

## Biochar impact on herbicides behavior in the soils: an approach in Brazil

### *Impacto do biochar no comportamento de herbicidas em solos: um enfoque no Brasil*

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**Abstract** - The application of biochar to soils because of beneficial effects is proven by many international researchers and this can increase herbicides sorption and reduce effectiveness on weed management. Positive impacts are reported in relation to the environmental behavior of herbicides, since the increase of the sorption reduces the leaching of these products to groundwater. Negative impacts are reported in relation to agronomic management of herbicides, since the sorption increase reduces the availability of these products in the soil, reducing the residual effect for weed control. In Brazil, biochar is produced by several private companies and pyrolysis units, but the cost for production is still very high, probably due to lack of government incentive, low use of producers, and awareness of the benefits. Although biochar has been used for several decades in other countries, in Brazil there are still few studies developed by soil researchers, and biochar efficiency on the bioavailability of herbicide in the soil is still unknown by many weed science Brazilian researchers. Against the above, the objective of this review was to evaluate the bioavailability of herbicides in biochar-amended soils and highlight the research with biochar in Brazilian conditions, besides presenting the benefits to soil with biochar addition. Little is known about the herbicides behavior in Brazilian soils amended with biochar, which can be used with greater intensity in modern agriculture. So more research is needed under our conditions to really we understand the dynamics of this product in the soil.

**Keywords:** black carbon, retention, management practices, soil behavior

**Resumo** - A aplicação de biochar (biocarvão) em solos por causa dos efeitos benéficos é comprovada por muitos pesquisadores internacionais e isto pode aumentar a sorção dos herbicidas e reduzir a eficácia destes no manejo das plantas daninhas. Impactos positivos são relatados em relação ao comportamento ambiental dos herbicidas, pois o aumento da sorção reduz a lixiviação destes produtos para as águas subterrâneas. Impactos negativos são relatados em relação ao manejo agrônômico dos herbicidas, pois o aumento da sorção reduz a disponibilidade destes produtos no solo, diminuindo o efeito residual para o controle das plantas daninhas. No Brasil, o biochar é produzido por várias empresas privadas e unidades de pirólise, entretanto, o custo para produção ainda é muito alto,

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provavelmente por falta de incentivo do governo, baixo uso dos produtores e consciência dos benefícios. Embora o biochar seja utilizado há várias décadas em outros países, no Brasil ainda há poucos estudos desenvolvidos por pesquisadores na área de solos, e a eficiência do biochar na biodisponibilidade de herbicidas no solo ainda é desconhecida por muitos pesquisadores brasileiros na área de plantas daninhas. Diante do exposto, o objetivo desta revisão foi avaliar a biodisponibilidade de herbicidas em solos modificados com biochar e destacar a pesquisa com biochar em condições brasileiras, além de apresentar os benefícios ao solo com a adição do biochar. Pouco se sabe sobre o comportamento de herbicidas em solos brasileiros modificados com biochar, que pode ser utilizado com maior intensidade na agricultura moderna. Então, mais pesquisas são necessárias sob nossas condições para realmente entender a dinâmica deste produto no solo.

**Palavras-chave:** carbono preto, retenção, práticas de manejo, comportamento no solo

## Introduction

Biochar is produced through the by-product of a thermal process conducted under low oxygen or oxygen-free conditions (pyrolysis) to convert any vegetative biomass to biofuel, according to Clay and Malo (2012). Pyrolysis is a process that involves the application of heat to biomass in order to concentrate the heat and collect the by-products (Khorram et al., 2016). It is an interesting alternative, mainly for the treatment of biomass residues in general, aiming at its direct application of soil or composing the compost. The main difference between pyrolysis and incineration is that by pyrolysis it is possible to recover condensable gases (pyroligneous or bio-oil) and those that do not condense, but with high combustion power providing additional energy for the processing unit. Although, chars and charcoal-like materials occur naturally in soils and are considered part of the soil organic carbon (SOC) pools (Skjemstad et al., 1996). High fertility associated with anthropogenic soils (e.g. *Terra Preta de Índio*) in the Amazon has been related to the high SOC content in the form of char and the practice of 'slash and char' by the pre-Columbian indigenous people of the Amazon (Glaser et al., 2001).

Thus, in addition to the natural biochar found in nature, biochar can be artificially produced, and there are a wide variety of end-products that can be manufactured depending on processing parameters and initial raw feedstocks, living or dead vegetables

(Bridgewater, 2003). It is important to note that the parameters of the pyrolytic process, such as temperature, heating rate, and pressure, can change the recovery amounts of each end-product, energy values of the bio-oils and the physicochemical properties of the biochar (Yaman, 2004).

Biochar has emerged as a viable option for sequestering carbon (C) in soil (Lehmann et al., 2006). However, agronomic responses to biochar application are likely to be influenced by several aspects of chemical composition of the biochar: the total and available plant nutrients, the liming equivalence, the presence of toxic constituents, and the surface properties of biochar (Singh et al., 2010). Depending on the type and amount of biochar applied, the changes in soil properties associated with the application (e.g. soil pH, electrical conductivity) as well as the physicochemical properties of the char itself, may impact the use, rates, efficacious properties, and fates of pesticide used in agronomic management, such as herbicides (Clay and Malo, 2012).

The great concern of researchers is that addition of biochar in the soil can potentiate sorption processes, and it may have negative impacts on weed management, reducing herbicide efficacy, consequently it will be necessary to apply higher doses of herbicides (Clay and Malo, 2012). On the other hand, positive impacts are also reported with the addition of biochar in soil, such as the increased sorption capacity of herbicides, due to

carbonaceous sorbents of biochar, providing reduced leaching of these products into the groundwater. Other positive points that increased sorption may be beneficial in terms of reducing herbicide residues in rotation or succession crops, thus it can eliminate the carryover effect (Beesley et al., 2011). In view of this situation, there is a growing demand on studying biochar under tropical conditions, such as in Brazil, which has one of the largest areas of the Amazon with natural biochar and already has private companies that produce biochar through the pyrolysis of different feedstocks.

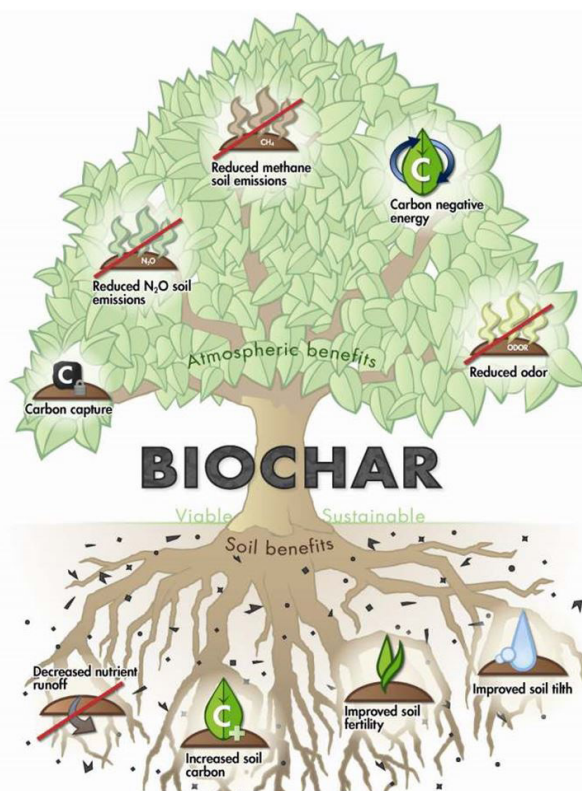
According to data from International Biochar Initiative (IBI, 2017) in South America there are not regional biochar groups that help support local biochar research and projects applicable to that geographical area. Although biochar has been used for several decades in other countries, in Brazil there are still few studies developed by soil researchers, and the influence of biochar on the bioavailability of herbicides in the soil is still unknown by many weed scientist Brazilian. Given the above, the objective of this review was to evaluate the bioavailability of herbicides in biochar-amended soils and highlight the research with biochar in Brazilian conditions, besides presenting the benefits to soil with biochar addition.

## Environment and soil agricultural benefits of biochar

The interest in the effects of biochar application on plant growth, soil properties, and environmental contaminants has spurred a significant amount of research in recent years (Ippolito et al., 2012). Biochar is posing many benefits to the environment, agriculture and economy in the longer run, so it is highly recommended to incorporate it in agriculture practices (Rehman and Razzaq, 2017). Spokas et al. (2012) reported that although current economics may not be favorable for large-scale production agriculture utilization of biochar, the potential exists for biochar to provide environmental quality benefits and to improve nonproductive or degraded soils. On the other hand, intensive study of biochar-rich dark earths

in the Amazon (*Terra Preta de Índio*) has led to a wider appreciation of biochar's unique properties as a soil enhancer (IBI, 2017).

Biochar can be an important tool to increase food security and cropland diversity in areas with severely depleted soils, scarce organic resources, and inadequate water and chemical fertilizer supplies. Biochar also improves water quality and quantity by increasing soil retention of nutrients and pesticides for plant and crop utilization, which these products can be unavailable to crop and weed. More nutrients stay in the soil instead of leaching into groundwater and causing pollution (IBI, 2017). As a soil corrector, biochar creates a recalcitrant C reserve with a negative charge, serving as a network that removes  $\text{CO}_2$  from the atmosphere. The large range of these atmospheric and soil benefits caused by the addition of biochar are illustrated in Figure 1.



**Figure 1.** Atmospheric and soil benefits of biochar. Source: IBI (2017).

In agriculture, biochar has several effects, as reported above, as interference in the bioavailability of nutrients to the crop, which the increase in nutrient retention capacity reduces the total fertilizer need. Singh et al. (2010) reported that feedstock source and/or pyrolysis temperature significantly influence charge properties and the contents of C, nutrients, and liming potential of biochars. It is thus important to characterise biochars in relation to their properties, thereby allowing users to select the most suitable biochar for a specific soil application; for example, nutrient-rich and high cation exchange capacity (CEC) biochars could potentially be applied to degraded, nutrient poor soils, or biochars with high acid-neutralising capacity could be applied to alleviate soil acidity. However, further research on the forms and bioavailability of nutrients present in biochar is required.

CEC of the biochar is affected by the type of feedstock used and by the pyrolysis temperature. High temperatures cause CEC to be low due to loss of functional groups. With the maturation of the biochar its CEC increases due to the formation of functional groups such as carboxyl and other oxygenates on its surface. At the same time, aging causes a substantial reduction of the anion exchange capacity (AEC) derived from the disappearance of the positive charge from the surface.

It is necessary to take into account the use of biomass, as it has other uses in the ecosystem, and combine them with human needs. It is important to consider possible conflicts between energy production and biochar versus food production. However, the use of waste as soil covers, to protect its surface, in balance with the use of biochar. While biochar will improve soil quality and productivity, cover crop may be useful to control water and wind erosion. As a consequence, not all biomass should be used for biochar production.

All these issues and others deserve special attention and more studies, especially in tropical regions, such as in Brazil.

## **Agricultural use of biochar in Brazil**

In Brazil, field experimentation with use of biochar started about 15 years ago and the first studies were focused on Amazonian lands. Maia et al. (2011) reported that biochar technology is being studied by Embrapa and their partners together with other low carbon practices such as no-tillage cropping systems, integrated crop-livestock-floresty systems, forestation and degraded land restoration. To produce biochar from native forest destruction is nonsense in any environmental analysis. Besides, sustainability is a concept that is increasingly present in industrial management, with recent initiatives taking place in the private forestry sector (Maia et al., 2011).

Carvalho et al. (2013) reported that wood biochar application provided an increase in soil pH, K, Ca, Mg, CEC, Mn and nitrate while decreasing Al content and potential acidity of aerobic rice growth and grain yield in a clayey Rhodic Ferralsol in the Brazilian Savannah. Effects of biochar on soil properties may change with time, leading to responses quite different from those observed in this study.

In other studies Eykelbosh et al. (2015) found that biochar (charcoal produced from pyrolyzed filtercake) attenuated dissolved organic carbon leaching, likely through stabilization of complex compounds already present in a Brazilian sugarcane soil, but did not lessen  $\text{NO}_3^-$  fluxes. Thus, biochar amendments in vinasse application areas may decrease carbon leaching.

Petter and Madari (2012) described that the technology of using biochar as soil conditioner also in the Brazilian Savannah is a promising future alternative to improve soil properties and the production of crops such as soybeans and aerobic rice in a sustainable manner. Biochar use in order to improve soil properties has been studied (Maia et al., 2011), but its real potential as reducing the herbicide bioavailability is still little understood, mainly in Brazil.



## Biochar use and herbicides behavior in soils

Several studies have demonstrated that biochar amendment can lead to higher irreversible sorption of herbicides (Yang et al., 2006; Yu et al., 2006; Cabrera et al., 2011, 2014; Eibisch et al., 2015; Mendes et al., 2017). The irreversible sorption process of herbicide on biochar included surface-specific sorption, entrapment into micropores, and partitioning into condensed with carbonaceous material (Khorram et al., 2016). Sorption to biochar may ultimately increase herbicide persistence in the environment because they will be protected from microbial degradation (Beesley et al., 2011). A summary of selected recently reported studies developed in the world using biochars and their influences on can be found in Table 1.

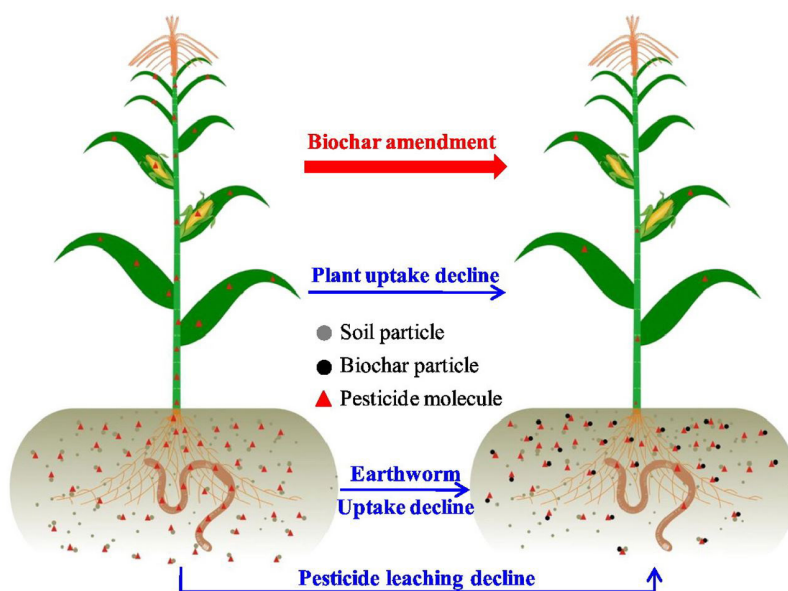
According to Petter and Madari (2012), as there is partial oxidation of the edges of the aromatic structures of the biochar, there is an increase in the exposure of charges. These characteristics may increase interaction with ionizable or non-ionizable molecules, since the physicochemical composition of organic matter soil is highly variable. The contribution of biochar

is given by the increase of total organic carbon, humic acid and humina (Petter et al., 2016).

This presents a challenge to manage organic contaminants, such as herbicides; sorption can reduce short-term environmental risk but may not always ultimately be remedially beneficial (Beesley et al., 2011). This depends on the sorption strength and factors inherent to the contaminant, char and soil which can influence retention over time.

The lack of information on biochar use and impact in Brazil requires more research in this area, on the other hand there are several biochar regional groups worldwide and these groups often hold conferences and meetings, provide updates on regional biochar projects to their members, undertake projects such as field tests and biochar production, advocate for policy on the local and regional levels, write and publish reports, and provide a network of people all working in a similar geographic area (IBI, 2017).

Based on the scientific reports cited in the previous sections, a schematic diagram of the effects of biochar amendment on the environmental behavior of herbicides in soil is shown in Figure 2, according to Khorram et al. (2016). The same



**Figure 2.** A schematic diagram of biochar amendment effects on the environmental behavior of pesticides (e.g. herbicides) in soil. Source: Khorram et al. (2016).

**Table 1.** Summary of selected recently reported studies using biochars and their influences on herbicides behavior of different chemical group.

Amendment types	Herbicide	Chemical group	Endpoints	Effect	Reference
Wheat ash (1%).	Diuron	Phenylurea (not ionizable)	Sorption	Sorption increased in amended soils by a factor of 4 on a unit mass basis.	Yang and Sheng (2003)
Wheat derived char (0.05, 0.5 and 1%).	Diuron	Phenylurea (not ionizable)	Sorption Microbial degradation	Sorption increased by a factor of 7-80 with 1% amendment. Diuron degradation reduced by >10% with 0.5% amendment.	Yang et al. (2006)
<i>Eucalyptus</i> spp derived biochar (450 °C) 0.1, 0.5, 1.0, 2.0 and 5.0% application rates.	Diuron	Phenylurea (not ionizable)	Sorption	Sorption capacity increased in amended soils by a factor of 7-80.	Yu et al. (2006)
<i>Eucalyptus</i> spp derived biochar (50 °C) 0.1, 0.2, 0.5, 0.8 and 1.0% application rates.	Diuron	Phenylurea (not ionizable)	Sorption	Sorption capacity increased in amended soils by a factor of 5-125.	Yu et al. (2006)
Poplar branches (350 °C) 0.5–1%.	2,4-D and acetochlor	chloroacetamide (not ionizable)	Leaching	Leaching decreased 40-65%.	Li et al. (2013)
Sawdust-derived biochar.	Atrazine and acetochlor	Triazine (weak base) and chloroacetamide (not ionizable)	Sorption	K <sub>d</sub> increased by a factor of 1.5 for acetochlor. Atrazine sorption also increased.	Spokas et al. (2009)
Wheat straw 0.5 and 1%.	Trifluralin and atrazine	Dinitroaniline (not ionizable) and triazine (weak base)	Biodegradation	Biodegradation decreased 5–25%.	Nag et al. (2011)
Hardwood 450-500°C (0.1-5%).	Atrazine	Triazine (weak base)	Mineralization	C mineralization increased in soil	Jablonowski et al. (2013)
Dairy manure, 200 °C 4h, 350 °C 4h.	Atrazine	Triazine (weak base)	Sorption	Sorption increased in biochar-amended soils	Cao et al. (2009)
Elm, oak, maple woodchips and barns 450 °C	Atrazine and simazine	Triazines (weak bases)	Sorption	Faster sorption particle size biochar, competitive sorption solid/solution, pH effect, pH<7	Zheng et al. (2010)
Charcoal derived biochar (350 °C).	Terbuthylazine	Triazine (weak base)	Sorption	Sorption increased in amended soils by a factor of 2.7.	Wang et al. (2010)

Source: Adapted from Beesley et al. (2011) and Mesa and Spokas (2011).

Table 1. Continued...

Amendment types	Herbicide	Chemical group	Endpoints	Effect	Reference
Sawdust-derived biochar (700 °C).	Terbuthylazine	Triazine (weak base)	Sorption and desorption	Sorption increased in amended soils by a factor of 63 and desorption decreased.	Wang et al. (2010)
Biochar produced from olive mill waste feedstock (700 °C).	Aminocyclopyrachlor	Pyridine carboxylic acid (weak acid)	Sorption	Reduced the aqueous herbicide concentration.	Rittenhouse et al. (2014)
Wood chip pellets (>500 °C), macadamia nut shells (850 °C), and hardwood (540 °C) 10%.	Aminocyclopyrachlor and bentazone	Pyridine carboxylic acid (weak acid) and benzothiazinone (weak acid)	Sorption	Sorption increased 18-240%.	Cabrera et al. (2014)
Biochar produced from poultry litter and wheat straw feedstocks (400 °C).	Fluridone and norflurazon	Unclassified (weak acid) and Pyridazinone (not ionizable)	Sorption	Sorption increased in 24 and 36 times, respectively.	Sun et al. (2012)
Corn digestate derived biochar (750 °C) 0.5%.	Isoproturon	Urea (not ionizable)	Sorption	The amount of in situ available herbicide was reduced by a factor of 10–2283 in treatments with biochar.	Eibisch et al. (2015)
<i>Eucalyptus</i> sp (0.1-1%)	Isoproturon	Urea (not ionizable)	Sorption and desorption Biodegradation	Sorption and hysteresis increased; desorption, degradation, and mineralization decreased in amended soils.	Sopeña et al. (2012)
Biochar produced from sugarcane bagasse, soybean stover, wood chips, etc.	MCPA, nicosulfuron, terbuthylazine, and indaziflam	Aryloxyalkanoic acid (weak acid), Sulfonyleurea (weak acid), Triazine (weak base), and Fluoroalkyltriazine (weak acid)	Sorption	Sorption increased for all herbicides.	Trigo et al. (2014)
Hardwood sawdust (500 °C), hardwood (540 °C), and wood pellets (>500 °C) 2%.	MCPA and fluometuron	Aryloxyalkanoic acid (weak acid) and phenylurea (not ionizable)	Sorption and desorption Leaching	Sorption increased 240-5200%, desorption decreased 85-3000%, and leaching decreased 10-75%.	Cabrera et al. (2011)
Beech wood (550 °C) 1.5%.	Imazamox	Imidazolinone (strong acid)	Sorption and desorption	Sorption increased <5% and desorption decreased ~3%.	Dechene et al. (2014)

Source: Adapted from Beesley et al. (2011) and Mesa and Spokas (2011).

authors affirmed that biochar demonstrated a clear and prominent potential to remedy soils contaminated with pesticides, including herbicides, by increasing soil sorption capacity, decreasing desorption and mobility of pesticides in soil, decreasing bioavailability of pesticides in soil pore water, which is considered to be the fraction bioavailable for soil organisms. Also, by improving soil microbial activity by providing essential nutrients and 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 herbicide-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 contaminated with herbicide are necessary (Khorram et al., 2016). As already reported in this review, biochar is seen as beneficial in alleviating climate change, improving crop productivity, remedying the polluted environment, and recycling agricultural waste (Tang et al., 2013). The benefits of biochar are multiple, interrelated and include direct and indirect effects on the environment. The biochar remediation effect will help remove the contaminants and make the soil cleaner and healthier which will ensure the normal growth of various crops. Because several biochar benefits are all linked together and form a virtuous circle once an aspect is triggered, biochar may potentially be an attractive alternative in modern society to solve environmental and food problems faced by the rapid increase in population.

These same authors affirmed that it is important to emphasize that we should not ignore the different points of view based on solid arguments. Variation of the results suggests that the current application of biochar to the soil is not a one-size fit-all paradigm, rather than the comprehensive

consideration of the properties associated with each case in particular.

The several potential benefits described by Tang et al. (2013), incorporated into the fact that biochar produced from a variety of biomass can potentially be an environmentally beneficial tool for environmental remediation, stimulates increased research on biochar in the world and initiates in this area in Brazil (Novotny et al., 2015). The same authors affirmed that biochar is a technology of particular interest for Brazil, since its “inspiration” is from the historical Amazon Dark Earth, and also because Brazil is the world’s largest charcoal producer, generating enormous residue quantities in form of fine charcoal and due to the availability of different residual biomasses.

### **Herbicides behavior in biochar-amended brazilian soils**

The increase in sorption and decrease in desorption show that the application of biochar is an important alternative for the remediation in soil leaching of diuron, especially in sandy soils (Petter et al., 2016), interfering negatively the weed management. In view of the high cost of biochar production in Brazil, this material has not yet been applied to soil, mainly in field conditions.

Biochar addition to soil has been reported to reduce the microbial degradation of pesticides due to sorption of the active compound. Jablonowski et al. (2013) investigated whether the addition of hardwood biochar alters the mineralization of atrazine in two atrazine-adapted soils from Belgium and Brazil at different moisture regimens. These authors found that biochar addition resulted in an equally high or even in a significantly higher atrazine mineralization compared to the soils without biochar, and the extent of atrazine mineralization was more influenced by the specific soil than by the addition of biochar. It was concluded that biochar amendment up to 5% by weight does not negatively affect the mineralization of atrazine by an atrazine adapted soil microflora.

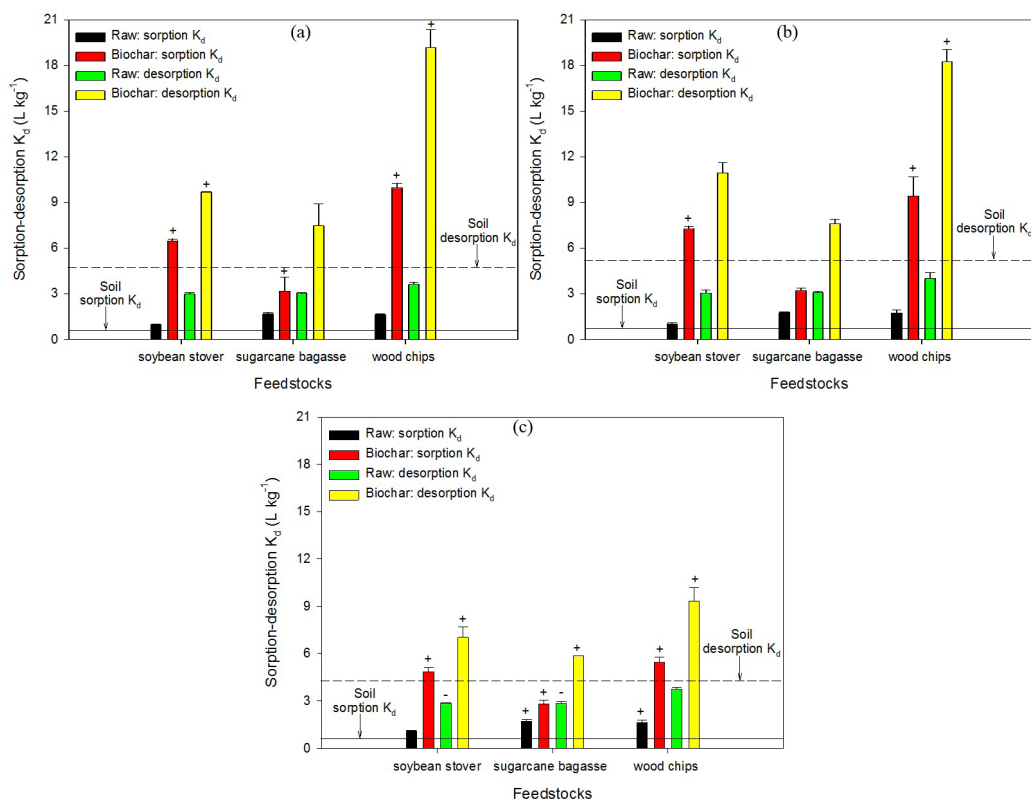


It is important to note that biochar effects on some soil physical, mechanical and hydrological properties have not been given the emphasis these attributes deserve, especially at field scale. Data from well-designed and properly implemented long-term field experiments are needed to develop credible recommendations for use by land managers and policy makers (Mukherjee and Lal, 2014).

These same authors also reported that various soil-biochar combinations at field scale should be tested for at least two successive seasons to allow for sufficient field-ageing of biochar before a conclusion can be derived on crop yield. Life-cycle and cost-benefit analyses are required to establish threshold biochar application rates

under specific soil-biochar-crop scenarios. Thus, full cost-benefit analyses are required with consideration of both environmental and agronomic factors for biochars derived from various sources to assess the economic value of biochar.

A model to represent the data of the sorption and desorption coefficients ( $K_d$ ) in biochar-amended and unamended soils is proposed by Clay and Malo (2012). Thus, Mendes et al. (2016) evaluated the effect of amending soils with soybean stover, sugarcane bagasse, and wood chips derived biochars or raw feedstocks on the sorption-desorption of metolachlor applied in different soils from three US states (Minnesota, silt loam; Illinois, silty clay loam; and Pennsylvania, silt loam) (Figure 3).



**Figure 3.** Sorption-desorption  $K_d$  (L kg<sup>-1</sup>) of metolachlor applied in soils from three US states [Minnesota, silt loam (a); Illinois, silty clay loam (b); and Pennsylvania, silt loam (c)] from the soil-only systems and with soybean stover, sugarcane bagasse, and wood chips derived biochars or same raw feedstocks. A “-” sign above the color bars indicates lower sorption-desorption  $K_d$  and a “+” sign indicates great sorption-desorption  $K_d$  than unamended soil (Dunnett’s test at  $p < 0.05$ ). The vertical bars associated with each column represent the standard deviation ( $\pm$ SD) of each mean value ( $n = 2$ ). Source: Mendes et al. (2016).

A batch sorption test was used to determine the concentration of  $^{14}\text{C}$ -metolachlor in a pseudo-steady state with soil and biochar-soil systems at 10% (w/w). Based on the sorption  $K_d$  values, metolachlor was considered a relatively low sorption herbicide to the unamended three soils, with  $K_d = 0.55 \pm 0.04$ ,  $0.61 \pm 0.08$ , and  $0.54 \pm 0.05 \text{ L kg}^{-1}$  to MN, IL, and PA, respectively (Figure 3). Sorption of metolachlor increased up 18 times in all amended soils with biochar as compared to the unamended soil and desorption increased up 4 times. Biochar produced from wood chips feedstock was the most effective biochar that we assessed for reducing (73-83%) the aqueous herbicide concentration. Therefore, the composition of the biochar in the amended soils can play an important role in the practical remediation by sorption-desorption of metolachlor, because these biochars reduced the herbicide concentration.

## Final considerations

Overall, little is known about the behavior of herbicides in tropical soils amended with biochar. Then, more research is needed under our conditions to really understand the dynamics of this product in the soil.

The use of biochar in soils for agronomic purposes significantly reduces the bioavailability of the herbicides with a consequent direct effect in weed management, what may require increased doses to maintain the efficiency of the product when compared to the application in biochar-unamended soil. On the other hand, if small fields are contaminated with herbicides, the use of biochar as a bioremediation tool is potentially important because this technique is efficient to remove high amounts of the product.

Most biochar and herbicide behavior research were developed in laboratory and greenhouse, therefore the addition of biochar in the soil still requires more research under field conditions, since, in field, climate changes are important and influence the mineralization process, the soil

physicochemical properties, and other factors such as soil erosion and heavy rain.

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