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Impacts of Biochar (Black Carbon) Additions on the Sorption and Efficacy of Herbicides

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1. Introduction

The aim of this chapter is to review the effect of biochar on the fate and efficacy of herbicides. The increasing use and need of energy worldwide, together with the depletion of fossil fuels make the search and use of renewable energy sources a priority. Biomass is recognized as a potential renewable energy source, and pyrolysis is considered the most promising thermo-chemical conversion of biomass into bioenergy products (Özçimen & Karaosmanoğlu, 2004). Burning biomass in the absence of oxygen (pyrolysis) yields three products: a liquid (bio-oil), solid, and a gas (Bridgwater, 2003), with the traditional use of these products as renewable fuel and energy sources. Biochar currently lacks a universal definition, as can been seen in the range of definitions in the literature. According to Azargohar & Dalai (2006) *biochar can be considered the solid product of pyrolysis* and Sohi et al., (2010) define it as *biomass-derived char intended specifically for application to soil*. Warnock et al. (2007) defined biochar as the *term reserved for the plant biomass derived materials contained within the black carbon (BC) continuum*. We recommend that the term biochar be defined as the **solid residual remaining after the thermo-chemical transformation of biomass whose main intended purpose is as a means of C sequestration**. However, to retain the "biochar" classification there are two restrictions: 1) biochar itself cannot be used as a fuel source (although the utilization of the energy during production of the biochar is acceptable and encouraged) and 2) excludes those forms of black C derived from non-renewable (fossil fuel) resources [e.g. coal, petroleum, tires] (Lehmann et al., 2006).

The origin of charcoal in the environment can be natural or synthetic. In the first case, wildfire and volcanic processes are responsible for its formation (Scott, 2010; Scott & Damblon, 2010); meanwhile in the second case, thermal processes such as combustion and pyrolysis convert biomass into a char (residual solid product). Pyrolysis is described by Bridgwater (2003; 2006) as thermal decomposition in absence of oxygen, and is always the first step in the processes of gasification and combustion. Production of charcoal is favored by low temperatures and very long residence time conditions (Bridgwater, 1992). According to Goldberg (1985) black carbon is produced by the incomplete combustion of fossil fuels and vegetation that comprises the range of products of char, charcoal, graphite, ash, and

soots, so biochar can be considered as a heterogeneous mixture of solid residues (Figure 1) (Hedges et al., 2000; Forbes et al., 2006; Jones et al., 1997; Spokas, 2010). In a study comparing oxidative stability of soot versus biochar, using a reference thermal stability method (OTC-375) (Gustafsson et al., 1997; 2001; Elmquist et al., 2004) it was observed that synthetic chars did not survive this analytical condition, with nearly 100% of the C oxidized at 375 °C. Thereby, the authors concluded that pyrolysis biochars are of a lower stability when compared to the natural chars (soot) in environmental sediments (Elmquist et al., 2006). In a recent review, this variability in the stability of biochars was placed in context of the spectrum of potential black C products with the molar ratio of oxygen: carbon (O:C) being suggested as a surrogate for biochar stability in soils (Spokas, 2010).
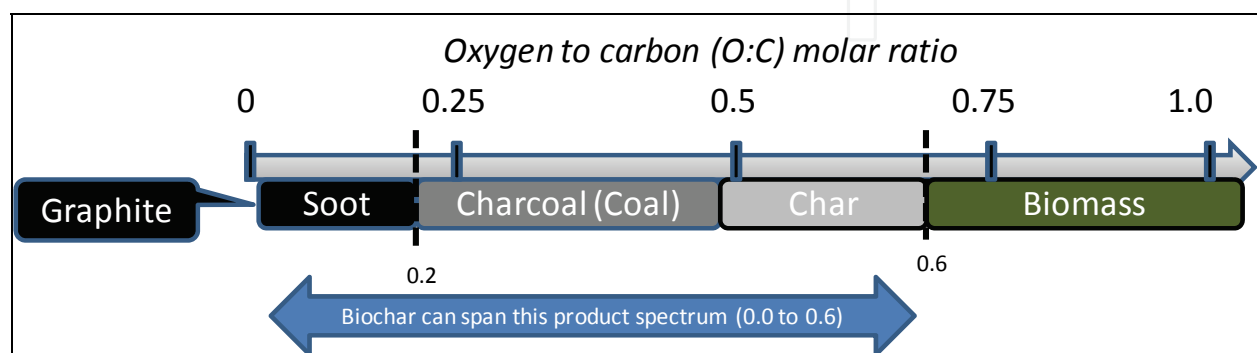

Fig. 1. Spectrum of black C products based on the oxygen to carbon ratio in the residual solid product. Adapted from Hedges et al. (2000), Bansal & Goyal (2005) and Spokas (2010).

For Bansal & Goyal (2005), activated carbon is a term that includes a wide range of processed amorphous carbonaceous materials with increased microcrystalline structure. Common parent materials for activated carbon are nutshells, peat, wood, coal (lignite or bituminous), and petroleum coke (Hassler, 1974). Activated carbon's superior adsorptive properties are due to their high surface area, micropore structure, high porosity, high sorption capacity, and high degree of surface reactivity (Pradhan & Sandle, 1999). Preparation of activated charcoal involves two steps: 1) the carbonization of the raw material (typically at temperatures below 800 °C) in an inert atmosphere, followed by 2) the activation by chemical or thermal methods of the carbonized product (Hassler, 1974; Yalcin & Sevinc, 2000). Chemical treatments both provide an opportunity to unify the surface behavior as well as to customize the overall surface area and porosity of the activated char (Hassler, 1974; Szymanski et al., 2002; Marsh & Rodríguez-Reinoso, 2006).

In summary, biochar properties are attributed to its characteristics, which depend on the pyrolysis conditions, temperature and time, as well as the feedstock used. There is renewed interest in the soil application of biochar as a means of increasing C sequestration and combating climate change. Biochar is a carbon-rich residue and the C is in a form that is more resistant to degradation than the original parent biomass whose primary purpose is as a vehicle for C sequestration, but the stability of the biochar spans the entire black C spectrum (e.g. Spokas, 2010). The land areas that are targeted for biochar applications are primarily agricultural land, due to the potential positive secondary impacts that biochar additions have on overall soil fertility as well as plant growth and yield (e.g. Busscher et al., 2010; Chan et al., 2007; Glaser et al., 2002; Novak et al., 2009; Sohi et al., 2010; Piccolo et al., 1996).

The application of organic materials to soils has been known for some time to increase herbicide sorption and reduce efficacy (e.g. Birk & Roadhouse, 1964; Weber et al., 1969).

Overall, there is the assumption that increased soil sorption could reduce leaching of agrochemicals to groundwater, thus improving overall water quality. On the other hand, increased sorption leads to decreased efficacy of soil applied herbicides thereby eliminating the residual action of these chemicals for weed management. The reader is encouraged to consult other chapters in this book, as well as Kookana et al. (1998), Gevao et al. (2000) and Laird & Koskinen (2008) for a review of herbicide sorption and fate in the soil environment. The impacts on the fate and dissipation of herbicides with biochar additions is still a developing research area, with only a limited number of biochars and soils that have been evaluated to date. To overcome this shortcoming, this chapter will review the existing literature and compile the results of the individual studies to examine if any overall conclusions can be gleamed from the data to date. In particular, production conditions (e.g. temperature, pyrolysis type, residency time) as well as parent material (biomass type) will be compiled to assess any dependency on these parameters as a function of herbicide efficacy, dissipation, and sorption. This review will provide insights for the future directions of herbicide-biochar research.

2. Charcoal, coal, ash and activated carbon: non-biochar additions

As mentioned in the introduction, biochar is the specialized name given to the spectrum of charred biomass products that are intended as a means of C sequestration. However, there has been some research conducted with non-biochar materials (e.g. activated charcoal applications and wood ashes). Activated charcoal starts as charred C prior to the activation process (e.g. steam, acid, or base activation) that optimizes sorption. Occasionally, the source of the C does not also fall within the biochar definition of a biomass (e.g. fossil fuels [coal], used tires, etc.).

There are minor differences in the overall chemical composition of activated charcoals compared to biochars, with the only significant difference being biochars possess higher oxygen contents (5-25%; e.g. Della Rocca et al., 1999; Brewer et al., 2009; Spokas & Reicosky, 2009; Zimmerman, 2010) than the corresponding activated charcoal (<10%; Yalcin & Sevinc 2000; Otowa et al., 1997) and natural black C forms (<7%; Hargrave et al., 1986; Ghetti, 1986; Hofrichter et al., 1997). The most striking difference is in surface area, with activated charcoals typically being >1000 m^2 g^{-1} and biochars are often two orders of magnitude smaller (<50 of m^2 g^{-1}; e.g. Della Rocca et al., 1999; Brewer et al., 2009; Spokas & Reicosky, 2009; Zimmerman, 2010). Thereby, activated charcoals possess an increased potential for herbicide and other organic chemical sorption, as illustrated by activated charcoal's use as absorbent for analytical chemistry quantification methods (e.g. Betz et al., 1989).

2.1 Effect of carbonaceous materials on pesticide sorption

Sorption is one of the main processes that determine the fate of pesticides applied to soils. Soil sorption is characterized by a partition constant K_d, which is the concentration of pesticide in the solid phase divided into the pesticide concentration at the liquid phase at the equilibrium (Wauchope et al., 2002). Sorption isotherms of organic compounds on soils or amended soils are usually fitted to the Freundlich model, especially when the adsorption takes place on heterogeneous surfaces (Calvet, 1989):

$$C_s = K_f \, C_e^{1/n} \tag{1}$$

where C_s is the concentration of pesticide sorbed, C_e is the equilibrium aqueous-phase concentration, K_f is the Freundlich capacity coefficient, and $1/n$ is the Freundlich exponent, which describes the degree of nonlinearity of the isotherm. When n=1, the Freundlich model reduces to a linear model.

Sorption isotherms can also be fitted to a Langmuir model, which assumes that the sorbent surface has a finite number of sorption sites and the sorptive energy is the same in all the sites (i.e. all sites are identical). Furthermore, each sorptive site is occupied only by a single molecule and there are no interactions between the sorbed molecules. Thereby, the maximum sorption a monolayer of sorbates on the surface of the sorbent can be given by:

$$q = QbC_e/1+bC_e \tag{2}$$

where q is the amount of sorbed pesticide per unit mass of soil, C_e is the equilibrium pesticide concentration in solution, Q is the Langmuir adsorption capacity, and b is the Langmuir affinity coefficient.

Among the carbonaceous materials more used as soil amendments are chars, especially wheat char, charcoal, ash, and activated carbon. Pesticide sorption increases in all cases when soils are amended with the carbonaceous materials (Table 1). Wang & Xing (2007) hypothesized that the sorption of organic compounds to un-charred biomass is dominated by absorption mechanisms, whereas adsorption becomes the dominant process with charred materials, largely due to the newly created atomic surfaces and micropores. In the case of wheat char and atrazine, one of the herbicides most used worldwide, the K_f value sorption on the amendment was 2012 (Loganathan et al., 2009), and the K_f increased by a factor of 5 in a sandy loam soil and of 4.3 in a clay loam soil, when both soils were amended with 1% (w/w) of wheat char. Sorption of pentachlorophenol, an organochlorine compound used as herbicide, insecticide, fungicide, algaecide, and disinfectant, was studied on three soils with different amendments (char, humic acids and peat), by Li et al. (2009). The highest sorption of pentachlorophenol in all the soils was observed when the soils were amended with char, followed by humic acids, and peat. Sorption was a function of organic carbon content (Li et al., 2009). The authors reported a 2.5-20 fold increase in the K_f values following the char addition. Zhang et al. (2006) studied the sorption of the pesticide benzonitrile in soil, wheat char and soil amended with the char at a rate of 1% (w/w) with the results of 40.5, >99, and 96.5% respectively, sorbed of the total of the pesticide initially applied. The wheat char was the dominant sorbent phase in the soil amended system, attributing approximately 90% of benzonitrile sorption to the wheat char and 10% to the soil. The sorption of benzonitrile on ash, 1% (w/w) amended soil and unamended soil was studied by Zhang et al. (2004), and a 10 fold increase was observed in the pesticide sorption on the silt loam soil amended with the wheat char. Sorption of the herbicide diuron on soil, char, ash, and amended soil has also been studied (Toth & Milham, 1975; Sheng et al., 2005; Yang et al., 2004; 2006; and Yang & Sheng, 2003a; 2003b). In the study by Toth & Milham (1975), ash was found to adsorb appreciable quantities of diuron from solution. Yang & Sheng (2003a) observed an increase in the sorption of diuron which ranged between 400-2500 times, when wheat and rice ash were used as sorbents and compared to the sorption on a silt loam soil. Increasing amounts of char added to soil, from 0.01 to 1% (w/w), resulted in an increase in sorption, directly proportion to the ash content.

Aged ash was compared as sorbent to fresh or non aged amendment by Yang & Sheng (2003b), and diuron sorption was found to decrease in the aged ash due to the competitive sorption of the dissolved organic matter present in the aged amendment. The competitive

Author	Pesticide	Amendment	Soil
Loganathan et al., 2009	Atrazine	Wheat char (1% w/w) 12.9% C, SA 10.1 $m^2 g^{-1}$	SL, 9% clay , 1.3% C CL, 32% clay, 2.1% C
Zhang et al., 2006	Benzonitrile	Wheat char (1% w/w)	SiL, 23% clay, 1.2% C
Li et al., 2009	Pentachlorophenol	Willow woods shavings char 400ºC, 2h (2% w/w) SA 292 $m^2 g^{-1}$	SiL, 27% clay, 2.6% C CL, 32% clay, 0. 9% C SiL, 11% clay, 0.8% C
Sheng et al., 2005	Diuron Bromoxynil Ametryne	Wheat char (1% w/w) SA 10.1 $m^2 g^{-1}$	SiL, 23% clay, 1.2% C
Yang et al., 2006	Diuron	Wheat char SA 10.1 $m^2 g^{-1}$	SiL, 23% clay, 1.2% C
Qiu et al., 2009a	Atrazine Dichlobenil	Wheat char (0.1-1% w/w)	SL
Zhang et al., 2005	Benzonitrile	Wheat char	SiL, 23% clay, 1.2% C
Sobek et al., 2009	Fenuron Metoxuron Diuron Isoproturon Linuron Chlorotoluron Metobromuron Chlorbromuron Monolinuron	Black carbon (Fork-lift diesel soot)	
Qiu et al., 2009b	2,4-D Prometon Propanil	Black carbon (Rice straw) SA 1085 $m^2 g^{-1}$	
Yang et al., 2004	Diuron Bromoxynil Ametryne	Commercial AC SA 776 $m^2 g^{-1}$ Wheat carbon SA 310 $m^2 g^{-1}$	
Xu et al., 2008	Clomazone	Burned rice straw (0.01-1% w/w)	SiL
Yamane and Green, 1972	Ametryne	Charcoal	SiC (subsoil)
Mukherjee, 2009	Atrazine	Charcoal (2.5% w/w)	SL, 17% clay, 0.4% C
Crepeau et al., 1991	Prometon, Prometryn 2,4-D, Carbofuan Dinoseb, Feanmiphos	Coal AC	SL, 10% clay, 0.4% C
Sudhakar & Dikshit, 1999	Endosulfan	Wood charcoal	
Sudhakar & Dikshit, 2010	Endosulfan Atrazine Monocrotophos	Wood charcoal	

Table 1. (Continued) (AC: Activated Carbon; CA: Carbonaceous adsorbent; SA: Surface Area; SL: Sandy loam; SiL: Silt loam; S: Sandy)

Author	Pesticide	Amendment	Soil
Keerthinarayana & Bandyopadhyay, 1997	Lindane	Wood charcoal	
Cui et al., 2009	Pentachlorophenol	Rice straw ash, 11.4% OC (1-10% w/w)	Sediment
Hiller et al., 2007 2008	MCPA	Wheat ash, 11.8% C (1% w/w)	SL, 11% clay, 1.2% C S, 0.6% clay, 0.5% C
Hiller et al., 2009	MCPA	Wheat ash, 11.8% C (1% w/w)	SL, 11% clay, 1.2% C S, 0.6% clay, 0.5% C
Al Qodah et al., 2007	Deltamethrin Lambda-Cyhalothrin	Oil shale ash	
Yang and Sheng, 2003a	Diuron	Rice ash, 6%OC Wheat ash 14%OC (0.01- 1%/w)	SiL, 23% clay, 1.2%
Yang and Sheng, 2003b	Diuron Atrazine	Wheat ash 14% OC (1% w/w)	SiL, 23% clay, 1.2%
Wang et al., 2009	2,4,6-Trichlorophenol	Wheat ash 77% OC SA 410 $m^2 g^{-1}$	
Zhang et al., 2004	Benzonitrile	Wheat ash 13% C (1% w/w) SA 10.1 $m^2 g^{-1}$	SiL, 23% clay, 1.2%
Gupta et al., 2006	2,4-D Carbofuran	CA SA 380 $m^2 g^{-1}$ AC SA 710 $m^2 g^{-1}$	
Hilber et al., 2009	Dieldrin	AC SA 1200 $m^2 g^{-1}$ (0.02-0.08% w/w)	SiL, 9% clay, 2.2%
Domingues et al., 2007	α-cypermethrin	AC SA 972 $m^2 g^{-1}$	
Hu et al., 1998	MCPB Imazalil Bentazone MCPP Dinoseb PCP Imidacloprid Linuron	AC SA 1340 $m^2 g^{-1}$	
Guo et al., 1993	Alachlor	AC 95.4% C (0.5-2.1 t C ha^{-1})	S, 5% clay, 0.9% O
Guo et al., 1991	Atrazine Alachlor	AC 95.4% C (0.5-2.1 t C ha^{-1})	S, 5% clay, 0.9% O

Table 1. (Continued) (AC: Activated Carbon; SA: Surface Area)

Author	Pesticide	Amendment	Soil
Hale et al., 2009	DDT DDD DDE DDMU	AC TOG SA 935 m² g⁻¹ ACRS SA 900 m² g⁻¹	Water Sediment
Tomaszewski et al., 2007	DDT	AC TOG SA 935, F400 SA 1100 AC830 SA 900, ACRS SA 900	Sediment
Lafrance et al., 1991	Aldicarb Lindane Pentachlorophenol	AC	
Bandala et al., 2006	Aldrin Dieldrin Heptacchlor Heptachlor Epoxide	Activated vegetal carbon	
Matsui et al., 2003	Simazine Simetryn Asulam	AC Coal based AC Wood based	
Ayranci and Hoda, 2005	Ametryn Aldicarb Dinoseb Diuron	AC-cloth SA 2500 m² g⁻¹	

sorption with atrazine was also studied, and a slight decrease in diuron sorption in presence of atrazine in the soil and in the amendment was also observed. The effect of the pH on pesticide sorption on the organic amendments was also studied by Li et al. (2009) with the result of an increase of sorption with the decrease in pH, which changes the pentachlorophenol species, and increases the static repulsion between the sorbent surface and the anionic form of the pesticide. However, it has been suggested that the presence of oxygenated groups on char could mask the impact of pH on the sorption of herbicides (Tessmer et al., 1997). Yang et al. (2004) did not observe any effect of pH on diuron sorption on activated carbon, due probably to the low density of functional groups on the surface of the activated carbon. Sheng et al. (2005) examined wheat char and 1% (w/w) char amended soil and hypothesized that the London forces between herbicide molecules and the electrically neutral char surface did not change with the pH. However, Yang et al. (2004) observed a decrease in diuron sorption with the pH increase on wheat char, because of the alteration of the surface charge properties by the deprotonation of the functional groups over the pH range. Contrary to the above charcoal studies, Sheng et al. (2005) also reported the same pH effect when diuron was sorbed only to soil, attributing the fact to the increase of the dissociation of the acidic groups with the increase in pH, increasing the hydrophilic of the organic matter, and reducing diuron sorption. Furthermore, Sheng et al. (2005) and Yang et al. (2004) also examined the pH effect on the sorption of the herbicides ametryne and bromoxynil. Both observed that sorption of bromoxynil on soil, wheat char, activated carbon and char-amended soil was higher at low rather than at high pH. The pK_a of this compound is 4.06, so at pH< 4.06 the herbicide is in the molecular form and at pH>4.06 in anionic form. The deprotonation of the phenolic hydroxyl group and the interactions and repulsion between the anion and the charge of the soil or amendment surfaces are the responsible for the sorption decrease with increasing pH of bromoxyinil. Ametryne is a basic herbicide, with pK_a of 4.1, at pH< 4.1 the compound is mostly in cationic form and at pH > 4.1 in molecular form. Sheng et al. (2005) studied the effect of 2 pH values, 3 and ~6.5, and found higher sorption of ametryne at lower pH on soil, wheat char and wheat char amended soil, in this case, the higher sorption occurs when the pesticide is in ionic form, due probably to electrostatic interactions of ametryne cations and the charges of the soil or char surface. Yang et al. (2004) included a value more of pH= 4 in the study and observed a different effect of pH on ametryne sorption. Ametryne sorption on activated carbon increased with the increase in pH, as result of the deprotonation of the herbicide molecule at low pH. However, when the sorbent was wheat char the highest sorption was observed at the intermediate pH, followed by the lower pH and the higher pH. The authors considered that the increase in sorption when the pH increased from 2 to 4 is due to the net result of the adsorption increase because of the ametryne deprotonation and the desorption decrease because of deprotonation of the functional groups of the sorbent surface. Yamane & Green (1972) also reported an increase on ametryne sorption on a silty clay soil when charcoal was added. Higher sorption of the herbicide at lower pH on the non amended soil was observed, but with the addition of charcoal to the soil the effect of pH on sorption of ametryne was the opposite, increasing the herbicide affinity for charcoal with protonation. For clomazone, a rice crops herbicide, Xu et al. (2008) reported an increase in sorption with the addition of burned rice straw to the soil, with an increase of 1.5 and 3 times in the K_f values when a silt loam soil was amended with the 0.1 and 0.5% (w/w) respectively. The acidic herbicide MCPA and the effect of wheat ash as soil amendment on its sorption were studied by Hiller et al. (2007; 2008; 2009). The authors observed that the isotherms of MCPA on wheat ash

fitted to a Langmuir equation, but sorption on soil and ash amended soil did not fit to any model and calculated the K_d values, with a 15 and 10 fold increase when the sandy loam and the sandy soil were amended with 1% (w/w) of wheat ash. Activated carbon was used as amendment of a sandy soil for sorption of the herbicide alachlor (Guo et al., 1993). The soil was amended with the waste activated carbon at a rate of 0.5-2 t C ha-1, increasing the value of K_f by a factor of 5-14 as compared with the non amended soil. Digested sewage sludge and animal manure were also studied as amendments, but waste activated carbon was more efficient in alachlor sorption. Konstantinou & Albanis (2000) examined the impact of coal fly-ash additions on the impact of 6 herbicides (atrazine, propazine, prometryne, propanil, molinate, propachlor). Their particular coal fly-ash had a carbon content of 2%, which is significantly lower than the typical charcoal. They showed that the adsorbed amounts of herbicides increased with the amount of fly ash addition, up to the amount sorbed by the "pure" fly ash. The adsorption coefficient (K_f) was exponentially related to the fly ash percent.

2.2 Effect of carbonaceous materials on herbicide desorption

The process of desorption has been less studied as compared to sorption. A pesticide that is sorbed to soil particles has to be desorbed to be available for transport and degradation. Desorption of atrazine in one step, successive steps and followed by solvent extraction for soil, char and char amended soil was performed by Loganathan et al. (2009). The multiple steps desorption was more efficient than the one step process, showing hysteresis in the sandy loam and clay loam soils and the amended soils. After the successive steps and solvent extraction desorption the amount of atrazine remaining sorbed on the char amended soils were higher than in nonamended soils. The successive desorption isotherms could be fitted to the Freundlich, Langmuir, and a combination of both equations. Desorption of MCPA is influenced by the presence of wheat ash in a sandy and sandy loam soil, decreasing MCPA desorption from 77 to 21% in the non amended and wheat ash amended sandy loam soil, and from 45 to 11% in the non amended and amended sandy soil (Hiller et al., 2007; 2008; 2009). MCPA desorption at high concentration (57 mg L-1) the percentage of herbicide desorbed from the wheat ash was similar to the percentages desorbed from the amended soils, however, at the low concentration (5.7 mg L-1) decreased the desorption of MCPA from the amendment. This fact could be propably due to the limited number of sorption sites of high energy binding available, which are occupied first at low concentration; to the extent of concentration is increasing, these sites are not available and herbicide molecules are retained to low energy sites and can be desorbed more easily. The same amendment was used for the desorption study of benzonitrile by Zhang et al. (2004). These authors evaluated the herbicide desorption from the nonamended soil and from the amendment, and observed a similar desorption of benzonitrile, but with different kinetics, slower desorption from wheat ash than from the silt loam soil, because of stronger sorption of benzonitrile on ash surface than on soil organic matter. Karanfil & Kilduff (1999) observed that the surface acidity (by activation) was a vital factor in the sorption of hydrophobic compounds. Increases in acidity caused a corresponding increase in surface polarity, which correspondingly resulted in reduced sorption. Konstantinou & Albanis (2000) also observed that the amount of herbicide desorbed with water decreased with increased fly-ash content. Thereby, indicating that the amount of potential available herbicide in the soil system decreases but fly-ash could be utilized to reduce the mobility of the herbicide in the soil system.

2.3 Effect of carbonaceous materials on pesticide degradation

The addition of organic amendments to soil can have contrasting effects on pesticide biodegradation; some authors have reported an increase as result of the microbial stimulation by the amendments, and others report a degradation decrease with the amendment, due to a lower pesticide bioavailability to microorganisms because of the increase in sorption.

For the herbicide atrazine, Loganathan et al. (2009) reported a decrease in mineralization of the herbicide in the 1% (w/w) wheat char amended soils as compared to the soils slurries, attributing the atrazine bioavailability decrease to the increase in sorption of the herbicide on the char amendment. Guo et al. (1991) suggested that atrazine and alachlor degradation could be inhibited by the presence of waste activated carbon, and stimulated by other uncharred amendments, such as municipal sewage sludge and manure. An increase on atrazine degradation by the addition of organic amendments to a sandy loam soil was also reported by Mukherjee (2009). Among the amendments studied, charcoal was included, although it was the amendment that had a lower decrease in atrazine degradation, as compared to rice straw, sawdust and farm yard manure. Qiu et al. (2009a) observed enhanced degradation of atrazine increasing the amount of wheat char added to the sandy loam soil from 0.1 to 1%. These increases were hypothesized to result from the nutrients present in char, and especially P, which could stimulate the microorganisms' activity thereby enhancing the biodegradation. Coapplication of another herbicide, dichlobenil resulted in a reduction of atrazine degradation in the soil and char amended soils, in comparison with the degradation of atrazine applied as the only herbicide. The suppression on the degradation of one herbicide by the metabolism of the other one applied could be due to the toxicity of the second compound or its metabolites, or by the competition for nutrients (Qiu et al., 2009a). Similar results were obtained for dichlobenil degradation as the only herbicide and coapplied with atrazine. Yang et al. (2006) observed a decrease and slower degradation of diuron in the 0.5% char amended soil as compared to the soil non-amended, with degradation lower than 40% and 55% respectively of the amount of diuron initially applied and after 10 weeks of study. Bioavailability of diuron to soil microorganisms was decreased by the presence of wheat char in the soil, due to the increase in herbicide sorption. For the weak acidic herbicide MCPA, a decrease in biodegradation because of wheat ash amendment was also reported by Hiller et al. (2009). The half-life of MCPA increased by a factor of 4.5 in the sandy loam soil with the 1% (w/w) wheat ash amendment, and correspondingly increased by 2.6 times in the sandy soil. The lower degradation of MCPA in the amended soils might be due to the increase in sorption, but also to the lower desorption observed.

Biodegradation of benzonitrile has been extensively studied by Zhang et al. (2004; 2005; 2006). In the first study a decrease in the biodegradation of benzonitrile in the 1% (w/w) wheat ash amended soil was reported. During the study the authors proved that there was no abiotical degradation of the organic compound and dissolved organic C did not affect its biodegradation. Reduction in the benzonitrile biodegradation was due to the combination of increased sorption and slow sorption from the ash and the acclimation period of the microorganisms. In the second study, initial degradation of benzonitrile was faster in the the soil amended than in the soil free of char, because of the dissolved nutrients of the wheat-residue derived char, which stimulated the cell growth and degradation in the amended soil. Degradation process was followed by a slower phase due to the adsorptive decrease by

the presence of char. In the last work the authors studied the effect of initial benzonitrile concentration on the degradation. In the non-amended soil higher degradation was observed at lower benzonitrile concentration, however, in char amended soil, the higher initial concentration, the higher degradation. At the highest concentration a higher degradation was observed in the amended soil as compared to the non amended one, which could be attributed to the increase and stimulation of the microbial activity by the nutrients of the char. No significant pH effect was observed for benzonitrile degradation in char and char-amended soil, probably due to the high affinity sorption of benzonitrile by char that did not vary with pH.

2.4 Effect of carbonaceous materials on pesticide leaching

The addition of rich carbon amendments to soils can decrease pesticide leaching, as consequence of the increase in sorption. Crepeau et al. (1991) studied the mobility of the pesticides: 2,4-D, carbofuran, dinoseb, fenamiphos, prometon and prometryn in a sandy soil, two charcoals and the soil amended with three charcoals and activated carbon at three rates: 4:1, 7:1, and 10:1 (dry weight soil/weight coal carbon). The highest retention of the pesticides was observed with the activated carbon at the rates of 7:1 and 10:1. Leaching of pesticides also decreased with the addition of charcoal to the sandy soil. Leaching of alachlor was studied by Guo et al. (1993) in three different conditions, unsaturated flow, saturated flow and alternation of saturated and unsaturated flow in soil amended with activated carbon, municipal sewage sludge and animal manure at three rates of C content. In all cases the highest alachlor retention and recovery at the end of the study was observed in the waste activated carbon amended soil, which is in accordance with the higher sorption reported by the authors.

3. Impacts of biochar additions

The use of biochar as soil amendment is highly recommended because of the properties and benefits this amendment provides to soil and environment. As it was previously mentioned, among the properties of biochar are its high stability to degradation, and nutrient retention. Numerous works deals with the effect of biochar on soil properties (Warnock et al., 2007; Chan et al., 2007; 2008; Asai et al., 2009; Novak et al. 2009; 2010; Steinbeiss et al., 2009; Van Zwieten et al., 2010; Busscher et al., 2010; Sohi et al., 2010; Gaskin et al., 2010; Singh et al., 2010). There are limited studies (Table 2) detailing the effect of biochar soil amendments (fitting the definition of biochar) on pesticides and agrochemicals fate. Due to the fact that biochar is a black C the studies outlined in Section 2 (Table 1) are also applicable.

The use of biochar could contribute to the increase of pesticides sorption on soil, decreasing its mobility and reducing the contamination risks of surface and ground waters. The knowledge of biochar properties, which depends on the feedstock and pyrolysis conditions, is vital (Section 1). The characterization of biochar used in studies should be conducted and this data should be included in the manuscript, which would enable the comparison of the effects of the amendment on the pesticides behavior in soils across different studies. This comparison would allow the determination of the optimum pyrolysis conditions to yield biochar with the most appropriate properties to reduce the environmental contamination risks associated with the use of agrochemicals.

3.1 Effect of biochar on herbicide sorption

Triazine herbicides are among the more studied pesticides in the works about the effect of biochar on pesticide sorption. Spokas et al. (2009) observed an increase on atrazine sorption when a sandy loam soil was amended with 5% (w/w) biochar. The biochar was produced by fast pyrolysis at 500 °C of sawdust and had a surface area of 1.6 m^2 g^{-1}. The effect of biochar on atrazine sorption was greater at lower atrazine concentrations, and no effect of biochar addition was observed at the highest concentration of atrazine studied (17 µg mL^{-1}). These authors also studied the sorption of acetochlor, a chloroacetanilide herbicide, and reported a greater sorption of the herbicide in the soil amended with biochar, increasing the Freundlich K$_f$ value from 4.1 to 6.6 µg$^{1-1/n}$ mL$^{1/n}$ g^{-1} with the amendment.

Wang et al. (2010) studied the effect of biosolids and two biochars on terbuthylazine sorption on sandy volcanic ash soil and forest topsoil. Pine (*Pinus* spp.) wood was the feedstock for both biochars, BC350 was produced at 350 °C and BC700 at 700 °C and were applied to soil at a rate of 1% (w/w). Sorption isotherms of terbuthylazine on soil and soil amended was described by a Freundlich model. The highest increase in sorption was observed when the soil was amended with BC700, followed by BC350. The authors found that the organic matter in the amendments had higher sorption capacity to the herbicide than endogenous organic matter in the landing soil, with lower content on organic carbon (OC). Sorption of atrazine to biochar was studied by Cao et al. (2009) and Cao & Harris (2010). The biochar feedstock was dairy manure and was produced at 200 and 350 °C in the first study and in the second were included the temperatures of 100 and 500 °C. Sorption of atrazine in the first study was higher on BC200 than on BC350, which was correlated to the organic carbon content (31 and 26% respectively) and the polymer aliphatic fraction. No significant differences were observed by the authors on the sorption of atrazine in single or binary solute (with Pb) systems when the adsorbent were the biochars, indicating limited sorption competition between Pb and atrazine. In the second study, the higher sorption of atrazine was observed with BC200, with higher OC content than BC350, but lower than BC100. It is thought that the lower sorption in BC100 with higher content on OC is due to the suppression of sorption by high dissolved organic C competing for sorption sites.

Zheng et al. (2010) have also studied the sorption of two triazine herbicides, atrazine and simazine, on biochar. The feedstock of this biochar was green waste which was a mixture of maple, elm and oak woodchips and bark. The pyrolysis temperature was set at 400 °C and biochar was separated in different fractions according to the particle size. Higher and faster sorption of atrazine and simazine occurred with the smaller particle size of biochar. The authors also reported an increase in sorption affinity of the biochar for the herbicides with the decrease in the solid/solution ratio and higher sorption at pH < 7, but, no pH effect at values ≥ 7 was observed. Sorption isotherms of the herbicides as single or double solute system were adjusted and fit to Freundlich models, and competitive sorption was observed for both herbicides. According to Zheng et al. (2010) biochar can be considered a heterogeneous sorbent with combined adsorption and partition mechanisms, which occurs on carbonized and non-carbonized fractions of the biochar. A biochar produced from red gum wood at two temperatures (450 and 850 °C) were used to study the sorption of the pesticides diuron and pyrimethanil on soil by Yu et al. (2006 and 2010) respectively. The sandy loam soil was amended with BC450 at rates from 0.1-5% (w/w) and from 0.1 to 1% for BC850. The sorption data were fitted to a Freundlich model and it was reported that there was an increase in the non-linearity behavior of the sorption with the increasing amendment rate, at the highest biochar rate data was better described by a Langmuir model.

Reference	Pesticide	Biochar	Soil	Effect
Yu et al., 2009	Carbofuran Clorpyrifos	Red gum wood chips 450 °C 2h (0.1-1% w/w) SA 27 m² g⁻¹ 850 °C 1h (0.1-1% w/w) SA 566 m² g⁻¹	SL, 11% clay	↓ Dissipation ↑DT$_{50}$ > BC 850 ↓ Plant uptake ↓Bioavailability
Yu et al., 2006	Diuron	Red gum wood chips 450 °C 2h (0.1-5% w/w) SA 27 m² g⁻¹ 850 °C 1h (0.1-1% w/w) SA 566 m² g⁻¹	SL, 11% clay	↑ Sorption + > amount BC 850 ↑ Sorption irreversibility > amount BC 850 > microporosity
Spokas et al., 2009	Atrazine Acetochlor	Sawdust 500ºC (5% w/w) SA 1.6 m² g⁻¹	SiL, 23% clay, 2.6% OC	↑ Sorption ↓ Dissipation ↓ Bioavailability
Jablonowski et al., 2010	Atrazine	Hardwood 450-500ºC (0.1-5% w/w) SA 200 m² g⁻¹	C, 49.4% clay, 3.2%OC SiL, 7.8% clay, 1.3%OC	↑ Mineralization C Soil
Cao et al., 2009	Atrazine	Dairy manure, 200 °C 4h, 350 °C 4h		↑ Sorption BC 200
Wang et al., 2010	Terbuthylazine	Pinus radiata wood Commercial charcoal 350ºC (1% w/w) Sawdust 700 °C (1% w/w)	S Landing soil, 1.2% OC Forest topsoil, 5.1% OC	↑ Sorption BC 700 ↓ Desorption
Yang et al., 2010	Chlorpyrifos Fipronil	Cotton straws 450ºC 2h (0.1-1% w/w) SA 3.9 m² g⁻¹ 850 °C 1h (0.1-1% w/w) SA 159 m² g⁻¹	CL, 33% clay	↓ Dissipation> 1% BC 850 ↓ Bioavailability ↓ Plant uptake
Yu et al., 2010	Pyrimethanil	Red gum wood chips 450 °C 2h (0.1-1% w/w) SA 27 m² g⁻¹ 850 °C 1h (0.1-1% w/w) SA 566 m² g⁻¹	SL, 11% clay	↑ Sorption + > amount BC 850 ↑ Sorption irreversibility > amount BC 850
Sopeña et al., 2010	Isoproturon	Eucalyptus sp (0.1-1% w/w)	SL , 1.3% OC	↑ Sorption ↓ Desorption ↑Hysteresis ↓ Degradation↓ Mineralization
Cao & Harris, 2010	Atrazine	DM BC 100ºC 4h SA~1.8 m² g⁻¹ BC 200ºC 4h SA~2.7 m² g⁻¹ BC 350ºC 4h SA~7 m² g⁻¹ BC 500ºC 4h SA~13 m² g⁻¹		↑ Sorption BC 200
Zheng et al., 2010	Atrazine Simazine	Elm, oak, maple woodchips and barns 450ºC SA 6.7-7.6 m² g⁻¹		> faster sorption < particle size BC Competitive sorption solid/solution , pH effect pH<7

Notes: SA: Surface area; BC: Biochar; DM: Dairy Manure; SL: Sandy loam; SiL: Silt loam; S: Sandy; C: Clay; and CL: Clay loam.

Table 2. Summary of biochar amendment studies on herbicide fate

The amount of diuron sorbed did increase with the biochar amount added to the soil. Biochar additions, even small additions, increased diuron sorption as compared with the non-amended soil. This clearly illustrates that presence of carbonaceous material, even in small amounts, can dominate sorption of organic compounds in soils. Similar results were obtained for the sorption of pyrimethanil on the same soil and using the same amendments rates and biochars (Yu et al., 2010). Higher sorption was observed in the soil amended with BC850, as compared to the amended BC450 soil, which is in accordance with the surface area of biochar, 566 and 27 m^2 g^{-1}, respectively. The authors suggested that sorption of the pesticide on the biochar amended soil was a combination of surface adsorption and absorption into biochar micropores. The increase of sorption and non linearity of the isotherms with the increase of biochar amendment was also observed by Sopeña et al. (2010) in the study of isoproturon sorption in a sandy loam soil. Biochar feedstock was red gum wood, but no further information about the biochar production and characteristics was reported thus limiting the comparison to other biochar results.

3.2 Effect of biochar on pesticide desorption

Studies of pesticide desorption have been reported by Yu et al. (2006; 2010), Wang et al. (2010), and Sopeña et al. (2010). In this first study of Yu et al. (2006), diuron desorption isotherms for a sandy loam soil amended with different rates of biochar produced at 450 and 850 °C were fitted to Freundlich models. Sorption-desorption hysteresis on the amended soils was observed, and irreversibility of the sorption increased with the increase in the amount of biochar applied to the soil. Sorption irreversibility was greater in the soil amended with the highest rate of BC850, which was attributed to the higher micro-porosity of this amendment as compared to BC450. In the second study pyrimethanil desorption was calculated as the percentage of the initial amount of herbicide adsorbed on the soil free of biochar and on the amended soil. Isotherms were not calculated and neither adjustment to any sorption model was performed. The authors observed a decrease on the percentage of pyrimethanil desorbed when the amount of biochar increased in the amended soils and lower herbicide desorption from the soil amended with BC850 than with BC450. The lower desorption reported for the BC850 could be due to the higher surface area (566 vs. 27 m^2 g^{-1}) and the higher number of micropores, maximum peak of pore size distribution at 0.49 vs. 1.1 nm, as compared to BC450. Desorption isotherms of terbuthylazine in unamended and amended soils were well described by the Freundlich model (Wang et al., 2010). The authors reported a lower desorption of terbuthylazine adsorbed on the soils treated with biochar, especially with BC700, than in the soils no amended. These biochars were not characterized, as to surface area and microporosity, but again the biochar produced at higher temperature shows a slower and lower desorption of the herbicide adsorbed. In case of isoproturon desorption the data also fitted well to Freundlich model and lower desorption of the herbicide with the increase in the biochar/soil ratio was observed by Sopeña et al. (2010).

3.3 Effect of biochar on pesticide degradation

The effect of biochar on the dissipation and degradation of pesticides in amended soils has been reported for the herbicides atrazine (Spokas et al., 2009; Jablonowski et al., 2010), acetochlor (Spokas et al., 2009), isoproturon (Sopeña et al., 2010), and the insecticides chlorpyrifos (Yu et al., 2009; Yang et al., 2010), fipronil (Yang et al., 2010), and carbofuran (Yu et al., 2009). Spokas et al. (2009) reported a lag phase of 11 days in the dissipation of

atrazine in the non-amended and biochar amended silt loam soil. After that time dissipation was greater in the unamended soil. An increase in the degradation of atrazine was found by Jablonowski et al. (2010), in a clay soil adapted to atrazine, and amended with biochar from hardwood at 450-500 °C. The increase in mineralization and degradation of the herbicide is attributed to the stimulation of the soil microflora by the nutrients provided by biochar. Spokas et al. (2009) did not observe any lag phase for acetochlor dissipation, and the amendment of soil with biochar decreased the herbicide dissipation. The time of disappearance of the 50% of the initial amount of herbicide applied (DT$_{50}$) was calculated and increased from 9.7 days in the non amended soil to 34.5 d in the biochar amended soil. An increase in persistence of isoproturon in a sandy soil with biochar amendment was also reported by Sopeña et al. (2010) and DT$_{50}$ increased from 2.2 d in the unamended soil to 5.6 d in the 2% (w/w) biochar amended soil. The amendment of a clay loam soil with biochar produced at 450 and 850 °C from cotton straws also caused a decrease in chlorpyrifos and fipronil dissipation (Yang et al., 2010). The dissipation decrease was higher with the higher content of biochar, and BC850 was more effective in reducing the loss of both insecticides. Under non sterilized conditions chlorpyrifos DT$_{50}$ increased from 21 to 44 and 56 d with the 1% (w/w) BC450 and BC850 amendments, respectively. Furthermore, fipronil DT$_{50}$ increased from 27 d in the non amended soil to 48 and 60 d with the 1% BC450 and 850, respectively. Under sterilized conditions DT$_{50}$ were 2 and 3 times higher for chlorpyrifos and fipronil, which implies that degradation of the pesticides is mainly biotic. It was suggested that the decrease in pesticide dissipation in the soils was due to the lower bioavailability of chlorpyrifos and fipronil to the soil microorganisms, because of an increase in sorption and lower desorption promoted by the biochar. Yu et al. (2009) also reported a decrease in carbofuran and chlorpyrifos dissipation in a sandy loam soil when the soil was amended with biochar produced from red gum wood chips at 450 and 850 °C. These authors also found a decrease in pesticide dissipation with the increasing content of biochar, being BC850 more effective in the reduction of the insecticides dissipation. Carbofuran DT$_{50}$ increased from 12 d in the non amended soil to 33 d in the 1% (w/w) BC850 amended soil and for chlorpyrifos the increase in DT$_{50}$ was from 12 to 43 d with the addition of 1% BC850 to the soil. The effect of the presence of plants on the insecticides dissipation was also studied, with the result of faster loss of pesticide residues with the presence of plants in all soils, and especially in the soil amended with BC850. This could be due to the combination of effects of uptake by the plants and increase in degradation of the pesticides, because of the stimulation of microbial and biochemical activity.

3.4 Effect of biochar on pesticide plant uptake

Little research is reported on the effect of biochar on plant uptake of pesticides. Yu et al. (2009) used spring onion to study the effect of the biochar produced from red gum wood chips at 450 and 850 °C as amendment of a sandy loam soil on the plant uptake of chlorpyrifos and carbofuran. In the study of Yang et al. (2010) Chinese chives uptake of chlorpyrifos and fipronil from a clay loam soil amended with biochar prepared from cotton straw residue at 450 and 850 °C was determined. In both studies higher biomass production was observed in the cultivated soils amended with biochars than in the control soils, with the BC850 resulting in a larger increase than the BC450 amendment. In the soils spiked with carbofuran, greater biomass was produced from spring onion than in the soils spiked with chlorpyrifos. Soils cultivated with Chinese chives produced higher biomass in the soil

spiked with chlorpyrifos as compared with fipronil. It was shown in the two studies that BC850 was more effective in reducing the uptake of the insecticides by the plants. The total amount of plant uptake of the pesticides in the whole plant or in parts of the plant decreased with the increasing content (0.1, 0.5, 1% w/w) of biochar in the soil, being the 1% BC850 treatment the most effective in the reduction of the total pesticide plant uptake (75% for carbofuran and 90% for chlorpyrifos in case of spring onion, and 52% for fipronil and 81% for chlorpyrifos in Chinese chives) as compared with the control or non amended soil.

4. Impact of biochar characteristics

There are several studies about pyrolysis conditions and biochar properties focused on soil quality improvement, but as mentioned above, reports on the study of biochar on the effect of pesticides fate are scarce. Thus, it is difficult to assess all the factors that predict biochar properties for the increase in sorption and retention, and decrease in leaching and mobility of herbicides to avoid environmental pollution associated to the use of agrochemicals. However, some trends can be elucidated from the available data.

4.1 Type of pyrolysis process

The first condition that appears to have an influence on herbicide sorption is the type of pyrolysis process. Biochar properties can be very varied and depend on the feedstock, the conditions of the thermal process used, and the changes post-pyrolysis caused by aging or activation treatments (Laird et al., 2009). The yield of gas, liquid or solid products also depends on the thermal process conditions. The yield of biochar follows the order: slow pyrolysis > intermediate pyrolysis > fast pyrolysis > gasification. The slow pyrolysis process implies low temperature, around 400 °C, and residence times of several minutes. The temperature of the fast and intermediate pyrolysis processes is moderate, around 500 °C, and the residence time is of ~1 second and 10-20 s, respectively. In gasification the temperature is higher, around 800 °C and the residence time is longer, more than 5 minutes (Bridgwater, 2006). Although the process with lower temperature yields the higher amount of char, temperatures lower than 400 °C produces biochar with low pH, CEC, and small surface area, which make it not suitable for improving soil quality (Lehmann, 2007), or increasing pesticide sorption on soil, decreasing its dissipation and availability (Yu et al., 2006; 2009; 2010; Wang et al., 2010; Yang et al., 2010). According to Sohi et al. (2010) feedstock is an important factor to determine the function of biochar in soil, but there is no consensus about the optimal feedstock in terms of soil use and energy production. The concentration of bases in biochar depends on the mineral content of the biomass used, and the ash content of the biochar on the type of feedstock, for example, softwood produces a biochar with lower content on ash than hardwood and corn or wheat wastes (Laird et al., 2009). Woody chars are considered to be more highly condensed, more aromatic and with higher surface area as cotton straw derived chars (Yang et al., 2010).

4.2 Pyrolysis temperature

Temperature is a key factor on biochar properties, such as surface area, microporosity, and stability. Brewer et al. (2009) reported different physical and chemical properties of the chars produced by fast pyrolysis and gasification than from the chars prepared by slow pyrolysis. The process temperature determines the type of carbon present in the biochar, being

reaction time less decisive. In the studies, which deal with the effect of biochar on pesticide sorption, dissipation and bioavailability in soils, the authors report better properties to the biochar produced at higher temperature, as consequence of the higher surface area and microporosity. Yu et al (2006) observed higher hysteresis and sorption irreversibility of diuron with the biochar produced at 850 °C as compared to the one produced at 450 °C. The microporosity was greater in BC850 than in BC450, and diuron molecules sorbed could be retained in the micropores or have caused a slow and prolongued sorption phase, which may have led to the apparent hysteresis due to non equilibrium process. Yang et al. (2010) considered that temperature is more important than feedstock material on the biochar effectiveness in treatment of contaminated soils. Wang et al. (2010) observed a higher sorption of the herbicide terbuthylazine in the soil amended with biochar produced at 700 °C than at 350 °C, although the feedstock was the same. In Fig. 2 we have plotted the data of Freundlich K_f parameter for some pesticides sorbed to the biochar and temperature pyrolysis. Granted there are a limited number of studies with sufficient data to compare, but the hypothesis is that higher temperature biochars appear to possess a higher capacity for sorption than the lower temperature biochars. However, since there are limited studies that present sufficient characterization data on the biochar, this conclusion requires further investigation.
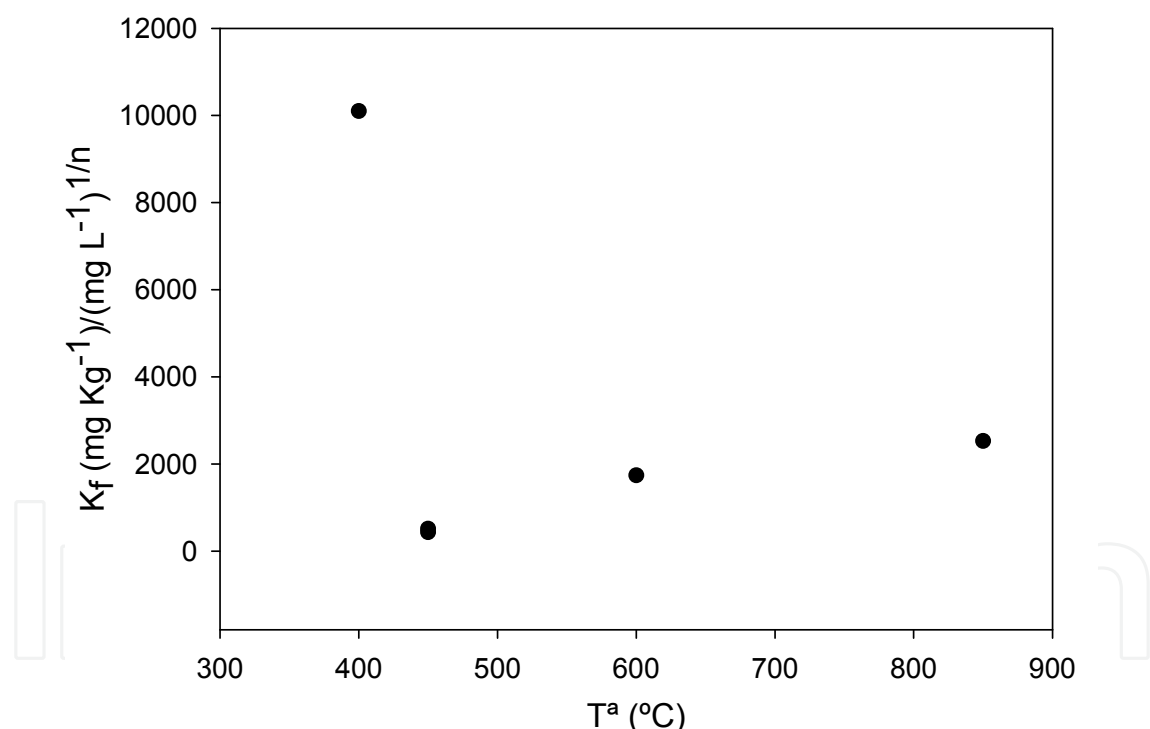

Fig. 2. Freundlich sorption parameter K_f correlated with the pyrolysis temperature (T^a). [Data of sorption on char from Zheng et al., 2010 (Table 2); Li et al., 2009, (Table 1); Aroguz, 2006 and Hameed et al., 2009].

4.3 Surface area
Fig. 3 displays the overall relationship between surface area and observed K_f sorption coefficient for various biochars. There is a relationship between surface area and sorption. However, due to the scatter in the graph, there is the suggestion that surface area is not the

fundamental parameter and potentially the chemistry of the surface groups would be a better predictor variable as has been shown for activated charcoals (e.g. Bello et al., 2002).

5. Conclusions

Overall, the comparison of the impact of biochar on herbicide sorption is narrow due to the limited number of studies utilizing biochar. Furhermore, the lack of information within these studies to properly characterize the biochar material used further limits the ability to compare results. However, based on the analogous observations with non-biochar materials (Table 1), the overall conclusions are that biochar additions (Table 2) will:

- increase sorption,
- decrease dissipation rates,
- decrease leaching and movement of the herbicide in the soil, and
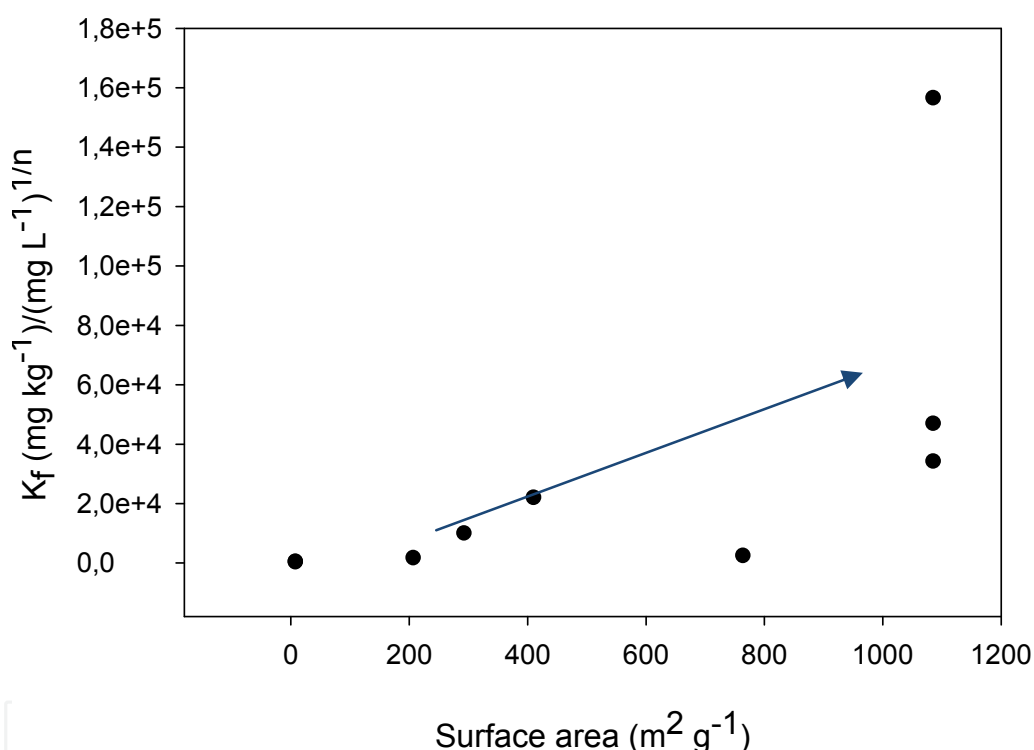- reduce the bioavailability of the herbicide, which could lead to reduced efficacy.

Fig. 3. Freundlich sorption parameter K_f correlated with the surface area determination of the biochar. [Data presented from Zheng et al., 2010 (Table 2); Li et al., 2009; Qiu et al., 2009b; Wang et al., 2009, (Table 1); Aroguz, 2006 and Hameed et al., 2009].

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Herbicides and Environment

Edited by Dr Andreas Kortekamp

Herbicides are much more than just weed killers. They may exhibit beneficial or adverse effects on other organisms. Given their toxicological, environmental but also agricultural relevance, herbicides are an interesting field of activity not only for scientists working in the field of agriculture. It seems that the investigation of herbicide-induced effects on weeds, crop plants, ecosystems, microorganisms, and higher organism requires a multidisciplinary approach. Some important aspects regarding the multisided impacts of herbicides on the living world are highlighted in this book. I am sure that the readers will find a lot of helpful information, even if they are only slightly interested in the topic.

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