analysis. The quantification of the herbicide was performed by means of high-performance liquid chromatography technique (HPLC) coupled to diode-array detector (Model Waters 600E chromatograph and Waters 996 detector), and Empower software as the data acquisition and processing control system. A Kinetex C18 of 150 mm length x 4.6 mm internal diameter (i.d.) and 5 μ m particle size (Phenomenex) column was used for the determination under the following analytical conditions: flow rate of 1 mL/min, 25 μ L injection volume, mobile phase 40:60 (v/v) CH₃OH/0.01 M H₃PO₄ (pH 2.2) and UV detection at 220 nm. Under these conditions mesotrione eluted at 5.8 min.

The detection and quantification limit were 0.005 and 0.01 mg/L calculated as the concentration resulting in an S/N ratio of 3:1 and 10:1, respectively. The analysis of the metabolite AMBA was also performed by means of HPLC using the specific analytical conditions: flow rate of 1 mL/min, 25 μ L injection volume, mobile phase 20:80 (v/v) CH₃OH/0.01 M H₃PO₄ (pH 2.2) and UV detection at 225 nm. The detection and quantification limit were 0.005 and 0.01 mg/L, respectively.

RESULTS AND DISCUSSION

Characterization of the biochars. Typical variation in biochars properties were observed after aging in soil (Table 1): C content, SSA and dissolved organic carbon (DOC) decreased and N and ash content increased^{11,14,27–29}. Lower SSA values are associated with blockage of BC pores by organic matter and/or destruction of the physical pore connectivity.^{30–32} Aging of the BC also enhances the polarity (O/C) of the material.¹¹

The bands between 675 and 890 cm⁻¹ in FT-IR spectra are assigned to the out-of-plane bending aromatic C-H bonds^{33,34} (Figure 2), which can overlap with those characteristic of carbonate salts, which usually appear in biochars produced at 500 °C. Most likely, this can become significant in the case of ABC_ID and ABC_SC, since these biochars contained greater amounts of ash and Ca (Table 1 and Table S2). The broadband appearing only in the fresh BC at 1180 cm⁻¹ is typically assigned to the C-O stretching vibration, present in cellulose-derived materials.^{33,35} However, in this range the bands may overlap with the O-H stretching modes of phenolic compounds.¹ The bands appearing at 1430 and 1600 cm⁻¹ were attributed to the C=C stretching vibration of the aromatic ring bonds, which are more intense in aged biochars. The band at 1600 cm⁻¹ can also be attributed to the tension mode of carbonyl groups -C=O of conjugated ketones and quinones as well as the ionized carboxyl group (-COO⁻), while the band at 1700 cm⁻¹

¹ is attributed to carboxyl groups mainly in its molecular form (-COOH).^{33,36} The surface functionalization of the aged samples derived in greater O content which could contribute to the enhancement of metal content in ABC_ID and ABC_WI, specifically, regarding Fe, Al and Ca for ABC_SC (Table S2).

Degradation of the labile fraction¹⁸ or partial solubilization and/or leaching can be the reason for the lower DOC of the aged BC^{12,27,30,32} The latter has been also associated with the oxidation of the material, since most of the water-soluble fraction contains O-moities,³⁷ which is supported by the higher % O of the aged samples (Table 1) and higher intensity of the band in the FTIR (Figure 2). Additionally, the characteristics of the remained DOC was treatment-dependent. For instance, fresh BC and aged ABC_SC showed higher fluorescence intensity at wavelengths ranging between 380-480 nm (Figure 3), where more condensed soluble fraction tends to fluoresce.²⁴ Conversely, ABC_WI and ABC_ID presented fluorescence maximum < 380 nm wavelength values (Figure 3), typical of more polar and less condensed materials.⁹ Differences between samples can also be related to the presence of metals, which associate differently with the DOC.^{31,37-39}

Sorption of mesotrione on biochar samples and on unamended soil and soil amended with biochar. Sorption data of mesotrione at a single initial concentration of 1 mg/L on fresh and aged biochars is compiled in Table 2. Accordingly, only significant sorption ($p < 0.05$) was measured in the case of ABC_WI (Table 2). The low sorption registered for the fresh BC was expected since the sorption on biochars increases with temperature of pyrolysis, and, overall, the sorption of anionic compounds on carbonaceous materials is usually low.^{9,40} Regarding the aged samples, a completely different behavior was observed between biochars: while ABC_ID and ABC_SC did not show significant sorption, similarly than that observed for the fresh BC ($p > 0.05$) (Table

2), ABC_WI had a high sorption capacity for mesotrione, with a K_d of 145 L/kg (40 % of sorption percentage) (Table 2). Mesotrione has a pK_a of 3.2, hence being an ionizable compound present in solution in mainly as anion at the pH at which the sorption experiment was performed,⁴¹ always > 7.8 (Table 2). This fact would explain the limited sorption of mesotrione to BC, due to the repulsion between negatively charged molecules and, according to their zeta potential values (Table 1), negative surface of fresh and ABC_SC and ABC_ID.^{26,40,42}

Despite differences observed in the compositional chemistry among aged samples, ABC_WI displayed a completely different sorption behavior with a high affinity for mesotrione (Table 2). Most likely, the differences observed in DOC can contribute direct or indirectly to this high mesotrione sorption. The presence of specific DOC compounds can provide additional sorption sites suitable for the herbicide^{43,44} or the different association with the mineral fraction after aging, as suggested previously,⁹ could be responsible for these observations. The affiliated mineral fraction (i.e., ash) could provide sorption sites for dissolved organic carbon, which could favor the sorption of mesotrione on ABC_WI. It has been demonstrated the presence of a complex coating of BC surface during the aging process,¹³ which could contain carbonates. This can be seen in Figure S2. It has been previously reported that the interaction of mineral phases with BC surfaces can produce different effects. For instance,⁴⁵ have recently found that the mineral treatment of a BC prepared at 700 °C enhanced the sorption of the antibiotic sulfamethoxazole, whereas the opposite occurred when the BC was prepared at 400 °C. This brings to light that mineral interactions with carbonaceous materials is still inconsistent and further investigation on this topic is needed.⁴⁶

Desorption of mesotrione was analyzed after its sorption on ABC_WI. The results indicated that the amount of herbicide sorbed was not recovered, which can be attributed

to strong binding to the BC surface and/or to chemical degradation catalyzed by BC or metal species.⁴⁷

The addition of the biochars to soil only changed the sorption behavior of mesotrione in ABC_WI-amended soil. The percentages were similar to those obtained with the isolated material (Table 2 and Table 3). Despite the significant differences, sorption was < 13 % for all cases except for soil amended with ABC_WI which reached almost 40% (Table 3). The K_d value calculated for mesotrione in soil is in line with those found in the literature, ranging between 0.13-5.0 L/kg.^{41,48,49} Variations among mesotrione sorption in soil can be attributed to different pH and OC content of the soils, which are the main parameters that dictate its sorption behavior.⁴¹ The enhancement of mesotrione sorption in ABC_WI-amended soil was a consequence of its ability to remove the herbicide from the solution. However, keeping in mind the K_d of mesotrione obtained for ABC_WI of 145 L/kg (Table 2), this would result in a theoretical calculated K_d value of 2.95 L/kg, according to the expression $K_{d-mixture} = K_{d-soil} f_{soil} + K_{d-sorbent} f_{sorbent}$,⁵⁰ instead of 1.32 L/kg, which is the experimental value. This indicates that the sorption capacity of BC are altered as a function of the soil contact. This was observed for another BC prepared also at 800 °C, although this was freshly applied to soil at a rate of 5% and 10%.⁴⁸

Mesotrione dissipation in soil amended with fresh and aged biochar. Figure 4 and Figure S3 show the dissipation curves for mesotrione in unamended soil and in soil amended with fresh and aged BC under aerobic conditions. The fitting of the dissipation data of mesotrione to first-order and sigmoidal kinetic equations are compiled in Table 4 and represented in Figure 4 and Figure S3. Mesotrione dissipation fitted better to the sigmoidal kinetic, as shown by the corresponding χ^2 values (Table 4) and corroborated by the visual evaluation of the experimental dissipation data for either unamended or

amended soils (Figure 2). When a compound is used as microbial growth substrate, its degradation curves usually are described by a sigmoidal equation, with a lag phase due to the adaptation of microorganisms and/or to an increase in the number (or activity) of degrading microorganisms.²⁵ Additionally, the degradation of mesotrione in soil has been proved to follow mainly biodegradation pathways.^{22,49} These hypotheses agree with our observations.

The dissipation of mesotrione in unamended soil occurred very fast, rendering a DT₅₀ of 5.4 days (Table 4). This has also been reported for mesotrione in other types of soils with TD₅₀ values ranging between 4.5 and 34 days.^{22,23,41,49} Specifically, Chaabane et al. (2008)⁴⁹ attributed the rapid degradation of mesotrione in soil to some reduction of the corresponding amino group owing to the hypothetical presence of specific microflora. This assumption was in good agreement with the better fitting of dissipation curves to a sigmoidal curve here proposed.

The addition of the biochars to soil only had significant effect on mesotrione dissipation in the case of ABC_WI-amended soil (Figure 4), with TD₅₀ of 8.6 days, which is greater compared to the other treatments ($p < 0.05$) (Table 4). Enhancement of mesotrione persistence was also observed after the addition to soil of green compost and sewage sludge, and it was attributed to an increase in herbicide sorption.²² This phenomena has been frequently described for the dissipation of pesticides in soils amended with BC,^{44,51} although not always the addition of organic amendments increases the persistence of a particular compounds, since in some cases microorganisms prefer to use the organic amendment as a carbon source.⁵²

The sorption percentage of mesotrione from the total amount extracted at different incubation times is shown in Figure 5. It is worthy to highlight that the non-recovered amounts are considered non-bioavailable, due to degradation or strong sorption.

Accordingly, greater mesotrione sorption was calculated for ABC_WI-amended soil in comparison to either unamended or BC-amended soil, particularly important at 1 and 4 days after the herbicide spiking ($p < 0.05$). There was a progressive increase in the sorption, which was not observed in the rest of treatments (Figure 5). This can reasonably be attributed to slow sorption kinetics on BC particles.^{26,52} Nevertheless, at 7 days, the amount of mesotrione sorbed was similar for all cases except for the fresh- BC amended soil ($p > 0.05$). However, it has to be considered that at this time of the experiment, mesotrione soil residues in ABC_WI-amended soil were 2-fold greater than in the other treatments ($p < 0.05$), which would explain the greater TD_{50} value. It was also remarkable that the experiment ended at 11 days of herbicide application, since at this time no mesotrione was extracted. The monitoring of the metabolite AMBA during the experiment was also performed and the compound was only detected after a week of mesotrione application, corroborating its biodegradation pathway.

Leaching of mesotrione in soil amended with fresh and aged biochar. The breakthrough curves (BTCs) of mesotrione in unamended soil and BC-amended soils is shown in Figure 6 and Table 5 summarizes the mass balance and relevant data of the leaching experiment.

In contrast to the dissipation experiment, the addition of BC to soil affected differently the leaching of the herbicide. As a result, the total amounts leached were significantly different among treatments ($p < 0.05$), variable amounts of mesotrione were detected in unamended and amended soil with BC and followed the order: unamended > ABC_ID > BCF > ABC_SC > ABC_WI-amended soil (Figure 6 and Table 5). Only ABC_WI-amended soil controlled the downward movement of mesotrione through the soil column. This was also supported by the very low maximum concentration of mesotrione, C_{max} , detected in leachates (Figure 6 and Table 5), whereas higher C_{max}

concentrations in leachates were observed for the other treatments (Table 5). This fact was expected due to the higher sorption capacity measured in the sorption and incubation experiments. In general, greater sorption of pesticides after BC addition to soil has been demonstrated to reduce the movement of highly mobile pesticides through the soil profile when compared to untreated BC soils.^{44,53} Mendes et al.⁴⁸ also reported limited leaching of mesotrione in a BC amended soil respect to an unamended soil, although these authors used higher doses of BC.

Nevertheless, for unamended soil and BC-amended soils, without including ABC_WI, there was no correlation between the sorption capacity of the sorbents, as determined by the batch methodology and during the incubation experiment, and the position at which C_{max} was detected, since, in these the treatments, very low amounts of mesotrione were sorbed (Table 3). This would have resulted also in lower and similar V_P position and total amount leached (Table 5). It has been pointed out the difficulties to link sorption and dissipation with the leaching of pesticides.⁵⁴ Discrepancies found regarding the sorption behavior and dissipation versus the leaching could have resulted from the rapid degradation of the pesticide together with dynamic and saturated conditions of the leaching experiment compared to those environments occurring in the batch and incubation experiments.^{25,55} Likewise, the concentration of the oxygen inside the soil column can be limited affecting the redox conditions, which indirectly can affect the degradation capacity of the specific microorganisms.⁵⁶

Extraction of the soil columns at the end of the leaching experiment revealed that mesotrione remained in the soil columns neither for unamended nor for BC -amended soil (fresh or aged), apart from ABC_WI-amended soil (Table 5). In these cases, herbicide residues were not detected after the extraction of the soil columns (Table 5). For ABC_WI-amended soil, 8% of mesotrione applied to the top of the column remained in

the first 0-5 cm of soil, where the amendment was added (Table 5). This result was consistent with the smaller amounts leached and longer DT₅₀ as compared to unamended and the rest of the BC-amended soils (Table 4, Figure 4). Moreover, it corroborates that when a soil amended with BC displays high affinity for a compound, it prolongs the persistence in the rhizosphere of BC-amended soil, protecting the compound from degradation. The amount of mesotrione not recovered was also greater for ABC_WI-amended soil and it was calculated by the subtraction of the amount applied and the sum of the amounts leached and extracted. Among the causes attributed to this fact, are found the degradation of the herbicide within the soil column and the formation of strongly bound mesotrione residues,⁵⁷ which is in line with that data aforementioned for the desorption. For the rest of treatments, fast degradation was likely the reason of not recovered amount since very low value of DT₅₀ were calculated for these cases. The metabolite AMBA was detected neither in leachates nor at different depths of the columns.

In summary, this work demonstrates that the potential sorption capacity of BC material towards mesotrione changes with time and is soil-dependent. The sorption behavior of aged biochars for mesotrione was affected by the type of dissolved organic carbon and likely, by its indirect effect due to interactions with the mineral fraction of soils, which, we can conclude, to be a key factor when appraising the impact of BC amendment in the fate of pesticides in soils. Further investigations regarding BC–metals interactions are still required. When the aged BC showed affinity for mesotrione, dissipation was enhanced and leaching was controlled, being slow sorption the main sorption mechanism. Likewise, there was no consistency between dissipation and leaching through soil profile, which brings to light the difficulties not only to predict sorption but also to relate dissipation and mobility of pesticides in soils, most likely, due

to the rapid degradation of mesotrione in soil. Since we have demonstrated that the aging effect varied with the type of soil the BC is aged, further investigations are needed matching BC properties in long-term scales with the features of specific compounds, mostly when there are rapidly degraded to control the bioavailability of pesticides.

ABBREVIATIONS USED

ABC_ID, biochar aged in Idaho; ABC_SC, biochar aged in South Caroline; ABC_WI, biochar aged in Wisconsin; AMBA, 2-amino-4-methylsulfonylbenzoic acid; BC, biochar; BCF, fresh biochar; DOC, dissolved organic carbon; HPLC, high performance liquid cromathography; K_d , distribution coefficient; TD50, half-life.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at <http://pubs.acs.org>.

Figure S1, Different locations where the biochar was aged; Figure S2, SEM images of biochar samples; Figure S3, linear fit of mesotrione dissipation curves; Table S1, soil properties; Table S2, relevant metals present in biochar samples; Table S3, parameters of the sigmoidal fitting.

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479 **Notes**

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FIGURE CAPTIONS

Figure 1. Chemical structure of mesotrione.

Figure 2. FT-IR spectra of the biochars used indicating the main characteristic bands.

Figure 3. Emission fluorescence spectra of the DOC of the fresh and aged biochars at excitation wavelength of 254 nm. All spectra are normalized to the maximum.

Figure 4. Dissipation curves of mesotrione for unamended soil or soil amended with fresh aged biochars at 2%. Symbols correspond with experimental data points and bars indicate standard error of two independent replicates. Lines correspond to the fits to sigmoidal dissipation kinetics.

Figure 5. Percentage of mesotrione sorbed from the total amount extracted at different times of the incubation experiment.

Figure 6. Mesotrione breakthrough curves (BTCs) in unamended and amended soil: relative BTCs (left); cumulative BTCs (right).

Table 1. Some Characteristics of the Fresh and Aged Biochars Used in This Work

Biochar	% C	% H	% O ^a	% N	% Ash	SSA (m ² /g) ^b	pH ^c	H/C	O/C	Zeta potential (mV)	DOC ^d (mg/gBC)
BCF	80.1 ± 1.3	2.0 ± 0.1	17.5	0.1 ± 0.1	3.4 ± 0.2	226 ± 3	7.8 ± 0.2	0.03	0.22	-32.7 ± 0.8	7.6 ± 0.2
ABC_WI	77.9 ± 0.9	2.2 ± 0.1	19.3	0.6 ± 0.1	4.5 ± 0.1	218 ± 5	7.4 ± 0.3	0.03	0.25	-28.5 ± 2.3	2.2 ± 0.4
ABC_ID	73.3 ± 5.6	1.5 ± 0.1	24.4	0.8 ± 0.1	14.5 ± 0.1	204 ± 4	7.5 ± 0.1	0.02	0.33	-26.7 ± 3.3	1.8 ± 0.1
ABC_SC	64.9 ± 3.2	2.5 ± 0.5	31.8	0.8 ± 0.1	20.2 ± 0.1	195 ± 7	7.5 ± 0.1	0.04	0.49	-31.2 ± 3.9	1.9 ± 0.2

^a calculated assuming less than 1 % of S without ash content. ^b measured by physisorption of CO₂. ^c measured in a 1:2.5 water:biochar slurries. ^d dissolved organic carbon. ^e value ± standar deviation

Table 2. Distribution Coefficients and Percentages of Mesotrione on Fresh BC and Aged BC.^a

Biochar	Ads %	K _d (L/kg)	pH ^b
BCF	2.3 ± 1.0 ^c a	4.8 ± 2.0 a	7.8
ABC_WI	40.4 ± 7.5 b	145.4 ± 38.7 b	9.0
ABC_ID	6.3 ± 0.8 a	13.4 ± 1.8 a	9.2
ABC_SC	1.5 ± 0.1 a	3.1 ± 0.2 b	8.7

^a Different letters in each column indicate significant differences in values ($p < 0.05$). ^b final pH after sorption experiment. ^c value ± standard error

Table 3. Distribution Coefficients and Percentages of Sorption for Mesotrione in Unamended Soil and Soil Amended with Fresh and Aged Biochars. ^a

Treatments	Ads %	Kd (L/kg)	pH ^b
Unamended soil	2.3 ± 0.3 ^c a	0.05 ± 0.01 a	7.8
BCF-amended soil	6.6 ± 1.1 b	0.14 ± 0.03 b	8.1
ABC_WI-amended soil	39.7 ± 0.1 c	1.32 ± 0.01 c	7.8
ABC_ID-amended soil	7.2 ± 0.8 b	0.15 ± 0.02 b	7.8
ABC_SC-amended soil	12.7 ± 1.1 d	0.29 ± 0.03 d	7.8

^a Different letters in each column indicate significant differences in values ($p < 0.05$). ^b final pH after sorption experiment. ^c value ± standard error

Table 4. Dissipation Parameters for Mesotrione in Unamended Soil and Soil Amended with Fresh and Aged Biochar After Fitting the Data to First-Order and Sigmoidal Curves. ^a

	First-order			Sigmoidal		
	DT ₅₀	R ²	χ^2	DT ₅₀	R ²	χ^2
Unamended soil	2.99 (4.3-2.3) a	0.895	18.4	5.4 (5.1-5.6) a	0.990	8.0
BCF-amended soil	3.56 (2.8-4.8) a	0.913	16.1	5.7 (5.6-5.8) a	0.990	7.5
ABC_WI-amended soil	5.93 (4.9-7.5) b	0.876	16.7	8.6 (7.4-18.3) b	0.998	3.0
ABC_ID-amended soil	3.01 (4.6-2.2) a	0.858	21.2	5.5 (5.45-5.6) a	0.999	1.8
ABC_SC-amended soil	3.36 (5.0-2.5) a	0.865	20.1	5.7 (5.6-5.8) a	0.999	2.3

^a Different letters in each column indicate significant differences in values ($p < 0.05$).

Table 5. Summary of Mesotrione Leaching Data Extracted from the Relative and Cumulative Breakthrough Curves (BTCs) in Unamended and BC-Amended Soil. ^a

Treatment	V _P ^b	C _{max} (mg/L) ^c	Total leached (%)	Mesotrione extracted (%)	Not recovered amount (%)
Unamended soil	1.51	1.31 ± 0.07 ^d a	69 ± 1 a	< 1	31
BCF-amended soil	1.38	0.98 ± 0.03 b	53 ± 1 b	< 1	47
ABC_WI- amended soil	1.20	0.09 ± 0.02 c	3 ± 1 c	8 ± 1 ^e	89
ABC_ID- amended soil	1.51	1.26 ± 0.06 a	64 ± 1 d	< 1	36
ABC_SC- amended soil	1.46	0.82 ± 0.03 b	43 ± 1 e	< 1	57

^a Different letters in each column indicate significant differences in values ($p < 0.05$) ^b number of pore volume at which was detected the C_{max}. ^c C_{max} maximum concentration of mesotrione in leachates. ^d value ± standard error. ^e Extracted from the first 0-5 cm of soil

Figure 1. Chemical structure of mesotrione.

Figure 2. FT-IR spectra of the biochars used indicating the main characteristic bands.

Figure 3. Emission fluorescence spectra of the DOC of the fresh and aged biochars at excitation wavelength of 254 nm. All spectra are normalized to the maximum.

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