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Review

Biochar: A review of its impact on pesticide behavior in soil environments and its potential applications

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ABSTRACT

Biochar is produced from the pyrolysis of carbon-rich plant- and animal-residues under low oxygen and high temperature conditions and has been increasingly used for its positive role in soil compartmentalization through activities such as carbon sequestration and improving soil quality. Biochar is also considered a unique adsorbent due to its high specific surface area and highly carbonaceous nature. Therefore, soil amendments with small amounts of biochar could result in higher adsorption and, consequently, decrease the bioavailability of contaminants to microbial communities, plants, earthworms, and other organisms in the soil. However, the mechanisms affecting the environmental fate and behavior of organic contaminants, especially pesticides in biochar-amended soil, are not well understood. The purpose of this work is to review the role of biochar in primary processes, such as adsorption–desorption and leaching of pesticides. Biochar has demonstrable effects on the fate and effects of pesticides and has been shown to affect the degradation and bioavailability of pesticides for living organisms. Moreover, some key aspects of agricultural and environmental applications of biochar are highlighted.

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Introduction

Soil is a fundamental resource for agricultural production systems and plays important roles, including: (1) providing a suitable basis for the production of biomass (Jin et al., 2014), (2) regulating water flow and quality, (3) storing carbon and maintaining the balance of gases in the air, and (4) sustaining biodiversity (Zhou and Song, 2004). Nevertheless, the extensive use of pesticides over the last several decades is now threatening soil quality by imposing unacceptable toxic effects on living organisms (Zhou and Song, 2004; Vangronsveld et al., 2009). Hence, soil remediation using environmentally acceptable alternatives to counteract the presence of contaminated soil worldwide seems to be one of the most suitable approaches to address soil contamination (Mench et al., 2010; Powlson et al., 2011).

Previously, a wide range of remediation techniques, such as soil washing, soil flushing, soil vapor extraction and bioremediation, have been proposed to remediate contaminated soil; however, such methods are usually not applicable in fields due to characteristic deficiencies or new problems that emerge after their application, such as high costs of maintenance, fertility loss, nutrient leaching and soil erosion (Kumpiene et al., 2008; Powlson et al., 2011; Kong et al., 2014). Therefore, the in situ application of

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an amendment for contaminated soil in a cost-effective way has been introduced as a new alternative to meet remediation needs (Lehmann and Joseph, 2009). This method had less disruptive effects and can be used in pesticide-contaminated soil by: (1) binding pesticides to reduce their potential motility into water resources and living organisms, and (2) providing nutrients to promote plant growth and stimulate ecological restoration (Bernal et al., 2006; Vangronsveld et al., 2009). Furthermore because organic materials originate from biological matter, they require minimal pre-treatment before application to soil samples (Barrow, 2012).

One of the most suitable materials for this method is biochar, which is considered to be a carbon-rich byproduct of heating biomass (*e.g.*, agricultural crop residues, wood, and waste) after pyrolysis in the absence of oxygen. Although biochar was primarily introduced as a soil amendment due to its positive role in carbon sequestration, reductions of greenhouse gas emissions, and improvement of soil fertility (Spokas et al., 2009; Zhang et al., 2010; Gomez-Eyles et al., 2011), it has been attracting more attention for its powerful ability to reduce the bioavailability of pesticides (Cabrera et al., 2011; Barrow, 2012; Chen et al., 2012; Ahmad et al., 2014). It has also been recognized that the presence of biochar in soil not only enhances the sorption of different pesticides but also affects the nature of sorption mechanisms and the bioavailability of pesticide residues for living organisms (Yang and Sheng, 2003; Yu et al., 2006; Kookana et al., 2011). Moreover, the application of biochar in agricultural soil next to lakes or bodies of water may effectively reduce the contamination of underground water by decreasing the leaching of applied pesticides (Laird et al., 2010; Ahmad et al., 2014). Despite the increasingly documented research in recent years regarding the beneficial effects of biochar on pesticide sorption than soil organic matter (Xu et al., 2008; Atkinson et al., 2010; Lehmann et al., 2011, Wang et al., 2012; Tatarkova et al., 2013), the effects of biochar on adsorption mechanisms and the desorption behavior of pesticides as an effective means to affect the bioaccessibility and toxicological impact of pesticides have received less attention.

Therefore, the objective of this review was to assess the potential effects of biochar amendment on the environmental fate of pesticides in soil compartments based on adsorption–desorption, leaching, degradation, and bioavailability in biochar-amended soils. We placed emphasis on: (1) the effects of biochar on the environmental behavior of pesticides in soil (*i.e.*, adsorption, desorption, leaching, and degradation), (2) the influence of biochar on the bioavailability of pesticide residues for plants and earthworms in soil, and (3) the potential agronomic and environmental implications of biochar. In this context, the priority areas of future research are also identified.

1. Effect of biochar on the environmental behavior of pesticides in soil

1.1. *Adsorption–desorption*

Adsorption is usually the first process that begins immediately upon introduction of pesticides into the soil. Thus, the capability of biochar to adsorb pesticides may be an important factor that can affect other processes, such as chemical transport, leaching, bioavailability, and ecotoxicological impacts on non-target organisms (Kookana et al., 2011).

Numerous studies have reported the effects of biochar on the adsorption of pesticides in soil, and the results are summarized in Table 1. Biochar is one of the most efficient sorbents for several groups of pesticides (Martin et al., 2012; Schaumann, 2006). The adsorption capacity of biochar for pesticides depends on its physico-chemical properties, such as organic carbon content, specific surface area (SSA), and porous structure (Spokas et al., 2009; Dechene et al., 2014; García-Jaramillo et al., 2014; Sopena et al., 2012; Wang et al., 2010; Cabrera et al., 2014; Xu et al., 2008). High organic carbon contents, high SSAs, and more porous structures result in higher adsorption capacities. Spokas et al. (2009) reported the high adsorption capacity of 5% (W/W) sawdust biochar to atrazine and acetochlor in a sandy loam soil sample, which was attributed to the high carbon content (69%) and SSA (1.6 m^2/g) of biochar. Wang et al. (2010) reported that the highest adsorption level of terbuthylazine was found in soil amended with pine wood biochar produced at 700°C due to its higher carbon content and SSA compared with that produced at 350°C. Sopena et al. (2012) reported that the adsorption capacity of 2% (W/W) biochar from *Eucalyptus dunni*, which had a high SSA, for isoproturon was nearly 5 times higher for amended soil than for the unamended soil. Similarly, García-Jaramillo et al. (2014) reported that the adsorption capacity of 2% (W/W) composted olive waste biochar, with a high SSA of 27 m^2/g, for trycidazole in biochar-amended soil was 4 times higher than in the unamended soil. Cabrera et al. (2014) indicated that the herbicides aminocyclopyrachlor and bentazone were nearly completely sorbed by silt loam soil amended with high SSA biochar produced from wood pellets.

Although the adsorption capability of biochar is considered to be a key factor that affects the environmental behavior of pesticides, desorption or the release behavior of pesticides adsorbed onto biochar should be carefully investigated due to its association with the bioavailability and efficacy of pesticides (Kookana et al., 2011). Several studies have reported the reversible pesticide adsorption of biochar in amended soil samples. Reversible adsorption can occur through different mechanisms: (1) the swelling of a sorbent during adsorption process, which results in macro-pore network deformation (Sopena et al., 2012; Khorram et al., 2015), and (2) weak binding between the tested pesticides and biochar components (Tatarkova et al., 2013; Khorram et al., 2015). One of the most suitable ways to predict the reversibility of pesticide adsorption is by comparing hysteresis coefficient values (calculated by dividing the adsorption exponents by the desorption exponents $H = (1/nf_{des})/(1/nf_{ads})$) between unamended and biochar-amended soils. An increase in this value could be interpreted as a sign of partial reversibility (Cabrera et al., 2011). Sopena et al. (2012) reported that the addition of 2% (W/W) biochar led to the reversible adsorption of isoproturon in soil, which may have resulted from micropore deformation because the hysteresis coefficient value of the biochar-amended soil was higher than that of the unamended soil. In our previous study, a higher H value was observed in soils amended with 2% of rice hull biochar compared with that of unamended soil; this demonstrated that some parts of the adsorbed fomesafen was desorbed during the one-step desorption experiment. This phenomenon was also explained by the kinetic effects of rice hull biochar, which had relatively low surface areas and resulted in easier detachment of the weakly attached fomesafen molecules from the biochar micropores (Khorram et al., 2015). Yu et al. (2006, 2010) observed adsorption reversibility of diuron and pyrimethanil in soil amended with red gum wood chip biochar produced at 850°C, which may have resulted from the presence of greater micropores as the main sites for entrapping pesticide molecules.

However, several studies have demonstrated that biochar amendment can lead to higher irreversible adsorption of the tested pesticides (Table 1). The irreversible adsorption process of biochar to a pesticide included surface-specific adsorption, entrapment into micropores, and partitioning into condensed structures (Yu et al., 2010; Wang et al., 2010; Sopena et al., 2012). Red gum wood biochar was reported as a suitable candidate for the irreversible adsorption of pyrimethanil in sandy loam soil (Yu et al., 2010). Tatarkova et al. (2013) found that the application of 1% (W/W) wheat straw biochar as an amendment decreased the desorption rate of MCPA (4-chloro-2-methylphenoxyacetic acid) from 64.2% in the unamended soil to 55.1% in the biochar-amended soil. Wang et al. (2010) also reported slower and lower desorption rates of the herbicide terbuthylazine in soil amended with sawdust biochar produced at 700°C followed by biochar produced at 350°C.

1.2. Leaching

The addition of biochar can enhance adsorption and decrease desorption of pesticides, thus altering their mobility. The effects of biochar on the mobility of pesticides have been investigated in many different studies (Table 1). The addition of rich carbon amendments to soil has been shown to usually decrease pesticide leaching in soil due to an increase in adsorption by the entrapment of pesticides into the micropore network and/or pore deformation of the biochar particles (Larsbo et al., 2013; Li et al., 2013; Marin-Benito et al., 2013). Delwiche et al. (2014) observed a remarkable reduction in atrazine leaching in homogenized soil columns amended with pine chip biochar, which was mainly attributed to the presence of more macropore structures that played a significant role in entrapping and accumulating more atrazine molecules around biochar particles. Meanwhile, pore deformation in biochar has been shown to result in reduced leaching of pesticides in homogenized soil (Yu et al., 2006; Sander and Pignatello, 2007). Similarly, we previously observed that rice hull biochar significantly decreased the leaching of fomesafen, which was attributed to pore deformation of biochar (Khorram et al., 2015).

It is noteworthy that asymmetrical leaching breakthrough curves of pesticides in biochar-amended soil relative to those in unamended soil indicated a time-dependent interaction between pesticides and soil components, which resulted in non-equilibrium adsorption. Previous observations with other chemicals have indicated that organic matter amendments could result in a greater OM% and a consequent increase in non-equilibrium adsorption effects, such as asymmetrical BTCs (with or without tails), on pesticide leaching (Marin-Benito et al., 2009).

1.3. Degradation

Because of their highly microporous and carbonaceous nature, biochar is a particularly interesting material when considering its impact on the biodegradation of pesticides with time. The results from some studies on the biodegradation of pesticides in biochar-amended soil are summarized in Table 1. Pesticide biodegradation was enhanced in biochar-amended soil due to microbial stimulation by the amendment (Lopez-Pineiro et al., 2013; Qiu et al., 2009a; Zhang et al., 2005, 2006). Qiu et al. (2009a) reported that the degradation of atrazine was increased by increasing the amount of wheat char in soil from 0.1% to 1%. This may have resulted from an increase in nutrients by the biochar especially phosphorus, which could have stimulated the activity of microorganisms and consequently enhanced biodegradation. An increase in the degradation of atrazine in clay soil amended with hardwood biochar produced at 450–500°C has also been attributed to the stimulation of the soil microflora by the nutrients added by biochar (Jablonowski et al., 2010). Lopez-Pineiro et al. (2013) reported that the addition of composted olive mill waste compounds significantly decreased the half-life of MCPA. This effect was attributed to an increase in microbial biomass due to the addition of available organic substrates, which constituted the most readily available source of energy for soil microorganisms. In addition, the presence of higher dissolved organic carbon content in the organic compounds may have resulted in the lower adsorption of pesticide molecules by biochar particles due to the competition between pesticide molecules and dissolved organic carbon for occupying the available adsorption sites. Therefore, pesticide availability for degradation has been shown to increase in soil solutions, and soils amended with these organic compounds have lower pesticide persistence compared with unamended soils (Marin-Benito et al., 2014).

As shown in Table 1, pesticide biodegradation may have also decreased because of the increase of adsorption, which resulted in lower pesticide bioavailability for microorganisms (Jones et al., 2011; Muter et al., 2014). Soil amended with organic compounds usually possess lower dissolved organic carbon (DOC) content and most likely adsorb more of the pesticide fractions; this leaves fewer bioavailable pesticide molecules for microorganisms, resulting in the decrease of pesticide degradation (Muter et al., 2014; Nag et al., 2011). Jones et al. (2011) illustrated that the degradation rate of simazine in biochar-amended soil was only approximately 10% of that in unamended soil over a 21-day incubation period. This may have been because most of the applied simazine was adsorbed by biochar particles with low DOC content. Similarly, the degradation half-life of MCPA increased from 5.2 days in unamended soil to 21.5 days in soil amended with 1% (W/W) wheat straw biochar. This observation may be attributed to the strong sorption affinity of biochar and thus a decrease in MCPA concentration in the soil solution where this herbicide was more available to soil microorganisms (Tatarkova et al., 2013). It has also been shown that the degradation half-life of fomesafen significantly increased from 34.6 days in unamended soil to 50.8, 82.7 and 160.3 days in soils amended with 0.5%, 1% and 2% rice

Table 1 – Selected reports on adsorption, desorption and leaching of pesticides in soils amended with biochars.

Biochar type	Application rate (%)	Pyrolysis temp. (°C)	Soil type	Pesticide	Adsorption	Desorption	Leaching	Reference
Wood chip pellets	10	>500 (slow pyrolysis)	Silt loam	Aminocyclopyrachlor	95%–240%↑ [a]			Cabrera et al. (2014)
				Bentazone	20%–35%↑			
Macadamia nut shells	10	850 (flash pyrolysis)	Silt loam	Aminocyclopyrachlor	18%–25%↑			Cabrera et al. (2014)
				Bentazone	13%↑			
Hardwood	10	540	Silt loam	Aminocyclopyrachlor	Up to 50%↑			Cabrera et al. (2014)
				Bentazone	~40%↑			
Beech wood	1.5	550	Sandy loam	Imazamox	<5%↑	~3%↓ [b]		Dechene et al. (2014)
Composted alperujo	2	500	Sandy loam	Tricyclazole	400%–500%↑	Up to 450%↓	Not changed	García-Jaramillo et al. (2014)
Hardwood sawdust	2	500 (fast pyrolysis)	Sandy loam	Fluometuron	340%–365%↑	600%–730%↓	Not changed	Cabrera et al. (2011)
				MCPA	Up to 55%↑	85%–300%↓		
Hardwood	2	540	Sandy loam	Fluometuron	300%–310%↑	520%–590%↓	10%↓ [c]	Cabrera et al. (2011)
				MCPA	240%–330%↑	Insignificant	12%↓	
Wood pellets	2	>500 (slow pyrolysis)	Sandy loam	Fluometuron	2800%–2900%↑	2700%–3000%↓	77.5%↓	Cabrera et al. (2011)
				MCPA	2800%–5200%↑	900%–950%↓	28.7%↓	
Red gum wood	0.5	450	Clayey silt		K_f by a factor of 2↑	K_f by a factor of 2.1↑		
			Sandy silt	Acetamiprid	K_f by a factor of 1.7↑	K_f by a factor of 1.4↑		Yu et al. (2011)
			Paddy soil		K_f by a factor of 1.2↑	K_f by a factor of 1.2↑		
Paper mill sludge	1	550	Ferrosol	Diuron	448%↑			Martin et al. (2012)
	5			Artrazine	515%↑			
Poultry manure	1	550	Ferrosol	Diuron	~220%↑			Martin et al. (2012)
				Artrazine	~270%↑			
Wheat derived	0.05–1	–	Silt loam	Diuron	K_f by a factor of 7–80↑			Yang et al. (2006)
Pinus radiata sawdust	1	700	Typic Udivitrand	Terbuthylazine	K_f by a factor of 63↑	K_f by a factor of 2.9↑		Wang et al. (2010)
Pinus radiata charcoal	1	350	Typic Udivitrand	Terbuthylazine	K_f by a factor of 2.7↑	K_f by a factor of 1.3↑		Wang et al. (2010)
Mixed sawdust	5	500	Silt loam	Atrazine	Not given	Not given		Spokas et al. (2009)
				Acetochlor	K_f by a factor of 2.6↑	Not given		

Pig manure	5	350	Not given	Carbaryl	K_f by a factor of 2.06↑	Not given		Zhang et al. (2010)
				Atrazine	K_f by a factor of 1.40↑	Not given		
Pig manure	5	700	Not given	Carbaryl	K_f by a factor of 2.85↑	Not given		Zhang et al. (2010)
				Atrazine	K_f by a factor of 2.77↑	Not given		
Wood chips of:	1	450	Typic Dystrochrept	Simazine	K_f by a factor of 1.12↑	Not given	Up to 30%↓	Jones et al. (2011)
	10		(high fertility)		K_f by a factor of 1.7↑	Not given		
Fraxinus excelsior L.,								
Fagus sylvatica L.								
Quercus robur L.								
Eucalyptus	1	600	Natric Haploxeralf	Simazine	K_f by a factor of 1.34↑	Not given	Up to 50%↓	Jones et al. (2011)
marginatus wood chips	10		(low fertility)		K_f by a factor of 2.2↑	Not given		
Mixture of:	1	500	Loamy	Isoproturon	Insignificant	Not given	97.2%↓	Larsbo et al. (2013)
Wheat seed coat,					Up to 70%↑	Not given	18%↓	
chaff and residue			Clayey	Imidacloprid	100%↑	Not given	97.7%↓	
					65%↑	Not given	49%↓	
Red gum wood	0.1	500	Sandy loam	Isoproturon	31%–35%↑	30%–42%↓		Sopena et al. (2012)
(*Eucalyptus dunni*)	1				58%–67%↑	73%–81%↓		
	2				120%–130%↑	97%–120%↓		
Pine wood	1	700–750	Silty loam	Atrazine			52%↓	Delwiche et al. (2014)
Poplar branches	0.5–1	350	Ferrallitic soil	2,4-D			40%–65%↓	Li et al. (2013)
				Acetochlor			34%–53%↓	
Wheat straw	1	300	Calcaric Fluviso	MCPA	253%↑	15%↓	35%↓	Tatarkova et al. (2013)
Charcoal	1–5	Not given	Paddy soil (fine-silty, mixed)	Isoproturon	K_f by a factor of 1.43↑		11%–84%↓	Si et al. (2011)
			Alfisol (fine-loamy, mixed)		K_f by a factor of 1.28↑		7%–78%↓	
			Vertisol (coarse-loamy, mixed)		K_f by a factor of 1.86↑		35%–80%↓	

[a] Biochar amendment increased the adsorption of pesticides in soils.
[b] Biochar amendment decreased the desorption of pesticides in soils.
[c] Biochar amendment decreased the leaching of pesticides in soils.
[d] K_f represented adsorption equilibrium constant.

hull biochar, respectively (Khorram et al., 2015). The increase in the persistence of fomesafen may be explained by the high adsorption capacity of biochar and little availability of pesticide for microbial degradation resulting from its larger surface area and micro-porous structure (Lopez-Pineiro et al., 2013).

2. Effect of biochar on the bioavailability of pesticide residues in soil

2.1. Plant growth and pesticide uptake

The effects of biochar on the plant uptake of pesticides have been examined in a few studies (Table 2). The addition of biochar into soil usually decreases the bioavailability of pesticides because the adsorbed pesticide molecules are not in the bioavailable fractions of the soil pore water environment (Khorram et al., 2015). Yu et al. (2009) reported that spring onions planted in soil amended with red gum wood chips had significantly lower residue levels of chlorpyrifos and carbofuran compared with plants grown in unamended soil. Similarly, Yang et al. (2010) reported that a 1% cotton straw biochar amendment decreased the total residue levels of chlorpyrifos and fipronil in Chinese chives (*Allium tuberosum*) to 19% and 48% of those grown in the control treatment, respectively. This lower pesticide uptake by plants cultivated in biochar-amended soil was attributed to increased sequestration of pesticides due to the porous nature of biochar, which provided more adsorption sites for the pesticide molecules than unamended soil organic matter. The significant reduction in phytotoxicity of air-dried sewage sludge after the application of biochar was also attributed to binding of the contaminants by biochar due to the increased presence of micro- and macropores, which may have acted as suitable sorption sites for the xenobiotics (Oleszczuk et al., 2012). Similarly, Yang et al. (2006) showed that the addition of wheat straw biochar enhanced the sorption of diuron in soil and thus decreased its uptake by barnyard grass. In another study, the decreased plant uptake of fomesafen was directly linked to the higher adsorption capacity of biochar (Khorram et al., 2015).

Meanwhile, biochar amendment has been shown to stimulate plant growth, partially due to the higher nutrient release and water holding capacity of biochar-amended soil (Cheng et al., 2008; Lehmann et al., 2011; Rogovska et al., 2014). The positive effects of biochar on plant growth are likely a result of different mechanisms. It has been demonstrated that biochar can act as a slow-release source of nutrients, can provide macro- (potassium and phosphorus) and micronutrients (copper), and improve soil physicochemical properties such as water holding capacity, pH, and aeration (Lehmann et al., 2011). Moreover, the oxidation of the surface of biochar and the formation of carboxyl groups likely result in an increased capacity for cation exchange (Cheng et al., 2008), which has a higher ability to retain nutrients (*e.g.*, Ca^{2+}, K^{+}, and Mg^{2+}). Rogovska et al. (2014) showed that maize grain and biomass yields increased by 11% to 55% in response to biochar amendments during the first year, respectively. Similarly, the fresh weight and height of corn grown in soil amended with 0.5%, 1% and 2% rice hull biochar increased by 65%–63.7%, 78%–134%, and 106%–181%, respectively, compared with those grown in the unamended control soil; this indicates that the biochar amendments could effectively eliminate the harmful effects of fomesafen on corn growth (Khorram et al., 2015). Yu et al. (2009) reported that spring onions planted in soil amended with red gum wood chips had significantly higher quantities of biomass compared with plants grown in unamended soil. Yang et al. (2006) also showed that the addition of wheat straw biochar into soil increased barnyard grass survival rates and fresh weights.

2.2. Earthworm uptake of pesticides

Although the effects of biochar on pesticide bioavailability to earthworms appears to be the most-studied topic of all the soil fauna effects, few short-term studies have been conducted to address this subject, and several of these studies present contradictory results (Table 2). Biochar amendment most likely decreases pesticide bioavailability to earthworms through: (1) increased adsorption capacity of biochar particles, or (2) decreased food consumption by earthworms. Earthworms are able to absorb organic chemicals in soil via dermal contact (through the skin) and direct ingestion of soil particles (Hickman and Reid, 2008). The relative contributions of the two uptake routes strongly depend on the burrowing and feeding habits of the worms.

Generally, pesticides that are dissolved in solutions around soil particles are weakly associated with active sites of soil/biochar surfaces and are considered to be bioavailable for earthworms for environmental dermal uptake (Lu et al., 2004). The decrease of pesticide bioavailability for earthworms is due to the enhanced adsorption by active sites on the surface of biochar, which leads to a reduced pesticide concentration in the soil solution. Biochar amendment in soil could decrease pesticide bioavailability for earthworms, which may mainly be attributed to the high adsorption capacity of biochar. Wang et al. (2012) found that the addition of two types of red gum wood biochar to soil led to a predominant decrease in the bioavailability of chlorantraniliprole through the higher adsorption capacity of biochar compared with soil organic matter. Similar results were observed when rice hull biochar was used as the soil amendment to evaluate the uptake of fomesafen by earthworms (Khorram et al., 2015). In this study, the concentration of fomesafen in earthworms in the soils amended with 0.5%, 1%, and 2% biochar declined by 14.2%–22.1%, 32.2%–37.7%, and 49.5%–52.9%, respectively, compared with those in the unamended soil. The decrease of fomesafen concentration in *in situ* pore water from 0.284–2.42 mg/kg in the unamended soil to 0.096–0.67 mg/kg in the 2% biochar-amended soil clearly demonstrates the higher adsorption capacity of biochar, which is the main reason for the decreased availability of fomesafen for earthworms.

However, several studies have found that the decrease in bioavailability of pesticides for earthworms in biochar-amended soil was most likely due to lower food availability, in which the earthworms preferred to ingest the char and soil mixture (Gomez-Eyles et al., 2011). Wang et al. (2014) reported that the concentration of atrazine in *Metaphire guillelmi* was approximately 2.6 times higher than that in *Eisenia foetida*. The difference in bioaccumulation potentials between *E. foetida* and

Table 2 – Selected reports on the degradation and bioavailability of pesticides in biochar-amended soils.

Biochar type	Application rate (%)	Pyrolysis temp. (°C)	Soil type	Pesticide	Degradation (comparison to control)	Bioavailability	Tested organisms	Reference
Wood chips of *Fraxinus excelsior* L., *Fagus sylvatica* L. and *Quercus robur* L.	1 10	450	Typic Dystrochrept (high fertility)	Simazine	Up to 55%↓ * Up to 80%↓			Jones et al. (2011)
Eucalyptus marginatus wood chips	1 10	600	Natric Haploxeralf (low fertility)	Simazine	Up to 57%↓ 90%↓			Jones et al. (2011)
Red gum wood	0.1 1 2	500	Sandy loam	Isoproturon	Insignificant 28%↓ Up to 40%↓			Sopena et al. (2012)
Wheat straw	1	300	Calcaric Fluviso	MCPA	Up to 65%↓			Tatarkova et al. (2013)
Charcoal	1–5	Not given	Paddy soil (fine-silty, mixed) Alfisol (fine-loamy, mixed) Vertisol (coarse-loamy, mixed)	Isoproturon	3%–24%↓ 79%–98%↓ 56%–84%↓			Si et al. (2011)
Red gum wood	0.5	450	Clayey silt Sandy silt Paddy soil	Acetamiprid	85%↓ 54%↓ 68%↓			Yu et al. (2011)
Wheat straw	0.5 1	Not given	Calcarosol Ferrosol	Atrazine	10%–15%↓ 12%–25%↓			Nag et al. (2011)
Wheat straw	0.5 1	Not given	Calcarosol Ferrosol	Trifluralin	5%–8%↓ Up to 15%↓			Nag et al. (2011)
Shattered wooden boxes and wood pellets	5.3 4.1	725	Loamy sand Sandy	MCPA	150 times lower 320 times lower			Muter et al. (2014)
Wheat straw	5.3 4.1	725	Loamy sand Sandy	MCPA	190 times lower 380 times lower			Muter et al. (2014)
Red gum wood	0.5–1	450	Sandy loam	Carbofuran Chlorpyrifos	34%–47%↓ 30%–40%↓	12%–33%↓ ** Up to 27%↓	Spring onion (*Allium cepa*).	Yu et al. (2009)
Red gum wood	0.5–1	850	Sandy loam	Carbofuran Chlorpyrifos	55%–73%↓ 50%–82%↓	45%–74%↓ 50%–89%↓	Spring onion (*Allium cepa*).	Yu et al. (2009)
Cotton straws	0.1–1	450	Clay loam	Chlorpyrifos Fipronil	5%–55%↓ 13%–42%↓	6%–53%↓ 3%–22%↓	Chinese chives (*Allium tuberosum*)	Yang et al. (2010)
Cotton straws	0.1–1	850	Clay loam	Chlorpyrifos Fipronil	12%–77%↓ 16%–84%↓	11%–82%↓ 8%–51%↓	Chinese chives (*Allium tuberosum*)	Yang et al. (2010)
Red gum wood	0.5	450 850	Loam	Chlorantraniliprole		25%–52%↓ 85%–92%↓	Earthworm (*Eisenia foetida*)	Wang et al. (2012)
Red gum wood	0.5	450 850	Clay sandy	Chlorantraniliprole		37%–48%↓ 80%–92%↓	Earthworm (*Eisenia foetida*)	Wang et al. (2012)
Red gum wood	0.5	450 850	Clay loam	Chlorantraniliprole		30%–50%↓ 92%–97%↓	Earthworm (*Eisenia foetida*)	Wang et al. (2012)
Red gum wood	0.5	450 850	Sandy loam	Chlorantraniliprole		50%–66%↓ 93%–96%↓	Earthworm (*Eisenia foetida*)	Wang et al. (2012)
Pine-wood shavings	0.5 2	400	Clay loam	Atrazine		25%–67%↓ 57%–89%↓	Earthworm (*Eisenia foetida*) Earthworm (*Metaphire guillelmi*)	Wang et al. (2014)

* Biochar amendment decreased the degradation of pesticides in soils.
** Biochar amendment decreased the bioavailability of pesticides in soils.

M. guillelmi was likely attributed to differences in their feeding ecology and uptake routes. *E. foetida* is an epigeic species that feeds mainly on plant litter or manure, while *M. guillelmi* is an anecic species that feeds mainly on litter or litter mixed with mineral surface soil and can process a large amount of soil (Shan et al., 2010). The bioaccumulation of atrazine in *E. foetida* was largely through dermal absorption from the pore water, and its equilibrium concentration depended on the desorption potential of atrazine from the soil particles to the pore water. Compared with the relatively passive uptake mechanism of *E. foetida*, the bioaccumulation of atrazine in *M. guillelmi* involved more aggressive processes resulting from the ingestion of large amounts of soil particles. In addition, although most of the experiments used *E. foetida* as a model organism because it is reasonably tolerant to contaminants and is widely available and responsive in laboratory assays, it may not be the most suitable species because it is a litter dwelling compost species that does not inhabit mineral soil (Lowe and Butt, 2007). Therefore, further studies with native species must be conducted to obtain more information on the mechanisms of pesticide uptake and potential effects of biochar on earthworm populations.

3. Environmental and agricultural implications

3.1. Environmental benefits

It is generally accepted that reducing the bioavailability of pesticides is one of the most appropriate methods to remediate pesticide-contaminated soil and water because this leads to decreased pesticide accumulation and toxicity in plants and animals (Sohi, 2012). It has been extensively reported that biochar can significantly reduce soil contamination by adsorbing and sequestering pesticides or their metabolites (Chen et al., 2008; Yu et al., 2011; Tatarkova et al., 2013; Ahmad et al., 2014; Khorram et al., 2015). Biochar can be considered an ameliorant to reduce the bioavailability of pesticides in the environment with the additional benefits of soil fertilization and climate change mitigation (Sohi, 2012). Jones et al. (2011) reported that strong sorption of simazine by biochar suppressed its leaching into the groundwater. Tatarkova et al. (2013) reported that biochar produced from wheat straw resulted in a remarkable decrease in the dissipation and plant uptake of MCPA in soil due to its high sorption capabilities, which consequently reduced its bioavailability. Cao and Harris (2010) showed that dairy manure biochar had an appreciable adsorption capability for atrazine and exhibited a removal rate as high as 77% from an aqueous solution. The results indicated that dairy manure could be converted into biochar as an effective adsorbent for applications in environmental remediation. Therefore, the increased sorption and decreased dissipation of pesticides in the presence of biochar may lower the risk of environmental contamination and human exposure from the perspective of ecosystems and human health (Kookana et al., 2011).

Biochar can also be considered an efficient way to manage waste streams originating from animals or plants and consequently be used to decrease the associated pollution loading into the environment. The production of biochar from waste biomass is economical and beneficial because this process produces green energy and the generated biochar can be used to mitigate climate change (Barrow, 2012). Waste biomass has been extensively used to produce biochar from various sources, such as crop residues, forestry waste, animal manure, food processing waste, paper mill waste, municipal solid waste, and sewage sludge (Cantrell et al., 2012; Li et al., 2013; Ahmad et al., 2014; Khorram et al., 2015). However, several variables in the production of biochar, including pyrolysis conditions and feedstock types, may affect its exact role in environmental management. Thus, the examination of the efficacy of biochar on the mobility/stabilization of pesticides in multi-element contaminated soil is necessary before utilizing biochar for environmental applications.

3.2. Agricultural applications

In addition to the benefits that biochar offers by significantly reducing soil contaminants through adsorption and/or sequestration of pesticides or their metabolites, biochar amendments also have the potential to serve as soil conditioners by changing the physicochemical and biological properties of soil, such as increasing soil pH, cation exchange capacity (CEC) and soil buffering (Lehmann and Joseph, 2009). Kimetu and Lehmann (2010) reported that the decrease in maize crop yields in the Western Kenyan Highlands, which was due to the continuous cultivation over 100 years, increased by up to 70% when biochar amendment was utilized; this increase in yield may mainly be attributed to the improvement in the physical properties of soil such as pH and water holding capacity. Biochar-amended soil usually exhibits higher soil water contents and nutrient retention compared with unamended soil (Tang et al., 2013; Ahmad et al., 2014). Cui et al. (2014) observed a decrease in adsorption but an increase in desorption of phosphorous on ferrihydrite in the biochar-amended soil. Uzoma et al. (2011) reported that maize grain yields significantly increased by 150% and 98% in the soil amended with cow manure biochar at 15 and 20 tons/ha, respectively. This enhanced plant growth was potentially related to improvements in soil properties and nutrient availability following the biochar amendment. Tammeorga et al. (2014) illustrated that the use of biochar as a soil amendment could improve soil poor water retention capacities and nutrient deficiencies that were the limiting factors in subtropical and temperate soils. Wood biochar application at 3 and 6 tons/ha in sandy clay loam soil reduced drought stress and consequently enhanced wheat yield, which may have been due to increased water availability (Blackwell et al., 2010; Solaiman et al., 2010).

Biochar can also improve crop productivity through an increase in crop resistance to disease (Elad et al., 2010; Harel et al., 2012; Noguera et al., 2012). It has been demonstrated that biochar amendments significantly reduce the severity of fungal foliar diseases caused by *Botrytis cinerea* and *Oidiopsis sicula* in tomatoes and peppers (Elad et al., 2010). Similarly, Harel et al. (2012) observed an increase in strawberry yields of up to 35% in biochar-amended soil compared with those grown in unamended soil; this was because wood and greenhouse waste biochar could induce systematic resistance against *B. cinerea*, *Colletotrichum acutatum*, and *Podosphaera aphanis*. The results of real-time PCR at the molecular level have also suggested that biochar addition stimulates a range of general defense pathways. Noguera et al. (2012) reported that biochar increased rice biomass production by increasing leaf protein turnover as a result of enhanced protein catabolism/anabolism.

4. Conclusions and future research directions

Based on the scientific reports cited in the previous sections, a schematic diagram of the effects of biochar amendment on the environmental behavior of pesticides in soil is shown in Fig. 1. Biochar has demonstrated a clear and prominent potential to remediate pesticide-contaminated soils through the following: (1) increasing adsorption capacity for pesticides; (2) decreasing desorption and mobility of pesticides in soil layers; (3) decreasing bioavailability of pesticides in soil pore water, which is considered the bioavailable fraction for soil organisms; (4) improving soil microbial activity by providing essential nutrients; and (5) improving soil physicochemical properties such as pH, CEC, and water holding capacity.

Nevertheless, it is noteworthy that although biochar amendment has been extensively studied as a potential technology for the remediation of pesticide-contaminated soil, many aspects still need to be further studied in detail because the available results are insufficient and sometimes contradictory. Future research topics to address current questions about the efficacy of biochar amendment for soil remediation mainly include the following.

To date, the applications of biochar for the remediation of contaminated soil have mainly been conducted in the laboratory, greenhouses or small plot experiments. Therefore, large-scale field trials are essential before operational scale remediation projects are implemented.

Because biochar characteristics vary widely with the use of different biomass materials and pyrolysis conditions, it is vital to optimize production systems to produce biochar products specifically designed for remediation work according to the nature of the pesticides and environmental conditions.

Biochar has a strong sorption capacity for pesticides, and it seems that biochar amendment can lead to an accumulation of pesticide residues in the amended soils, which could act as a new source of pollution. Therefore, the long-term environmental fate of sequestered pesticides must be evaluated.

Surface functional groups and the chemistry of biochar can be altered due to aging, oxidation, or microbial degradation. It is generally accepted that the adsorption capacity of biochar decreases with time due to the aging process. Hence, more specific studies on the aging process will likely help elucidate the exact application rate and frequency of biochar amendments to maximize remediation efficiencies.

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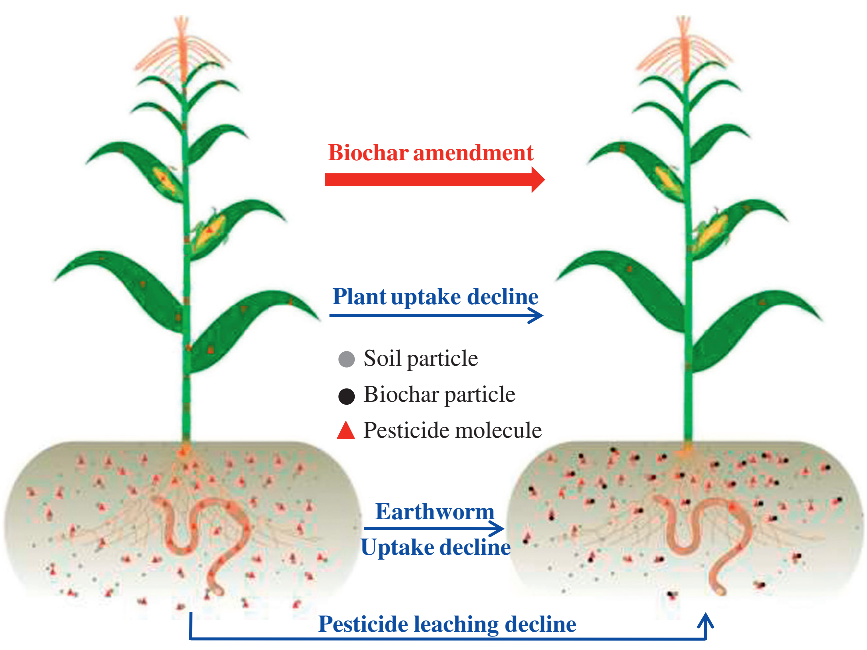

Fig. 1 – A schematic diagram of biochar amendment effects on the environmental behavior of pesticides in soil.

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