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Degradation Process of Herbicides in Biochar-Amended Soils: Impact on Persistence and Remediation

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Abstract

Biochar is a solid material derived from different feedstocks that is added to the soil for various agronomic and environmental purposes, such as nutrient sources and CO₂ emission mitigators. In modern agriculture, the application of herbicides directly in the soil is common for pre-emergent weed control; however, biochars may interfere in the degradation processes of these agrochemicals, increasing or decreasing their persistence. Long persistence is desirable for some herbicides in determined cultivation systems, especially in monoculture, but persistence is undesirable in crop rotation and/or succession systems because the subsequent cropping can be sensitive to the herbicide, causing carryover problems. Therefore, knowing the interactions of biochar-herbicide is essential, since these interactions depend on feedstock, pyrolysis conditions (production temperature), application rate, biochar aging, among other factors; and the physical-chemical characteristics of the herbicide. This chapter shows that the addition of biochar in the soil interferes in the persistence or remediation processes of the herbicide, and taking advantage of the agricultural and environmental benefits of biochars without compromising weed control requires a broad knowledge of the characteristics of biochar, soil, and herbicide and their interactions.

Keywords: bioavailability, sorption, weed control, pollution soil

1. Introduction

Herbicides are the pesticides most applied in modern agriculture for weed control worldwide, in pre-emergency, directly in the soil, or in post-emergence in leaves. Regardless of the application of herbicides, these reach the soil and may persist with residual effect (carryover) or contaminate the non-target organism and environment. The behavior of the herbicide in the soil is governed by the physico-chemical properties of the molecule and the soil and can have retention, transport, and transformation processes [1]. In transformation processes, the herbicide molecule is degraded into secondary compounds (metabolites) by physical (photodegradation), chemical, and biological processes (**Figure 1**) [2].

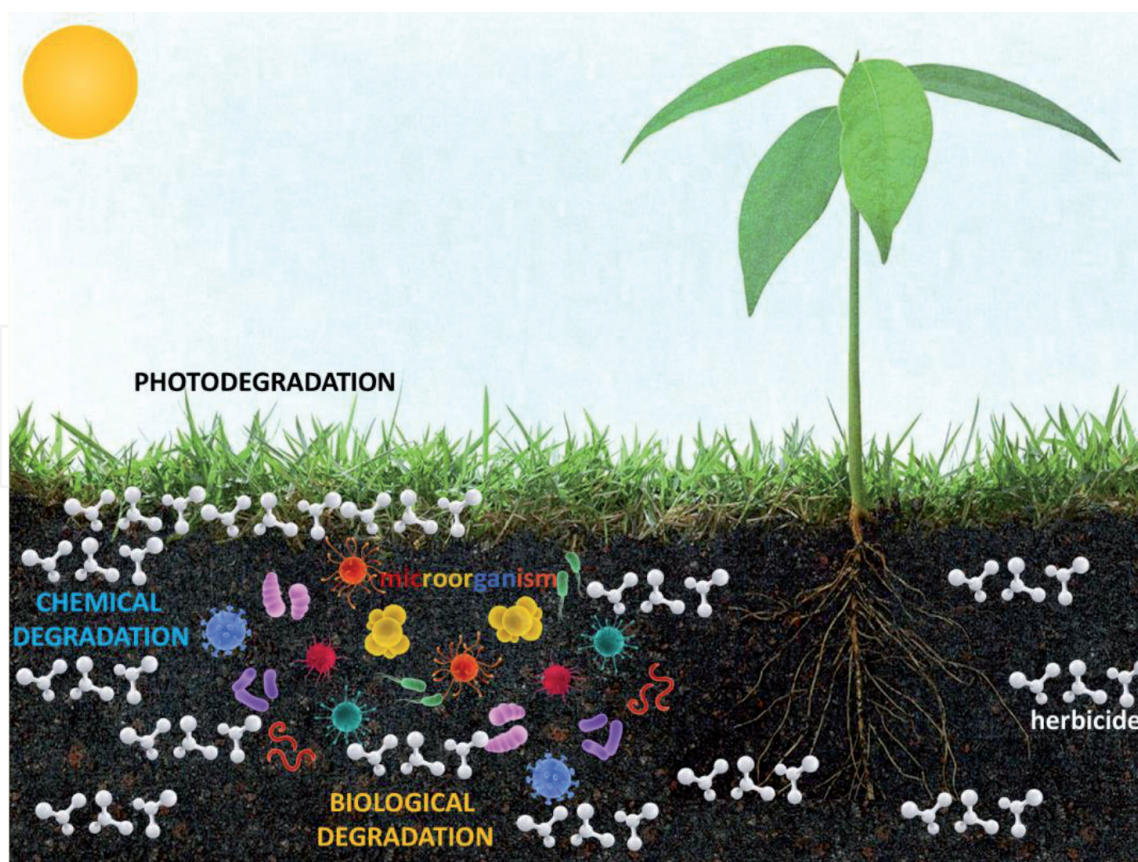


Figure 1.
Degradation process (chemical, biological, and photodegradation) of herbicides in the soil.

Biological degradation is the most common way to dissipate the herbicides in the environment, and it is carried out mainly by the soil microbiota which use the herbicide molecules as an energy source and transforms it into compounds without herbicidal action, the process is also known as detoxification [3, 4]. The chemical complexity of the herbicide determines the higher or lower facility of microorganisms to degrade the molecules, characterizing it in low or high persistence in the soil [5], being measured by degradation or dissipation half-life time (DT_{50}) in laboratory or field conditions, respectively [2].

The degradation of herbicides in the soil by microorganisms can be aerobic (with oxygen) or anaerobic (without oxygen). In the presence of oxygen, the herbicide is mineralized in CO_2 and water. Without oxygen, the herbicide is mineralized in CH_4 , CO_2 , and water [6]. The efficiency of aerobic degradation of herbicides is higher than the anaerobic. The aerobic bacteria oxygen act as an oxidizing agent, and they are present in the region of the soil where there is a higher content of organic matter (OM) and an excellent soil-water-air ratio for the microbiota [7]. In conditions of absence of oxygen, the herbicide can become more persistent in the soil and its degradation pathways are different from microorganisms with aerobic metabolism [8].

The addition of organic materials, like biochar, in the soil directly influences the microbial community, responsible for herbicide degradation [9]. Biochar is a carbonaceous material produced by different feedstocks in pyrolysis conditions with the limited presence of oxygen. Naturally, biochar is found in the anthropogenic soil, known as “Terra Preta de Índio”, i.e., Amazonian Dark Earths in the Amazon, which gave rise to synthetic biochar produced worldwide [10]. Pyrolyzed feedstocks and pyrolysis conditions determine the physico-chemical properties of biochar, such as nutrient content, porosity, specific surface area, among others.

In agricultural soils, the biochar has been added to increase porosity, water-holding capacity, reduce acidity, sequester carbon, reduction of greenhouse gas emissions, plant growth promotion, improve soil fertility, and immobilize (remediation) herbicides by increasing sorption and microbial diversity [11]. This chapter showed that is possible to recommend the addition of biochar in the soil to interfere in the persistence or remediation processes of the herbicide.

2. Biochar characteristics

Biochar is the carbon-rich product resulting from the pyrolysis of organic residues such as wood, animal wastes, crop residues, and biosolids [12]. The feedstock usually determines the chemical composition, quantity of macropores, and nutrient content in biochar. Pyrolysis conditions (such as temperature, heating rate, and residence time) determine the morphology and surface structure changes in feedstock and C/H content [11]. The dominant properties affecting herbicide sorption and degradation by biochar include porosity, specific surface area, pH, functional groups, carbon content and aromatic structure, and mineralogical composition [13].

More porous structures and higher specific surface area will result in higher sorption capacities and lower degradation of herbicides [13]. Higher pH of biochar can accelerate the hydrolysis of organophosphorus and carbamate herbicides in the soil through the alkali catalysis mechanism [14]. Surface functional groups including carboxylic ($-\text{COOH}$), hydroxyl ($-\text{OH}$), lactonic, amide, and amine groups are essential for the sorption capacity of biochar [15, 16]. Carbon content and aromatic structure can increase herbicide sorption and reduce their bioavailability to be degraded [13]. The mineralogical composition can reduce the bioavailability of herbicides through surface chelation and/or surface acidity mechanisms [17].

Biochar amendment also affects the degradation of herbicides in the soil in several ways and the effects can be either stimulatory or suppressive [18]. Biochar may contain available nutrients that stimulate overall microbial activity and, thus, degradation of herbicides [19, 20]. However, the degradation of herbicides in biochar-amended soils is most commonly reduced because herbicide sorption increases [21]. Biochar also sorbs dissolved organic carbon (OC), which can contribute to co-metabolic biodegradation [22]. Some changes in the degradation rate can be a result of indirect effects of biochar amendment, e.g., changes in soil pH, albedo, and aeration [18].

3. Microbial diversity in biochar-amended soils

Soil correction with biochar can affect the soil microbiota in different ways: (1) It can provide an increase in the microbiota [23, 24]; (2) It can negatively affect the resident microbiota by the amount of organic substances (volatile compounds) formed in the production of biochar [25, 26]; or (3) It may not effect the soil microbiota [27, 28]. The possible interaction mechanisms of biochar and soil microbiota are exemplified in **Figure 2** [29, 30]. The physical–chemical structures of the biochar surface (macro and micropores, roughness, surface load, and hydrophobicity) are a refuge for the soil microbiota [31, 32], where microorganisms can find nutrients and ions adsorbed in biochar particles useful for their growth [29, 33]. In addition, biochars can contain significant amounts of organic substances (volatile organic compounds and free radicals) [34, 35], improve the soil's physical–chemical properties, which are important for microbial growth by modifying habitats (aeration, water content, and pH) [36], affect the enzymatic activity of the soil [37, 38],

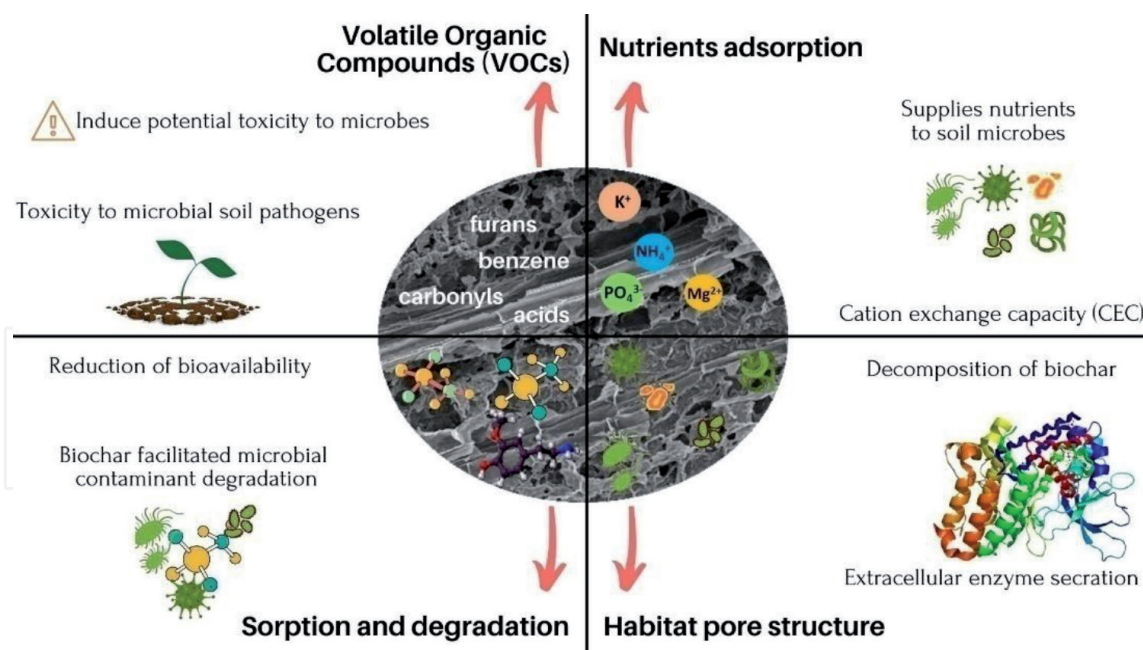


Figure 2.

Interactions between biochar and soil microbiota and environmental effects. Source: Adapted from Zhu et al. [29].

and increase the sorption of herbicides, reducing the bioavailability and toxicity of these agrochemicals for the soil microbiota [29, 39, 40].

Biochar-amended soil has a higher respiratory rate and microbial communities due to carbon mineralization by soil microorganisms [41]. Microbial biomass carbon and nitrogen increased by 18% and 63% with the application of 1% of sugarcane bagasse biochar [42]. The role of biochar nutrients in the biodegradation of coexisting dichlobenil and atrazine in soil by their respective bacterial degraders was evaluated. The degradation increased with increasing biochar content, due to nutritional stimulation on microbial activities [43]. The application of hardwood-derived biochar increased atrazine mineralization by stimulating atrazine-adapted microflora compared to unamended soil [19]. Soil amended with biochar derived from wheat straw increased the abundance and diversity rate of bacteria and fungi beneficial to plants in the rhizosphere of wheat seedlings [24]. In addition, these microorganisms use fomesafen as a source of nutrients, which favors their proliferation from the soil [24]. The change and proliferation of the soil microbiota with the addition of biochar is related to the chemical characteristics of biochar (mainly pH and nutrient content) and physical properties (pore size, pore-volume, and specific surface area), OM content, and water retention that provide favorable conditions for soil microbiota [28]. Although soil microbial biomass is generally benefited with the addition of biochar, the response depends on the type of raw material, pyrolysis temperature, and biochar application rate, since these factors directly interfere with the physical–chemical characteristics of biochar and consequently on the response of the microbiota in herbicide degradation. The proposed mechanisms involved in biochar and microbiota interactions require further studies to elucidate the impact of biochar on soil microbial activity.

4. Influence of biochar amendment in soil on the herbicide degradation

Herbicides are applied to the soil to control weeds during a certain time after application; however, long persistence may affect the subsequent crop, a process known as carryover. Therefore, the process of degradation of the herbicide is

important for the dissipation of herbicides in the soil when the intention is the remediation of the product. However, under agronomic conditions in which a residual effect of the herbicide on the soil is desired for weed control, the addition of biochar can reduce the persistence of the product, consequently reducing its effectiveness in management [2, 9, 44].

The degradation of herbicide molecules into secondary compounds (metabolites) can occur by biotic (biological degradation) or abiotic (hydrolysis, reduction, oxidation, and photolysis) processes [45]. Biodegradation, carried out by the soil microbiota (bacteria, fungi, protozoa, and actinomycetes), is the main decomposition pathway for most herbicides [13, 46]. Microorganisms can use herbicide molecules as an energy source and transform them into compounds without herbicide action, a process known as catabolism, or through co-metabolism, in which herbicide degradation requires the presence of a growth substrate that is used as primary carbon and energy source [3, 47], i.e., microorganism does not obtain energy or benefit from the herbicide degradation. The transformation process is usually mediated by non-specific enzymes that are capable to transform various organic compounds [4]. Herbicides have varied susceptibility to microbial degradation depending on the complexity of the molecule that influences low or high persistence in the soil [5].

Microbial degradation generally reduces the DT_{50} of herbicides in the soil; however, the addition of biochar, according to studies performed, may increase or decrease the DT_{50} values, depending on the herbicide and pyrolyzed feedstock (**Table 1**). The high sorption capacity for herbicides in the biochar-amended soil decreases herbicide degradation, providing a higher DT_{50} than the unamended soil [46, 49]. For example, less atrazine degradation was observed in amended soils with sugarcane bagasse biochar (0.5% w/w) (**Table 1**), increasing in 15 days the DT_{50} of the herbicide in relation to unamended soil [49]. Flumioxazin DT_{50} increased by ~10 days when bamboo biochar (10% w/w) was added compared to unamended soil (**Table 1**) [51]. The DT_{50} of 2-methyl-4-chlorophenoxyacetic acid (MCPA) increased from 5.2 days (unamended soil) to 21.5 days in amended soil with 1% of wheat straw biochar [59].

The application of biochar can also increase soil microbial activity, improving herbicide degradation [29, 60]. The increase in microbial biomass may be due to the addition of available organic substrates, which are the main energy source readily available to soil microorganisms [55]. The high content of dissolved OC in the soil MO can reduce herbicide sorption by biochar particles, as dissolved OC competes with herbicide molecules to occupy available biochar sorption sites [61]. Biochar also sorbs dissolved OC, which can contribute to co-metabolic biodegradation [22]. Some changes in degradation rate may result from indirect effects of biochar amendment, e.g., changes in soil pH and aeration [18]. The highest degradation of oxyfluorfen was observed in amended soils with different rates of application of rice husk biochar, decreasing DT_{50} between 2 and 23 days compared to unamended soil (**Table 1**) [50]. Alachlor mineralization increased up to 50% using biochar derived from soybean stoves, sugarcane bagasse, and wood chips compared to unamended soil (**Table 1**) [58].

Photolysis and hydrolysis are the main abiotic processes involved in herbicide degradation [48, 62]. Photolysis or photodegradation occurs when herbicides are exposed to sunlight [63] and can be direct (a herbicide molecule absorbs light energy, is later excited and transformed) or indirect (species photochemically produced in the soil matrix react with the herbicide molecule triggering its degradation) [64]. Water degrades herbicides by dividing large molecules into smaller molecules, breaking them in the process called hydrolysis [65]. The hydrolysis of herbicides in the soil can be influenced by several factors such as dissolved ion

Location (Country)	Soil texture (%)				Feedstock	Application rate (%) ^b	Pyrolysis temperature (°C)	Herbicide	DT ₅₀ (biochar- amended soil)	DT ₅₀ (unamended soil)	References	
	Sand	Silt	Clay	OM ^a								
Australia	n.a.	n.a.	36.1	2.4	Wheat straw	0.5	450	Atrazine	61.5 ^d	76.5 ^d	Nag et al. [44]	
						1			57.9 ^d			
	n.a.	n.a.	28	4.0		0.5			65.9 ^d			68.6 ^d
						1			52.0 ^d			
Australia	n.a.	n.a.	36.1	2.4	Wheat straw	0.5	450	Trifluralin	73.6 ^d	75.4 ^d	Nag et al. [44]	
						1			71.1 ^d			
	n.a.	n.a.	28	4.0		0.5			63.2 ^d			66.4 ^d
						1			61.2 ^d			
Brazil	n.a.	n.a.	n.a.	n.a.	Industrial- production of charcoal	3	350-550	Sulfometuron- methyl	52.1	36.6	Alvarez et al. [48]	
						6			55.4			
China	n.a.	n.a.	n.a.	3.2	Sugarcane bagasse	0.2	500	Atrazine	38.5	28.1	Huang et al. [49]	
						0.5			45.0			
				2.0		0.2			35.5	23.7		
						0.5			41.2			
				3.6		0.2			41.2	39.8		
						0.5			54.8			

Location (Country)	Soil texture (%)				Feedstock	Application rate (%) ^b	Pyrolysis temperature (°C)	Herbicide	DT ₅₀ (biochar- amended soil)	DT ₅₀ (unamended soil)	References
	Sand	Silt	Clay	OM ^a							
China	21.4	51.4	27.2	2.8	Coal	1.5	n.a. ^c	Isoproturon	53.3	54.6	Si et al. [46]
						5			60.8		
						8			71.4		
	27.9	33.6	38.5	1.5		1.5			67.9	16	
						5			102		
						8			136		
	44.9	39.5	15.6	1.2		1.5			58.2	15.2	
						5			88.9		
						8			107		
China	32.1	24.7	43.2	0.84	Rice husk	0.5	500	Oxyfluorfen	59	65	Wu et al. [50]
						1			57		
						2			53		
	73.2	12.3	14.5	0.98		0.5			104	108	
						1			85		
						2			77		
	55	23.1	21.9	2.2		0.5			43	45	
						1			42		
						2			35		

Location (Country)	Soil texture (%)				Feedstock	Application rate (%) ^b	Pyrolysis temperature (°C)	Herbicide	DT ₅₀ (biochar- amended soil)	DT ₅₀ (unamended soil)	References
	Sand	Silt	Clay	OM ^a							
China	77.4	4.4	18.2	1.5	Cornstalk	10	500	Flumioxazin	15.4	11.1	Chen et al. [51]
					Rice husk		500		16.7		
					Bamboo		700		23.2		
	21	17	62	1.7	Cornstalk		500		18.5	11.5	
					Rice husk		500		22.3		
					Bamboo		700		25.4		
	6.8	55.3	37.9	3.8	Cornstalk		500		20.5	15.4	
					Rice husk		500		22.6		
					Bamboo		700		29.2		
	3.7	64.7	31.6	4.3	Cornstalk		500		21.0	20.8	
					Rice husk		500		24.7		
					Bamboo		700		30.7		
Germany	30.1	62.5	7.8	1.2	Hardwood	0.1	500	Atrazine	74.0 ^d	72.4 ^d	Jablonowski et al. [19]
						1			72.4 ^d		
						5			68.0 ^d		
	24.4	25.2	50.3	3.1		0.1			53.0 ^d	42.6 ^d	
						1			49.8 ^d		
						5			44.4 ^d		

Location (Country)	Soil texture (%)				Feedstock	Application rate (%) ^b	Pyrolysis temperature (°C)	Herbicide	DT ₅₀ (biochar- amended soil)	DT ₅₀ (unamended soil)	References
	Sand	Silt	Clay	OM ^a							
India	56.6	29.6	13.8	n.a.	Rice straw	0.25	350	Bispyribac- sodium	10.7	27.1	Sharma et al. [39]
						0.5			11.5		
						1			12.1		
						0.25	550		8.8		
						0.5			9.9		
						1			11.2		
Latvia	89.2	8.9	1.9	n.a.	Wood chips	5.3	725	MCPA	1986 ^f	94.5 ^f	Muter et al. [52]
						4.1			3854 ^f	11.1 ^f	
					Wheat straw	5.3			1636 ^f	94.5 ^f	
						4.1			15.3 ^f	11.1 ^f	
Malaysia	40	21.5	37.9	0.99	Oil palm empty fruit bunches	1	300	Imazapic	46.2	34.6	Yavari et al. [53]
								Imazapyr	53.3	38.5	
					Rice husk			Imazapic	40.7	34.6	
								Imazapyr	46.3	38.5	

Location (Country)	Soil texture (%)				Feedstock	Application rate (%) ^b	Pyrolysis temperature (°C)	Herbicide	DT ₅₀ (biochar- amended soil)	DT ₅₀ (unamended soil)	References	
	Sand	Silt	Clay	OM ^a								
Russia	3.1	30.4	66.5	n.a.	Woods (<i>Betula</i> sp. and <i>Piceaabies</i>)	1	400	Diuron	47	40	Zhelezova et al. [18]	
						10			42			
						20			56			
						30			45			
						1		Glyphosate	187			17
						10			151			
						20			131			
						30			51			
	83.7	8.8	7.5	n.a.		1	Diuron	58	112			
						10		33				
						20		35				
						30		40				
						1	Glyphosate	83	182			
						10		66				
						20		78				
						30		53				

Location (Country)	Soil texture (%)				Feedstock	Application rate (%) ^b	Pyrolysis temperature (°C)	Herbicide	DT ₅₀ (biochar- amended soil)	DT ₅₀ (unamended soil)	References
	Sand	Silt	Clay	OM ^a							
Spain	24	47	30	1.3	Hardwood (<i>Caryatomentosa</i>)	2	350	Clomazone	97	29	Gámiz et al. [54]
							400		77		
							700		99		
					Hardwood (<i>Caryaillinoensis</i>)		350	107			
							400	65			
							700	67			
					Hardwood (<i>Caryatomentosa</i>)		350	Bispyribac- sodium	n.a.	21	
							400		n.a.		
							700		84		
					Hardwood (<i>Caryaillinoensis</i>)		350	n.a.			
							400	n.a.			
							700	33			

Location (Country)	Soil texture (%)				Feedstock	Application rate (%) ^b	Pyrolysis temperature (°C)	Herbicide	DT ₅₀ (biochar- amended soil)	DT ₅₀ (unamended soil)	References
	Sand	Silt	Clay	OM ^a							
Spain	43	32	23	0.9	Olive mill waste	2.5	n.a.	Metribuzin	39	22	López-Piñeiro et al. [55]
						5			48		
					Olive mill waste plus leaves	2.5			13		
						5			17		
	53	32	14	0.6	Olive mill waste	2.5			49	35	
						5			52		
					Olive mill waste plus leaves	2.5			19		
						5			22		
	43	14	42	0.9	Olive mill waste	2.5			40	29	
						5			43		
					Olive mill waste plus leaves	2.5			18		
						5			16		
USA	n.a.	n.a.	n.a.	0.7	Sugarcane bagasse	0.2	350	Metribuzin	54	25	White Junior et al. [56]
					Sugarcane bagasse	0.1	700		25		
	n.a.	n.a.	n.a.	0.8	Sugarcane bagasse	0.2	350	74	57		
					Sugarcane bagasse	0.1	700	39			
	n.a.	n.a.	n.a.	1.2	Pine wood	0.4	400	39	28		
USA	22	55	23	>2	Mixed sawing	5	500	Acetochlor	34.5	9.7	Spokas et al. [57]
USA	n.a.	n.a.	n.a.	n.a.	Soybean waste	10	500	Alachlor	4.6 ^e	10.4 ^e	Mendes et al. [58]
					Sugarcane bagasse		350		3.4 ^e		
					Wood bark (grape)		500		3.8 ^e		
^a Organic Matter; ^b Application rate in relation to soil mass (ww ⁻¹); ^c Data not available; ^d Degradation (%); ^e Mineralization (%) to CO ₂ ; ^f Herbicide concentration after incubation period (µg kg ⁻¹).											

^aOrganic Matter; ^bApplication rate in relation to soil mass (ww^{-1}); ^cData not available; ^dDegradation (%); ^eMineralization (%) to CO₂; ^fHerbicide concentration after incubation period ($\mu g\ kg^{-1}$).

Table 1.
Effect of biochar amendment in soil on the degradation half-live time (DT₅₀ - days) of different herbicides.

concentration, soil pH, and content of clays and metal oxides capable of catalyzing this herbicide degradation process [14, 66].

The application of biochar can influence the degradation of herbicides by hydrolysis and photolysis, since persistent free radicals existing or photogenerated in biochars can react with the herbicide by the activation of other free radicals such as hydroxyl, sulfate, anion, and superoxide [67, 68]. In addition, the increase in soil pH, the presence of active groups on the mineral surface of biochar, and the high sorption of herbicides have a direct effect on the chemical degradation processes of herbicides [64, 66]. Atrazine was hydrolyzed by 27.9% in the presence of biochar derived from pig manure (700°C) after 12 h due to the mineral surface and dissolved metal ions released from biochars that catalyze hydrolysis [66]. In contrast, imazapic and imazapyr were resistant to degradation by hydrolysis in amended soil with biochar derived from empty fruit bunch of oil palm and rice husk, and their DT₅₀'s increased by ~6 to 12 days because the photodegradation rate diminished [53] (**Table 1**). The addition of biochar to the soil at 1 or 5% inhibited the photodegradation of metribuzin and its metabolites deamino (DA), deaminodiketo (DADK), and diketometribuzin (DK), which increased their DT₅₀'s due to the immobilization of these compounds the surface layer of the biochar [64]. Therefore, the application of biochar has a direct impact on herbicide degradation processes and should be constantly examined for its application in the soil.

5. Factors affecting herbicide degradation in biochar-amended soils

The impact on the degradation of herbicides due to their high sorption in the biochar particles depends on the rate of biochar applied to the soil. The application of different rates of application of hardwood biochar in Rhodic Ferralsol soil increased atrazine degradation by 49% (0.1% of biochar), 51% (1.0% of biochar), and 62% (5.0% of biochar) after 88 days of incubation (**Table 1**) [19]. DT₅₀ of isoproturon in unamended Alfisol was 16 days, however, when biochar was added at 1.5 and 5%, DT₅₀ increased to 67 and 136 days, respectively (**Table 1**) [46], i.e., the persistence of isoproturon is prolonged as the rate of biochar added to the soil increases. DT₅₀ of fomesafen increased from 34.6 days in unamended soil to 51, 83, and 160 days in amended soils with rice husk biochar at 0.5, 1, and 2%, respectively [61]. The increased persistence of fomesafen can be explained by the higher sorb capacity of biochar and, therefore, little bioavailability of the herbicide for microbial degradation.

Pyrolysis temperature defines the physicochemical characteristics of biochars [69]. Generally, biochar produced at relatively high pyrolysis temperatures (>500°C) presents an increase in specific surface area, microporosity, and hydrophobicity, improving herbicide sorption [70]. However, even with higher herbicide sorption capacity, degradation at high pyrolysis temperatures may be more intensified than low temperatures. The addition of sugarcane bagasse biochar produced at 700°C in clay soil decreased the DT₅₀ of metribuzin from 57 (unamended soil) to 39 days, but when biochar was produced at 350°C, DT₅₀ went from 57 to 74 days (**Table 1**) [56]. These conflicting results could be due to the impact of ash on the alkalinity of the soil amended with biochar produced at 700°C (20.3% of ash), which increased the soil pH and improved the conditions for the degradation of metribuzin, and to the greater amount of dissolved OC from biochar produced at 350°C (3.78 mg g⁻¹), which is more preferred by microorganisms as substrate, increasing the persistence of the herbicide. The variation in pyrolysis temperature of eucalyptus wood residue biochar affected the total hexazinone unavailable (mineralized + non-extractable residue) being higher for 850°C (46%) and 950°C

(49%) compared to biochar pyrolysed at 650°C (33%) and 750°C (42%) [71]. The addition of biochar did not alter the mineralization of hexazinone, but it did reduce the bioavailability of this herbicide in the soil due to the greater amount of non-extracted residue, reducing the risk of environmental contamination [71].

Aging alters the properties of biochar, affecting the degradation of herbicides, however, these changes are not fully elucidated [72]. Glyphosate showed no variation in degradation in two tropical soils (Ultisol and Alfisol) amended with eucalyptus biochar aged [73]. The aging of soil-wood biochar mixtures (*Betula* sp. and *Piceaabies*) decreased glyphosate and diuron sorption compared to fresh biochar amended soil [18]. In addition, herbicide degradation was not affected by changes or biochar aging in the soils studied [18]. The degradation of S-metolachlor was not affected with the addition of three macadamia nutshell biochars aged [74]. The persistence of mesotrione in different soils amended with fresh and aged biochar was similar to unamended soils [75]. In contrast, the extractable amounts of picloram were 20 and 50% lower for soils amended with fresh and aged oak wood biochar, respectively, in relation to unamended soil [76]. The addition of 10% fresh biochar from the olive oil industry increased the DT₅₀ of metribuzin from 20 (unamended soil) to 30.2 days, however, the DT₅₀ decreased to 6.4 days with the addition of aged biochar, possibly because microorganisms in soil aged with biochar used metribuzin as a source of carbon and energy instead of the labile fraction of soil OM (**Table 1**) [55]. The effects of biochar on herbicide degradation in soils should not be generalized due to the different characteristics of biochars and the complexity of the soil system. The variation of temperature and application rate of biochar can bring different degradation responses for each herbicide studied. Furthermore, the aging of biochar in the soil can influence the bioavailability of herbicides in soil solution by altering the sorption capacity of the biochar; therefore, the conditions of pyrolysis, type of feedstock as well as aging must be taken into consideration when planning its use in agriculture and for soil remediation purposes [18].

6. Simultaneous use of herbicides and biochar

In an agricultural context, the property of biochar that offers potential for herbicide sorption (environmental remediation) can also decrease the efficacy of herbicides applied to the soil, influencing their bioavailability and susceptibility to leaching and consequently their degradation [77]. The bioavailability of diuron and microbial degradation was reduced in soils amended with rice straw biochar, which decreased the effectiveness of diuron to jungle rice (*Echinochloa colona*) control [78]. The addition of wheat straw biochar to the soil inactivated the herbicides atrazine and trifluralin, resulting in increased seed germination and biomass of annual ryegrass (*Lolium rigidum*). In this study, the efficacy of the herbicides for ryegrass control was achieved when the application doses were four times higher than recommended [44]. In a bioassay with *Echinochloa colona*, injuries 9 days after planting decreased with increasing application rates of rice straw biochar indicating that sorption of clomazone increased and directly influenced the bioavailability of herbicide in the soil [79]. The control efficiency of S-metolachlor was evaluated on green foxtail (*Setaria viridis*) in soil amended with wood biochar at different application rates (0, 0.5, 1, and 2%) [80]. *S. viridis* control at the highest application rate (2%) was lower than the other application rates evaluated, however, better than the control treatments (no herbicide) [80].

The biochar applied to soil also influences the soil physicochemical properties and the improved nutritional availability of these directly impacts crop growth and consequently weed growth [81]. Soil amended with walnut shell biochar

(5 Mg ha⁻¹) for 4 years was evaluated for weed control [82]. Weed density was dramatically higher in biochar-amended soils (60-78%) compared to unamended soil, being related to increased nutrient availability and improvements in soil physico-chemical properties such as cation exchange capacity (CEC), density and porosity, increased soil aeration, and water retention. The application of 2 Mg ha⁻¹ of cow bonechar prevented weed control by indaziflam which is related to the increase of soil fertility, especially the phosphorus and carbon content, and to the increase of pH because it is a basic material [83]. In addition, goosegrass (*Eleusine indica*) and crabgrass (*Digitaria horizontalis*) accounted for about 99.7% of the entire weed community infestation [83].

On the other hand, the decrease in efficacy depends on the characteristics of the herbicide evaluated. The dose of pretilachlor to inhibit 50% of *E. colona* emergence and biomass was higher in soil amended with rice-husk biochar, however, the effectiveness of pendimethalin in controlling *E. colona* was not influenced by the application rate of biochar [84]. The effectiveness on metribuzin in soils amended with biochar was evaluated by White Junior et al. [56]. The addition rates of biochar did not alter Palmer (*Amaranthus palmeri*) emergence, and it is possible that the residual activity was sufficient to reduce germination at any rate of biochar [56].

The addition of biochar to soil increases the sorption of different herbicides and reduces their effectiveness, which may result in the need for higher herbicide application rates, additional application times, or more weed control operations required [85]. Residual herbicides, applied in pre-emergence, can not provide good weed control regardless of soil type after biochar application. This does not necessarily mean that biochar should be avoided, however, when biochar is applied to the soil, management practices need to be adjusted to obtain appropriate weed control [86].

7. Conclusions

Modifying soil characteristics with biochar is a world-renowned emerging practice for either environmental and/or agronomic purposes, and the benefits these carbonaceous materials bring to the soil are clear. However, the pyrolysis conditions for biochar production directly interfere with the physical-chemical properties of the produced material, which govern the biochar-herbicide interactions. If the objective is to apply the herbicide in pre-emergence after the addition of biochar in the soil, care should be taken, as biochar can decrease or increase the persistence of the chemical product, interfering in the effectiveness of weed control over time. On the other hand, if the objective is herbicide remediation in contaminated soils, the interference of biochar in the bioavailability of the herbicide in the soil solution to increase soil microbiological diversity should be known.

Acknowledgements

The authors wish to thank the Coordination for the Improvement of Higher Education Personnel (CAPES - 88887.479265/2020-2100) and Foundation for Research Support of the State of Minas Gerais - Brazil (FAPEMIG - APQ-01378-21) for the financial support.

Conflict of interest

The authors declare no conflict of interest.

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