PLANTA DANINHA

SOCIEDADE BRASILEIRA DA
CIÊNCIA DAS PLANTAS DANINHAS
<http://www.sbcpd.org>

ISSN 0100-8358 (print)
1806-9681 (online)

Literature Review

EFFECT OF ORGANIC MATTER ON THE BEHAVIOR AND CONTROL EFFECTIVENESS OF HERBICIDES IN SOIL

Efeito da Matéria Orgânica no Comportamento e Eficácia de Controle de Herbicidas no Solo

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ABSTRACT - With extensive use of herbicides in agricultural areas, the risk of contamination of groundwater and surface water by these products has become a worldwide concern. Practices of application or maintenance of soil organic residues that have begun to be used in agriculture for soil nutrition have demonstrated other benefits besides nutrient supplementation, such as reduced mobility and increased soil degradation of herbicides. Because it is the final destination of herbicides, soil and its constituents, especially organic matter in tropical soils, play a prominent role in processes that encompass the dynamics of herbicide molecules. In this context, it is necessary to know the influence of the organic matter and its constituents on the behavior of the herbicides. This review discusses the main relationships of organic matter in the retention, transport, and transformation processes of herbicides in the soil, as well as the interference in the weed control effectiveness of these products. Because of this, knowing the influence of organic matter in the various processes related to the behavior of herbicides in the soil allows us to adopt more appropriate management practices regarding both weed control and remediation of contaminated areas. However, despite the wide range of information on the subject in the literature, each situation is distinct due to the wide variation in the behavioral response of the products to the different types of organic material present in the soil.

Keywords: sorption, mobility, biodegradation, organic carbon

RESUMO - Com o uso extensivo de herbicidas em áreas agrícolas, os riscos ambientais de contaminação de águas subterrâneas e superficiais por esses produtos têm se tornado preocupação mundial. Práticas de aplicação ou manutenção de resíduos orgânicos no solo que começaram a ser empregadas na agricultura para a nutrição dos solos têm demonstrado outros benefícios, como redução da mobilidade e aumento da degradação de herbicidas no solo. Por ser o destino final dos herbicidas, o solo e seus constituintes, principalmente a matéria orgânica em solos tropicais, exercem papel de destaque nos processos que abrangem a dinâmica das moléculas de herbicidas. Nesse contexto, há necessidade de se conhecer a influência da matéria orgânica e seus constituintes no comportamento dos herbicidas. Esta revisão de literatura tem por objetivo apontar as principais relações da matéria orgânica nos processos de retenção, transporte e transformação dos herbicidas no solo, além da interferência dela na eficácia de controle de plantas daninhas. Nesse sentido, conhecer a influência da matéria orgânica nos diversos processos relacionados ao comportamento dos herbicidas no solo permite adotar práticas de manejo mais adequadas no que se refere tanto ao controle das plantas daninhas quanto à remediação de áreas contaminadas. Contudo, apesar da ampla gama de informações a respeito do assunto na literatura,

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Received: September 21, 2018
Approved: November 26, 2018

Planta Daninha 2019; v37:e019214401

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Doi: 10.1590/S0100-83582019370100110

cada situação é distinta, devido à grande variação da resposta comportamental dos produtos diante dos diversos tipos de materiais orgânicos presentes no solo.

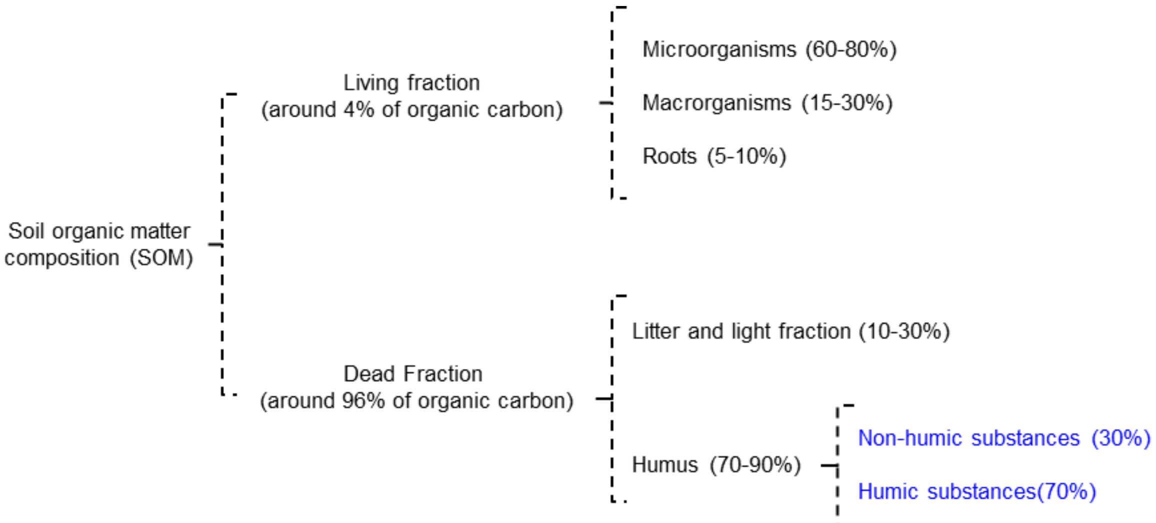
Palavras-chave: sorção, mobilidade, biodegradação, carbono orgânico.

INTRODUCTION

The application of herbicides is commonly used in agricultural systems, as it is a practical and efficient method for weed control. However, after being applied, herbicides may follow different paths in the environment, and the soil its main destination (Oliveira and Brighenti, 2011). Among the soil components, soil organic matter (SOM) has been reported to be an important factor in the retention of herbicides, the reduction of soil profile mobility and the potential for environmental decontamination (López-Piñeiro et al., 2013; Bonfleur et al., 2015; Tejada and Benítez, 2017). In addition to increasing the microbiological activity of soils, SOM also accelerates the biodegradation processes of herbicides (Gómez et al., 2014). Thus, changes made by organic matter (OM) in the soil can decrease the mobility of herbicides in the soil profile and play an important role in the management of environmental pollution due to the use of these molecules (Rojas et al., 2013).

The SOM may be defined as any material originating from animals or plants in the soil (litter, root exudates, and soluble humic compounds) either fresh or at different stages of decomposition (Stevenson, 1994). Typically, SOM is estimated by the organic carbon content (OC), which can vary in quantity and quality depending on the source, and it is subdivided into living (4%) and dead (96%) portions (Figure 1). Theoretically, the dead SOM is divided into non-humidified (less stable) and humidified fractions (greater stability). The higher stability of this last fraction is related to the greater binding constancy with the mineral fraction of the soil and resistance to soil decomposition (Stevenson, 1982). The less stable fraction is generally composed of carbohydrates (5-10%), lignin (10-30%), proteins and peptides (10-20%) and fractions soluble in alcohol and ether, such as fats, oils, greases, and pigments (5%) (Guerra et al., 2008). The most stable compounds are derivatives of the chemical and biological degradation of organic waste, consisting of polyphenols, mainly carboxyl groups (-COOH) and phenolics (-OH). Most of the soil cation exchange reactions occur due to the dissociation of these compounds and the generation of negative charges in the soil (Novotny and Martin-Neto, 2008).

In clay soils, SOM is responsible for 30-40% of the cation exchange capacity (CEC) and 50-60% in of the CEC in sandy soils (Verdade, 1956). Alves et al. (2001), when analyzing the humic



Fonte: Adapted from Theng et al. (1989).

Figure 1 **-** Scheme of the organic matter composition of the soil.

substances of vermicompost, verified a higher degree of aromatic structures in the samples of soils altered with these materials, which gave them greater CEC, and contributed to the greater sorption of the alachlor, in relation to the unchanged soils. In addition, negative charges of CEC are pH-dependent, and as pH increases, as happens in agricultural soils where the acidity must be corrected for cultivation, there is a dissociation of the organic groups and significant increase of their loads (Silva and Mendonça, 2007). According to Bayer and Mielniczuk (1999), in highly weathered tropical and subtropical soils, SOM has great importance to nutrient supply, cation retention, complexation of toxic and micronutrient elements, physical stability, aeration, infiltration and water retention, as well as the maintenance of microbial activity. Its contribution to the cation retention was estimated to be between 20% and 90% of the CEC of the soils (Raij, 1981; Canellas et al., 2003; Alvarez-Puebla et al., 2005; Bayer and Mielniczuk, 2008). The retention of cations is the main process that interferes in the behavior of the herbicides in the soil by the SOM, favoring the reduction of leaching and the availability of the herbicide molecules to degradation.

The content of SOM and CEC in soils may correlate with sorption of herbicides and reductions in their bioavailability (Bailey and White, 1964). The bioavailability of herbicides is inherent to absorption processes and weed control, as well as the availability of products to microbial degradation and their reduction as a contaminant in the environment. Song et al. (2010) found lower phytotoxicity of chlorotoluron in wheat plants in soils altered with sewage sludge and straw, indicating a lower bioavailability of the herbicide absorbed in the soil.

The origin of the organic material added to the soil influences the composition of the SOM and its interaction with herbicides. Different materials, such as straw, biochar (charcoal), bonechar (animal charcoal), sewage sludge, crop residues and agroindustrial waste, have been studied not only to increase soil OC and nutrient contents, but also to influence herbicide behaviors in soil (Fenoll et al., 2014a; Rittenhouse et al., 2014; Tejada and Benítez, 2017; Mendes et al., 2018a,b). Therefore, this literature review has as its objective to point out the main relationships of SOM to the retention, transport and transformation processes of herbicides in the soil, in addition to the its interference of in weed control efficiency.

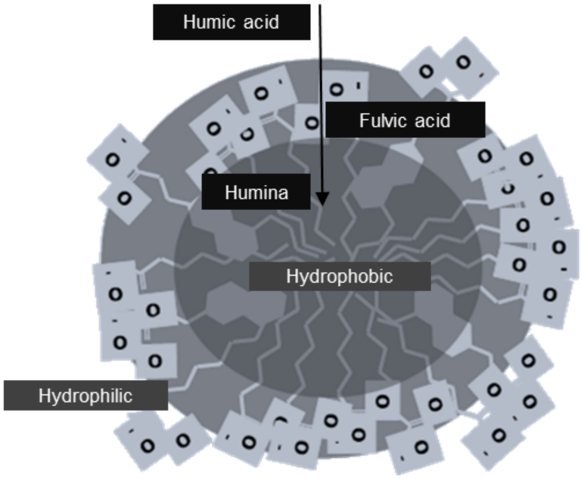
ORGANIC MATTER OF THE SOIL IN RETENTION OF HERBICIDES

Retention, characterized by sorption to the soil particles, is the main process that regulates the behavior of herbicides in the soil. It can help to explain and predict the other processes of herbicide dissipation in the environment, such as mobility and degradation (Iglesias et al., 2010). The affinity of a molecule is expressed by the sorption constant, K_d (ratio of the concentration of the molecule in the soil colloids to its equilibrium concentration in the soil solution). Mendes et al. (2014) found a significant correlation between the K_d of diuron, hexazinone, and sulfometuron-methyl and the levels of SOM and CEC of Brazilian soils. The K_d increases with the OC content of the soil and, therefore, the values of K_d are generally normalized for the OC content of the soil, obtaining K_{oc} (Smernik and Kookana, 2015). However, this relation is not exact, due to the great variation in the forms and content of OC present in the soils. Nevertheless, in the works reported, the K_f and K_{foc} coefficients (adjusted to the Freundlich model) are used to indicate sorption of the herbicides in soils.

The linkages between herbicide molecules and soil organic compounds can occur through physical forces, such as hydrogen bonds, van der Waals forces, electrostatic forces, covalent bonds, and hydrophobic interactions, simultaneously acting on the sorption of the same molecule (Prata and Lavorenti, 2000). According to Silva et al. (2014), the major forces acting on the surface of SOM are the hydrogen bonds, with carboxylic, phenolic, and amide groups, as well as hydrophobic bonds at the sorption sites increased in the soil by the addition of organic residues. According to Gleber and Spadotto (2004) the sorption forces between herbicides and SOM are classified as very strong (K_{oc} > 5,000 L kg^{-1}), strong (K_{oc} 600-4,999 L kg^{-1}), moderate (K_{oc} 100-599 L kg^{-1}) and weak (K_{oc} 0.5-99 L kg^{-1}).

Among the soil SOM fractions, the humic substances are the primary adsorbents of herbicides (Cox et al., 2000). Humic substances are divided according to their degree of humification (fulvic acid < humic acid < humin), so that each fraction exerts a distinct effect on the behavior of the herbicides. The more lipophilic herbicides have greater sorption and, the higher the K_{ow} value of the herbicide, the greater its retention potential on hydrophobic surfaces, such as the organic matter of the soil (higher degree of humification) (Oliveira and Brighenti, 2011; Silva et al., 2014). In the literature, there are reports of the positive correlation between the aromatic C of the humic acids and the K_{oc} values of the herbicides (Ahmad et al., 2001; Ahangar et al., 2008; Mitchell and Simpson, 2013). For linuron, Dorado et al. (2005) found higher retention affinity in soils with humic acids. Ferri et al. (2005) verified values of K_d and K_{oc} six and nine times, respectively, higher for alachlor for humins, in relation to humic acids. This is due to the higher oxidation and the aliphatic character of the humin fractions, so that the bonding with functional groups oxygenated by hydrogen bonds and the hydrophobic bonds with those with aliphatic groups favored the connections with alachlor and humin. Chefetz et al. (2000) showed ten times higher values for humin hydrophobic compounds K_{oc}. However, this fact can vary among the soils and the chemistries of the SOM present; the sorption behavior is affected by the heterogeneity and nature of the supramolecular structures of the humic substances in the soil (Piccolo, 2001; Simpson et al., 2002). In accordance with the supramolecular structures of the humic substances in the soil (Figure 2), it is possible to verify that the higher degree of humification of the humic substances favors the hydrophobic bonding of herbicides. This is contrary to the lower degree of humification, which may favor the retention of herbicides by hydrogen bonds. In addition, there are other factors that can alter the sorption behavior of herbicides in the SOM, such as their interaction with soil minerals.

Celis et al. (1999) found lower sorption for 2,4-D in montmorillonite-ferrihydrite complexes coated with humic acids, indicating the blockage of action sites by these substances. Cox et al. (2000) indicated the competition of dissolved organic matter (DOM), present in liquid commercial humic acids, with soil sorption sites of montmorillonite for simazine. In this same sense, Arroyave et al. (2016) verified that humic acids reduce the sorption of glyphosate onto goethite, because there was saturation of the surface of the mineral by this humic substance.



Fonte: Adapted from Sutton and Sposito et al. (2005).

Figure 2 **-** Structural model of the humic substances according to the degree of humification in the soil.

The physical-chemical properties of the soil exert effects on soil retention and behavior of soil herbicides, such as SOM content, iron and manganese clays and oxides, pH, cation exchange capacity, specific surface area, porosity, moisture, and the presence and diversity of microorganisms (Costa et al., 2004). Herbicides can be retained by both the organic fraction and the mineral fraction of the soils (Elkhattabi et al., 2007). The mineral fraction may have a significant contribution in the sorption of polar herbicides or in soils with low levels of SOM (Celis et al., 1999). When present, SOM exerts influence on the increase of soil CEC (Ramos et al., 2018), contributing to an increase of herbicide binding and retention sites in the soil. However, this SOM can also be chemically protected, forming organomineral complexes, and it can be responsible for variations in the sorption coefficients of the herbicides (Silva et al., 2014). Bonfleur et al. (2006) found that, after physical fractionation of tropical Latosols under a no-tillage system, the sorption of alachlor, bentazone, and imazethapyr increased. These results indicated that the organomineral complexes might have led to the blockade of sorption sites in the SOM by the mineral, which, after being broken down, made the sites available to herbicides.

Among the physicochemical properties of herbicides, the K_{ow} (octanol-water partition coefficient) is what most indicates the affinity of the molecules for the organic fractions of the soil. The connections between nonionic and neutral herbicides are favored with the addition of organic material to the soil, since these residues increase the number of hydrophobic soil binding sites (Procópio et al., 2001; Silva et al., 2014). Nègre et al. (2001), comparing sorptions of herbicides from the imidazolinones group, reported that the more apolar nature of imazaquin (log K_{ow} = 1.09) conferred greater binding affinity for SOM than imazapyr (log K_{ow} = 0.11). Rojas et al. (2013) found lower values of K_{oc} in soils amended with organic residues for atrazine (131-462 L kg^{-1}), when compared with alachlor (173-1545 L kg^{-1}), due to the more hydrophobic character of the last herbicide.

Another important physicochemical property is the acid dissociation constant (pK_a) for sorption in the SOM, because in soils with SOM, the abrupt pH variations are smaller. In agricultural soils where pH should be close to neutrality, ionizable herbicides, such as weak acids, can be found in the anionic form, because the pH is higher than pKa, and there is less sorption at the SOM sites. For Cañero et al. (2012), there were higher dissolved OC levels in soils altered with organic waste from olive oil production. These residues lowered the pH values, so that bentazone sorption (pKa = 3.2) was higher (K_f = 1.70 $\mu mol^{1"1/n}$ kg^{-1} $L^{1/n}$) at lower pH values (5.3), due to the higher number of molecules in the molecular (non-ionized) form with increasing pH. For nonionic and neutral herbicides, the affinity with SOM is more pronounced, especially when these compounds are more hydrophobic. For non-ionic herbicides such as isoproturon, moderately hydrophobic (log K_{ow} = 2.5), and strongly hydrophobic diflufenican (log K_{ow} = 4.9), Benoit et al. (2008) found greater sorption for diflufenican (K_{oc} = 604-4780 L kg^{-1}) when compared to isoproturon (K_{oc} = 25-179 L kg^{-1}), regardless of the size of the particulate SOM and the management system.

A good comparison of the effect of SOM on herbicide retention is cropping systems. In a no-tillage system, Ding et al. (2002) verified a higher aromaticity of humic acids (5.3%) and humin (12.6%) compared to the conventional soil preparation system, due to the increase in the number of sorption sites. Similarly, the same authors indicated that sorption of metolachlor was more pronounced in no-tillage system (K_{foc} = $4.19x10^4$ µg (g of OC)$^{-1}$), when compared to the conventional system (K_{foc} = $3.75x10^4$ µg (g of OC)$^{-1}$). For metolachlor and atrazine, the amounts of the sorbed compounds increased according to the increase of surface OC in direct seeding systems (Pusino et al., 1992; Levanon et al., 1993). In addition to the straw, the use of exogenous OM in cropping systems, such as the application of biochar (coal derived from vegetal biomass), has affected the retention and dynamics of herbicides in the soil. This is due to the high OC contents, higher surface areas and more porous structures, which result in higher herbicide sorption capacities (Mesa and Spokas, 2011; Mendes et al., 2018b). Several studies have indicated higher sorption of herbicides, such as atrazine, MCPA, aminocyclopyrachlor and terbuthylazine in soils modified with biochar and bonechar (Wang et al., 2010; Martin et al., 2012; Tatarková et al., 2013; Cabrera et al., 2014).

Within the retention process, there is not only the permanent sorption of herbicides to soil particles, but also a reversible process called desorption. In soil, the herbicide may be strongly bound to and retained on a surface or be weakly bound and return to the soil solution (Wu et al., 2011). When complexed with SOM, this binding force becomes larger and, consequently, there is a reduction in the desorption capacities of molecules. Petter et al. (2016) indicated a reduction of 30-57% desorption of diuron in altered soil with 16 Mg ha^{-1} biochar. Still, when sorption is practically irreversible, there is no desorption of the product; there is a phenomenon called hysteresis (Silva et al., 2007). In this sense, Passos et al. (2013) indicated the occurrence of sulfentrazone hysteresis in the Neossolo Regolítico because of its higher OC (2.96%).

When the desorption process becomes irreversible, the herbicidal molecules may be strongly bound to humic substances, forming what is known as bound residue. These residues are not extractable from the soil with the use of solvents without alteration of the molecule or matrix (soil), which, when formed, reduces the bioavailability of the herbicides in the soil (Führ et al., 1987; Prata and Lavorenti, 2000). Therefore, SOM is primarily responsible for the formation of this bound residue (Prata and Lavorenti, 2000). According to Khan (1991), the herbicide molecules are strongly retained by the humic fractions because of processes involving sorption to the external surfaces and penetration by the internal spaces of the organic substances. Elkhattabi et al. (2007) found that 65% of isoproturon, in the form of bound residue (residue not extracted), was associated with SOM, with the highest accumulation in fulvic acid and humin fractions at the end of the incubation period (30 days). Similarly, Barriuso et al. (1991) found 15% to 40% of the atrazine bound residue associated with organic compounds in the soil. Furthermore, they indicated that 59% of the bound residue of this herbicide was in soil with 7% OC. However, even while in the form of bound residue, and unavailable for degradation and transport, as well as for weed control, herbicides can still be remobilized. Thus, the role of SOM in this process will be discussed later.

The factors affecting the sorption processes determine the other routes to be taken by the herbicides in the soil. The bioavailability for weed absorption can be altered with the addition of OM in the soil, and there may be a reduction in the risk of phytotoxicity of the herbicide (Szmigielski et al., 2009; Gannon et al., 2014; Schneider et al., 2015). For acidic, polar, and low pK_a herbicides, this influence of OM on the behavior of the product in the environment may be lower, since they have low affinity of sorption with the SOM (Stevenson, 1972). Thus, retention is a balancing factor between the effectiveness of the herbicide and the dissipation in the environment, by means of transport and/or degradation. The effect of SOM in these two processes will be discussed in the next few topics.

ORGANIC MATTER OF SOIL IN TRANSPORTATION OF HERBICIDES

Among the processes of herbicide transport in the soil, leaching is important because of the potential contamination of the groundwater. According to Prata et al. (2003), the leaching process is influenced by the content and type of SOM, composition, size, and distribution of soil particles, pH, soil density, pore size, and distribution, and is the main form of transport within the soil of non-volatile and water-soluble molecules.

According to Oliveira (2001), to be leached, the herbicide must be in soil solution or adsorbed to small particles, such as clays, low molecular weight fulvic and humic acids, amino acids, peptides and sugars, among others. These different fractions can contribute in different ways to the transport of the herbicides in the soil. Haberhauer et al. (2002) identified higher MCPA leaching in soil columns with humic acids dissolved in solution; and in columns with fulvic acids, the retention was greater. Due to the more hydrophilic character ($\log K_{ow} = -0.81$) of MCPA, the connection with the less hydrophobic fraction of the humic substances (fulvic acid) was favored. Therefore, the origin and composition of the total carbon present in the soils interfered in the mobility of the herbicide. In this context, different materials can be presented as potential minimizers of herbicide leaching. For soils altered with olive oil residues (fresh, composted and aged), López-Piñeiro et al. (2013) found a reduction in the amount of metribuzin that was leached in Mediterranean soils, indicating that, irrespective of the degree of humification, there was a reduction in leaching with the application of these organic residues in the soil.

According to Briceño et al. (2007), agronomic practices such as the incorporation of organic waste have often been carried out to reduce herbicide leaching. As for flazasulfuron, Tejada and Benítez (2017) found lower concentrations (3.5, 5.4, and 6.9 µM) of this herbicide in leachates of altered soils with organic residues (urban solid waste, chicken manure and bovine manure), in relation to the soil without these materials (8.9 µM). By studying the behavior of the triazines and triazinones herbicide groups, Fenoll et al. (2014a) observed a reduction in herbicide leaching in soils altered with compound of sheep manure, coffee grounds, composting of pine bark and coconut fiber. Mendes et al. (2018a), in soils amended with bonechar (coal derived from bovine bones) applied superficially, they obtained total retention of the herbicides aminocylopyrachlor and mesotrione, indicating the potential of bonechar to be a remover of this material. Mendes et al. (2016) found higher oxadiazon concentrations above the 0.10 m depth in the soil profile, 64 days after herbicide application, and low concentrations of herbicides at the other depths. This was due to the higher affinity of the herbicide for the SOM contents (4.3 and 4.9%) present in soils, resulting in less product mobility. This relationship allowed greater herbicide efficacy in the more superficial layers in which the seed bank is found and a lower groundwater contamination risk.

In addition to the type of organic material present and the characteristics of the herbicide, the soil physical conditions interfere with the water flow and entrapment of the molecules. The OM plays a fundamental role in soil aggregation and porosity. Bonfleur et al. (2015), in a sorption study with several herbicides, found a higher positive correlation in the sorption of alachlor, bentazon and imazethapyr with aggregates of a tropical soil, larger than the clay particles, that were formed by clay and OC. With sorption in these soil aggregates, the leaching reduction of these herbicides occurred in the soil profile. Moreover, soil aggregation generally reduces water flow in the soil profile and herbicide movement, as more water-soluble herbicides are more likely to leach (Alletto et al., 2010), due to the influence of the flow of water in this process. As for porosity, organic materials and aggregation increase the number of pores and the water retention capacity in the soil. Delwiche et al. (2014) found a reduction of 52% in the leaching of atrazine in columns modified with biochar derived from pine, due to the greater presence of micropores, which played a significant role in the entrapment and accumulation of the herbicide around the biochar particles.

A fraction of the OM can be dissolved in the soil solution (dissolved organic matter, DOM). The DOM has its origin from the percolation of the litter and the activity of the soil microbial biomass, molecular organic acids, and macromolecular structures (enzymes, humic acids, polyphenols and amino sugars) (Traversa and D'Orazio, 2008). This fraction is composed of organic colloids dispersed in solution is due to their high surface charge (Barriuso et al., 2011). Cox et al. (2004) and Williams et al. (2002) have stated that limitations on the role of SOM in the reduction of herbicide leaching should be taken into account, since the presence of DOM may favor leaching through herbicide interactions (facilitated transport), as well as interactions on soil surfaces (sorption competition).

In addition to leaching, the molecules can be transported by runoff. The use of systems that increase the organic material on the soil, as well as the aggregation of the particles in its profile, promotes the reduction of this effect. Sauer and Daniel (1987) affirmed that no-tillage systems reduced the runoff of atrazine and alachlor, generally superior to conventional farming systems, because the straw reduced the erosion of the soil particles in which the herbicide may be retained. In addition to runoff minimization, the physical effects of MOS include improving aggregation, increasing the number of micropores, and decreasing the number of macropores in the soil, which can alter herbicide leaching in the profile. Cox et al. (2001) observed that the reduction in large pores by the addition of sewage sludge to the soil led to a reduction in the movement of simazine. Cañero et al. (2012) indicated an increase in the total number of pores of soils altered with organic residues of olive oil production, obtaining a greater sorption of bentazone (K_f = 1.70 $\mu mol^{1"1/n}$ kg^{-1} $L^{1/n}$) and, consequently, a lower risk of leaching. This indicates that several factors related to or associated with SOM along with sorption of the herbicide may affect the mobility of the herbicides in the soil.

Volatilization is also a type of herbicide transport in the environment. This process occurs from water or soil to the atmosphere. According to Blasioli et al. (2011), the transport of herbicides between these interfaces depends on characteristics of the molecule (moisture, porosity, density, SOM and clay), soil moisture (porosity, density, SOM and clay), and soil moisture content, as well as the concentration in the environment and climatic conditions (temperature, humidity, and wind speed). Thus, volatilization is a process directly influenced by sorption, as are other types of transport. In this sense, the OC content of the soil can be determinant in the reduction of the loss of herbicide to the environment by volatilization. For clomazone, a herbicide with high volatility (19.2 mPa at 20 ^{o}C) (PPDB, 2018), Loux et al. (1989) verified that soil with high OC content decreased the volatilization losses of this product due to the increase of the sorption. On the other hand, even with the low sorption of the 2,4-D to SOM there was low volatilization of that product, because this process does not depend only on the sorption. In this case, it was due to the low H (4.0×10^{-06} Pa m^3 mol^{-1}) (PPDB, 2018) and rapid rate of degradation (Jury et al., 1983).

The SOM can also contribute to the loss of the herbicide by volatilization. Whang et al., (1993) reported a higher percentage of atrazine volatilization (0.9%) in conservation planting when compared to conventional planting. Mills et al. (1989) found that more than 40% of the clomazone applied in a no-tillage system did not reach the soil surface, and was intercepted by the straw and volatilized. Wienhold and Gish (1994) also observed higher volatilization of alachlor and atrazine under conservation tillage in relation to conventional cultivation. Both works indicated that the presence of organic material on the soil contributes to the increase of the volatilization of the products, due to the greater exposure of the herbicides to the environment. However, these last authors verified that the scenario was altered after the first rain, because the products are exposed to the soil particles, and were subject to the other behaviors in the environment, such as sorption and degradation.

The losses of herbicides by the transport processes are higher with volatilization (up to 90% of the total applied), followed by runoff (about 10% of the total applied) and leaching (4% of the total applied) (Plimmer, 1992; Oliveira Jr., 2002). Even with the lowest loss percentages, the runoff and leaching processes are those that directly contribute to the contamination of groundwater and surface waters, and leaching is the process that contributes most to water pollution. (Flury, 1996). The SOM, whether it comes from no-tillage system, agroindustrial, or natural soil residues, generally reduces the losses of herbicides by transport in the soil, since the higher the sorption, especially in OC in the soil, the lower the transport is (Alister et al., 2011). It acts on this reduction through sorption, physical barriers, or improvement of water retention conditions in soils (Jiang et al., 2011; Silva et al., 2018; Alletto et al., 2012). However, soil DOM can have the opposite effect on herbicides (Ding et al., 2011; Navarro et al., 2012), with the fundamental leaching of herbicides in the soil profile, for effects on weed seeds and roots (Oliveira, 2001). Thus, the lower the transport of herbicides in the soil, the lower the risks of environmental contamination by them are.

ORGANIC MATTER OF THE SOIL IN THE TRANSFORMATION OF HERBICIDES

Herbicides commonly have their degradation favored in environments with active soil microbiota. According to Gómez et al. (2014), the organic compounds increase the microbiological activity of the soil. To degrade the herbicides, the microorganisms need energy which is variable and dependent on the chemical composition of the SOM and soil inherent factors (Tejada et al., 2010; Tejada and Benítz, 2011; Tejada et al., 2011). Fenoll et al. (2014a) observed that, for unamended soils with organic residues, the half-lives ($t_{1/2}$) of the triazine and triazinone groups of herbicides were higher. In this case, atrazine, for example, had the 139-day $t_{1/2}$ changed to 39 days with the addition of sheep manure to the soil and to five days with coconut fiber. The authors affirm that it was not possible to generalize the occurrence of this reduction, since each material exerted a different effect on the microbiota and the degradation of the herbicides. Thus, for soils altered with solid residues from the olive oil extraction process, Albarrán et al. (2003) found that the biodegradation of simazine was reduced because of the microbial preference for the SOM added to the soil compared to the herbicide. For propanil, Fenoll et al. (2014b) found $t_{1/2}$ values between 2.3 and 6.8 days in soils altered with sheep manure, coffee grounds, pine bark and coconut fiber, when compared to the unchanged soil, where $t_{1/2}$ was 1-7 days. However, Gigliotti et al. (2005) did not find any relationship between the addition of municipal residue compound to the soil and the degradation of triflusulfuron-methyl, obtaining a $t_{1/2}$ of 17 days with soil amendment and 18 days for unchanged soils. Most of the available soil carbon is in the first few centimeters of the soil profile. However, even in the deeper layers, where total carbon content is low, herbicide biodegradation may be the most important process that prevents the leaching of these compounds (Kalbitz et al., 2000; Cheyns et al., 2012). Therefore, soil microorganisms do not specialize in a specific substrate, but use all available carbon compounds (Egli, 1995). Cheyns et al. (2012) verified that, by adding glucose to the soil as a source of carbon to *Chelatobacter heintzii* SalB, at low concentrations (10 mg of C L^{-1}), there was an increase in the degradation of atrazine. This fact indicated that even with low concentrations of organic carbon, as with depth in the soil profile, there might be degradation of herbicides. However, there is variation as to the type of material present.

In addition to increasing the microbial population in the soil by serving as an energy source, SOM can aid in degradation processes in other ways. According to Tejada and Benítez (2017), the excretion of enzymes by microorganisms may contribute to the chemical degradation of herbicides. These enzymes may be associated with complex humus-enzymes; catalysts of the degradation processes are more stable than the free enzymes in the soils (Tejada and Benítez, 2011). Mandelbaum et al. (1993) showed that the relationship between the high content of SOM and the formation of hydroxyiatrazine (a non-toxic metabolite resulting from atrazine degradation) is due to the increase in enzymatic activity in soils, even in situations where there is no microbial degradation.

Another function of SOM in herbicide transformation is the possibility of remobilization of residues bound to the soil. This occurs because the microorganisms with the ability to make these compounds become bioavailable in the soil (Khan and Ivarson, 1981). According to

Lavorenti et al. (1998), remobilization is the process related to the new form of organization that happens with the herbicides after they are bound residues and become bioavailable to the soil solution, which is still a form of remediation of areas contaminated by the herbicide. However, this process may be slow, since the cycling of SOM itself occurs rather slowly (Bollag, 1991). Peixoto et al. (2005), in agreement with this fact, verified a low remobilization of atrazine associated to the humic substances, even in soil with the addition of glucose and organic material as energy sources for the degrading microbiota. Loiseau and Bariuso (2002) indicated that the presence of atrazine bound residue (10-40% of total applied) depended on the presence of microflora capable of mineralizing the triazine ring of this herbicide, since this product was associated with humic acids and formed residues bound to SOM.

The transformation of herbicides, in addition to being carried out by microorganisms, can occur by abiotic means, and SOM can interfere in these degradation processes. Elazzouli et al. (2002) reported that the presence of humic acids in water induced an increase in the photodegradation of imazethapyr, because when it is sorbed to humic substances, it exerts a protective effect on them, and is more exposed to photolysis (Kononova, 1966). This increase of the photolysis of herbicides in the presence of humic substances can also be indirect, with the sensitization of photochemical reactions, through the generation of reactive oxygen species (Albanis et al., 2002; Kraemer et al., 2009). These species become capable of diffusing up to 1 mm deep in the soil, causing indirect photolysis, compared to the direct reaction by light, which occurs only 0.3 mm deep. However, Elazzouli et al. (2002) reported that the presence of humic acids reduces the photolysis of herbicides, since the photolysis of imazethapyr decreased in the presence of humic acids in aqueous solution, due to the competition between the substances for light. Albanis et al. (2002) found that the protective effect could also be caused by SOM, so that in soil with a higher content of SOM (2.3%), there were longer half-life values obtained for the herbicides triasulfuron and thifensulfuron-methyl, in relation to the soil with a lower SOM content (0.9%). Similarly, Curran et al. (1992) emphasized the importance of SOM in the photolysis of herbicides applied in pre-emergence, as this protection occurs as a function of sorption of the herbicides to the SOM particles, which was verified by other transport and transformation processes, where herbicide retention was the determining factor in the fate of these products in the soil.

In general, the degradation of herbicides in the soil can be potentiated when associated with the presence of SOM. Environmentally, it is interesting that there is a reduction in the persistence of an herbicide, indicating reduced environmental contamination. For weed control, soil residuals, as well as carryover, associated with the presence of SOM are important points to be discussed and verified, since they interfere directly in herbicide management. However, on both sides of the discussion, the interference of SOM and its importance in agricultural management is clear, because in each situation, there will be a different possibility of the interaction of the herbicides with the SOM.

ORGANIC MATTER OF THE SOIL IN THE EFFECTIVENESS OF WEED CONTROL

SOM is intrinsically linked to herbicide efficacy in weed control, as it directly influences herbicide behavioral factors, such as the bioavailability of product absorption, which regulates management success (Ferri et al., 2002). The bioavailability of the herbicides in the soil depends on the particular characteristics of each molecule. When the molecules have higher retention in SOM, such as in the case of nonionic and neutral herbicides, due to the greater affinity with the hydrophobic components of SOM, there is a lower availability for weed absorption and control. Mendes et al. (2016) found greater $t_{1/2}$ of dissipation values (9 days) for oxadiazon (nonionic herbicide, with log K_{ow} of 5.33) in soil containing incorporated organic material, compared to soil without the addition of organic material ($t_{1/2}$ = 6 days). The authors indicated that even with a short $t_{1/2}$ of dissipation; the herbicide remained more concentrated in the first centimeters of the soil, especially when in the presence of organic material. According to Jursík et al. (2010), this herbicide, when persisting in the soil, may be bioavailable for absorption by weeds. Another major influence of SOM on weed control can be observed in leaching studies. Inoue et al. (2008) analyzed the leaching of diuron in two soils and concluded that their movement was restricted to the superficial layers of the soil (0-10 cm). Even when they used a high dose of the herbicide

(3.2 kg ha^{-1}), the movement did not increase significantly, and it was practically undetectable after 15 cm of depth. Consequently, the accumulation of biomass in the indicator species used in the study was lower, due to the high concentration of the herbicide in these superficial soil layers.

Knowing that SOM favors sorption of herbicides, the intensity with which the management affects the residual activity of these products depends mainly on the effects on the content and infiltration of water and on the content of SOM (Ferri et al., 2002). To illustrate this fact, we mention the direct sowing system, which can promote an increase of the density and the OC content in the superficial layers of the soil and, consequently, favor the sorption of the herbicides (Ferri et al., 2002). These authors concluded that the values obtained from K_{oc} suggest that the higher retention capacity of acetochlor in direct seeding was not only associated with the higher OC content, but also with the characteristics of the SOM. Monquero et al. (2008) verified in their studies that the residual effect of isoxaflutole was higher in soil with higher SOM contents and clayey texture, but this fact does not always necessarily mean greater efficacy. The same authors verified that the application of an ametryn + clomazone mixture on sugarcane straw at doses of 10 and 15 t ha^{-1} adversely affected their effectiveness. Furthermore, the diuron + hexazinone mixture with no straw in the soil proved to be effective at control until 40 days after application (DAA). However, in the treatment with 15 t ha^{-1} of straw, there was a profound reduction in the effectiveness of this herbicide at 10 DAA. The fact can be explained by the greater retention of the mixture by the SOM (straw) of the system. Oliveira et al. (2001) evaluated the effect of straw and the mixture of atrazine and metolachlor on weed control in corn. The authors concluded that the low precipitation (10 mm) during the first weeks after application might not have been sufficient to remove metolachlor from the straw, contributing significantly to the reduction in grass control; therefore, when the no-tillage system is used, this herbicide is expected to be less effective.

In addition to the effects related to the retention and increase of the residual effect of the herbicides, when associated with SOM in direct sowing system, a reduction in their persistence can occur when SOM is in the soil. Monquero et al. (2008) indicated that the efficacy of isoxaflutole with 15 t ha^{-1} of straw was lower from 20 DAA for medium textured soil and 40 DAA for clayey soil, and the cause was linked to the biodegradation of the product. This occurs with the increase in soil moisture content and SOM in the raw cane system, due to the large accumulation of straw. This increase favors the soil microbial community, which will degrade the herbicide faster, which limits efficiency, requires higher doses and, consequently, increases production costs.

The bioavailability of the herbicides and the residual effect vary according to the interaction of the herbicide with the SOM. The characteristics of SOM may interfere with this herbicide availability, as verified by Toth et al. (1999), where the phytotoxicity of diuron was reduced in soil with addition of ash, due to the sorption of the herbicide in this material. Still, for diuron, soils with addition of wheat straw coal and rice biochar had sorption values 400 and 2,500 times greater than soil with 2.1% of OM (Yang and Sheng, 2003). Loganathan et al. (2009) verified the same effect of reducing the availability of atrazine in soil with wheat charcoal. The differences between the materials added to the soil under different management systems also contribute to the change in bioavailability of herbicides. According to Gámiz et al. (2012), the addition of olive mill residues to the soil promotes an increase in the persistence of fluometuron, due to its sorption to the SOM, and, consequently, the availability of the product for efficacy in weed control. In addition to sorption, SOM may increase the possibility of degradation of the product, which reduces its control efficacy, as verified by Said-Pullicino et al. (2004), who found that the addition of municipal waste to the soil promoted the abiotic degradation potential of triasulfuron (hydrolysis). In addition to reducing the bioavailability of herbicides, the organic material present on the soil surface can exert a physical effect of preventing the germination of weeds (Favarato et al., 2014; Campiglia et al., 2015) and/or an allelopathic effect (Khan et al., 2016; Shahbyki et al., 2018) on these, with the possibility of reducing the use of herbicides. In this sense, the increase of residual herbicide doses, with the justification that a significant amount of the product is retained in the straw and does not reach the soil, is not valid in all situations. The herbicide is wasted, and there is a consequent increase of costs and damages to the environment if the herbicide is applied without the actual need of use (Oliveira et al., 2001).

The residual effect of herbicides in areas that have a high content of SOM may increase due to the high retention of the material. Depending on the physico-chemical characteristics of the herbicides and the soils, the herbicides may return to the soil solutions or become strongly adhered as bound residue. There are studies that demonstrate that the dissipation of herbicides is dependent on SOM. Mendes et al. (2016) observed that oxadiazon $t_{1/2}$ was higher in MOS treated soils than in those without treatment. Melo et al. (2010) studied the residual effects of sulfentrazone, isoxaflutole, and oxyfluorfen in three different soils. Sulfentrazone had a high residual effect in the three studied soils; the greater residual effect of oxyfluorfen was observed in the sandy loam soil, and isoxaflutole had more residual effect in the loam soil with a high content of SOM.

For herbicides that have higher affinities for SOM and, consequently, high sorptions, there is a great reduction of degradability, and the residual effect on the soil may be more pronounced. In the same sense, for herbicides whose sorption ratio is low relative to the SOM (ionizable), there are greater chances of dissipation of these herbicides in the environment, with reduced residual effects. According to the several studies cited, the importance of SOM for the regulation of herbicide performance and the influence it exerts on weed control are clear. The farmer who aims at reducing costs and effective weed control should know that understanding the dynamics of SOM is essential.

The addition or maintenance of SOM is of utmost importance not only for the nutritional, biological, and physical benefits of the soil, but also for the possibility of reducing the risks of contamination of soil and water resources by herbicides. Research on this subject has been conducted for several years, and a wide variety of information is available. However, they are not definitive, since each organic material, soil type and herbicide molecule interacts in a different way and can generate information different from others found in the scientific literature. On the other hand, knowing the influence of OC and SOM fractions allows us to adopt adequate management practices in situations where herbicides are present. These include the use of higher doses of herbicides in soils with higher contents of SOM and clay (Agostinetto et al., 2015) and prevention of contamination of water resources by herbicides with application of agricultural residues in soil (Rodríguez-Cruz et al., 2012). Furthermore, application of herbicides under straw, with attention to drought periods and/or affinity of the herbicide with straw (Rossi et al., 2013) may be necessary. The reduction in the persistence of herbicides can be accomplished with the use of organic materials in soil, in addition to promoting the growth of the microbiota (Fenoll et al., 2014a), and remediation of soils contaminated with herbicides (Madalão et al., 2015; Trevisan et al., 2016).

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