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BIOCHAR ADDITIONS TO AGRICULTURAL SOILS: IMPACTS ON THE BEHAVIOR OF MOBILE HERBICIDES

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Thesis submitted to the Federal Rural University of the Semi-Arid, in partial fulfillment of the requirements for the degree of Doctor of Science in Plant Science.

Research area: Weed management

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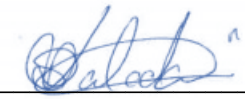

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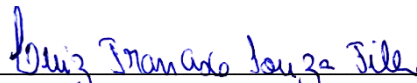

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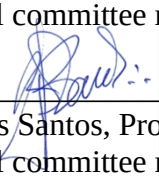

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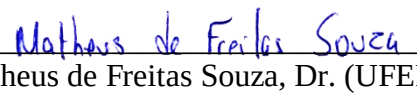

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To my beloved parents, Francisco de Queiroz Porto Filho and Lúcia Formiga Ramos Porto, for their love, education, dedication and to always guide me to a better version of myself.

I dedicate

To GOD, for the presence in every moment of my life, especially the difficult ones, granting me the opportunity of learning and revealing its power and its glory.

I offer

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Teach me, LORD, the way of your decrees, that I may follow it to the end. Give me understanding, so that I may keep your laws and obey it with all my heart. Direct me in the path of your commands, for there I find delight.

(Psalm 119: 33-35)

RESUMO

PORTO, Maria Alice Formiga. **Adição de biocarvão em solos agrícolas: Impactos no comportamento de herbicidas móveis.** 2019. 77f. Tese (Doutorado em Fitotecnia) – Universidade Federal Rural do Semi-Árido (UFERSA), Mossoró-RN, 2019.

Herbicidas móveis têm um alto potencial de contaminação das águas subterrâneas. Assim, o biocarvão tem sido proposto como alternativa para reter herbicidas e modificar a comunidade microbiana do solo, limitando o transporte de herbicidas e outros contaminantes no solo e em fontes de água. O objetivo desta pesquisa foi avaliar o efeito das alterações do biocarvão na sorção-dessorção e mineralização de herbicidas móveis em solos agricultáveis. No capítulo um, a sorção-dessorção foram avaliadas usando o método de equilíbrio de batelada com cinco concentrações de hexazinone, metribuzin e quinclorac. O solo foi alterado com biocarvão de eucalipto (*Eucalyptus grandis*), casca de arroz (*Oryza sativa*) e bambu nativo (*Merostachys skorvotzii*) na proporção de 0 (controle - sem alterações) e 1% (m m^{-1}), correspondentes a 0 e 12 t ha^{-1}, respectivamente. A maior sorção em solo não alterado seguiu a ordem decrescente de herbicidas: quinclorac (65,9%)> metribuzin (21,4%)> hexazinone (16,0%). O biocarvão de bambu nativo proporcionou a maior sorção comparado aos solos alterados com biocarvão de casca de arroz e eucalipto para os três herbicidas. A maior dessorção nos solos não alterados seguiu a ordem decrescente de herbicidas: metribuzin (18,35%)> hexazinone (15,9%)> quinclorac (15,1%). A adição de biocarvão de bambu nativo proporcionou a menor dessorção entre as modificações do solo para os três herbicidas. No capítulo dois, a sorção e dessorção foram avaliadas usando o método de equilíbrio de batelada com cinco concentrações do metribuzin. Três solos foram alterados com biocarvão de madeira de uva (*Vitis vinifera* L.) e pinheiro loblolly (*Pinus taeda* L.) na concentração de 0 (controle - sem alterações) e 5% (m m^{-1}), correspondentes a 0 e 60 t ha^{-1}, respectivamente. A mineralização da ^{14}C-metribuzin foi realizada em frascos biométricos a uma concentração de 4 mg kg^{-1} (concentração alvo). O $^{14}CO_2$-metribuzin liberado da mineralização foi aprisionado em solução de hidróxido de sódio a 0,4 M (NaOH) analisada em cada tempo de amostragem (1, 3, 7, 14, 21, 28, 35 e 42 dias). A sorção do metribuzin nos três solos não alterados seguiu a ordem decrescente: drummer (61,3%)> oakville (24,56%)> ipava (22,35%). O biocarvão de madeira de uva (82,6 - 83,3%) apresentou a maior quantidade sorvida em comparação com o biocarvão de pinheiro loblolly (43,9 - 68,4%) nos três solos. O solo ipava forneceu a maior quantidade de metribuzin dessorvida entre os solos não alterados, tanto na primeira (40,52%) quanto na segunda (57,97%) etapas de dessorção. O biocarvão de pinheiro loblolly forneceu a menor quantidade dessorvida

na primeira (16,4 - 29,5%) e segunda (24,7 - 42,5%) etapa de dessorção entre os dois biocarvões nos três solos. As duas etapas consecutivas de dessorção do metribuzin mostraram que mais de 65% do metribuzin sorvido foram retidos nos solos alterados com biocarvão de madeira de uva. A mineralização do metribuzin nos solos drummer, ipava e okaville foi baixa em relação à concentração de herbicida aplicada. A adição de biocarvão de madeira de uva e pinheiro loblolly reduziu a mineralização e aumentou a quantidade de metribuzin não extraível, mas esse efeito foi observado apenas em alguns solos. Como conclusão, a adição de biocarvão é uma boa alternativa para aumentar a sorção e evitar o transporte de herbicidas móveis em solos agrícolas.

Palavras-chave: material carbonáceo, herbicida lixiviável, persistência, modificação do solo.

ABSTRACT

PORTO, Maria Alice Formiga. **Biochar additions to agricultural soils: Impacts on the behavior of mobile herbicides**. 2019. 77p. Thesis (D.Sc. in Plant Science) – Federal Rural University of the Semi-Arid (UFERSA), Mossoró-RN, 2019.

Mobile herbicides have a high potential for contaminating groundwater. Biochar have been proposed as an alternative to retain herbicides and modify soil microbial community, thus, limiting the transport of herbicides and other contaminants in soil and water sources. The objective of this research was to evaluate the effect biochar amendments on sorption-desorption and mineralization of mobile herbicides in agricultural soils. In chapter one, sorption-desorption were evaluated using the batch equilibrium method at five concentrations of hexazinone, metribuzin and quinclorac. Soil was amended with eucalyptus (*Eucalyptus grandis*), rice hull (*Oryza sativa*), and native bamboo (*Merostachys skorvotzii*) biochar at rate of 0 (control – unamended) and 1% (w w^{-1}), corresponding to 0 and 12 t ha^{-1}, respectively. The highest sorption in unamended soil followed the decreasing order of herbicides: quinclorac (65.9 %) > metribuzin (21.4 %) > hexazinone (16.0 %). Native bamboo biochar provided the highest sorption in comparison to rice hull and eucalyptus biochar amended soils for the three herbicides. The highest desorption in unamended soil followed the decreasing order of herbicides: metribuzin (18.35 %) > hexazinone (15.9 %) > quinclorac (15.1 %). Addition of native bamboo biochar provided the lowest desorption among the biochar amendments on the three herbicides. In chapter two, sorption and desorption were evaluated using the batch equilibrium method at five concentrations of metribuzin. Three soils were amended with grape wood (*Vitis vinifera* L.) and loblolly pine (*Pinus taeda*) biochars at rate of 0 (control – unamended) and 5% (w w^{-1}), corresponding to 0 and 60 t ha^{-1}, respectively. Mineralization of ^{14}C-metribuzin was performed in biometer flasks at a rate of 4 mg·kg^{-1} (target concentration). The $^{14}CO_2$-metribuzin released from mineralization was trapped in 0.4 M sodium hydroxide solution (NaOH) analyzed at each sampling time (1, 3, 7, 14, 21, 28, 35 and 42 days). Sorption of metribuzin on the three unamended soils followed the decreasing order: drummer (61.3 %) > oakville (24.56 %) > ipava (22.35 %). Grape wood biochar (82.6 – 83.3 %) showed the highest amount sorbed compared to loblolly pine biochar (43.9 – 68.4 %) in all the three soils. Ipava soil provided the highest amount of desorbed metribuzin among the unamended soils in both, first (40.52%) and second (57.97%) desorption step. Loblolly pine biochar provided the lowest amount desorbed on first (16.4 – 29.5 %) and second (24.7 – 42.5 %) desorption steps between the two biochars in all the three soils. The two consecutive steps of metribuzin desorption

showed that more than 65% of the sorbed metribuzin was retained in the soils amended with grape wood biochar. Metribuzin mineralization in drummer, ipava and okaville soil was low in comparison to the initial concentration applied. The addition of grape wood and loblolly biochar decreased mineralization and increased the non-extractable amount of metribuzin, but this effect was only observed for some soils. As conclusion, the addition of biochar is a good alternative to increase the sorption and avoid the transport of mobile herbicides in agricultural soils.

Keywords: carbonaceous material, leachable herbicide, persistence, soil amendment.

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SUMMARY

1 INTRODUCTION

Agriculture has been a cauldron of evolutionary change ever since its inception thousands of years ago, and with its modernization in recent decades, significant increases in agricultural production and productivity have been achieved. Considering that the next decade should be of major changes of the global population, which is expected to reach 8.5 billion people by 2030 (UNDESA, 2015), the agricultural production will need to expand even more to keep pace with the demands of our growing population.

Allied to the increase of agricultural production, the use of pesticides also increased and its potential impacts on the environment and public health have now been getting extensive attention, especially because the constant and inappropriate use over the last several decades led to the accumulation of residues exceeding the self-purification capacity of the soil (VANGRONSVELD et al., 2009), which resulted in serious soil pollution and deteriorated soil quality. For instance, residual of imazethapyr in soil can cause serious damage to oilseed rape cultivation (MEHDIZADEH, 2019). Tomato crop was highly sensitive to residual of aminopyralid and aminocyclopyrachlor in soil (SINGH et al., 2019). Also, microorganisms' activity and diversity in the rhizosphere decreased with residual of fomesafen in soil (HU et al., 2019).

Among the pesticides used in agriculture, herbicides are widely used as a tool to control weeds in many crops. Nonetheless, given the wide range of compounds, the use of highly mobile herbicides are getting especial attention because it poses some far-reaching consequence due to their potential runoff and leaching through the soil, leading to contamination of surface and ground water (BATTAGLIN et al., 2001; GUZZELLA et al., 2006; DORES et al., 2008; LAPWORTH et al., 2015; LE COADOU et al., 2017; RENDÓN-VON OSTEN et al., 2017). Even when applied at technically recommended rates and with the correct technology, most molecules do not reach the target and ends up reaching the soil, where it tends to be sorbed by the soil components or stay in solution and liable to be leachable. In addition, a variety of herbicides are applied directly to the soil, acting on weed pre-emergence, and usually have a long persistence, which may contaminate the environment or affect crops planted the following year.

In regards to the herbicides already detected in the environment, the quinclorac, hexazinone and metribuzin were frequently found in water (BATTAGLIN et al., 2001; KJÆR et al., 2005; RESGALLA et al., 2007; LE COADOU et al., 2017). This fact is associated with the characteristics that favor the mobility or persistence in the environment. For example, quinclorac has low solubility (0.065 mg L^{-1}) in water (PPDB, 2019). However, this herbicide has long persistence in soils and allows the leaching to the deeper layers or runoff to rivers in areas with high rainfall indices (MATTICE et al., 2010; LIU et al., 2014; ADAMS et al., 2015). Quinclorac was detected in water sources near to irrigated rice fields in Brazil under average concentrations ranging from 1.34 to 6.97 µg L^{-1} among seven hydrographic basins analyzed (RESGALLA et al., 2007).

Hexazinone and metribuzin have high solubility in water (33,000 and 1050 mg L^{-1}, respectively) and low to moderate persistence in soil (half-life of approximately 90 and 50 days, respectively), properties highly favorable to the leaching in agricultural soils (POT et al., 2011; REIS et al 2017; TRAVLOS et al., 2017). Hexazinone was detected in water resources with maximum level concentration of 0.21 µg L^{-1} near sugarcane crops in the state of São Paulo, Brazil (MACHADO et al., 2016) and in bottled water samples under concentration of 1.4 ng L^{-1}, considered as natural mineral water in France (LE COADOU et al., 2017). Also, metribuzin was found in surface waters in the Midwestern of United States in concentrations up to 0.400 µg L^{-1} (BATTAGLIN et al., 2001). Based on these reports and the negative impacts caused by the use of herbicides, efficient strategies have been developed to remove herbicides by soil remediation (CHENG et al., 2016) using sustainable and environment-friendly alternatives, for example, the addition of biochar to agricultural soils.

Biochar refers to the carbonaceous pyrogenic material formed during the energy production process from biomass in a dry carbonization process known as pyrolysis, which is the thermal decomposition of biomass under limited supply of oxygen or oxygen-free conditions (LEHMANN et al., 2006). During the thermal degradation, biomass undergoes a variety of physical, chemical and molecular changes, where basically, the biological material is fractionated into gases (biogas) and oils (bio-oil and tar), both with high combustion power and destined to the primary production of bioenergy. Simultaneously, the carbon-rich solid, non-volatiles are collected as biochar.

The origin of biochar was found in indigenous tribes of the Amazon, which deposited residual biomass of burning material in the soil and increased fertility over extended periods, originating the anthropogenic soil *Terra Preta de Índio* (LEHMANN; JOSEPH, 2009). Based on the characteristics of high fertility and high agricultural potential in intensely weathered

soils, *Terra Preta de Índio* has encouraged studies with biochar, its properties, and the mechanisms responsible for its performance when applied to soil (LEHMANN; JOSEPH, 2009). A wide range of agricultural and organic materials has been proposed to produce biochar such as crop residues, food and forestry wastes, as well as animal manures. Thus, given the diversity of feedstock, biochar is not a homogenous product, showing varying complexity and heterogeneous chemical and physical properties. According to Lehmann; Joseph (2009), biochar mainly consists of disordered stacks of sheets of aromatic compounds (graphene) cross-linked randomly, where nutrients may be embedded or separated from the carbonaceous matrix (AMONETTE; JOSEPH, 2009).

Other characteristics of biochars includes its surface chemistry, which may assume acidic, basic, hydrophobic or hydrophilic behavior (LEHMANN; JOSEPH, 2009), where the contribution of each characteristic to the material depends on the feedstock and the production condition of biochar. For instance, biochars with higher hydrophobicity surface may increase sorption of hydrophobic compounds (ZHANG et al., 2011). In general, freshly made biochar is hydrophobic and contains few polar surface functional groups; however, the surface of biochar oxidizes when exposed to water and oxygen from soil, forming carboxyl and other oxygen-containing functional groups. Additionally, biochar contains an inorganic portion composed by metals originally from the feedstock, which is referred as the ash content of biochar, and it is concentrated as volatile materials are released during pyrolysis process.

In general, the changes on biochar properties can be related to their function in every aspect. The pyrolysis temperature, heating rates and feedstock type used to produce biochar are important factors that influence the physico-chemical properties of the obtained product, which in turn display a range of results when used as soil amendment. For example, the action of heating biomass via pyrolysis in higher temperatures results in a more graphitized (aromatic) biochar, with greater specific surface area and reduced surface functional groups. Moreover, the increase in temperature decreases the mechanical strength of the biochar, resulting in a larger quantity of small particles due to the higher occurrence of breaks. In contrast, lower pyrolysis temperatures produce biochars with low specific surface area, which implies partitioning and specific interactions with functional groups on the surface of the biochar (LIU et al., 2016). These biochar characteristics eventually help to immobilize rhizospheric heavy metals and pesticides (SPOKAS et al., 2009; BOLAN et al., 2014) on its surface and restricts their mobility into the crops.

Nowadays, the addition of biochar in the soil has gained attention for its ability to increase sorption and decrease the amount of available pesticides, thereby, limiting its activity and

biodegradation over time. Several studies have been conducted to evaluate the effects of biochar application on the herbicides environmental behavior in a series of soil and water, such as acetochlor (SPOKAS et al., 2009), alachlor (MENDES et al., 2017), atrazine (DENG et al., 2017; ZHENG et al., 2010), diuron (MARTIN et al., 2012; PETTER et al.,2017), fomesafen (KHORRAM et al., 2017), S-metolachlor, sulfentrazone (GRABER et al., 2012). Based on these researches, the affinity of biochar for organic compounds is hypothesized to be determined mainly by its surface area, structural porosity, and surface chemistry.

For instance, imazamox, picloran and terbuthylazine partitioned to soil more strongly (>85%) when the soil was amended with oak wood biochar compared to fresh feedstock (<16%), and the main factor that governed this increase was attributed to water-soluble components on the biochar (GÀMIZ et al., 2019). Similarly, atrazine also sorbed more strongly (up to 79%) to soil amended with 0.5% of sugarcane biochar. In addition, aminocyclopyrachlor and bentazone were almost completely sorbed by the soil amended with the biochar produced from wood pellets, which was related to the specific surface area and dissolved organic carbon content of the biochar (CABRERA et al., 2014). In general, the increase in sorption dictates the behavior of pesticides, since once sorbed, there is less availability of access of the molecule to microorganisms (DING et al., 2017), resulting in lower degradation rates and lower leaching potential.

Leaching is one of the most important mechanism that control the distribution of agrochemicals in the environment, which corresponds to the vertical transportation of the pesticide in the soil profile with the rainwater or irrigation that infiltrates the pores. For a pesticide to be available for leaching, plant uptake or microbial degradation it must be present in solution (i.e. not sorbed). Furthermore, it is relevant to mention that several factors related to soil, climate and the compound molecule influence their transport on the soil profile (OLIVEIRA; BRIGHENTI, 2011), however sorption is one the most important parameters which determine herbicide capacity to leach, and so capable to reach groundwater.

Based on this, the use of biochar can be an alternative to promote the retention of herbicides with high mobility in soil, such as quinclorac, hexazinome and metribuzin and avoid the contamination of water sources. With this concept, the objective of this study was to evaluate the effect biochar amendments on sorption-desorption and mineralization of mobile herbicides in agricultural soils.

REFERENCES

ADAMS, J. W.; LYM, R. G. Quinclorac and aminocyclopyrachlor movement in sandy soils. **Invasive Plant Science and Management**, v. 8, n. 3, p. 269–275, 2015.

AMONETTE, J. E.; JOSEPH, S. Characteristics of biochar: microchemical properties. In: LEHMANN, J.; JOSEPH, S. (org.). **Biochar for environmental management science and technology**. London: Earthscan, 2009. p. 34-51.

BATTAGLIN, W. A. et al. **Concentration of selected sulfonylurea, sulfonamide, and imidazolinone herbicides, other pesticides, and nutrients in 71 streams, 5 reservoir outflows, and 25 wells in the Midwestern United States**, Denver: US Geological Survey, 2001.

BOLAN, N. et al. Remediation of heavy metal(loid)s contaminated soils–to mobilize or to immobilize?. **Journal of Hazardous Materials**, v. 266, n. 1, p. 141-166, 2014.

CABRERA, A. et al. Influence of biochar amendments on the sorption–desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil. **Science of the Total Environment**, v. 470, n. 1, p. 438-443. 2014.

CHENG, C. et al. Reduction of diuron efficacy with biochar amendments. **International Journal of Environmental Science and Development**, v. 7, n. 7, p. 480-485, 2016.

DENG, H. et al. Influence of biochar amendments to soil on the mobility of atrazine using sorption-desorption and soil thin-layer chromatography. **Ecological Engineering**, v. 99, p. 381-390, 2017.

DING, Y. et al. Potential benefits of biochar in agricultural soils: A review. **Pedosphere**, v. 27, p. 645-661, 2017.

DORES, E. F. et al. Pesticide levels in ground and surface waters of Primavera do Leste Region, Mato Grosso, Brazil. **Journal of Chromatographic Science**, v. 46, n. 7, p. 585-590, 2008.

GÁMIZ, B. et al. Changes in sorption and bioavailability of herbicides in soil amended with fresh and aged biochar. **Geoderma**, v. 337, n. 1, p. 341-349, 2019.

GRABER, E. R. et al. High surface area biochar negatively impacts herbicide efficacy. **Plant and Soil**, v. 353, n. 1, p. 95-106, 2012.

GUZZELLA, L. et al. Herbicide contamination of surficial groundwater in Northern Italy. **Environmental Pollution**, v. 142, n. 2, p. 344-353, 2006.

HU, H. et al. Fomesafen impacts bacterial communities and enzyme activities in the rhizosphere. **Environmental Pollution**, v. 253, n. 1, p. 302-311, 2019.

KHORRAM, M. S. et al. Effects of aging process on adsorption–desorption and bioavailability of fomesafen in an agricultural soil amended with rice hull biochar. **Journal of Environmental Sciences**, v. 56, n. 1, p. 180-191, 2017.

KJÆR, J. et al. Leaching of metribuzin metabolites and the associated contamination of a sandy Danish aquifer. **Environmental Science and Technology**, v. 39, n. 21, p. 8374-8381, 2005.

LAPWORTH, D. J. et al. Persistent and emerging micro-organic contaminants in Chalk groundwater of England and France. **Environmental Pollution**, v. 203, n. 1, p. 214-225, 2015.

LE COADOU, L. et al. Quality survey of natural mineral water and spring water sold in France: Monitoring of hormones, pharmaceuticals, pesticides, perfluoroalkyl substances, phthalates, and alkylphenols at the ultra-trace level. **Science of The Total Environment**, v. 603, n. 1, p. 651-662, 2017.

LEHMANN, J.; JOSEPH, S. Biochar for Environmental Management: An Introduction. In: LEHMANN, J.; JOSEPH, S. (org.). **Biochar for Environmental Management.** 2ª ed. Routledge:Earthscan, 2015. p. 33-46.

LEHMANN, J. et al. Biochar sequestration in terrestrial ecosystems: a review. **Mitigation and Adaptation Strategies for Global Change**, v. 11, n. 2, p. 395-419, 2006.

LIU, M. et al. Identification and characteristics of an endophytic quinclorac degrading bacterium Bacillus megaterium Q3. **Plos One**, v. 9, n. 9, p. 108012-108020, 2014.

LIU, C. et al. Biochar increased water holding capacity but accelerated organic carbon leaching from a sloping farmland soil in China. **Environmental Science and Pollution Research**, v. 23, n. 2, p. 995-1006, 2016.

MACHADO, C. S. et al. Chemical contamination of water and sediments in the Pardo River, São Paulo, Brazil. **Procedia Engineering**, v. 162, n. 1, p. 230-237, 2016.

MATTICE, J. D. et al. Analysis of river water for rice pesticides in eastern Arkansas from 2002 to 2008. **Journal of Soil and Water Conservation**, v. 65, n. 1, p. 130-140, 2010.

MARTIN, S. M. et al. Marked changes in herbicide sorption-desorption upon ageing of biochars in soil. **Journal of Hazardous Materials**, v. 231-232, n. 1, p. 70-78, 2012.

MEHDIZADEH, M. Sensitivity of oilseed rape (Brassica napus L.) to soil residues of imazethapyr herbicide. International **Journal of Agriculture, Environment and Food Sciences**, v. 3, n. 1, p. 46-49, 2019.

MENDES, K. et al. Evaluating agricultural management effects on alachlor availability: tillage, green manure, and biochar. **Agronomy**, v. 7, n. 4, p. 64-79. 2017.

NOVOTNY, E. H. et al. Biochar: pyrogenic carbon for agricultural use - a critical review. **Revista Brasileira de Ciência do Solo**, v. 39, n. 2, p. 321-344, 2015.

OLIVEIRA, M. F.; BRIGHENTI, A. M. Comportamento dos herbicidas no ambiente. In. OLIVEIRA JÚNIOR et al. (org.). **Biologia e manejo de plantas daninhas**. Curitiba, Brasil: Omnipax. 2011. p. 263-304.

PETTER, F. A. et al. Biochar increases the sorption and reduces the potential contamination of subsurface water with diuron in sandy soil. **Pedosphere**, v. 160, n. 1, p. 1-11, 2017.

POT, V. et al. Metribuzin transport in undisturbed soil cores under controlled water potential conditions: experiments and modelling to evaluate the risk of leaching in a sandy loam soil profile. **Pest management science**, v. 67, n. 4, p. 397-407, 2011.

REIS, F. C. et al. Leaching of Diuron, Hexazinone, and Sulfometuron-methyl Applied Alone and in Mixture in Soils with Contrasting Textures. **Journal of Agricultural and Food Chemistry**, v. 65, n. 13, p. 2645-2650, 2017.

RENDÓN-VON OSTEN, J.; DZUL-CAAMAL, R. Glyphosate residues in groundwater, drinking water and urine of subsistence farmers from intensive agriculture localities: a survey in Hopelchén, Campeche, Mexico. **International Journal of Environmental Research and Public Health**, v. 14, n. 6, p. 595-608, 2017.

RESGALLA, C. et al. Risk analysis of herbicide quinclorac residues in irrigated rice areas, Santa Catarina, Brazil. **Ecotoxicology**, v. 16, n. 8, p. 565-571, 2007.

SINGH, V. et al. Activated charcoal reduces pasture herbicide injury in vegetable crops. **Crop protection**, v. 117, n. 1, p. 1-6, 2019.

SMEBYE, A. et al. Biochar amendment to soil changes dissolved organic matter content and composition. **Chemosphere**, v. 142, n. 1, p. 100-105, 2016.

SPOKAS, K. A. et al. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. **Chemosphere**, v. 77, n. 4, p. 574-581, 2009.

STEINER, C. et al. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. **Plant and Soil**, v. 291, n. 1, p. 275-290, 2007.

TRAVLOS, I. S. et al. Effects of the herbicides benfluralin, metribuzin and propyzamide on the survival and weight of earthworms (*Octodrilus complanatus*). **Plant, Soil and Environment**, v. 63, n. 3, p. 117-124, 2017.

United Nations. Department of Economic and Social Affairs, Population Division (UNDESA). **World Population Prospects: The 2015 Revision, Key Findings and Advance**

Tables; United Nations: New York, NY, USA, 2015. Disponível em: <https://www.un.org/en/development/desa/population/index.asp>. Acesso em: 30 ago. 2019.

VANGRONSVELD, J. et al. Phytoremediation of contaminated soils and groundwater: lessons from the field. **Environmental Science and Pollution Research**, v. 16, n. 7, p. 765-794, 2009.

ZHANG, G. et al. Sorption of simazine to corn straw biochars prepared at different pyrolytic temperatures. **Environmental Pollution**, v. 159, n. 10, p. 2594-2601, 2011.

ZHENG, W. et al. Sorption properties of greenwaste biochar for two triazine pesticides. **Journal of Hazardous Materials**, v. 181, n. 1, p. 121-126, 2010.

Chapter 1

SORPTION-DESORPTION OF MOBILE HERBICIDES IN A TROPICAL SOIL AMENDED WITH BIOCHARS

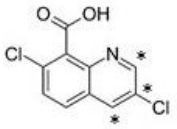
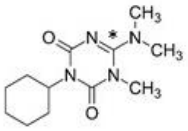
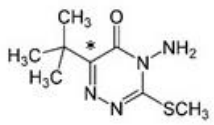
Abstract: Mobile herbicides have a high potential for contaminating groundwater. An alternative to reduce the mobility of herbicide is to apply to soils materials with high sorbent capacity, as biochars. The objective of this research was to evaluate the effect of eucalyptus, rice hull and native bamboo biochar amendments on sorption and desorption of hexazinone, metribuzin and quinclorac in a tropical soil. The sorption-desorption were evaluated using the batch equilibrium method at five concentrations of hexazinone (0.63, 1.25, 1.88, 2.50, and 3.13 mg L^{-1}), metribuzin (0.40, 0.80, 1.60, 3.20, and 6.40 mg L^{-1}) and quinclorac (0.31, 0.63, 0.94, 1.25, and 1.56 mg L^{-1}). Soil was amended with eucalyptus (*Eucalyptus grandis*), rice hull (*Oryza sativa*), and native bamboo (*Merostachys skorvotzii*) biochar at rate of 0 (control – unamended) and 1% (w w^{-1}), corresponding to 0 and 12 t ha^{-1}, respectively. The highest sorption in unamended soil followed the decreasing order of herbicides: quinclorac (65.9 %) > metribuzin (21.4 %) > hexazinone (16.0 %). Native bamboo biochar provided the highest sorption compared to rice hull and eucalyptus biochar amended soils for the three herbicides. The highest desorption in unamended soil followed the decreasing order of herbicides: metribuzin (18.35 %) > hexazinone (15.9 %) > quinclorac (15.1 %). Addition of native bamboo biochar provided the lowest desorption among the biochar amendments on the three herbicides. As conclusion, the biochars differently affect the sorption and desorption of hexazinone, metribuzin, and quinclorac mobile herbicides in a tropical soil. The addition of eucalyptus, rice hull and native bamboo is a good alternative to increase the sorption of hexazinone, metribuzin, and quinclorac, thus reducing mobility and availability of these herbicides to non-target organisms in the soil.

Keywords: carbonaceous material, environmental contamination, leachable herbicides, retention process.

1 INTRODUCTION

Sharp criticism of the excessive use of weed control herbicides as a practice to maintain a high agricultural yield of crops is related to the ability of these molecules to contaminate the environment, mainly water sources such as rivers and groundwater. Among the herbicides already detected in water resources, the hexazinone [3-cyclohexy1-6-(dimethylamino)-1methyl-1,3,5-triazine-2-4(1*H*,3*H*)dione], metribuzin (4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4*H*)-one) and quinclorac (3,7-dichloro-8-quinolinecarboxylic acid) were molecules frequently found under concentrations up to 1.4 ng L^{-1}(LE COADOU et al., 2017), 1.76 µg L^{-1} (BATTAGLIN et al., 2001) and 6.97µg L^{-1} (RESGALLA et al., 2007), respectively. This fact is associated with the physico-chemical properties that favor the mobility or persistence in the environment. The structural formulas and physico-chemical properties of the three herbicides are shown in Table 1.

Table 1: Structures and physico-chemical properties of the three herbicides.

Property	Quinclorac	Hexazinone	Metribuzin
Structure			
Molecular formula	$C_{10}H_5Cl_2NO_2$	$C_{12}H_{20}N_4O_2$	$C_8H_{14}N_4OS$
Molecular weight (g mol^{-1})	241.1	252.3	214.2
Melting point (°C)	272.4	114.0	125.0
Vapor pressure (25 °C, mPa)	0.01	0.03	0.12
Water solubility (mg L^{-1} at 20 °C)	0.065	33000	10700
Log K_{ow}	2.95	1.85	1.75
pK_a(25 °C)	4.3	2.2	1.0
K_{oc} (L kg^{-1})	50	54	38
DT50 soil (d)	450	105	11.5

Source: Adapted from PPDB (2019).
DT50 soil: persistence, K_{oc}: soil sorption coefficients, Log K_{ow}: n-octanol/water partition coefficients, pK_a:acid dissociationconstant
*: Radiolabeled carbon in the herbicide molecule.

For example, quinclorac has low solubility (0.065 mg L^{-1}) in water (PPDB, 2019). However, this herbicide has long persistence in soils and allows the leaching to the deeper layers or runoff to rivers in areas with high rainfall indices (MATTICE et al., 2010; LIU et al., 2014; ADAMS; LYM, 2015). Quinclorac was detected in water sources near to irrigated rice fields in Brazil

under average concentrations ranging from 1.34 to 6.97 μg L^{-1} among seven hydrographic basins analyzed (RESGALLA et al., 2007).

Hexazinone and metribuzin have high solubility in water (33,000 and 1165 mg L^{-1}, respectively) and low to moderate persistence in soil (half-life of approximately 105 and 12 days, respectively) (PPDB, 2019), properties highly favorable to the leaching in agricultural soils (POT et al., 2011; REIS et al., 2017; TRAVLOS et al., 2017). Hexazinone was detected in water resources with maximum level concentration of 0.21 μg L^{-1} near to sugarcane crops in the state of São Paulo, Brazil (MACHADO et al., 2016) and in bottled water samples under concentration of 1.4 ng L^{-1}, considered as natural mineral water in France (LE COADOU et al., 2017). Metribuzin was detected in three groundwater samples in Denmark, with concentrations range of 0.01-0.02 μg L^{-1} (KJÆR et al., 2005). Also, metribuzin was found in more than 50% of the stream samples in the Midwestern of United States in concentrations up to 1.76 μg L^{-1} (BATTAGLIN et al., 2001). According to these authors, this concentration is not likely to be toxic to non target aquatic plants or humans, but they do add to the overall burden of metribuzin carried by streams.

Every day, tons of herbicides are released into the environment and their surroundings, which not only put human health at risk, but also affect biological processes of nature and the ecosystem services in the name of weed control. For instance, highly mobile or persistent herbicides may contaminate the environment or affect crops planted the following year. Solutions to mitigate the environmental contaminations by herbicides have been studied as an alternative to reduce the mobility of herbicides and, consequently, the contamination risk of water sources, through the sorption capacity of some materials, such as biochars. For example, biochars can increase the sorption (MAJUMDAR et al., 2007; LI et al., 2013) of mobile herbicides and avoid the leaching or surface runoff of molecules (MANDAL et al., 2017). However, the diverse range of biochar applications depends on its physico-chemical properties, which are governed by the pyrolysis conditions (heating temperature and duration) and the original feedstock (ENDERS et al., 2012).

Among these properties, the type of feedstock is one of the most important factors which determines the final characteristics of the biochar and its effect as a herbicide sorbent in soil, because its characteristics are affected by the nature of the original material. For instance, biochars derived from wood (*Pinus taeda*) biomasses often have higher surface area than grass (*Tripsacum floridanum*) biochar (Mukherjee et al. 2011), while wheat straw (*Triticum aestivum*) feedstock had higher cation exchange capacity than that of wood (*Picea abies*) biochar (KLOSS et al., 2012).

Commonly, biomass from agricultural activities are used to synthesize biochars, and eucalyptus, native bamboo and rice hull residues have been proposed as promising feedstocks controlling the environmental fate of herbicides in the soil (KHORRAM et al., 2017; KHORRAM et al., 2018; KEARNS et al., 2019; WU et al., 2019). Each feedstock used to produce biochar has specifically chemical and physical properties able to sorb organic pollutants. For example, the eucalyptus, bamboo chips and rice hull biochars increased the sorption of the atrazine and imidacloprid herbicides in the soil after the amendment with these materials (Mandal et al., 2017). Graber et al. (2012) related a similar effect for eucalyptus woodchips biochars and sulfentrazone.

Other biochars synthesized from the residues of sugarcane and pinewood increased metribuzin sorption in agricultural soils (WHITE JUNIOR et al., 2015), and switchgrass biochar increased sorption of the same herbicide from aqueous solution (ESSANDOH et al., 2017). Another example, poplar woodchip biochar increased the sorption of hexazinone (LI et al., 2013) and biochar prepared from cow bone (bonechar) increased the sorption of quinclorac in a tropical soil (MENDES et al., 2019).

Given the diverse properties of biochars, and its ability to sorb significant amounts of different contaminants, limited researches were developed to evaluate the effects of biochars from different feedstocks, added as an amendment to soil, in order to reduce the movement of highly mobile herbicides. Thereby, studies approaching biochar produced from the diverse feedstock should be performed to select those with the best performance. In this scenario, the objective of this research was to evaluate the effect of eucalyptus, rice hull and native bamboo biochar amendments on sorption and desorption of quinclorac, hexazinone, and metribuzin in a tropical soil.

2 MATERIAL AND METHODS

2.1. Tropical soil

Tropical soil samples were collected from the surface layer (0–30 cm depth) in an area with no herbicide application history, close to sugarcane fields of Carpina, PE, Brazil (S 7° 50′ 35″; W 35° 16′ 21″), after pre-cleaning the native vegetable layer. After drying, samples were sieved through a 4.0-mm mesh and stored at room temperature. The soil is an Ultisol (Soil Taxonomy, 1999), classified as an Argissolo according the Brazilian Soil Classification System (SANTOS et al., 2018) and following chemical andphysical properties: cation exchange capacity (CEC) =

17 $mmol_c\ kg^{-1}$, pH (H_2O) = 6.52, organic carbon (OC) = 0.35%, clay = 43%, silt = 8% and sand = 49%. Soil particle analysis was made using the hydrometer method (GEE; BAUDER, 1986). Soil pH was measured in a 1:2 soil/deionized water suspension. The OC content was determined by wet oxidation of the organic matter using potassium dichromate, according to Walkley-Black method (ENANG et al., 2018).

2.2. Biochar

Three biochars were prepared from eucalyptus (*Eucalyptus grandis*), rice hull (*Oryza sativa*) and native bamboo (*Merostachys skorvotzii*). Biochar was milled and homogenized in mechanical mill with a mesh 0.6x0.3 mm. The biochar was added to soil at 0 (control – unamended) and 1% (w w^{-1}) ratio, corresponding to 0 and 12 t ha^{-1}, respectively, assuming a soil bulk density of 1.2 g cm^{-3} and depth of 10 cm. Elemental analyses of biochars were conducted by the Brazilian Agricultural Research Corporation (EMBRAPA) (Colombo, PR, Brazil) using inductively coupled plasma optical emissions spectrometry (ICP-OES) (Optima 3000, Perkin Elmer). Biochar pHs were measured in 1:10 biochar:deionized water slurries after shaking for 12 h. OC content was determined by dichromate oxidation (ENANG et al., 2018). Selected physico-chemical properties of the biochar are listed in Table 2.

Table 2. Physico-chemical properties of three biochars.

Property	Value		
Feedstock	Eucalyptus	Rice	Bamboo
Temperature (°C)	450	700	500
Heating rate (°C min^{-1})	1.7	10.0	10.0
SSA($m^2\ g^{-1}$)	155.45	6.81	48.41
Moisture (%)	3.63	4.32	5.07
Ash (%)	5.81	48.88	13.68
Volatile matter (%)	27.75	4.69	13.17
Fixed carbon (%)	62.82	42.12	68.08
pH (H_2O)	7.69	9.38	8.65
S (%)	0.005	0.004	0.037
C (%)	74.52	44.14	45.36
H (%)	1.98	0.85	6.89
N (%)	0.47	0.43	0.35
O (%)	23.03	54.57	47.38
O/C	0.31	1.24	1.04
H/C	0.03	0.02	0.15
(O+N)/C)	0.32	1.25	1.05

SSA = specific surface area, C: carbon, H: hydrogen, N: nitrogen, O: oxygen, S: sulfur.
Source: Brazilian Agricultural Research Corporation (EMBRAPA).

2.3. Thermogravimetric and specific surface area of biochar analysis

The thermal degradation of samples under inert atmosphere was carried out in a thermogravimetric instrument (Shimadzu DTG-60H, Kyoto, Japan) using N_2 as a carrier gas (50 mL min^{-1}) and heating rate of 10°C min^{-1} up to 900°C.

The samples were milled and sieve in a 100 sieve and prepared under vacuum at 200°C for 24 h to prevent the influence of humidity. The specific surface area (SSA) studies were performed by nitrogen sorption isotherms at 77 K in a BET surface area analyzer (NOVA 1200e - Quantachrome Instruments, Boynton Beach, FL, USA), using the BET equation.

2.4. Herbicides

[triazine-6-^{14}C] hexazinone (radiochemical purity 99.7%, specific activity 3.14 MBq mg^{-1}) purchased from Izotop (Budapest, Hungary) and analytical standards with purities of 99.9% (Sigma Aldrich, Saint Louis, MO, USA), and five solutions (0.63, 1.25, 1.88, 2.50, and 3.13 mg L^{-1}) were prepared. [ring-6-**^{14}**C] metribuzin (radiochemical purity 98.0%, specific activity 5.43 MBq mg^{-1}) purchased from Izotop (Budapest, Hungary) and analytical standards with purities of 99.8% (Sigma Aldrich, Saint Louis, MO, USA), and five solutions (0.40, 0.80, 1.60, 3.20, and 6.40 mg L^{-1}) were also prepared. [2,3,4-^{14}C] quinclorac (radiochemical purity 99.5%, specific activity 1.50 MBq mg^{-1}) and pure analytical standards (chemical purity 99.4%,) were provided by Basf (Ludwigshafen, Germany) and five solutions (0.31, 0.63, 0.94, 1.25, and 1.56 mg L^{-1}) were prepared. Radiolabeled and non-radiolabeled standards were carefully mixed in 0.01 mol L^{-1} $CaCl_2$. The lowest concentration corresponded to the maximum rate recommended by the manufacturer and 2, 3, 4, and 5-times this rate, respectively.

2.5. Sorption-desorption studies

Studies were performed at the Ecotoxicology Laboratory of the Center of Nuclear Energy in Agriculture - CENA, University of São Paulo - USP, Piracicaba, State of São Paulo, Brazil. The methodology was established according to the guidelines of the OECD-106, Sorption - Desorption Using a Batch Equilibrium Method" (OECD, 2000).

Each experimental unit consisted of a 50 mL Teflon tube with a screw cap. 10 g of soil and 10 mL of 0.01 mol L^{-1} $CaCl_2$ solutions from each herbicides with different concentrations were added to the tubes, resulting in a soil-solution ratio of 1:1 (w v^{-1}). For the sorption studies, 120

μL aliquots of radiolabeled solutions were transferred to vials containing 10 mL of the scintillation solution. The concentrations of ^{14}C-herbicides in both cases were determined by liquid scintillation counting (LSC) after 15 minutes, using a Tri-Carb 2910 TR LSA counter (LSA PerkinElmer, Waltham, MA, USA).

The tubes were agitated in a horizontal shaker tabletop in a dark room with constant temperature (20 ± 2 °C) during 24 h to achieve the equilibrium concentration of the three herbicides, according to previous studies with hexazinone (SILVA et al., 2019), metribuzin (CARA et al., 2015) and quinclorac (DING et al., 2016). At the equilibration concentration, the tubes were centrifuged (Hitachi CF16RXII centrifuge, Hitachi Koki Co., Ltd., Indaiatuba, SP, Brazil) at 755 g for 15 min, and 1 mL aliquots of the supernatant from each tube were transferred in duplicate to scintillation vials containing 10 mL of the scintillation solution and analyzed by LSC to determine the concentration of the ^{14}C-herbicides solution by counting the radioactivity for 5 minutes. The herbicide sorbed amount was calculated using the difference between the initial concentration and the concentration in the supernatant after equilibration.

Desorption studies were performed immediately after sorption under the same conditions. For that, the supernatant remained from the sorption study was removed and a fresh $CaCl_2$ solution (10 mL, 0.01 mol L^{-1}) non-radiolabeled was added to the Teflon tubes containing the soil and the radiolabeled herbicide sorbed from the sorption study. The stirring procedures and determination of ^{14}C were the same as those one used for the sorption study. The desorbed amount was calculated as the difference between the radioactivity sorbed in the soil and in the remaining supernatant. The pHs of biochar-amended soil were determined on slurries with a soil/deionized water ratio of 1:2. All sorption-desorption analysis were done in duplicates

2.6. Sorption-desorption model

Sorption coefficients (K_f and *1/n*) were calculated from the slope and intercept of the Freundlich equation: $C_s = K_f \times C_e^{1/n}$; where C_s is the concentration (mg kg^{-1}) of herbicide sorbed onto the soil after equilibration; K_f is the equilibrium Freundlich constant (mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}); C_e is the herbicide concentration (mg L^{-1}) after equilibration; and *1/n* is the degree of linearity of the isotherm. Percentage of metribuzin on biochar amended and unamended soils were calculated as: % sorption = $[(C_i - C_e)/C_i] \times 100$, where C_i is the herbicide initial liquid concentration, and C_e is the equilibrium liquid concentration. The equilibrium constant K_{foc} sorption standard for the OC content of the soil was adjusted using the following formula: $K_{foc} = (K_f/(\%OC)) \times 100$.

The desorption ($K_{f(desorption)}$) coefficients were also calculated for comparison to the sorption $K_{f(sorption)}$. Desorption coefficients K_f and $1/n$ were determined in a similar manner to the sorption coefficients, using a plot of the amount of remaining chemical sorbed at each desorption step measured for each equilibrium concentration of the sorption isotherm. The percentage of metribuzin desorbed from biochar amended and unamended soils were calculated as: % desorption = $[(C_i - C_e)/C_i] \times 100$, where C_i is the herbicide concentration sorbed onto soil, and C_e is the equilibrium liquid concentration after desorption step. The hysteresis coefficient (H) for the sorption-desorption isotherms was calculated according to the formula $H = (1/n_{desorption})/(1/n_{sorption})$, where $1/n_{sorption}$ and $1/n_{desorption}$ are the Freundlich slopes obtained for the sorption and desorption isotherms, respectively (BARRIUSO et al., 1994).

2.7. Statistical analysis

Hexazinone, metribuzin and quinclorac sorption–desorption coefficients (K_f and K_d) data were analyzed descriptively according to the standard error of the mean. Figures were plotted using Sigma Plot® (version 10.0 for Windows, Systat Software Inc., Point Richmond, CA, USA).

3 RESULTS AND DISCUSSION

3.1. Characterization of biochars

After feedstock pyrolysis, the eucalyptus biochar showed the highest carbon content (C) (74.52%), followed by rice hull (44.14%) and native bamboo (45.36%) biochars (Table 2). The nitrogen content among the biochars did not show variation, with 0.47, 0.43 and 0.35% for eucalyptus, rice hull and native bamboo, respectively (Table 2). Native bamboo biochar contained the highest hydrogen content (6.89%) compared to eucalyptus (1.98%) and native bamboo (0.85%) biochars (Table 2). The rice hull pyrolyzed at 700 °C by a heating rate of 10 °C min^{-1} permitted the synthesis of a biochar with higher oxygen content compared to the eucalyptus at 450 °C and 1.7 °C min^{-1} (Table 2). The H/C ratio was higher for native bamboo (0.15) compared to the other biochars (Table 2). For O/C and (O + N)/C ratio, the lowest values (0.31 and 0.32 respectively) were observed for eucalyptus biochar (Table 2).

Elemental analysis and H/C, O/C, and (O+N)/C ratios are important for assessing the degree of aromaticity and polarity of biochars (ZHAO et al., 2018). Pyrolysis of fresh materials

generally increases the aromaticity of the biochar due to dehydration, dehydrogenation and decarboxylation process (SULIMAN et al., 2016). The low rates for H/C, O/C and (O+N)/C indicate that eucalyptus biochar has higher aromaticity and lower polarity than bamboo and rice hull biochars. The proximity of O/C and (O+N)/C values between bamboo and rice hull biochars indicates that these materials have no polarity differences. The main difference between bamboo biochar and rice hull is the higher O/C ratio for rice hull. This last material (rice hull) presents a high amount of SiO_2 in their natural composition, favoring the synthesis of biochar with high O/C rate (ZHANG et al., 2018).

The eucalyptus biochar showed higher SSA (155.446 m^2 g^{-1}) compared to native bamboo (48.413 m^2 g^{-1}) and rice hull (6.807 m^2 g^{-1}) biochars (Table 2). In general, high temperature of pyrolysis increases the SSA (LI et al., 2019). However, in this study the high temperature of pyrolysis reduced the SSA. The pore enlargement and/or neighboring pore coalescence at temperatures above 500 °C contributes to this response, leading to a decrease in pore volume and SSA. In addition, as a result of softening, melting, fusing and carbonization, the pores of biochars may be partially blocked (FU et al., 2011).

In addition to the high temperature used for pyrolysis, the high heating rate to synthesize the rice hull and native bamboo biochars may have reduced the SSA. The higher heating rate promotes rapid volatilization of compounds, impairing the release these volatiles from the biochar (ANGIN, 2013). This fact may have occurred to the biochars in this study, where the amount of volatile matter followed the sequence: eucalyptus > native bamboo > rice hull. The presence of volatile compounds into biochar contributes to obstruction the pores of rice hull and native bamboo biochars, reducing the sorption of N_2 and, consequently, the SSA values. Angin (2013) observed a similar effect for safflower seed press cake, reporting a reduction in SSA due to the increase of heating rate and retention of volatile matter.

The rice hull (48.88%) biochar contained higher ash content than native bamboo (13.41%) and eucalyptus biochar (5.81%) (Table 2). The highest ash content of rice hull biochar might be related to their high temperature of pyrolysis (ZHANG et al., 2013). Some studies have attributed the increased ash percentage to the remains of this material in the lower-mass pyrolyzed biochar (FIDEL et al., 2017). This fact may have increased the percentage of ash in rice hull biochar compared to the other biochars. Another determining factor is the amount of silica present in the rice hull (ZHANG et al., 2018), which can easily transform in ash after pyrolysis step.

The pH values for eucalyptus, native bamboo and rice hull biochars were 7.69, 8.65 and 9.38, respectively (Table 2). The higher pH observed for rice hull is due to the higher content

of ash compared to the other biochars. Ash is primarily responsible for generating alkalinity in biochars because of the presence of alkaline reaction minerals such as Na^{+}, Ca^{2+} and Mg^{2+} (FIDEL et al., 2017). Increased pyrolysis temperature also increased the alkalinity of biochars derived from rice straw, eggshell (XU et al., 2019), rapeseed (ZHAO et al., 2018) and safflower seeds (ANGIN, 2013).

The thermogravimetric analysis showed the mass loss of the three biochars in the temperature range between 100 and 900 °C (Figure 1). All biochars showed a reduction in percentage mass loss (Figure 1). The first decrease in weight loss (25 to 100°C) for all biochars is mainly due to the evaporation of water physically sorbed and some extractives compounds, which indicated that the three raw feedstock possesses a moisture content around 5%.

The largest reduction was observed for biochar synthesized from eucalyptus (99%), followed by native bamboo (85%) and rice hull (45%) (Figure 1). The higher mass loss for eucalyptus biochar indicates that this material has lower recalcitrance compounds compared to other biochars (SULIMAN et al., 2016; ZHAO et al., 2018). Consequently, this biochar can suffer faster soil degradation, releasing CO_2 into the atmosphere as the deterioration process occurs. Unlike eucalyptus, biochars made from rice hull and native bamboo can fix C in the soil, contributing to the reduction of CO_2 emissions in the atmosphere (ONOREVOLI et al., 2018).

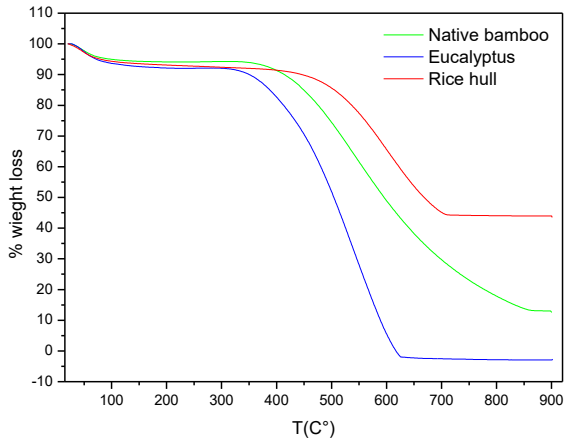


Figure 1. Thermogravimetric curves of biochar samples (native bamboo, eucalyptus, and rice hull) under nitrogen atmosphere.

Mass loss between temperatures of 200 to 400 °C for all biochars was low, only 10% on average (Figure 1). The mass reduction in this temperature range occurs mainly by the degradation of cellulose and hemicellulose, less thermostable compounds (LI; CHEN, 2018). For the biochars of this study, it can be observed that little cellulose and hemicellulose make up the pyrolyzed materials. At temperatures above 400 °C, mass loss increased exponentially

for the three biochars (Figure 1). This fact indicates the predominance of more thermostable compounds, such as lignin, in the biochar composition (LI; CHEN, 2018). The stability of lignin is due to the high molecular weight cross-linked polymer on phenyl propane derivatives, slowing down the dehydrate process (SADDAWI et al., 2012). Furthermore, lignin has various oxygen groups in its structure, increasing their thermal stability (BREBU; VASILE, 2010).

Although more thermostable, lignin is degraded at temperatures above 500 °C (LI; CHEN, 2018). For rice hull, the pyrolysis process produced a higher content of recalcitrant compounds with high thermostability compared to other biochars not degraded even at 900 °C. This property is essential to ensure biochar stability under conditions that favor the degradation of organic materials such as those occurring in soils (Angin, 2013).

3.2. Influence of biochars in sorption-desorption of three herbicides

3.2.1. Hexazinone

Sorption isotherms of hexazinone in biochar amended and unamended soil fitted to Freundlich model, with $R^2 \geq 0.98$ (Figure 2). The isotherms slopes ($1/n_{sorption}$) varied from 0.69 to 0.93 among all treatments. The sorption isotherms for the treatments with eucalyptus biochar and unamended soil were close to linearity for the tested concentrations, with 1/n values of 0.83 and 0.93, respectively (Table 3). This fact suggests a C-type isotherm; the sorbed rate of hexazinone does not reduce with increase of solution concentration. Differently, treatments with addition of rice hull and native bamboo were nonlinear, with 1/n of 0.69 and 0.74, respectively (Table 3). The nonlinear isotherms occur when relative sorption decreases in high solution concentration of herbicide (TAN et al., 2009). The reduction of relative sorption for hexazinone in soils amended with rice hull and native bamboo demonstrated the saturation of sorption sites available, impairing the sorption of molecules in soil solution (SUN et al., 2013). In addition, filling in the biochar surface binding sites may reduce hexazinone binding to the internal regions of the biochar from the steric hindrance between the herbicide molecules. The low SSA of native bamboo and rice hull may favor this steric hindrance due to rapid saturation of sorption monolayer (CHEFETZ; XING, 2009).

The sorption coefficients of hexazinone were lower compared to the other herbicides, both in amended and unamended soil (Table 3). The $K_{f(sorption)}$ values for hexazinone were equal to 0.17 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} (unamended soil), 0.18 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} (eucalyptus and rice hull biochar), and 0.24 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} (native bamboo biochar) (Table 3). The K_{foc} values were

48.57 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for unamended soil, and 51.42, 52.85, and 67.14 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for rice hull, eucalyptus and native bamboo biochar, respectively (Table 3). The addition of eucalyptus and rice hull biochars to the soil does not increase hexazinone sorption. On the other hand, the addition of biochar from native bamboo increased the sorption of hexazinone. The native bamboo biochar presented the highest H/C ratio, besides, a high O/C ratio, indicating a higher quantity of hydroxyl groups in relation to the other biochars. This property may favor hexazinone sorption due to hydrogen bonds between the biochar hydroxyls and the oxygen and nitrogen atoms present in the hexazinone molecule, causing higher herbicide sorption. Ćwieląg-Piasecka et al. (2018) also observed the effect of hydrogen interactions between 2,4-D or MCPA and hydrophilic portions on the surface of a humic acid (HA), which resulted in higher sorption of phenoxy acetic acids in HA.

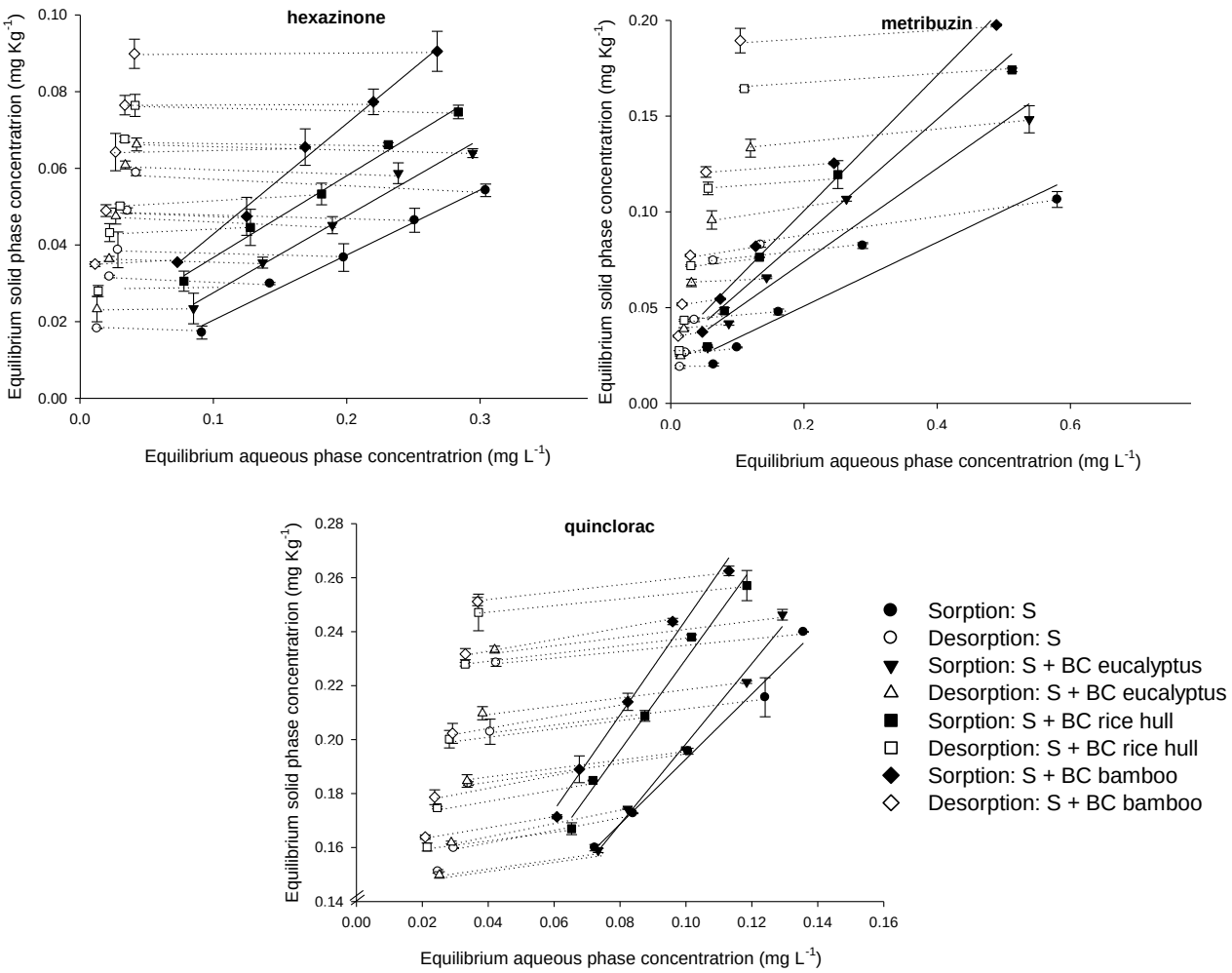


Figure 2. Freundlich sorption (●, ▼, ■, and ♦) and desorption (○, Δ, □, and ◊) isotherms of quinclorac, hexazinone and metribuzin mobile herbicides in the unamended soil and soil amended with three biochars (eucalyptus, rice hull, and native bamboo). S: tropical soil, BC: biochar. Error bars represent standard error of the mean (n = 2). Symbols may cover error bars.

Table 3. Freundlich sorption parameters and distribution coefficients at (K_d and K_{oc}) for the three herbicides in the unamended soil and soil amended with three biochars.

Herbicide	Sample	pH	$K_{f\ (sorption)}$	$K_{foc\ (sorption)}$	$1/n_{\ (sorption)}$	R^2
			($mg^{(1-1/n)}\ L^{1/n}\ kg^{-1}$)			
Hexazinone	S	6.52	0.17 (0.14-0.20)[a]	48.57 (40.00-57.14)	0.93 ± 0.10[b]	0.98
	S + BC eucalyptus	6.34	0.18 (0.15-0.22)	52.85 (42.86-62.85)	0.83 ± 0.10	0.99
	S + BC rice hull	6.09	0.18 (0.17-0.19)	51.42 (48.57-54.28)	0.69 ± 0.03	0.99
	S + BC bamboo	6.01	0.24 (0.21-0.26)	67.14 (60.00-74.28)	0.74 ± 0.04	0.98
Metribuzin	S	6.52	0.19 (0.18-0.20)	54.28 (51.43-57.14)	0.79 ± 0.03	0.97
	S + BC eucalyptus	6.34	0.26 (0.24-0.27)	72.86 (68.57-77.14)	0.74 ± 0.03	0.98
	S + BC rice hull	6.09	0.33 (0.31-0.34)	92.85 (88.57-97.14)	0.78 ± 0.01	0.97
	S + BC bamboo	6.01	0.34 (0.33-0.35)	97.14 (94.29-100.00)	0.71 ± 0.01	0.99
Quinclorac	S	6.52	0.81 (0.74-0.87)	229.85 (212.00-247.71)	0.62 ± 0.03	0.99
	S + BC eucalyptus	6.34	1.09 (1.02-1.16)	311.42 (291.42-331.43)	0.74 ± 0.03	0.98
	S + BC rice hull	6.09	1.21 (1.10-1.29)	341.43 (314.29-368.57)	0.72 ± 0.04	0.99
	S + BC bamboo	6.01	1.21 (1.11-1.23)	334.28 (317.14-351.43)	0.69 ± 0.05	0.99

S: tropical soil, BC: biochar.

[a] Number in parentheses are confidence intervals of the mean, $n = 2$.

[b] Mean 1/n value ± standard deviation of the mean.

The hydrophilicity of biochar is another important property for soil sorption of herbicides (SHI et al., 2015). The higher H/C value and high O/C and (O+N)/C values observed for native bamboo biochar may reduce its aromaticity. For herbicides with high solubility, such as hexazinone (33000 mg L^{-1} at 20 °C), the lower aromaticity may increase the affinity between sorbent and sorbate, contributing to the sorption of the herbicide present in the solution. The importance of affinity between soluble compounds with less aromatic biochars has also been reported by Yavari et al. (2016), which also identified higher sorption of herbicides with high water solubility (imazapic and imazethapyr) in biochars produced at low pyrolysis temperature with lower aromaticity.

Physico-chemical properties of biochars synthesized from eucalyptus and rice hull did not increase the sorption of hexazinone in amended soil. Eucalyptus biochar showed the highest aromaticity among biochars, with low O/C, H/C and (O+N)/C. Even with high SSA, a property that allows higher sorption of pollutants (ZHANG et al., 2013), the low number of polar groups that favor binding of soluble herbicides proved to be the crucial factor for low hexazinone sorption. For rice hull biochar, in addition to the low H/C ratio, the lower SSA may have contributed to similar sorption in biochar-unamended soil.

The hexazinone desorption from biochar amended and unamended soils fitted to Freundlich model with $R^2 \geq 0.96$ (Table 4). Furthermore, the desorption of hexazinone showed no hysteresis ($1/n_{desorption} > 1/n_{sorption}$) for both amended and unamended soils, with H for soil amended with biochar from eucalyptus, rice hull, native biochar and unamended soil of 1.18, 1.46, 1.11 and 1.07, respectively (Table 4). This fact occurs because the strength of hexazinone sorption is weak and permits the return of this compound to soil solution (CALDERÓN et al., 2004).

The percentage of hexazinone desorption showed values varying between 14.83-16.23%, for all treatments (Table 4). Rice hull biochar-amended soil favored the highest desorption of hexazinone. This fact might be attributed to the binding energy between biochar and the herbicide (GUIMARÃES et al., 2018), where herbicide molecules are retained to low energy sites and can be desorbed more easily. Although part of the sorbed hexazinone returns to soil solution, the permanence of a sorbed proportion, especially for treatment with native bamboo biochar, which has increased hexazinone sorption and may reduce the amount of herbicide in the solution. This behavior may reduce the bioavailability of the contaminant to non-target organisms as well as their leaching (RUBIO-BELLIDO et al., 2018).

Table 4. Freundlich desorption parameters and hysteresis coefficient (H) for the three herbicides in the unamended soil and soil amended with three biochars.

Herbicide	Sample	$K_{f\ (desorption)}$	$K_{foc\ (desorption)}$	$1/n_{\ (desorption)}$	R^2	H	Sorption	Desorption
		($mg^{(1-1/n)}\ L^{1/n}\ kg^{-1}$)					(%)	
Hexazinone	S	2.31 (1.98-2.52)[a]	660.00 (565.71-720.00)	1.00 ± 0.02	0.98	1.07	16.05	15.92
	S + BC eucalyptus	2.41 (1.68-3.57)	688.57 (480.00-1020.00)	0.98 ± 0.10	0.96	1.18	19.80	15.74
	S + BC rice hull	2.79 (2.43-3.20)	797.14 (694.29-914.29)	1.01 ± 0.04	0.96	1.46	23.97	16.23
	S + BC bamboo	1.68 (1.31-2.07)	480.00 (374.29-591.43)	0.82 ± 0.07	0.98	1.11	27.90	14.83
Metribuzin	S	1.09 (1.08-1.10)	311.43 (308.57-314.29)	0.82 ± 0.01	0.96	1.04	21.43	18.35
	S + BC eucalyptus	1.84 (1.68-1.98)	525.71 (480.00-565.71)	0.89 ± 0.03	0.97	1.20	29.70	17.27
	S + BC rice hull	2.36 (2.32-2.37)	674.29 (662.86-677.14)	0.91 ± 0.01	0.98	1.17	33.28	16.05
	S + BC bamboo	2.17 (2.03-2.31)	620.00 (580.00-660.00)	0.84 ± 0.01	0.99	1.18	37.62	14.67
Quinclorac	S	2.21 (2.17-2.22)	631.43 (620.00-634.29)	0.74 ± 0.01	0.94	1.19	65.91	15.08
	S + BC eucalyptus	3.62 (2.70-4.73)	1034.29 (771.43-1351.43)	0.87 ± 0.08	0.99	1.17	66.66	14.81
	S + BC rice hull	3.67 (2.91-4.07)	1048.57 (831.43-1162.86)	0.82 ± 0.07	0.99	1.14	70.58	12.71
	S + BC bamboo	3.03 (2.94-3.05)	865.71 (840.00-871.43)	0.76 ± 0.01	0.99	1.10	72.26	12.64

S: tropical soil, BC: biochar.

[a] Number in parentheses are confidence intervals of the mean, $n = 2$.

[b] Mean 1/n value ± standard deviation of the mean.

3.2.2. Metribuzin

The sorption isotherms of metribuzin on biochar amended and unamended soils are showed in Figure 2 and the data adjusted to Freundlich model, with $R^2 \geq 0.97$ (Table 3). The Freundlich isotherms for all treatments were nonlinear for tested concentrations, with $1/n_{sorption}$ values ranging from 0.71 to 0.79 (Table 4). Similar to the hexazinone, the sorption of metribuzin in the biochar amended and unamended soil decreases with increasing herbicide concentration in the solution. This sorption behavior in solid materials allows a better fit of nonlinear models, such as Freundlich, because they consider the reducing of affinity between sorbent and sorbate at higher concentrations (SANTOS et al., 2019; CHAGAS et al., 2019).

Freundlich sorption coefficients (K_f) in soil amended with native bamboo and rice hull biochar were about 1.3-fold greater than the unamended soil. The $K_{f(sorption)}$ values increased from 0.19 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} (unamended soil) to 0.26, 0.33 and 0.34 $mg^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for eucalyptus, rice hull and native bamboo biochar amended soil, respectively (Table 3). K_{foc} values followed the same trend as $K_{f(sorption)}$ for biochar amended soil and unamended soil (Table 3). K_{foc} values for metribuzin were 54.28 (unamended soil), 72.86 (eucalyptus biochar + soil), 92.85 (rice hull biochar + soil) and 97.14 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} (bamboo biochar + soil) (Table 3).

Unlike hexazinone, all biochars promoted an increase of sorbed amount of metribuzin. This herbicide has a more lipophilic character (Log K_{ow} = 1.75) than hexazinone (Log K_{ow} = 1.17) (Table 2), favoring the sorption of this molecule to the nonpolar groups of the biochars. However, this interaction between nonpolar groups via Van Der Waals binding explains only part of the metribuzin sorption. This fact can be attributed to the lower sorption of metribuzin to eucalyptus biochar (higher aromaticity) compared to rice hull and bamboo biochar (lower aromaticity). Electrostatic interactions between metribuzin and rice hull and bamboo biochars may have promoted the highest sorption observed. The metribuzin molecule has an amino radical ($-NH_2$) that can establish hydrogen bonds with oxygen atoms, widely present in rice hull and bamboo biochars, increasing the sorption observed in these biochars (ANTÓN-HERRERO et al., 2018).

The chemical properties of biochars were more critical for metribuzin sorption than SSA, a physical property. The largest SSA for eucalyptus biochar did not promote the largest sorption of metribuzin in relation to other biochars. SSA generally plays a fundamental role in the sorption capacity of biochars (ZHENG et al., 2010; ZHANG et al., 2016; XU et al., 2019). For example, White Jr. et al. (2015), using pinewood and sugarcane bagasse biochar synthesized at

different pyrolysis temperature, attributed the sorption increase of approximately 5 and 24-fold to the higher SSA of sugarcane bagasse biochar pyrolyzed at 700 °C compared to the same feedstock synthetized at 350 °C. This occurs because the pores number directly increase with SSA, providing a larger herbicide binding sites (DOWNIE et al., 2009). However, our study shows that metribuzin sorption was not related to the SSA of tested biochars, but due to the intrinsic chemical properties of feedstock.

The Freundlich model for desorption of metribuzin also showed an appropriate fit, with $R^2 \geq 0.96$ for all biochar amended and unamended soils (Table 4). The highest $K_{f(desorption)}$ value was observed for unamended soil (1.09 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) (Table 4). The increasing order for $K_{f(desorption)}$ in biochar amended soil was eucalyptus (1.84), native bamboo (2.17) and rice hull (2.36 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) (Table 4). The higher $K_{f(desorption)}$ value for metribuzin in amended soils indicated that the presence of organic material reduced metribuzin desorption. For more lipophilic herbicides such as metribuzin, the presence of interactions between nonpolar groups increases bond stability, reducing desorption. Both C content and aromatic structure are important factors affecting low desorption capability of biochar for herbicides, manly for lipophilic compounds (CHEN et al., 2008; CABRERA et al., 2014; LIAN; XING, 2017).

Also, the lower desorption rate observed in the concentrations tested for rice hull biochar may be related to the higher amount of oxygen in the pyrolyzed material. This atom can interact with the amino group of metribuzin molecule and increase sorption stability via electrostatic interaction. Studies have previously reported the importance of surface functional groups including carboxylic (–COOH), hydroxyl (–OH), lactonic, amide and amine groups for high sorption and low desorption capacity of biochar (LI et al., 2017; ANTÓN-HERRERO et al., 2018).

3.2.3. Quinclorac

Sorption data of quinclorac fitted the Freundlich equation ($R^2 \geq 0.98$). All treatments showed a nonlinear behavior for sorption at the tested concentrations, indicating the use of nonlinear models to compare differences between treatments. This herbicide showed the highest sorption coefficient (K_f = 0.81 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) in the unamended soil compared to the other herbicides (Table 3). The $K_{f(sorption)}$ values for quinclorac in biochar amended soils were of 1.09, 1.21, and 1.21 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for soil amended with eucalyptus, rice hull and native bamboo biochar, respectively (Table 3). K_{foc} value of quinclorac in unamended soil was 229.85 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}. For biochar amended soil, the K_{foc} was 311.42, 334.28, and 341.43

$mg^{(1-1/n)}\ L^{1/n}\ kg^{-1}$ in eucalyptus, native bamboo and rice hull, respectively (Table 3). The highest quinclorac sorption in the soil without biochar in relation to the other herbicides tested in this study can be attributed to its lower solubility (0.065 mg L^{-1}) and higher Log K_{ow} value (2.95) (Table 2). These herbicide properties favor the sorption of the molecule to soil colloids (CURRAN, 2016). The addition of eucalyptus biochar increased the quinclorac sorption rate by 25%. Similar to the herbicide metribuzin, the aromatic character of the biochar contributed to the increase of sorbed quinclorac. The aromatic ring present in the molecule quinclorac can bind to the nonpolar fractions of eucalyptus biochar, elevating the sorption this herbicide. Ćwieląg-Piasecka et al. (2018) demonstrated similar interactions between other pesticides and highly aromatic organic materials

Native bamboo and rice hull biochars demonstrated the same sorption capacity for quinclorac, increasing the sorption rate of this herbicide by 33% compared to the unamended soil. Like to the metribuzin, in addition to aromaticity, other chemical properties of native bamboo and rice hull biochars increased the sorption of quinclorac. Although quinclorac has aromatic groups, which give it low solubility in water, the existence of a -COOH and chlorine atoms attached to the aromatic ring may allow other bonds to biochar. The effect of these bonds becomes more evident in bamboo and rice hull biochars due to the presence of possible groups in these biochars that favor the occurrence of electrostatic and hydrogen bonds.

Desorption data of the quinclorac fit to Freundlich equation, with high coefficients of determination for all treatments ($R^2 \geq 0.94$) (Table 4). The quinclorac desorption isotherms in biochar amended and unamended soils are shown in Figure 2. The lowest $K_{f(desorption)}$ for quinclorac was observed in unamended soil, with value of 2.21 $mg^{(1-1/n)}\ L^{1/n}\ kg^{-1}$ (Table 4). The $K_{f(desorption)}$ for quinclorac in soil amended with eucalyptus, rice hull and native bamboo were 3.67, 3.62, and 6.12 $mg^{(1-1/n)}\ L^{1/n}\ kg^{-1}$, respectively, and did not differ statically (Table 4). Hysteresis indices ranged from 1.10 to 1.19 between treatments (Table 4).

Positive hysteresis indicates that quinclorac, although a part returns to soil solution, tends to remain sorbed to the soil in a metastable state (BORISOVER et al., 2019). Quinclorac desorption rate was lower for soil biochar amended and unamended soils compared to other herbicides. This fact indicates that for conditions tested in this research, sorption of quinclorac to soil and soil with biochar is more stable, probably due to lipophilic interactions between herbicide and sorbate. The low solubility of quinclorac increases the affinity of this herbicide to mineral and organic colloids since its affinity to aqueous solution is much lower (CURRAN, 2016). The lower desorption of quinclorac in biochar amended soils compared to unamended

soil is a result of the combination of lipophilic and hydrophilic interactions (mainly for bamboo and rice hull biochars), which increases bond stability (CURRAN, 2016).

4 CONCLUSIONS

The biochars differently affect the sorption and desorption of the herbicides hexazinone, metribuzin and quinclorac. The chemical properties (H/C, O/C, and (O+N)/C) of the biochars are more important than the physical properties (SSA) for sorption capacity of these herbicides. The lower aromaticity of biochar allows the sorption of different ionic herbicides. Of the three biochars, only native bamboo biochar was effective in increasing hexazinone sorption. For metribuzin and quinclorac, all biochars increased sorption and decreased desorption of these herbicides in the soil. The native bamboo biochar had the highest sorption capacity for the hexazinone, metribuzin and quinclorac. Eucalyptus, native bamboo and rice hull biochars can reduce mobility and availability of herbicides in the soil, therefore weed control will also be diminished if these herbicides are used in areas amended with biochar.

REFERENCES

ADAMS, J. W. et al. Quinclorac and aminocyclopyrachlor movement in sandy soils. **Invasive Plant Science and Management**, v. 8, n. 3, p. 269–275. 2015.

ANGIN, D. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. **Bioresource Technology**, v. 128, n. 1 p. 593-597, 2013.

ANTÓN-HERRERO, R. et al. Comparative adsorption of tetracyclines on biochars and stevensite: looking for the most effective adsorbent. **Applied Clay Science**, v. 160, n. 1, p. 162-172, 2018.

BARRIUSO, E. et al. Atrazine desorption from smectites. **Soil Science Society of America Journal**, v. 58, n. 6, p. 1632-1638, 1994.

BATTAGLIN, W. A. et al. **Concentration of selected sulfonylurea, sulfonamide, and imidazolinone herbicides, other pesticides, and nutrients in 71 streams, 5 reservoir outflows, and 25 wells in the Midwestern United States**. Denver: US Geological Survey, 2001.

BORISOVER, M. Accumulated Gibbs free energy as a quantitative measure of desorption hysteresis associated with the formation of metastable states. **Chemosphere**, v. 215, n. 1, p. 490-499, 2019.

BREBU, M.; VASILE, C. Thermal degradation of lignin – a review. **Cellulose Chemistry and Technology**, v. 44, n. 9, p. 353-363, 2010.

CABRERA, A. et al. Influence of biochar amendments on the sorption–desorption of aminocyclopyrachlor, bentazone and pyraclostrobin pesticides to an agricultural soil. **Science of the Total Environment**, v. 470, n. 1, p. 438-443, 2014.

CALDERÓN, M.J. et al. Hexazinone and simazine dissipation in forestry field nurseries. **Chemosphere**, v. 54, n. 1, p. 1-8, 2004.

CARA, I. G. et al. Assessment of some straw-derived materials for reducing the leaching potential of Metribuzin residues in the soil. **Applied Surface Science**, v. 358, n. 1, p. 586-594, 2015.

CHAGAS, P. S. F. et al. Multivariate analysis reveals significant diuron-related changes in the soil composition of different Brazilian regions. **Scientific Reports**, v. 9, n. 1, p. 7900-7912, 2019.

CHEFETZ, B.; XING, B. Relative role of aliphatic and aromatic moieties as sorption domains for organic compounds: a review. **Environmental Science and Technology**, v. 43, n. 6, p. 1680-1688, 2009.

CHEN, B. et al. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. **Environmental Science and Technology**, v. 42, n. 14, p. 5137-5143, 2008.

CURRAN, W. S. Persistence of herbicides in soil. **Crops and Soils**, v. 49, n. 5, p. 16-21, 2016.

ĆWIELĄG-PIASECKA, I. et al. Humic acid and biochar as specific sorbents of pesticides. **Journal of Soils and Sediments**, v. 18, n. 8, p. 2692-2702, 2018.

DING, C. et al. Removal of quinclorac herbicide from aqueous solution by chitosan/montmorillonite bionanocomposite. **Desalination and Water Treatment**, v. 57, n. 52, p. 24970-24981, 2016.

DOWNIE, A. et al. Physical properties of Biochar. In: LEHMANN J. L.; JOSEPH, S. (org.). **Biochar for Environmental Management, Science and Technology**. London: Earthscan, 2009, p. 13-32.

ENANG, R. K. et al. Assessing the effectiveness of the Walkley-Black method for soil organic carbon determination in tephra soils of cameroon. **Communications in Soil Science and Plant Analysis**, v. 49, n. 19, p. 2379-2386, 2018.

ENDERS, A. et al. Characterization of biochars to evaluate recalcitrance and agronomic performance. **Bioresource Technology**, v. 114, n. 1, p. 644-653, 2012.

ESSANDOH, M. et al. Adsorption of metribuzin from aqueous solution using magnetic and nonmagnetic sustainable low-cost biochar adsorbents. **Environmental Science and Pollution Research**, v. 24, n. 5, p. 4577-4590, 2017.

FIDEL, R. B. et al. Characterization and quantification of biochar alkalinity. **Chemosphere**, v. 167, n. 1, p. 367-373, 2017.

FU, P. et al. Effect of temperature on gas composition and char structural features of pyrolyzed agricultural residues. **Bioresource Technology**, v. 102, n. 17, p. 8211-8219, 2011.

GEE, G. W.; BAUDER, J. W. **Particle-size analysis 1.** Methods of soil analysis: Part 1—Physical and mineralogical methods. Madison: Agron. Monogr., 1986. p. 383-411.

GRABER, E. R. et al. High surface area biochar negatively impacts herbicide efficacy. **Plant and Soil**, v. 353, n. 1-2, p. 95-106, 2012.

GUIMARÃES, A. C. D. et al. Role of soil physicochemical properties in quantifying the fate of diuron, hexazinone, and metribuzin. **Environmental Science and Pollution Research**, v. 25, n. 13, p. 12419-12433, 2018.

KEARNS, J.P. et al. 2, 4-D adsorption to biochars: Effect of preparation conditions on equilibrium adsorption capacity and comparison with commercial activated carbon literature data. **Water Research**, v. 62, n. 1, p. 20-28, 2014.

KHORRAM, M. S. et al. Effects of aging process on adsorption–desorption and bioavailability of fomesafen in an agricultural soil amended with rice hull biochar. **Journal of Environmental Sciences**, v. 56, n. 1, p. 180-191, 2017.

KHORRAM, M. S. et al. The effects of biochar properties on fomesafen adsorption-desorption capacity of biochar-amended soil. **Water, Air, and Soil Pollution**, v. 229, n. 3, p. 60-73, 2018.

KJÆR, J. et al. Leaching of metribuzin metabolites and the associated contamination of a sandy Danish aquifer. **Environmental Science and Technology**, v. 39, n. 21, p. 8374-8381, 2005.

KLOSS, S. et al. Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. **Journal of Environmental Quality**, v. 41, n. 4, p. 990-1000, 2012.

LE COADOU, L. et al. Quality survey of natural mineral water and spring water sold in France: Monitoring of hormones, pharmaceuticals, pesticides, perfluoroalkyl substances, phthalates, and alkylphenols at the ultra-trace level. **Science of the Total Environment**, v. 603, n. 1, p. 651-662, 2017.

LI, H. et al. Mechanisms of metal sorption by biochars: biochar characteristics and modifications. **Chemosphere**, v. 178, n. 1, p. 466-478, 2017.

LI, J. et al. Effectiveness of low-temperature biochar in controlling the release and leaching of herbicides in soil. **Plant and Soil**, v. 370, n. 1-2, p. 333-344, 2013.

LI, S. et al. Predicting biochar properties and functions based on feedstock and pyrolysis temperature: A review and data syntheses. **Journal of Cleaner Production**, v. 215, n. 1, p. 890-902, 2019.

LI, S.; CHEN, G. Thermogravimetric, thermochemical, and infrared spectral characterization of feedstocks and biochar derived at different pyrolysis temperatures. **Waste Management**, v. 78, n. 1, p. 198-207, 2018.

LIAN, F.; XING, B. Black carbon (biochar) in water/soil environments: molecular structure, sorption, stability, and potential risk. **Environmental science and technology**, v. 51, n. 23, p. 13517-13532, 2017.

LIU, M. et al. Isolation, identification and characteristics of an endophytic quinclorac degrading bacterium Bacillus megaterium Q3. **PloS One**, v. 9, n. 9, p. 108012-108020, 2014.

MACHADO, C. S. et al. Chemical contamination of water and sediments in the Pardo River, São Paulo, Brazil. **Procedia Engineering**, v. 162, n. 1, p. 230-237, 2016.

MAJUMDAR, K.; SINGH, N. Effect of soil amendments on sorption and mobility of metribuzin in soils. **Chemosphere**, v. 66, n. 4, p. 630-637, 2007.

MANDAL, A. et al. Characterization of pesticide sorption behaviour of slow pyrolysis biochars as low cost adsorbent for atrazine and imidacloprid removal. **Science of the Total Environment**, v. 577, n. 1, p. 376-385, 2017.

MATTICE, J. D. et al. Analysis of river water for rice pesticides in eastern Arkansas from 2002 to 2008. **Journal of Soil and Water Conservation**, v. 65, n. 2, p. 130-140, 2010.

MENDES, K. F. et al. Cow bone char as a sorbent to increase sorption and decrease mobility of hexazinone, metribuzin, and quinclorac in soil. **Geoderma**, v. 343, n. 1, p. 40–49, 2019.

MUKHERJEE, A. et al. Surface chemistry variations among a series of laboratory-produced biochars. **Geoderma**, v. 163, n. 3-4, p. 247-255, 2011.

OECD - Organisation for Economic Co-operation and Development. **OECD Guidelines for the Testing of Chemicals**: Test Number 106, Adsorption – Desorption Using a Batch Equilibrium Method, OECD. Paris, 2000. 44 p.

ONOREVOLI, B. at al. Characterization of feedstock and biochar from energetic tobacco seed waste pyrolysis and potential application of biochar as an adsorbent. **Journal of Environmental Chemical Engineering**, v. 6, n. 1, p. 1279-1287, 2018.

PARTHASARATHY, P. et al. Study on kinetic parameters of different biomass samples using thermo-gravimetric analysis. **Biomass and Bioenergy**, v. 58, n. 1, p. 58-66, 2013.

POT, V. et al. Metribuzin transport in undisturbed soil cores under controlled water potential conditions: experiments and modelling to evaluate the risk of leaching in a sandy loam soil profile. **Pest Management Science,** v. 67, n. 4, p. 397-407, 2011.

PPDB - Pesticide Properties Database. **Creating Tools for Pesticide Risk Assessment and Management in Europe**. Hertfordshire: UK National Sources, 2019. Available from: <http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>. Acesso em: 20 ago. 2019.

REIS, F. C. et al. Leaching of diuron, hexazinone, and sulfometuron-methyl applied alone and in mixture in soils with contrasting textures. **Journal of Agricultural and Food Chemistry**, v. 65, n. 13, p. 2645–2650, 2017.

RENDÓN-VON OSTEN, J.; DZUL-CAAMAL, R. Glyphosate residues in groundwater, drinking water and urine of subsistence farmers from intensive agriculture localities: a survey in Hopelchén, Campeche, Mexico**. International Journal of Environmental Research and Public Health**, v. 14, n. 6, p. 595-608, 2017.

RESGALLA, C. et al. Risk analysis of herbicide quinclorac residues in irrigated rice areas, Santa Catarina, Brazil. **Ecotoxicology,** v. 16, n. 8, p. 565-571, 2007.

RUBIO-BELLIDO, M. et al. Assessment of soil diuron bioavailability to plants and microorganisms through non-exhaustive chemical extractions of the herbicide. **Geoderma**, v. 312, n. 1, p. 130-138, 2018.

SADDAWI A. et al. Commodity fuels from biomass through pretreatment and torrefaction: effects of mineral content on torrefied fuel characteristics and quality. **Energy Fuels**, v. 26, n. 11, p. 6466-6474, 2012.

SANTOS, H. G. et al. **Brazilian Soil Classification System**. Embrapa Solos- Brasília, DF: Embrapa, 2018.

SANTOS, L. O. G. et al. Effect of liming on hexazinone sorption and desorption behavior in various soils. **Archives of Agronomy and Soil Science**, v. 65, n. 9, p. 1183-1195, 2019.

SHI, K. et al. Natural oxidation of a temperature series of biochars: opposite effect on the sorption of aromatic cationic herbicides. **Ecotoxicology and Environmental Safety**, v. 114, n. 1, p. 102-108,2015.

SOIL TAXONOMY. **A basic system of soil classification for making and interpreting soil surveys.** Soil Survey Staff. Natural Resources Conservation Service, Washington, DC: US Department of Agriculture Handbook, 1999. p. 436.

SULIMAN, W. et al. Influence of feedstock source and pyrolysis temperature on biochar bulk and surface properties. **Biomass and Bioenergy**, v. 84, n. 1, p. 37-48, 2016.

SUN, K. et al. Impact of deashing treatment on biochar structural properties and potential sorption mechanisms of phenanthrene. **Environmental Science and Technology**, v. 47, n. 20, p. 11473-11481, 2013.

TAN, I. A. W. et al. Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2, 4, 6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. **Journal of Hazardous Materials**, v. 164, n. 3, p. 473-482, 2009.

TRAVLOS, I. S. et al. Effects of the herbicides benfluralin, metribuzin and propyzamide on the survival and weight of earthworms (Octodrilus complanatus). **Plant, Soil and Environment**, v. 63, n. 3, p. 117-124, 2017.

WHITE JR, P.M. et al. Sugarcane and pinewood biochar effects on activity and aerobic soil dissipation of metribuzin and pendimethalin. **Industrial Crops and Products**, v. 74, n. 1, p. 737-744, 2015.

WU, C. et al. Sorption, degradation and bioavailability of oxyfluorfen in biochar-amended soils. **Science of the Total Environment**, v. 658, n. 1, p. 87-94, 2019.

XU, D. et al. Effect of pyrolysis temperature on characteristics of biochars derived from different feedstocks: A case study on ammonium adsorption capacity. **Waste Management**, v. 87, n. 1, p. 652-660, 2019.

YAVARI, S. et al. Sorption-desorption mechanisms of imazapic and imazapyr herbicides on biochars produced from agricultural wastes. **Journal of Environmental Chemical Engineering**, v. 4, n. 4, p. 3981-3989, 2016.

ZHANG, K. et al. Characterization of biochar derived from rice husks and its potential in chlorobenzene degradation. **Carbon**, v. 130, n. 1, p. 730-740, 2018.

ZHANG, P. et al. Adsorption and catalytic hydrolysis of carbaryl and atrazine on pig manure-derived biochars: impact of structural properties of biochars. **Journal of Hazardous Materials**, v. 244, n. 1, p. 217-224, 2013.

ZHANG, X. et al. Effect of aging process on adsorption of diethyl phthalate in soils amended with bamboo biochar. **Chemosphere**, v. 142, n. 1, p. 28-34, 2016.

ZHAO, B. et al. Effect of pyrolysis temperature, heating rate, and residence time on rapeseed stem derived biochar. **Journal of Cleaner Production**, v. 174, n. 1, p. 977-987, 2018.

ZHENG, W. et al. Sorption properties of greenwaste biochar for two triazine pesticides. **Journal of Hazardous Materials**, v. 181, n. 3, p. 121-126, 2010.

Chapter 2

BIOCHAR ADDITIONS TO AGRICULTURAL SOILS: IMPACTS ON SORPTION-DESORPTION AND MINERALIZATION OF METRIBUZIN IN THREE AGRICULTURAL SOILS

Abstract: Addition of biochars to agricultural soils have been proposed as a soil amendment able to modify soil microbial abundance, activity and community structure, as well as to retain and limit the transport of herbicides and other environmental contaminants in soil and water sources. The objective of this research was to evaluate the effect of grape wood and loblolly pine biochar amendments on sorption-desorption and mineralization of metribuzin in three agricultural soils. Each soil was amended with grape wood (*Vitis vinifera* L.) and loblolly pine (*Pinus taeda*) biochars at rate of 0 (control – unamended) and 5% (w w^{-1}). Sorption and desorption studies were performed using the batch equilibrium method at five concentrations of ^{14}C-metribuzin (0.5, 1.5, 5.0, 10.0 and 20.0 mg L^{-1}). Mineralization of ^{14}C-metribuzin was performed in biometer flasks at a rate of 4 mg kg^{-1} (target concentration). The $^{14}CO_2$-metribuzin released from mineralization was trapped in 0.4 M sodium hydroxide solution (NaOH) and analyzed at each sampling time (1, 3, 7, 14, 21, 28, 35 and 42 days). Sorption of metribuzin on the three unamended soils followed the decreasing order: drummer (61.3 %) > oakville (24.56 %) > ipava (22.35 %). Grape wood biochar (82.6 – 83.3 %) showed the highest amount sorbed compared to loblolly pine biochar (43.9 – 68.4 %) in all the three soils. Ipava soil provided the highest amount of desorbed metribuzin among the unamended soils in both, first (40.52 %) and second (57.97 %) desorption steps. Loblolly pine biochar provided the lowest amount desorbed on first (16.4 – 29.5 %) and second (24.7 – 42.5 %) desorption steps between the two biochars in all the three soils. The two consecutive steps of metribuzin desorption showed that more than 65% of the sorbed metribuzin was retained in the soils amended with grape wood biochar. Metribuzin mineralization in drummer, ipava and okaville soil is low in relation to the initial concentration applied. The addition of grape wood and loblolly biochar reduces mineralization and increases the non-extractable amount of metribuzin, but this effect was only observed for some soils. Grape wood and loblolly biochars have great potential to reduce the risk of environmental contamination due to the application of metribuzin, since both biochars increased sorption and decreased mineralization of this herbicide.

Keywords: black carbon, herbicide degradation, mobile herbicide, soil amendment.

1 INTRODUCTION

Biochar has been defined as a solid carbon-rich residue remaining after the thermo-chemical transformation of biomass (crop and forest residues, food residues, wood and animal wastes, etc.) under oxygen-limited conditions, whose main intended purpose is as a means of carbon sequestration and combating climate changes (LEHMANN et al., 2006; WOOLF et al., 2010; BAMMINGER et al., 2018). In addition to the studies on the use of biochar focused on the global-warming effects, biochar amendment to soil has been reported as an alternative to reduce herbicide mobility (WHITE JR. et al., 2015; ESSANDOH et al., 2017; HASKIS et al., 2019) and, consequently, decreases the risk of contamination of water sources by increasing the sorption capacity of herbicides. However, the diverse range of biochar applications depends on its physico-chemical properties, which are governed by the pyrolysis conditions (temperature, holding time) and the original feedstock (ENDERS et al., 2012).

The type of feedstock is considered as one of the main factors influencing the biochar final characteristics and its effect as an herbicide sorbent in soil, because its properties are affected by the nature of the original material. Among these, the differences in characteristics such as surface area, pore structures, surface functional groups and element composition (GUIZANI et al., 2017). For instance, the addition of manure-based biochars provided higher soil cation exchange capacity than that of wood biochar (SINGH et al., 2010), while the treatment of soil with woodchip biochar resulted in higher saturated water contents than those ones with the dairy manure biochars (LEI; ZHANG, 2012).

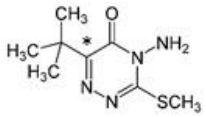
Additionally, biochars derived from wood biomasses often have higher surface area than grass biochar (MUKHERJEE et al., 2011), while wheat straw feedstock has higher cation exchange capacity (CEC) than that of wood biochar (KLOSS et al., 2012). According to Laird et al. (2009), the CEC of biochar depends on the mineral content of the biomass used, and the ashes (e.g. oxides, hydroxides and carbonates) of the biochar depends on the type of biomass, for example, softwood produces a biochar with lower content of ash than hardwood and corn or wheat wastes.

Considering the higher amounts of herbicides used in agronomic practices and the existence of contaminated water sources, either surface or groundwater (KHAN; BROWN, 2016; HAKOUN et al., 2017; MENCHEN et al., 2017), the interest in the application of biochar as a method for mitigating the herbicides environmental contamination effects is steadily increasing. For instance, relevant amounts of metribuzin were sorbed by wood biochar (Li et al., 2015). Furthermore, White Jr. et al. (2015) found that biochar synthetized from sugarcane

and pinewood affected metribuzin dissipation differently, according to the type of soil and the temperature that they were synthetized. In addition, switchgrass biochar has been shown to sorb metribuzin in both aqueous solution and lake water (ESSANDOH et al., 2017). Other benefits of adding biochar to soils include positive effects on soil microbial life (STEINER et al., 2007), as a toxic compound can be degraded by microorganisms to another less toxic compound, making it unavailable for environmental contamination.

Metribuzin [4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4*H*)-one] is an herbicide widely used for the control of grasses and broad-leaved weeds in soybeans, sugarcane, potatoes, wheat and numerous other crops, applied both pre- or post- emergence (PAPADAKIS; PAPADOPOULOU-MOURKIDOU, 2002; TOMLIN, 2009). In soil, metribuzin presents moderate affinity to organic carbon (K_{oc} = 38 mL g^{-1}) (PPDB, 2019), however it should be carefully monitored because of its relatively high (1,050 mg L^{-1}) water solubility and high mobility into deeper soil layers, thus a high potential to transfer into groundwater. The structural formulas and physico-chemical properties of metribuzin are shown in Table 1.

Table 1: Structure and physico-chemical properties of metribuzin.

Property	Metribuzin
Structure	
Molecular formula	$C_8H_{14}N_4OS$
Molecular weight (g mol^{-1})	214.2
Melting point (°C)	125.0
Vapor pressure (25 °C, mPa)	0.12
Water solubility (mg L^{-1} at 20 °C)	1165
DT50 soil (d)	11.5
K_{oc} (L kg^{-1})	38
Log K_{ow}	1.65
pK_a (25 °C)	1.0

Source: Adapted from PPDB (2019).
DT50 soil: persistence, K_{oc}: soil sorption coefficients,Log K_{ow}: n-octanol/water partition coefficients, pK_a:aciddissociationconstant
*: Radiolabeled carbon in the herbicide molecule.

For instance, metribuzin was found in surface waters in the United States (BATTAGLIN et al., 2001); in surface and groundwater close to agricultural areas in Brazil (DORES et al., 2008); in irrigation wells and groundwater in Portugal (CEREJEIRA et al., 2003) and other countries such as Norway (HAARSTAD; LUDVIGSEN, 2007) and Saudi Arabia (AL-WABEL et al., 2016). In addition, groundwater contamination carried out at a sandy test site in Denmark

detected up to 99% of metribuzin and its metabolites in the groundwater samples analyzed (KJÆR et al., 2005).

It is well known that herbicides have different fates when applied in the field, among others, uptake by plants, degradation process, movement, out-target, immobilization and unintentional discharge in the environment (TIRYAKI et al., 2010; HASKIS et al., 2019). To maximize the benefits offered by biochar on the environmental fate and activity of herbicides in the soil, it is important to develop an understanding of the herbicide's physico-chemical properties and their relationships to biochars from different feedstocks. Thus, optimizing biochar to increase sorption as well as increasing the soil microbial community to degrade and decrease the leaching process of mobile herbicides in the soil may require intentional selection of a biochar with the desired characteristics. Thus, the objective of this research was to evaluate the effect of grape wood and loblolly pine biochar amendments on sorption-desorption and mineralization of metribuzin in three agricultural soils.

2 MATERIAL AND METHODS

2.1. Soil characterization

Three soils from the state of Illinois (USA) were selected for this study: a silt loam (drummer) collected from Cham County, a silt loam (ipava) collected from Christian County, and a sandy soil (oakville) collected from Kan County (Figure 1). At each location, soil was collected from the upper 20 cm, air-dried, and passed through a 2 mm sieve. Soils' physico-chemical properties analysis were performed by WayPoint Analytical (Memphis, TN). Select properties of these soils are listed in Table 2. The soil pH was measured in water using a proportion of 1:1 soil:deionized water (w/v%), and the nutrients were measured by the Mehlich 3 extraction using Inductively Coupled Plasma (ICP). Soil organic matter (OM) was determined by weight loss-on-ignition (LOI) method, as described in Table 2.

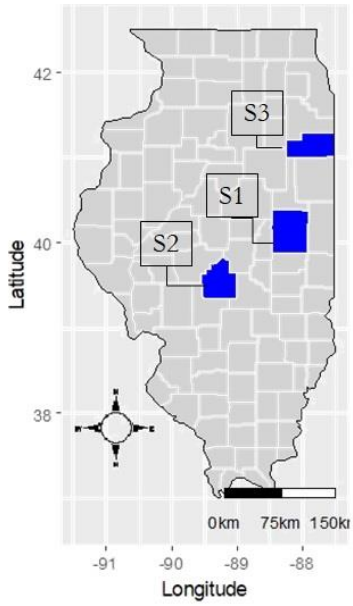


Figure 1. Illustration of the geographical distribution of the soil sampling locations. S1: Drummer, S2: Ipava, S3: Oakville.

Table 2. Physical and chemical properties of the three agricultural soils.

Soils	USDA soil type	OC	pH	CEC	Ca^{2+}	Mg^{2+}	K^{+}	P	Texture		
									Sand	Silt	Clay
		(%)	H_2O	(cmolc kg^{-1})	(mg L^{-1})				(%)		
D	silt loam	4.6	7.0	25.2	4052	450	351	71	43	49	8
I	silt loam	1.7	5.7	19.9	2667	228	129	39	21	64	15
O	sand	2.2	4.2	10.0	421	72	58	82	88	9	3

Soils (D: drummer, I: ipava, O: oakville), OM: organic matter, pH: hydrogen potential, CEC: cation exchange capacity, Ca^{2+}: calcium, Mg^{2+}: K^{+}: potassium, P: phosphorus.
Source: WayPoint Analytical.

2.2. Biochar amendment

Two biochars were prepared from residues of grape wood (*Vitis vinifera* L.) (GW) and loblolly pine (*Pinus taeda*) (LP) at USDA-ARS laboratory in Florence - SC, by heating for 4 hours at 700 °C with a N_2 sweep gas (4 L min^{-1}) during the entire pyrolysis process. The biochar was added to soil at 0 (control – unamended) and 5% (w w^{-1}) ratio, corresponding to 0 and 60 t ha^{-1}, respectively, assuming a soil bulk density of 1.2 g cm^{-3} and depth of 10 cm. All biochars were ground prior to use and sieved though 0.25 mm sieve to reduce sample heterogeneity. Selected physico-chemical properties of the biochars are listed in Tables 3 and 4.

Elemental analyses of biochars were conducted by the University of Minnesota Soil Testing and Research Analytical Lab (St. Paul, MN) using inductively coupled plasma optical emissions spectrometry (ICP-OES) (Optima 3000, Perkin Elmer). Biochar pHs were measured in 1:10 biochar:deionized water slurries after shaking for 12 h. Biochars were imaged using VEGA 3 LMU Spectrum Electron Microscope (SEM) (Tescan, Czech Republic), operating with a 20kV electron beam, to visually inspect their physical structure. Biochar samples were prepared in a sample holder (PELCO Tabs ™, Ted Pella, Inc., Redding, CA, EUA) using a carbon conductive adhesive. To reduce sample charging and improve image resolution, biochar samples were coated with a 9 nm layer of metal (GOLD) using a Q150R ES Coater (Quorum technologies Ltda, Laughton, East Sussex, England).

Table 3. Physico-chemical properties of the biochars.

Property	Value	
Feedstock	Grape wood	Loblolly pine
Temperature (°C)	700	700
Moisture (%)	2.42	1.37
Ash (%)	18.92	8.00
Volatile matter (%)	10.14	5.71
Fixed carbon (%)	70.95	86.29
pH (H_2O)	9.74	7.91
S (%)	0.053	0
C (%)	72.95	81.67
H (%)	0.50	0.87
N (%)	0.90	0.66
O (%)	6.68	8.80
H/C	0.15	0.10
O/C	0.07	0.08
(O+N)/C)	0.43	0.56

C: carbon, H: hydrogen, N: nitrogen, O: oxygen, S: sulfur.
Source: University of Minnesota Soil Testing and Research Analytical Lab.

Table 4. Particle size of the biochars.

Feedstock	Particle size (%)			
	<0.075 mm	0.075-0.3 mm	0.3-2 mm	>2 mm
Grape wood	0.23	14.25	81.31	4.20
Loblolly pine	1.02	9.10	79.10	9.89

Source: University of Minnesota Soil Testing and Research Analytical Lab.

2.3. Chemicals

^{14}C-labeled (triazine-6-^{14}C) metribuzin (radiochemical purity ≥ 99.0%, specific activity = 2.22 Bq/mmol) and its respective pure analytical standard (purity ≥ 99.0%) were obtained through Moravek Inc. (Brea, California) and Sigma Aldrich (Saint Louis, MO, USA), respectively. Metribuzin stock solutions were prepared in methanol and stored in the dark at 2 °C prior to use. Radiolabeled and non-radiolabeled standards were carefully mixed in 0.01 M $CaCl_2$ to prepare five solutions at concentration of 0.5, 1.5, 5.0, 10.0 and 20.0 mg L^{-1} of metribuzin.

2.4. Sorption-desorption studies

Sorption-desorption studies were performed in duplicate using the batch equilibration method, according Organization for Economic Co-operation and Development (OECD, 2000). For studies, a completely randomized experiment of 3 x 3 factorial design, with 3 different soils (drummer, ipava and oakville); 3 biochar amendments (control, grape wood and loblolly pine) and 2 replicates was established. A blank tube containing each solution (without soil or biochar) was included as a blank method. Each experimental unit consisted of a 50 mL Teflon centrifuge tube with Teflon-lined cap. Aliquots with 5 g of each soil were weighed out in tubes and 10 mL of metribuzin solution (116.7 BqmL^{-1}) were added to the respective treatment. The tubes were shaken horizontally in a tabletop shaker in a dark room at 20 ± 2 °C for 24 h. Shaking time was sufficient for equilibration (CARA et al., 2015). After equilibration, samples were centrifuged for 15 min at 1700 rpm and the supernatants were collected. Aliquots (1 mL) of the supernatant solutions were mixed with 5 mL scintillation cocktail [EcoLite(+)™, MP Biomedicals, LLC, Solon, OH] in 7 mL vials and thoroughly mixed. The solutions were analyzed for ^{14}C by liquid scintillation counting (LSC) for 5 minutes, using Hitachi AccuFLEXLSC-8000 (Hitachi-Aloka Medical, Tokyo, Japan). The amount of herbicide sorbed was calculated as the difference between the amount of herbicide in the initial solution and amount of herbicide in the final supernatant solution.

Desorption studies were performed immediately after sorption. After removal of 1 mL aliquot for sorption analysis, 10 mL of 0.01 M $CaCl_2$ solution were added to the Teflon tubes containing the soil/biochar and the radiolabeled herbicide sorbed from the sorption study, without removing the remaining supernatant. The tubes were shaken for 24 h to reach the equilibrium concentration, centrifuged for 15 min at 1700 rpm and 1 mL aliquots of the

supernatant was transferred to a 7 mL scintillation vial containing 5 mL of scintillation cocktail and analyzed by LSC for 5 minutes, as described in sorption step. For a second desorption step, additional 10 mL of 0.01 M $CaCl_2$ solution were added to the Teflon tubes containing the soil/biochar and the radiolabeled herbicide remained from the first desorption step, without removing the remaining supernatant. The amount of metribuzin desorbed was calculated as the difference between the radioactivity sorbed in the soil and in the remaining supernatant. The pH of the supernatant was measured directly in the sample tubes at the end of the study.

2.5. Sorption-desorption model

Sorption coefficients ($K_f$and *1/n*) were calculated from the slope and intercept of the Freundlich equation: $C_s = K_f \times C_e^{1/n}$; where C_s is the concentration (mg kg^{-1}) of herbicide sorbed onto the soil after equilibration; K_f is the equilibrium Freundlich constant (mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}); C_e is the herbicide concentration (mg L^{-1}) after equilibration; and *1/n* is the degree of linearity of the isotherm. Percentage of metribuzin on biochar amended and unamended soils were calculated as: % sorption = $[(C_i - C_e)/C_i] \times 100$, where C_i is the herbicide initial liquid concentration, and C_e is the equilibrium liquid concentration. The equilibrium constant normalized to the OC content of the soil (K_{foc}) was calculated by the following formula: $K_{foc} = (K_f/(\%OC)) \times 100$.

The desorption ($K_{f(desorption)}$) coefficients were calculated for comparison to the sorption $K_{f(sorption)}$. Desorption coefficients K_f and *1/n* were determined in a similar manner to the sorption coefficients, using a plot of the amount of remaining chemical sorbed at each desorption step measured for each equilibrium concentration of the sorption isotherm. The percentages of metribuzin desorbed from biochar amended and unamended soils were calculated as: % desorption = $[(C_i - C_e)/C_i] \times 100$, where C_i is the herbicide concentration sorbed onto soil, and C_e is the equilibrium liquid concentration after desorption step. The hysteresis coefficient (H) for the sorption-desorption isotherms was calculated according to the formula $H = (1/n_{desorption})/(1/n_{sorption})$, where $1/n_{sorption}$ and $1/n_{desorption}$ are the Freundlich slopes obtained for the sorption and desorption isotherms, respectively (BARRIUSO et al., 1994).

2.6. Mineralization study

Metribuzin mineralization study was conducted in a completely randomized 3 x 3 factorial design, with 3 soils (drummer, ipava, oakville) and 3 biochar amendments (control,

grape wood, loblolly pine) as the factors analyzed, and 2 replicates. Each experimental unit consisted of a 250 mL biometer flask equipped with a side tube, in which a 20 mL scint vial containing 4 mL of 1 M NaOH was placed to trap carbon dioxide (CO_2). Prior to the addition of metribuzin, soils (20 g) with and without amendments (1 g) were placed in flasks and deionized water was added adjusting to 75% of field capacity for each soil (ARIAS et al., 2016). At this time, used 1 mL less of water, considering that 1 mL of spike solution will be added seven days later. The samples were incubated for 7 days at 25 °C to stimulate microbial activity. Then, 1 mL of 80 mg L^{-1} (4,883.3 Bq mL^{-1}) ^{14}C-metribuzin solution was added dropwise using a microliter syringe at a rate of 4 mg kg^{-1} (target concentration) to the soil and vials with NaOH were positioned in the flasks.

Each biometer flask was weighed out after addition of the spike solution and repeated at each sampling time to check if the field capacity of soils were maintained. If necessary, deionized water was added to re-establish the soil moisture in field capacity. Soil samples were incubated at 25 °C for a period of 42 days. Vials with NaOH were removed for sampling and replaced with a new NaOH solution at each sampling time (1, 3, 7, 14, 21, 28, 35 and 42 days), and flasks were simultaneously aerated. To determine the amount of evolved $^{14}CO_2$, 1 mL aliquot of NaOH solution was mixed with 5 mL of scintillation cocktail in 7 mL vials, vortexed, and samples were left in the dark for 24 h prior to counting via LSC for 5 minutes.

At the end of the study (after 42 days of incubation), approximately 20 g of the soil/soil+biochar samples with ^{14}C-metribuzin were transferred to a Teflon tube and first extracted with 20 mL of 0.01 M $CaCl_2$ by shaking on a horizontal shaker at 200 rpm for 24 h. The soil slurries were then centrifuged at 1700 rpm for 15 min, and 1 mL aliquots of the supernatants were added to 5 mL scintillation cocktail and analyzed for ^{14}C by LSC. Then, additional 9 mL of supernatant were removed, totaling 10 mL less of $CaCl_2$ initially added. The supernatant removed was replaced with 20 mL of methanol (99% purity), where the proportion of $CaCl_2$ and methanol became 1:2 (w w^{-1}).

The second extraction was conducted by shaking on a horizontal shaker at 200 rpm for one hour and centrifuged at 1700 rpm for 15 min. Then, 1-mL aliquots of the supernatants were added to a 7 mL vials with 5 mL of scintillation cocktail and analyzed by LSC for 5 minutes to enable calculation of the percentage of metribuzin in the extracted ^{14}C, as previously described. The non-extractable ^{14}C-metribuzin was obtained by the difference between the amount of $^{14}CO_2$ evolved and the extractable herbicide in relation to the initial rate applied.

2.7. Statistical analysis

Metribuzin sorption–desorption coefficient (K_f), mineralization ($^{14}CO_2$ evolution), extractable and non-extractable (after 42 days of incubation) data were subjected to analysis of variance (ANOVA). Sorption–desorption averages were compared by Scott-knott honest significant differences (HDS) test ($p< 0.05$). Mineralization ($^{14}CO_2$ evolution), extractable and non-extractable averages of metribuzin were compared by Tukey honest significant differences (HDS) test ($p< 0.05$). The $^{14}CO_2$ evolution over the days of incubation was compared by the confidence interval due to the non-independence of the experimental units. Figures were plotted using Sigma Plot® (Version 13.0 for Windows, 201Systat Software Inc., Point Richmond, CA, USA).

3 RESULTS AND DISCUSSION

3.1. Effect of biochar on sorption of metribuzin

The sorption data fitted to the Freundlich model for all treatments, with R^2 values ≥ 0.93 (Table 5). The Freundlich isotherms were not linear for all treatments tested in this study, with *1/n* values varying between 0.74 and 0.93 (Table 5). Values of *1/n*< 1 demonstrate a reduction in sorption capacity of sorbate with increasing concentration of sorbate in solution (TAN et al., 2009). Regardless of soil type and type of biochar added, the highest concentration of metribuzin in the solution reduced the sorption rate of this herbicide in the substrate. This behavior is typical of herbicides (SANTOS et al., 2019; CHAGAS et al., 2019), and its occurrence is a result of metribuzin saturation in sorption sites. The effect of saturation is more pronounced when herbicide sorption is similar to monolayer type (KAMARAJ et al., 2018). In addition to saturation of the binding sites, the steric hindrance promoted by the substrate-sorbed metribuzin may impair further interactions with the herbicide molecules in the solution.

The $K_{f(sorption)}$values of metribuzin in the unamended soils were of 1.13, 1.24 and 4.19 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for ipava, oakville and drummer soils, respectively (Table 5). For the unamended soils, the highest $K_{f(sorption)}$ (72%) was observed for drummer, compared to the other soils (Table 6). The OC content was 58% higher than ipava and okaville soils (Table 2). This higher soil OC content was the main factor contributing to the higher sorption rate among the unamended soils. This soil property has been reported in different studies as an important factor affecting the sorption of different herbicides in the soil (GÁMIZ et al., 2019; SILVA et al., 2019), as well as for metribuzin (MAJUMDAR et al., 2007; OUKALI-HAOUCHINE et al., 2013; MENDES

et al., 2019). Organic molecules may establish hydrophobic interactions between nonpolar interfaces, and this effect increases the sorption of metribuzin in the OC. In addition, soil OC has other functional groups that may promote electrostatic attractions with amino, amide and azomethine groups present in the metribuzin molecule (LUDVÍK et al., 1998; PUBCHEM, 2019), contributing to the herbicide retention.

Table 5. Freundlich sorption parameters of metribuzin in biochar-amended and unamended soils.

Sample	pH (H_2O)	OC (%)	Sorption				
			$K_{f\,(sorption)}$	$K_{foc\,(sorption)}$	$1/n_{(sorption)}$	R^2 (%)	Sorption (%)
			$mg^{(1-1/n)}\,L^{1/n}\,kg^{-1}$				
D	7.00	4.6	4.19±0.23[a]	91.10±4.93	0.82±0.01[a]	0.99	61.28
D+GW	7.84	5.5	10.09±0.54	180.10±9.71	0.80±0.04	0.99	83.31
D+LP	7.68	5.6	5.11±0.06	92.83±1.08	0.79±0.01	1.00	68.42
I	5.70	1.7	1.13±0.01	66.46±0.58	0.94±0.01	0.93	22.35
I+GW	6.40	2.6	9.77±0.43	361.81±16.09	0.79±0.03	0.99	82.98
I+LP	6.25	2.7	2.31±0.03	88.94±1.19	0.79±0.02	0.98	43.93
O	4.20	2.2	1.24±0.00	56.15±0.06	0.93±0.00	0.96	24.56
O+GW	4.71	3.1	10.68±2.82	333.66±88.12	0.74±0.07	0.98	82.57
O+LP	4.61	3.2	2.97±0.03	95.71±0.85	0.74±0.02	0.99	52.02

Soils (D: drummer, I: ipava, O: oakville), Biochars (GW: grape wood, LP: loblolly pine), pH: hydrogen potential, OC: organic carbon.
[a]mean ± standard deviation of the mean (*n = 2*).

The ipava (1.13 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) and oakville (1.24 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) soils showed similar K_f when biochar was not added to these soils (Table 6). Another important property which affects the sorption of herbicides in soils is the clay content (AZCARATE et al., 2015; LI et al., 2015). The percentage of clay in ipava soil was 5-fold higher than in okaville soil, a fact that could result in higher sorption of metribuzin. However, this behavior was not observed. This fact can be attributed to the higher OC content. As mentioned above, this component is a suitable sorbent for metribuzin. Also, the lower pH in okaville soil may favor the sorption of metribuzin. In this pH, a higher amount of protonated molecules may allow its sorption by the negative charges in the soil. These factors may compensate the lower amounts of clay, equalizing sorption rate between ipava and okaville soils.

$K_{f(sorption)}$ values of metribuzin in drummer, ipava and oakville soils amended with grape wood biochar were 10.09, 9.77 and 10.68 $mg^{(1-1/n)}$ $L^{1/n}$ kg^{-1}, respectively (Table 5). The addition of grape wood biochar increased the sorption of metribuzin compared to biochar-unamended

soils (Table 6). There was no difference on sorption of metribuzin among the three soils amended with grape wood biochar (Table 6). Despite the difference on sorption of metribuzin among the biochar-unamended soils, the grape wood biochar equaled the sorption capacity among them. Notably, the affinity of metribuzin to this biochar is very high, allowing ipava and okaville soils to sorb higher concentrations of the herbicide, similar to drummer soil. This fact shows that biochar did not have a similar additive effect on the sorption rate of metribuzin in soils.

Table 6. Freundlich coefficients (K_f) of sorption and the two desorption steps of metribuzin on each soil (durmmer, ipava and oakville) and biochar amendments (grape wood and loblolly pine).

Soil	Sorption			Desorption 1			Desorption 2		
	Biochar								
	Unamended soil	GW	LP	Unamended soil	GW	LP	Unamended soil	GW	LP
D	4.19aB	10.09aA	5.11aB	35.56aA	29.63bA	18.33aB	4.17aB	5.60bA	4.15aB
I	1.13bB	9.77aA	2.31bB	2.04bB	48.41aA	5.92bB	0.64bC	6.84aA	2.09bB
O	1.24bB	10.68aA	2.98bB	2.81bB	47.45aA	6.23bB	0.85bC	6.40aA	2.37bB
CV	4.85			5.65			8.44		

Different letters indicate significant differences by Scott-knott test ($p \leq 0.05$). Lowercase letters distinguish the mean in the column and uppercase letters in the row. CV: coefficient of variation, Soils (D: drummer, I: ipava, O: oakville), Biochars (GW: grape wood, LP: loblolly pine)

Zhang et al. (2010) reported a 4.8-fold increase in phenanthrene sorption to a silty-loam soil and 723 times to another sandy-soil both amended with *Pinus radiata* biochar. Similar to our study, the additive effect on sorption of herbicide in soil with high OC was lower compared to the soils with low OC. Possibly, the lower number of sorption sites in the ipava and okaville soils favored the migration of metribuzin to biochar, providing a greater increase in sorption. The higher OC content in the drummer soil may have reduced the sorption capacity the biochar via competition for molecules of metribuzin in solution, allowing an increase of only 41% compared to the unamended soil.

$K_{f(sorption)}$ values of metribuzin in drummer, ipava and oakville soils amended with loblolly biochar were 5.11, 2.31 and 2.98 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}, respectively (Table 5). There was no difference on $K_{f(sorption)}$ values between the unamended soils and the addition of loblolly biochar (Table 6). The addition of loblolly biochar did not increase the sorption of metribuzin in any soils tested. Studies have shown that some biochars are not able to increase the sorption of some

herbicides in the soil. For example, Martin et al. (2012) did not observe an increase in atrazine sorption capacity when adding aged biochar compared to the control soil. The presence of fresh biochar synthesized from beech wood also did not increase the sorption of a metazachlor metabolite, metazachlor sulfonic acid (DECHENE et al., 2014). Factors such as low affinity between biochar and herbicide functional groups may make it impossible for interactions to occur, consequently increasing the sorption of the molecule (ZHANG et al., 2011; XIAO; PIGNATELLO, 2015; YAVARI et al., 2016). Another point is the low number of binding sites between biochar and herbicide, resulting in lower increases in pesticide sorption (WU et al., 2019).

The chemical composition between loblolly and grape wood biochars did not differ after pyrolysis (Table 3). However, the sorption capacity between these materials when added to the soil was extremely contrasting. The similar chemical composition does not reflect, in some cases, affinity between sorbent and sorbate. The arrangement of functional groups in the loblolly biochar may differ from those present in grape wood and have a lower affinity for metribuzin. Li et al. (2018) characterized biochars with similar C, H, N, and O content composition, but the presence of ester, alcohol, phenol and aliphatic groups was much higher in biochar synthesized from switchgrass compared to water oak wood biochar.

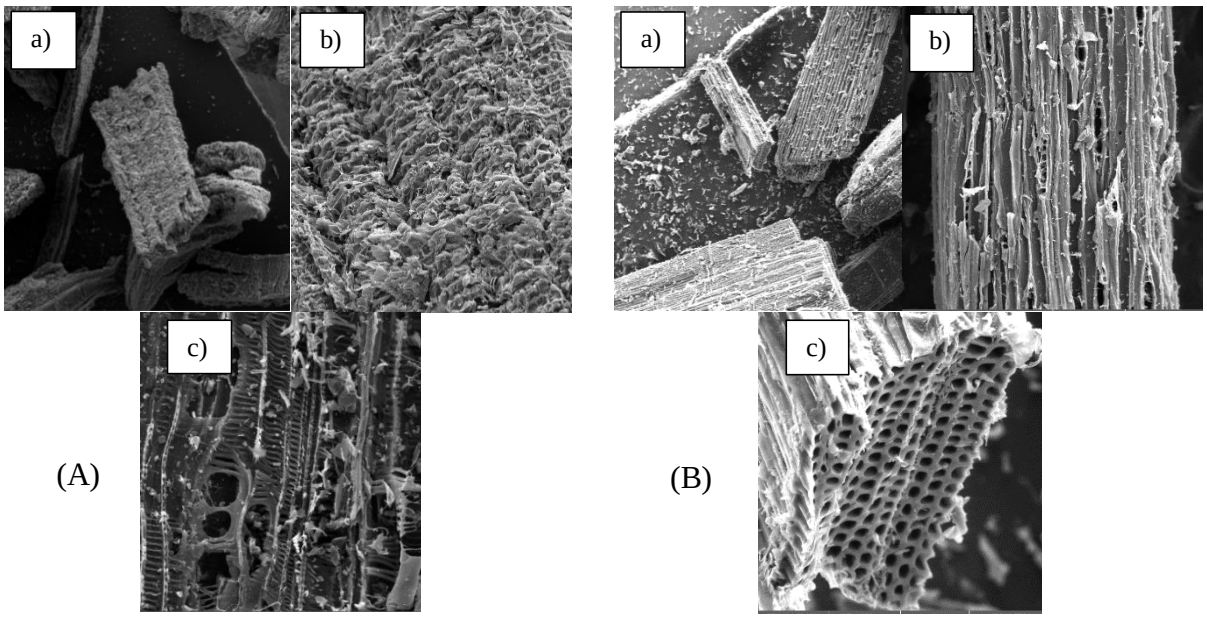


Figure 3. Scanning electron microscope (SEM) images of grape wood (A) and loblolly pine (B) biochars. Magnification is 100x (a), 500x (b), and 1000x (c).

Particle size may also contribute to the contrast observed for the sorption capacity of metribuzin in loblolly and grape wood biochars. Loblolly biochar showed lower particle size <

0.3 mm (10.12 %) and higher particle size > 2 mm (9.89%) compared to grape wood (< 0.3 mm = 14.48 % and > 2 mm = 4.20 %) (Table 4, Figure 3). This fact gives loblolly smaller area of sorption by volume of biochar added to the soil. Consequently, a smaller amount of metribuzin can be sorbed. Particle size has a direct effect on sorption of organo-pollutants in soil, and several studies have reported higher sorption capacity for high particle volume biochars (ESSANDOH et al., 2017; ZHELEZOVA et al., 2017; KANG et al., 2018; GÁMIZ et al., 2019).

3.2. Effect of biochar on desorption of metribuzin

Metribuzin first desorption data for the three unamended and biochar-amended soils fitted well to the Freundlich isotherms, with R^2 from 0.85 to 0.99 (Table 7, Figure 2). The desorption coefficients ($K_{f(desorption\ 1)}$) for the first desorption step on the unamended soils were of 2.0, 2.81 and 35.6 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for ipava, oakville and drummer soils, respectively (Table 7). The $K_{f(desorption\ 2)}$ from the second desorption step were 0.64, 0.85 and 4.17 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for ipava, oakville and drummer soils, respectively (Table 7). The lowest desorption observed for the drummer soil is due to the stable bonds between metribuzin and sorbent particles of this soil. The higher OC content of drummer soil, in addition to increasing sorption, reduced herbicide desorption to soil solution, even after two desorption processes. Soil OC can establish electrostatic bonds; and aging renders difficult to break covalent bonds (Tunega et al., 2019; Gaonkar et al., 2019), preventing the return of metribuzin to the soil solution.

The $K_{f(desorption\ 1)}$ for drummer soil (29.63 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) was lower than for ipava (48.41 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) and okaville (47.45 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) soils in the presence of grape wood biochar (Table 6). For the second desorption, there were no differences among soils in the presence of grape wood biochar (Table 6). The presence of grape wood biochar on drummer soil increased metribuzin desorption to soil solution compared to the unamended soil and other soils (ipava and okaville) amended with biochar. Although grape wood biochar has increased the sorption of metribuzin on drummer soil, the increase in desorption rate is unfavorable to reduce the mobility of this herbicide in the environment, which may lead to higher contamination of water resources (FARIA et al., 2018; PASSOS et al., 2019). Conversely, the presence of grape wood biochar on ipava and okaville soils showed higher potential to reduce environmental contamination, since in these soils there was an increase in sorption and a reduction in desorption.

Table 7. Freundlich desorption parameters and hysteresis coefficients (H) for metribuzin in biochar-amended and unamended soils.

Samples	First desorption						Second desorption					
	K_f (desorption)	K_{foc} (desorption)	*1/n* (desorption)	R^2	H	Desorption (%)	K_f (desorption)	K_{foc} (desorption)	*1/n* (desorption)	R^2	H	Desorption (%)
	$mg^{(1-1/n)} L^{1/n} kg^{-1}$						$mg^{(1-1/n)} L^{1/n} kg^{-1}$					
D	35.56± 1.20[a]	773.03± 25.99	1.26± 0.01 [a]	0.98	1.54	19.69	4.17± 0.71 [a]	90.67± 15.47	1.037± 0.05 [a]	0.99	1.26	29.45
D+GW	29.63± 3.76	529.03± 67.11	0.92± 0.03	0.91	1.15	9.04	5.60± 0.27	99.98± 4.85	0.97± 0.02	1.00	1.22	13.69
D+LP	18.33± 0.48	333.30± 8.65	0.96± 0.03	0.96	1.21	16.36	4.15± 0.04	80.57± 0.64	0.95± 0.00	0.99	1.20	24.72
I	2.04± 0.44	119.91± 25.89	0.94± 0.11	0.98	1.00	40.52	0.64± 0.04	37.94± 2.25	0.93± 0.02	0.99	0.98	57.97
I+GW	48.41± 13.12	1792.83 ± 485.78	0.85± 0.10	0.95	1.08	8.67	6.84± 0.15	253.33± 5.50	0.96± 0.03	1.00	1.22	12.32
I+LP	5.92± 0.27	227.83± 10.39	0.90± 0.03	0.97	1.15	29.47	2.09± 0.01	80.57± 0.32	0.88± 0.01	0.99	1.12	42.50
O	2.81± 0.15	127.58± 6.82	0.53± 0.64	0.99	0.57	39.08	0.85± 0.03	38.53± 1.17	0.92± 0.04	0.99	0.99	56.14
O+GW	47.45± 8.27	1482.86 ± 258.51	0.85± 0.08	0.85	1.15	8.10	6.40± 0.04	200.12± 1.13	0.95± 0.01	0.99	1.28	11.57
O+LP	6.23± 0.75	200.58± 24.16	0.83± 0.04	0.48	1.12	25.79	2.37± 0.37	76.41± 11.96	0.84± 0.03	0.98	1.14	37.51

Soils (D: drummer, I: ipava, O: oakville), Biochars (GW: grape wood, LP: loblolly pine).

[a]± standard deviation of the mean.

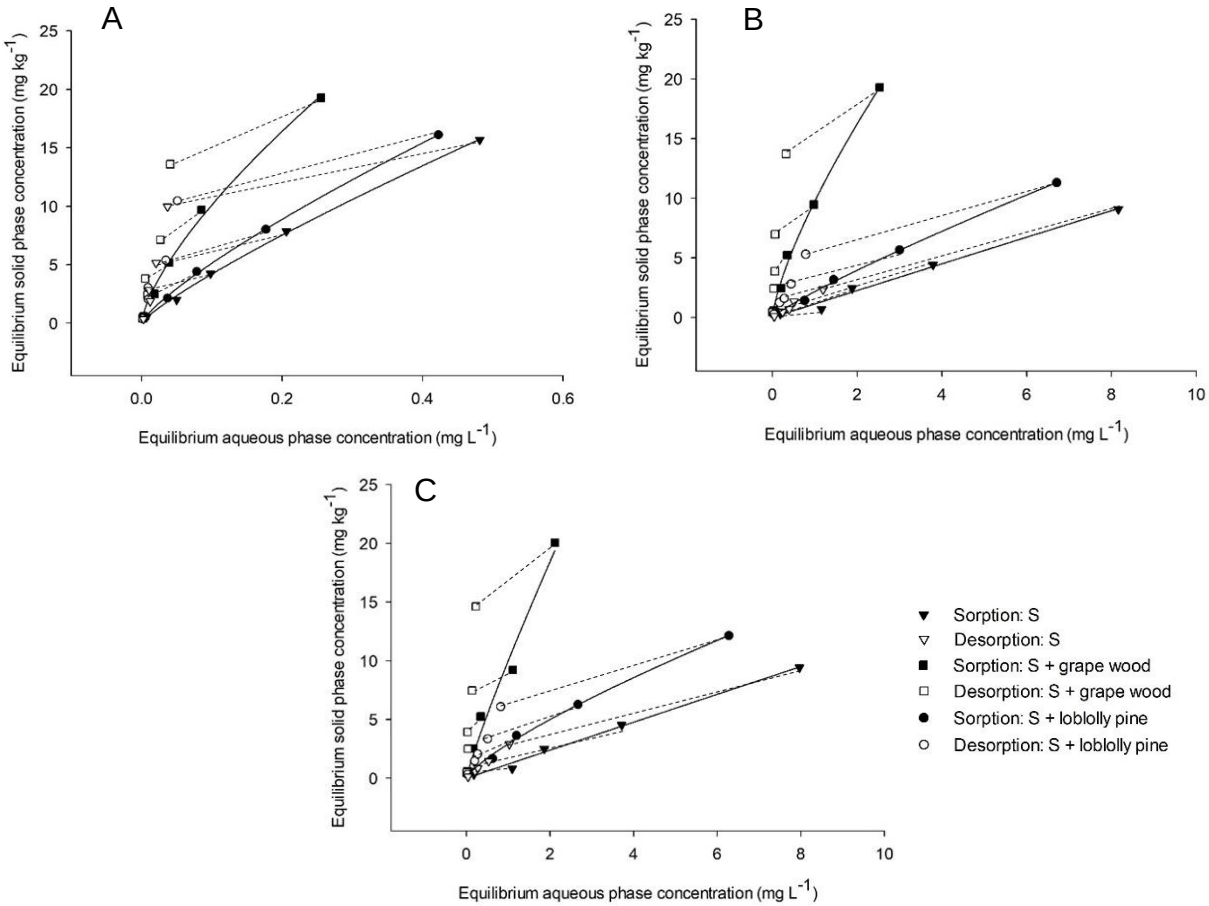


Figure 2: Freundlich isotherms for sorption (■, ● and▼) and first desorption (□, ○ and Δ) of metribuzin in three soils (A: Drummer, B: Ipava, C: Oakville) amended or not with biochars from grape wood or loblolly pine.

The ipava and oakville soils showed a very low sorption in the absence of biochar. The higher amounts of metribuzin sorbed on ipava and okaville soils amended with grape wood indicates that almost all herbicide was retained by the biochar. For drummer soil, part of the sorbed metribuzin may be bound to the soil colloids, with less stability, allowing the return of the herbicide to the soil solution. Studies have shown that biochars can sorb larger amounts of herbicides in a highly stable form, preventing their return to the soil water phase (KHORRAM et al., 2018; REN et al., 2018). Therefore, the metribuzin sorbed to grape wood biochar, when mixed with ipava and okaville soils, is more thermodynamically stable compared to drummer soil.

The $K_{f(desorption\ 1)}$ of drummer soil (18.33 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) was higher than ipava (5.92 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) and okaville (6.23 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) soils in the presence of loblolly biochar (Table 6). For the second desorption, the $K_{f(desorption\ 2)}$ were 4.15, 2.09 and 2.37 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} for drummer, ipava and okaville soils, respectively (Table 6). The behavior for the first and second desorption in the presence of loblolly biochar was similar. The drummer soil presented

lower metribuzin desorption compared to ipava and okaville soils. However, the presence of loblolly biochar increased the desorption of metribuzin on drummer soil compared to the unamended soil. This increase in desorption may be caused by lower contact of metribuzin to drummer soil colloids due to the presence of biochar, weakening interactions between herbicide and sorbent particles (MARCO-BROWN et al., 2019).

$K_{f(desorption\ 2)}$ values of ipava and okaville soils (2.09 and 2.37 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) amended with loblolly biochar were higher compared to them without biochar (ipava = 0.64 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1} and okaville = 0.85 mg $^{(1-1/n)}$ $L^{1/n}$ kg^{-1}) (Table 6). A reverse effect was observed for ipava and okaville soils in relation to drummer soil. In the first two soils, the presence of loblolly biochar reduced desorption of metribuzin. This fact demonstrates that this biochar may reduce the mobility of this herbicide on ipava and okaville soils. Even though loblolly biochar has sorbed a small amount of metribuzin, not changing the sorption rate, this portion sorbed by biochar was important to reduce desorption.

3.3. Mineralization of metribuzin

The mineralization of ^{14}C-metribuzin in drummer-free soil was similar to biochar-treated soil until 21 days after application (Figure 4A). After 21 DAA, mineralization was higher in the soil without biochar and with the presence of loblolly biochar (Figure 4A). In ipava soil, the difference between mineralization rates began at 14 DAA (Figure 4B). After this period, the increasing order of ^{14}C-metribuzin mineralization was soil + grape wood > soil + loblolly > soil without biochar (Figure 4B). For okaville soil, there were no differences in mineralization rate in any treatment and evaluation time (Figure 4C).

Days after metribuzin application, the mineralization in biochar-amended and unamended soils was similar. However, after a few weeks, the presence of biochar delayed mineralization in drummer and ipava soils. Possibly, this behavior was related to the amount of metribuzin available to be mineralized, moments after application. Although the sorption tests have shown higher sorption on biochar-amended soils, especially for grape wood biochar amendment, herbicide sorption in soils does not occur immediate (MARCO-BROWN et al., 2019; SPULER et al., 2019). Therefore, the amount of metribuzin in soil solution may be similar between the biochar-amended and unamended soils, allowing equal mineralization rate at initial weeks.

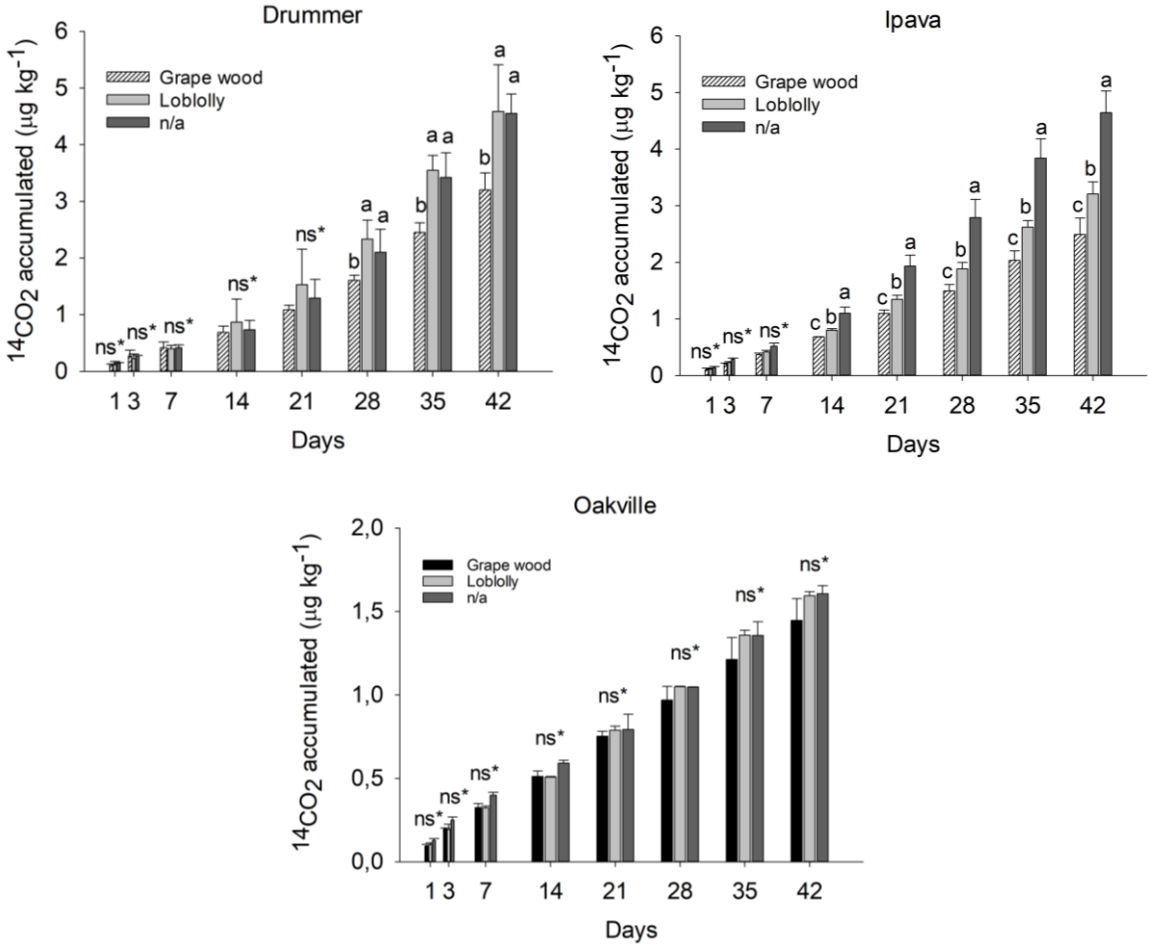


Figure 4. $^{14}CO_2$ mineralized (µg kg^{-1}) during 42 days of incubation from the soils (Drummer, Ipava, Okaville) with (Grape wood and Loblolly) and without (n/a) biochar. Lower case letters differ in the treatments with (Grape wood and Loblolly) and without (n / a) biochar within each evaluation period. Means do not differ by confidence interval at $p \leq 0.05$.

After 42 DAA, metribuzin mineralization values in the unamended soils were 4.6, 4.7 and 1.6 µg kg^{-1} for drummer, ipava and okaville, respectively (Table 8). The mineralized $^{14}CO_2$ rate in drummer and ipava soils was higher (65%) than okaville in the absence of biochar (Table 8). The main degradation route of metribuzin is carried out by soil microorganisms (JAISWAL et al., 2107; HUANG et al., 2018). The higher mineralization of metribuzin on drummer and ipava soils may be related to favorable conditions for degradation via microorganisms. Drummer and ipava soils have higher amounts of basic cations (Ca^{2+} and Mg^{2+}) and higher pH values. These conditions are ideal for microbial activity and may have promoted higher mineralization of metribuzin.

In contrast, okaville soil has not shown these same conditions in the soil; therefore, the lower microbiological activity in this soil may reduce metribuzin degradation. Allen; Walker

(1988) also observed a significant degradation of metribuzin in soil with higher pH and Ca^{2+} and Mg^{2+} contents. Metribuzin was 85% degraded after 26 days on a sandy-loam and pH 7.3. In this same soil, only 65% of metribuzin were degraded when the pH was adjusted to 6.4.

Table 8. $^{14}CO_2$ mineralized, total extracted ($CaCl_2$ + MeOH) and ^{14}C-metribuzin non-extractable (µg kg^{-1}) from the soil samples after 42 days of incubation.

	$^{14}CO_2$ mineralized (µg kg^{-1})					
	Drummer		Ipava		Okaville	
	Mean	SD	Mean	SD	Mean	SD
Grape wood	3.2 bA	1.2E-01	2.5 cB	1.2E-01	1.5 aC	5.3E-02
Loblolly	4.6 aA	3.3E-01	3.2 bB	8.5E-02	1.6 aC	9.8E-03
Unamended soil	4.6 aA	1.4E-01	4.7 aA	1.5E-01	1.6 aB	1.9E-02
	^{14}C-metribuzin extracted ($CaCl_2$ + MeOH) (µg kg^{-1})					
Grape wood	12.3 cA	1.7E+00	13.2 aA	8.0E-01	11.1 bA	5.4E-01
Loblolly	19.1 bA	1.1E+00	9.1 bB	3.5E-01	7.6 cB	1.1E+00
Unamended soil	29.0 aA	4.9E-01	12.4 aC	5.4E-01	15.1 aB	4.3E-02
	^{14}C-metribuzin non-extractable (µg kg^{-1})					
Grape wood	64.5 aB	1.8E+00	64.2 bB	9.2E-01	67.4 bA	4.9E-01
Loblolly	56.3 cC	7.3E-01	67.7 aB	2.7E-01	70.8 aA	1.0E+00
Unamended soil	46.5 bB	3.6E-01	62.9 bA	3.9E-01	63.3 cA	6.3E-02

Lowercase letters differ the mean in the column and uppercase letters in the row. SD= Standard deviation.

The $^{14}CO_2$–metribuzin evolution in okaville soil was lower than the other soils independent on the presence of biochar or not (Table 8). Despite the lower sorption of metribuzin in this soil, especially in the absence of biochar and with loblolly treatment, mineralization of this herbicide was extremely low. This fact emphasizes the importance of better conditions for microbiological activity in the metribuzin mineralization process. Also, the microbial community present in okaville soil may not exhibit the same efficiency in metribuzin degradation as other soils. Studies have shown that microbial activity is very important in the mineralization process, but the presence of specific microorganisms capable of performing this process is essential (HUANG et al., 2018).

The addition of grape wood biochar to drummer and ipava soils reduced the evolution of mineralized $^{14}CO_2$-metribuzin by 30 and 46%, respectively, compared to treatment without biochar (Table 8). Loblolly biochar reduced the evolution of mineralized $^{14}CO_2$-metribuzin only in ipava soil (Table 8). Higher sorption of metribuzin in soils with the addition of grape wood biochar reduced the herbicide concentrations in the water soil phase. This phenomenon made metribuzin unavailable to photodegradation, hydrolysis and metabolization processes via

microorganisms capable of mineralizing this herbicide. Eibisch et al. (2015) reported a similar behavior for the herbicide isoproturon, also a photosystem inhibitor. According to the authors, mineralization was significantly reduced after application of pyrochars and hydrochars to the soil in reasonable (0.5%) and high (5%) biochar residue additions due to the high sorption capacity.

The $^{14}CO_2$-metribuzin mineralized was higher in drummer soil compared to the other soils, with and without biochar application (Table 8). In this soil, higher sorption and lower desorption of metribuzin were observed. Thus, less mineralization was expected due to herbicide unavailability on degradation media. However, this behavior is not a general rule for all conditions. White Jr. et al. (2015) noted the addition of sugarcane bagasse biochar increased the sorption of metribuzin in a clay soil, but the herbicide half-life increased 18 days due to increased mineralization. These authors attributed the higher mineralization of metribuzin to the better conditions for more significant soil microbiological activity and the presence of a microbiota capable of metabolizing metribuzin. In our study, it was evident that the conditions inherent to the drummer soil were more important for the mineralization process than the sorption capacity of metribuzin to the sorbent particles.

3.4. Extractable and non-extractable metribuzin in soil

The addition of biochar to drummer soil reduced the amount of metribuzin extracted and increased the amount of this herbicide in the non-extractable (i.e. not extracted by the extractor used) fraction (Table 8). This behavior was not observed for ipava and okaville soils (Table 8). A larger portion of non-extractable metribuzin was observed for all biochar treatments (Table 8). Irreversible sorption of metribuzin is vital to reduce the mobility of herbicide in the environment. For drummer soil, the presence of biochars contributed to reduce the extractable quantities of metribuzin compared to other soils. Therefore, the amendment of this soil with grape wood and loblolly biochars is recommended to reduce metribuzin mobility and, consequently, the environmental risks of contamination associated to this herbicide.

The effect on the extractable and non-extractable portions of metribuzin on ipava and okaville soils is less significant than drummer soil. However, the addition of biochars in ipava and okaville soils may contribute to reduce metribuzin availability in the environment. The higher sorption rate or lower desorption rate is desirable when aiming to reduce water contamination and exposure to non-target organisms.

4 CONCLUSIONS

The physico-chemical properties (OC and clay content) of soils alter the sorption and desorption of metribuzin. Higher soil OC content increases sorption and decreases desorption of metribuzin in soil. The addition of grape wood biochar increased sorption and decreased desorption in all evaluated soils. The additive effect of grape wood biochar on sorption of metribuzin is higher in soils with lower OC content. The loblolly biochar is not able to increase metribuzin sorption in soils. However, the presence of this biochar decreased the return of sorbed metribuzin to the soil solution. Metribuzin mineralization in drummer, ipava and okaville soil is low in comparison to the initial concentration applied. The addition of grape wood and loblolly biochar decreases mineralization and increases the non-extractable amount of metribuzin, but this effect was only observed for some soils. Grape wood and loblolly biochars have great potential to reduce the risk of environmental contamination and persistence due to the application of metribuzin.

FINAL CONSIDERATIONS

There are many feedstocks that can be easily obtained and used for biochar production by the pyrolysis process, such as waste from agricultural processes. However, each feedstock has different characteristics, which will give rise to biochars with greater or lesser pesticide sorption capacity. In addition, combined to the different feedstocks, pyrolysis conditions are also important factors that must be considered in order to obtain biochars with good sorptive characteristics.

Regarding the weed control, it is a fact that the use of biochar reduces the mobility and availability of pesticides, thus, it can be stated that weed control will also be reduced if herbicides are used in biochar-treated areas (i.e. it might need higher rates of herbicides)

The use of biochar as a soil amendment is still an uncommon practice worldwide. Therefore, studies should be conducted to enable biochar technical recommendations for remediation of pesticides in soil or contaminated water resources.

REFERENCES

ALLEN, R.; WALKER, A., Effects of microbial inhibitors on the degradation rates of metamitron, metazachlor and metribuzin in soil. **Pesticide Science**, v. 22, n. 4, p. 297-305, 1988.

AL-WABEL, M. et al. Spatial distribution of pesticide residues in the groundwater of a condensed agricultural area. **Arabian Journal of Geosciences**, v. 9, n. 2, p. 120-130, 2016.

ARIAS, Y. P. et al. Halogen light thermogravimetric technique for determining the retained water in fine aggregates used for concrete mixing design. **Journal of Thermal Analysis and Calorimetry**, v. 123 n. 1, p. 127-134, 2016.

AZCARATE, M. P. et al. Sorption, desorption and leaching potential of sulfonylurea herbicides in Argentinean soils. **Journal of Environmental Science and Health**, v. 50, n. 4, p. 229-237, 2015.

BAMMINGER, C. et al. Offsetting global warming-induced elevated greenhouse gas emissions from an arable soil by biochar application. **Global change Biology,** v. 24, n. 1, p. 318-334, 2018.

BARRIUSO, E. et al. Atrazine desorption from smectites. **Soil Science Society of America Journal**, v. 58, n. 6, p. 1632-1638, 1994.

BATTAGLIN, W. A. et al. **Concentration of selected sulfonylurea, sulfonamide, and imidazolinone herbicides, other pesticides, and nutrients in 71 streams, 5 reservoir outflows, and 25 wells in the Midwestern United States**, Denver: US Geological Survey, 2001.

CARA, I. G. et al. Assessment of some straw-derived materials for reducing the leaching potential of Metribuzin residues in the soil. **Applied Surface Science**, v. 358, n. 1, p. 586-594, 2015.

CEREJEIRA, M. J. et al. Pesticides in Portuguese surface and ground waters. **Water Research**, v. 37, n. 5, p. 1055-1063, 2003.

CHAGAS, P. S. F. et al. Multivariate analysis reveals significant diuron-related changes in the soil composition of different Brazilian regions. **Scientific Reports**, v. 9, n. 1, p. 7900-7912, 2019.

DECHENE, A. et al. Sorption of polar herbicides and herbicide metabolites by biochar-amended soil. **Chemosphere**, v. 109, n. 1, p. 180-186, 2014.

DORES, E. F. et al. Pesticide levels in ground and surface waters of Primavera do Leste Region, Mato Grosso, Brazil. **Journal of Chromatographic Science**, v. 46, n. 7, p. 585-590, 2008.

EIBISCH, N. et al. Effect of pyrochar and hydrochar amendments on the mineralization of the herbicide isoproturon in an agricultural soil. **Chemosphere**, v. 134, n. 1, p. 528-535, 2015.

ENDERS, A. et al. Characterization of biochars to evaluate recalcitrance and agronomic performance. **Bioresource Technology**, v. 114, n. 1, p. 644-653, 2012.

ESSANDOH, M. et al. Adsorption of metribuzin from aqueous solution using magnetic and nonmagnetic sustainable low-cost biochar adsorbents. **Environmental Science and Pollution Research**, v. 24, n. 5, p. 4577-4590, 2017.

FARIA, A. T. et al. Tebuthiuron leaching in three Brazilian soils as affected by soil pH. **Environmental earth sciences**, v. 77, n. 5, p. 214-226, 2018.

GÁMIZ, B. et al. Changes in sorption and bioavailability of herbicides in soil amended with fresh and aged biochar. **Geoderma**, v. 337, n. 1, p. 341-349, 2019.

GAONKAR, O. D. et al. Soil organic amendments: impacts on sorption of organophosphate pesticides on an alluvial soil. **Journal of Soils and Sediments**, v. 19, n. 2, p. 566-578, 2019.

GUIZANI, C. et al. Biomass chars: The effects of pyrolysis conditions on their morphology, structure, chemical properties and reactivity. **Energies**, v. 10, n. 6, p. 796-814, 2017.

HAARSTAD, K.; LUDVIGSEN, G. H. Ten years of pesticide monitoring in Norwegian ground water. **Groundwater Monitoring and Remediation**, v. 27, n. 3, p. 75-89, 2007.

HAKOUN, V. et al. Factors controlling spatial and temporal patterns of multiple pesticide compounds in groundwater (Hesbaye chalk aquifer, Belgium). **Environmental Pollution**, v. 223, n. 1, p. 185-199, 2017.

HASKIS, P. et al. Effect of biochar on the mobility and photodegradation of metribuzin and metabolites in soil–biochar thin-layer chromatography plates. **International Journal of Environmental Analytical Chemistry**, v. 99, n. 4, p. 310-327, 2019.

HUANG, X. et al. Colonization of Paracoccus sp. QCT6 and enhancement of metribuzin degradation in maize rhizosphere soil. **Current microbiology**, v. 75, n. 2, p. 156-162, 2018.

JAISWAL, D. K. et al. Microbe Induced Degradation of Pesticides in Agricultural Soils. In: SINGH S. (org.).**Microbe-Induced Degradation of Pesticides**: Environmental Science and Engineering. Switzerland: Springer, Cham, 2017. p. 167-189.

KAMARAJ, R. et al. Facile one-pot electrosynthesis of zinc hydroxide for the adsorption of hazardous 2-(2-methyl-4-chlorophenoxy) propionic acid (MCPP) from water and its modelling studies. **Journal of Environmental Chemical Engineering**, v. 6, n. 2, p. 2017-2026, 2018.

KANG, S. et al. Effect of biochar particle size on hydrophobic organic compound sorption kinetics: Applicability of using representative size. **Science of the Total Environment**, v. 619, n. 1, p. 410-418, 2018.

KHAN, M. A.; BROWN, C. D. Influence of commercial formulation on leaching of four pesticides through soil. **Science of the Total Environment**, v. 573, n. 1, p. 1573-1579, 2016.

KHORRAM, M. S. et al. The effects of biochar properties on fomesafen adsorption-desorption capacity of biochar-amended soil. **Water, Air, and Soil Pollution**, v. 229, n. 3, p. 60, 2018.

KIM, S. et al. PubChem 2019 update: improved access to chemical data. **Nucleic Acids Research**, v. 47, n. 1, p. 1102-1109, 2019.

KJÆR, J. et al. Leaching of metribuzin metabolites and the associated contamination of a sandy Danish aquifer. **Environmental Science and Technology**, v. 39, n. 21, p. 8374-8381, 2005.

KLOSS, S. et al. Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties. **Journal of Environmental Quality**, v. 41, n. 4, p. 990-1000, 2012.

LAIRD, D. A. et al. Review of the pyrolysis platform for coproducing bio-oil and biochar. **Biofuels, Bioproducts and Biorefining**, v. 3, n. 5, p. 547-562, 2009.

LEHMANN, J. et al. Bio-char sequestration in terrestrial ecosystems–a review. **Mitigation and Adaptation Strategies for Global Change**, v. 11, n. 2, p. 403-427, 2006.

LEI, O.; ZHANG, R., Effects of biochars derived from different feedstocks and pyrolysis temperatures on soil physical and hydraulic properties. **Journal of Soils and Sediments**, v. 13, n. 9, p. 1561-1572, 2013.

LI, J. et al. Role of alumina and montmorillonite in changing the sorption of herbicides to biochars. **Journal of Agricultural and Food Chemistry**, v. 63, n. 24, p. 5740-5746, 2015.

LI, S.; CHEN, G., Thermogravimetric, thermochemical, and infrared spectral characterization of feedstocks and biochar derived at different pyrolysis temperatures. **Waste Management**, v. 78, n. 1, p. 198-207, 2018.

LUDVÍK, J. et al. Electrochemical reduction of metribuzin. **Electroanalysis:An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis**, v. 10, n. 13, p. 869-876, 1998.

MAJUMDAR, K.; SINGH, N. Effect of soil amendments on sorption and mobility of metribuzin in soils. **Chemosphere**, v. 66, n. 4, p. 630-637, 2007.

MARCO-BROWN, J. L. et al. Adsorption of picloram on clays nontronite, illite and kaolinite: equilibrium and herbicide-clays surface complexes. **Journal of Environmental Science and Health**, Part B, v. 54, n. 4, p. 281-289, 2019.

MARTIN, S. M. et al. Marked changes in herbicide sorption–desorption upon ageing of biochars in soil. **Journal of Hazardous Materials**, v. 231, n. 1, p. 70-78, 2012.

MENCHEN, A. et al. Pesticide contamination in groundwater bodies in the Júcar River European Union pilot basin (SE Spain). **Environmental Monitoring and Assessment**, v. 189, n. 4, p. 146, 2017.

MENDES, K. F. et al. Cow bone char as a sorbent to increase sorption and decrease mobility of hexazinone, metribuzin, and quinclorac in soil. **Geoderma**, v. 343, n. 1, p. 40-49, 2019.

MUKHERJEE, A. et al. Surface chemistry variations among a series of laboratory-produced biochars. **Geoderma,** v. 163, n. 3-4, p. 247-255, 2011.

OECD - Organisation for Economic Co-operation and Development. **OECD Guidelines for the Testing of Chemicals**: Test Number 106, Adsorption – Desorption Using a Batch Equilibrium Method, OECD. Paris, 2000. 44 p.

OUKALI-HAOUCHINE, O. et al. Factors affecting metribuzin retention in Algerian soils and assessment of the risks of contamination. **Environmental monitoring and assessment**, v. 185, n. 5, p. 4107-4115, 2013.

PAPADAKIS, E. N.; PAPADOPOULOU-MOURKIDOU, E., Determination of metribuzin and major conversion products in soils by microwave-assisted water extraction followed by liquid chromatographic analysis of extracts. **Journal of Chromatography A**, v. 962, n. 2, p. 9-20, 2002.

PASSOS, A. B. R. et al. Effects of liming and Urochloa brizantha management on leaching potential of picloram. **Water, Air, and Soil Pollution**, v. 230, n. 1, p. 12, 2019.

PPDB - Pesticide Properties Database. **Creating Tools for Pesticide Risk Assessment and Management in Europe**. Hertfordshire: UK National Sources, 2019. Disponível em: <http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>. Acesso em: 20 ago. 2019.

REN, X. et al. Desorption of atrazine in biochar-amended soils: Effects of root exudates and the aging interactions between biochar and soil. **Chemosphere**, v. 212, n. 1, p. 687-693, 2018.

SANTOS, L. O. G. et al. Effect of liming on hexazinone sorption and desorption behavior in various soils. **Archives of Agronomy and Soil Science**, v. 65, n. 9, p. 1183-1195, 2019.

SILVA, T. S. et al. Use of neural networks to estimate the sorption and desorption coefficients of herbicides: A case study of diuron, hexazinone, and sulfometuron-methyl in Brazil. **Chemosphere**, v. 236, n. 1, p. 124333-124348, 2019.

SINGH, B. et al. Characterization and evaluation of biochars for their application as a soil amendment. **Soil Research**, v. 48, n. 7, p. 516-525, 2010.

SPULER, M. J. et al. Sorption Kinetics of 2, 4-D and Diuron Herbicides in a Urea-Fertilized Andisol. **Journal of Soil Science and Plant Nutrition**, v. 19, n. 2, p. 313-320, 2019.

STEINER, C. et al. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. **Plant and Soil**, v. 291, n. 1, p. 275-290, 2007.

TAN, I. A.W. et al. Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2, 4, 6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. **Journal of Hazardous Materials**, v. 164, n. 2-3, p. 473-482, 2009.

TIRYAKI, O.; TEMUR, C. The fate of pesticide in the environment. **Journal of Biological and Environmental Sciences**, v. 4, n. 10, p. 29-38, 2010.

TOMLIN, C. D. S. (org.), 2009. **The Pesticide Manual**. British Crop Protection Council, Farnham, Surrey, UK : British Crop Protection Council, 2000

TUNEGA, D. et al. Adsorption process of polar and nonpolar compounds in a nanopore model of humic substances. **European Journal of Soil Science**, v. 70 n. 1, p. 1-11, 2019.

WHITE JR, P. M. et al. Sugarcane and pinewood biochar effects on activity and aerobic soil dissipation of metribuzin and pendimethalin. **Industrial Crops and Products**, v. 74, n. 1, p. 737-744, 2015.

WOOLF, D. et al. Sustainable biochar to mitigate global climate change. **Nature Communications**, v. 1, n. 6, p. 56-62, 2010.

WU, C. et al. Sorption, degradation and bioavailability of oxyfluorfen in biochar-amended soils. **Science of The Total Environment**, v. 658, n. 1 p. 87-94, 2019.

XIAO, F.; PIGNATELLO, J. J. Interactions of triazine herbicides with biochar: Steric and electronic effects. **Water Research**, v. 80, n. 1, p. 179-188, 2015.

YAVARI, S. et al. Sorption-desorption mechanisms of imazapic and imazapyr herbicides on biochars produced from agricultural wastes. **Journal of Environmental Chemical Engineering**, v. 4, n. 4, p. 3981-3989, 2016.

ZHANG, G. et al. Sorption of simazine to corn straw biochars prepared at different pyrolytic temperatures. **Environmental Pollution**, v. 159, n. 10, p. 2594-2601, 2011.

ZHANG, H. et al. Effect of Pinus radiata derived biochars on soil sorption and desorption of phenanthrene. **Environmental Pollution**, v. 158, n. 9, p. 2821-2825, 2010.

ZHELEZOVA, A. et al. Effect of biochar amendment and ageing on adsorption and degradation of two herbicides. **Water, Air, and Soil Pollution**, v. 228, n. 6, p. 216-228, 2017.