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Literature Review

SULFENTRAZONE: ENVIRONMENTAL DYNAMICS AND SELECTIVITY

Sulfentrazone: Dinâmica Ambiental e Seletividade

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ABSTRACT - Sulfentrazone is a pre-emergence herbicide that inhibits protoporphyrinogen oxidase (Protox). Its use has emphasis on areas like soybeans planted in lowlands, soybean, and sugarcane in areas of cerrado, and also in the implementation of eucalyptus afforestation. The use of sulfentrazone into resistant weed management programs mainly to glyphosate and acetolactate synthase (ALS) inhibitors has been successful. However, the information on the environmental behavior of this herbicide is limited, even more restricted when it refers to the lowland areas where problems are frequently observed regarding the selectivity of sulfentrazone, due to the soil and climatic peculiarities of this environment. In this context, the present review aims to describe the main characteristics of sulfentrazone to its environmental dynamics.

Keywords: triazolinone, pre-emergent, weed management, sorption.

RESUMO - O sulfentrazone é um herbicida com ação em pré-emergência que inibe a protoporfirinogênio oxidase (Protox). Sua utilização tem ênfase em áreas de expansão, como a soja em terras baixas, soja e cana-de-açúcar em áreas de cerrado, e também na implantação de florestamentos de eucalipto. A inserção do sulfentrazone em programas de manejo de plantas daninhas resistentes, principalmente ao glifosato e a inibidores da acetolactato sintase (ALS), vem obtendo sucesso. Contudo, as informações sobre o comportamento ambiental desse herbicida são limitadas, sendo ainda mais restritas quando se trata de áreas de terras baixas, onde frequentemente são observados problemas quanto à seletividade do sulfentrazone, em razão das peculiaridades edafoclimáticas desse ambiente. Nesse âmbito, esta revisão teve por objetivo relacionar as principais características do sulfentrazone com sua dinâmica ambiental e sua seletividade, compreendendo esses processos, a fim de otimizar sua utilização.

Palavras-chave: triazolinona, pré-emergente, manejo de plantas daninhas, sorção.

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INTRODUCTION

Sulfentrazone was the first herbicide of the triazolinones chemical group, marketed for the first time in 1991 by the FMC Corporation (Shaner, 2014). In Brazil, this herbicide is registered for the control of weeds in sugarcane, soybean, coffee, tobacco, citrus, pineapple, and eucalyptus (Brasil, 2018); however, on a worldwide scale, it can have other uses, which include non-agricultural areas and lawns (EPA, 2015). When applied in

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pre-emergence, this herbicide efficiently controls monocotyledonous, dicotyledonous, and cyperaceous weeds (Sweat et al., 1998; Blum et al., 2000; Wilson et al., 2002; Grey and Wehtje, 2005).

Sulfentrazone provides excellent control of weeds in soybean and sugarcane and is especially effective in difficult to control plants such as *Cyperus* spp., *Setaria* spp., *Amaranthus* spp., *Brachiaria* spp., *Panicum* spp., and *Ipomoea* spp. (Dirks et al., 2000; Walsh et al., 2015). Unlike other pre-emergent herbicides, it is a herbicide that can be used efficiently in pre-emergence in no-tillage systems as its high solubility allows it to reach the soil with little interference of straw (Rodrigues et al., 2000; Carbonari et al., 2016a).

In recent years, it has been used mainly on management programs of weeds resistant to herbicides that inhibit acetolactate synthase (ALS) and 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS) enzymes (Grey et al., 2000a; Hulting et al., 2001; Taylor-Lovell et al., 2001; Wilson et al., 2002; Krausz and Young, 2003; Grey et al., 2004; Reiling et al., 2006). For example, sulfentrazone associated with glyphosate can be used in the management of horseweed (*Conyza* spp.) and milkweed (*Euphorbia heterophylla*) to reduce selection pressure (Krausz et al., 1994; Krausz and Young, 2003). To date, only three cases of sulfentrazone-resistant weeds have been found in *Ambrosia artemisiifolia* in the United States, *Amaranthus hybridus* in Bolivia, and *Avena fatua* in Canada (Heap, 2018).

Expansion of soybean and sugarcane crops in Brazil, particularly the cultivation of rotating soybeans with irrigated rice in the lowlands of the Rio Grande do Sul State, and of both crops in cerrado soils, has led to new studies on the dynamics and behavior of sulfentrazone in these systems. These studies have addressed questions about the agronomic efficiency, persistence of the herbicide in the soil, leaching, and contamination of groundwater. Therefore, this review was carried out to better understand these processes by focusing on the insertion of this herbicide in the management of weeds in the soybean crop in an attempt to minimize potential risks to the environment.

The herbicide

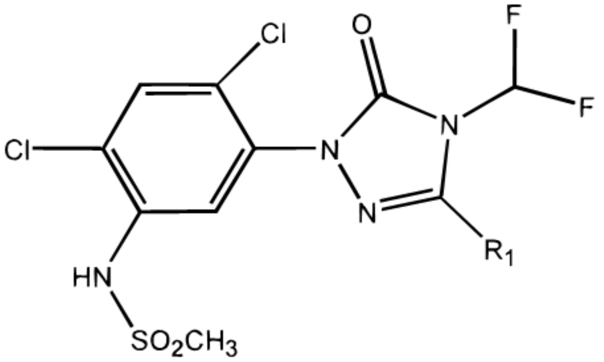
Sulfentrazone, N-[2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl]methanesulfonamide, is a herbicide of the chemical group aryl triazolinone (Shaner, 2014) which is weak acid (pKa 6.56). Its dissociation constant lies in the same pH range (pKa ± 1) of most agricultural soils. Therefore, pH is one of the most important extrinsic factors in its activity. Table 1 shows the structural form of sulfentrazone and its main metabolites, as well as the main physicochemical characteristics that will be used throughout the text to understand the behavior of this herbicide, in plants and the environment.

Mode of action

Sulfentrazone, as well as the other herbicides of the triazolinones group inhibit of the protoporphyrinogen oxidase (Protox), which is the last common enzyme on the synthesis route of chlorophyll and *heme* (Duke et al., 1991; Nandihalli and Duke, 1993; Dayan et al., 1997). Protox catalyzes the oxidation of six electrons of protoporphyrinogen to a highly conjugated tetrameric ring, the protoporphyrin (Duke et al., 1991; Nandihalli and Duke, 1993).

The molecule of the sulfentrazone is a bicyclic compound capable of competing with the substrate (protoporphyrinogen IX) for the binding site of the Protox in the chloroplast (Nandihalli and Duke, 1993; Nicolaus et al., 1993). Thus, the inhibition of Protox by sulfentrazone leads to the accumulation of protoporphyrinogen IX in chloroplasts. Differences in the concentration gradient inside and outside the chloroplasts lead the protoporphyrinogen IX to diffuse to the cytoplasm, where this compound is converted into protoporphyrin IX (Jacobs et al., 1991; Jacobs and Jacobs, 1993; Yamato et al., 1994). Protoporphyrin IX reacts with the Mg catalase in the chloroplast, forming the Mg-protoporphyrin IX (Dan Hess, 2000). In the cytoplasm, it reacts with light and oxygen producing reactive species (triplet protoporphyrin and singlet oxygen) (Matringe et al., 1989). These, in turn, remove hydrogen from unsaturated

Table 1 **-** Physico-chemical properties of sulfentrazone

Parameter/ characteristic	Description
Structure	
Herbicide	sulfentrazone (**R1= CH_3**)
Metabolites (1)	3-hydroxymethyl (**R1= CH_2OH**) 3-carboxylic acid (**R1= COOH**) 3-dimethyl(**R1=H**)
Density (g mL^{-1}) (2, 3)	0.53
Molecular weight (g mole^{-1}) (2, 3)	387.1899
Solubility in water (mg L^{-1}) (2, 3)	
pH 6	110
pH 7	780
pH 7.5	1600
Ionization (pKa(4)) (2, 3)	6.56
K_{ow}(5) (pH 7) (2, 3)	9.8
K_{oc}(6) (mL g^{-1}) (2, 3)	43
P_{vp}(7)(Pa at 25 °C) (2, 3)	$1.07x10^{-7}$
K_H(8) (atm m/mole)	$6.45x10^{-13}$

(1) (Dayan et al., 1996,1998) (2) (Shaner, 2014); (3) (Lewis et al., 2016); (4) Dissociation constant; (5) Octanol-water partition coefficient; (6) Organic carbon partition coefficient; (7) Vapor pressure; (8) Henry's Law Constant.

lipids producing a chain reaction of lipid peroxidation (Duke et al., 1991; Nandihalli and Duke, 1993; Jacobs et al., 1996) that destroying chlorophylls and carotenoids and causing rupture of membranes.

The mechanism of action of Protox inhibitory herbicides is dependent on light. However, secondary effects of sulfentrazone can be observed in its absence this includes reduction in the growth of soybeans hypocotyls (Li et al., 1999) and reduction in root development (Dayan et al., 1996).

Absorption and translocation

The sulfentrazone is absorbed by the roots and translocated by the xylem to the leaves until reaching the chloroplast where the Protox is located (Matringe et al., 1989); with light exposure, the first symptoms begin to appear (Wehtje et al., 1997).

It is a weak acid (pKa = 6.5) and thus, its absorption is dependent on the pH of the medium in which the plants are exposed due to the protonation of the sulfentrazone molecule at a pH below 6.5, which reduces its solubility and its availability in the soil solution (Grey et al., 1997; 2000a). However, absorption by the roots is higher when the molecule is in the protonated form. In this context, Ferrell et al. (2003) evaluated the absorption of sulfentrazone in tobacco plants grown with nutrient solution at pH 5.8, 6.5, and 7.8; these authors observed a decrease in absorption and higher accumulation of dry mass of the plants as the pH increased. It should be noted that in the soil, this same behavior cannot be observed because the higher protonation of the sulfentrazone molecule may favor soil sorption and reduce the amount of herbicide absorbed by the roots of the plants (Wehtje et al., 1997).

Leaves can also absorb sulfentrazone; however, its symplastic translocation in the phloem is low due to rapid leaf desiccation (Shaner, 2014), a typical symptom of Protox inhibiting herbicides. In the application to emerged seedlings, the efficiency of sulfentrazone can be increased due to leaf absorption; however, most of the herbicide is absorbed by the roots (Wehtje et al., 1997).

Metabolism in plants

Differential metabolism is the primary tolerance factor in soybean and tobacco plants (Dayan et al., 1996, 1997, 1998; Thomas et al., 2005; Fisher et al., 2006). After absorption, the sulfentrazone, still in the roots, is rapidly converted to its metabolites 3-hydroxymethyl, 3-carboxylic acid, and 3-dimethyl (Table 1).

In sulfentrazone tolerant species like soybean, the metabolism of the herbicide occurs rapidly as 90% is transformed into metabolites within 24 hours after application (Dayan et al., 1997). Dayan et al. (1996) also showed that the tolerant species *Senna obtusifolia* metabolized 91.6% of sulfentrazone in nine hours of absorption. On the other hand, the sensitive species *Cassia occidentalis* metabolized only 17% in this period.

The primary route of sulfentrazone metabolization occurs through substitution of the methyl group (CH_3). The exchange of this grouping at the 3-position of the triazole ring reduces its herbicidal activity (Dayan et al., 1997, 1998). In the first step of the metabolism, the hydroxylation of the methyl group to 3-hydroxymethyl (CH_2OH) occurs (Figure 1). Followed by the oxidation of this group and the formation of a carboxylic group, the 3-carboxylic acid (COOH), which is probably catalyzed by the cytochrome P450 monooxygenase (Dayan et al., 1997). The decarboxylation occurs until in the third step of metabolism, resulting in the 3-dimethyl metabolite (-H) (Leung et al., 1991; Dayan et al., 1997; Dayan et al., 1998; Shaner, 2014). In the secondary route of degradation, cleavage of the sulfentrazone takes place that produces a triazole ring, which is conjugated with a glycoside (Aizawa and Brown, 1999; Shaner, 2014).

Selectivity

The selectivity of sulfentrazone in plants involves several mechanisms like absorption, translocation, and differential metabolization (Thomas et al., 2005). However, the rapid sulfentrazone metabolization is attributed as the primary factor responsible for plant tolerance to sulfentrazone (Dayan et al., 1996,1997; FMC, 2004; Fisher et al., 2006).

Higher absorption of sulfentrazone by susceptible soybean cultivars was highlighted in the study by Li et al. (2000b) who detected a reduction of sulfentrazone absorption in 37% by a tolerant soybean cultivar, compared to a sensitive cultivar. In this context, the study by Carbonari et al. (2012) quantified the sulfentrazone in the sap of eucalyptus clones. These authors observed that the clones with the highest reduction in accumulation of dry mass also had a higher concentration of the herbicide in the sap, which indicated its higher absorption. When comparing the absorption, translocation, and metabolism of sulfentrazone from potato to *Chenopodium album* and *Datura stramonium,* Bailey et al. (2003) observed that only the amounts absorbed and translocated were lower in the plants and that the metabolism rate did not differ.

The lower rates of absorption and translocation favor plant selectivity since sulfentrazone needs to reach the chloroplast to inhibit Protox (Dayan et al., 1997; Swantek et al., 1998). This observation supports the condition that this herbicide is selective only at pre-emergence,

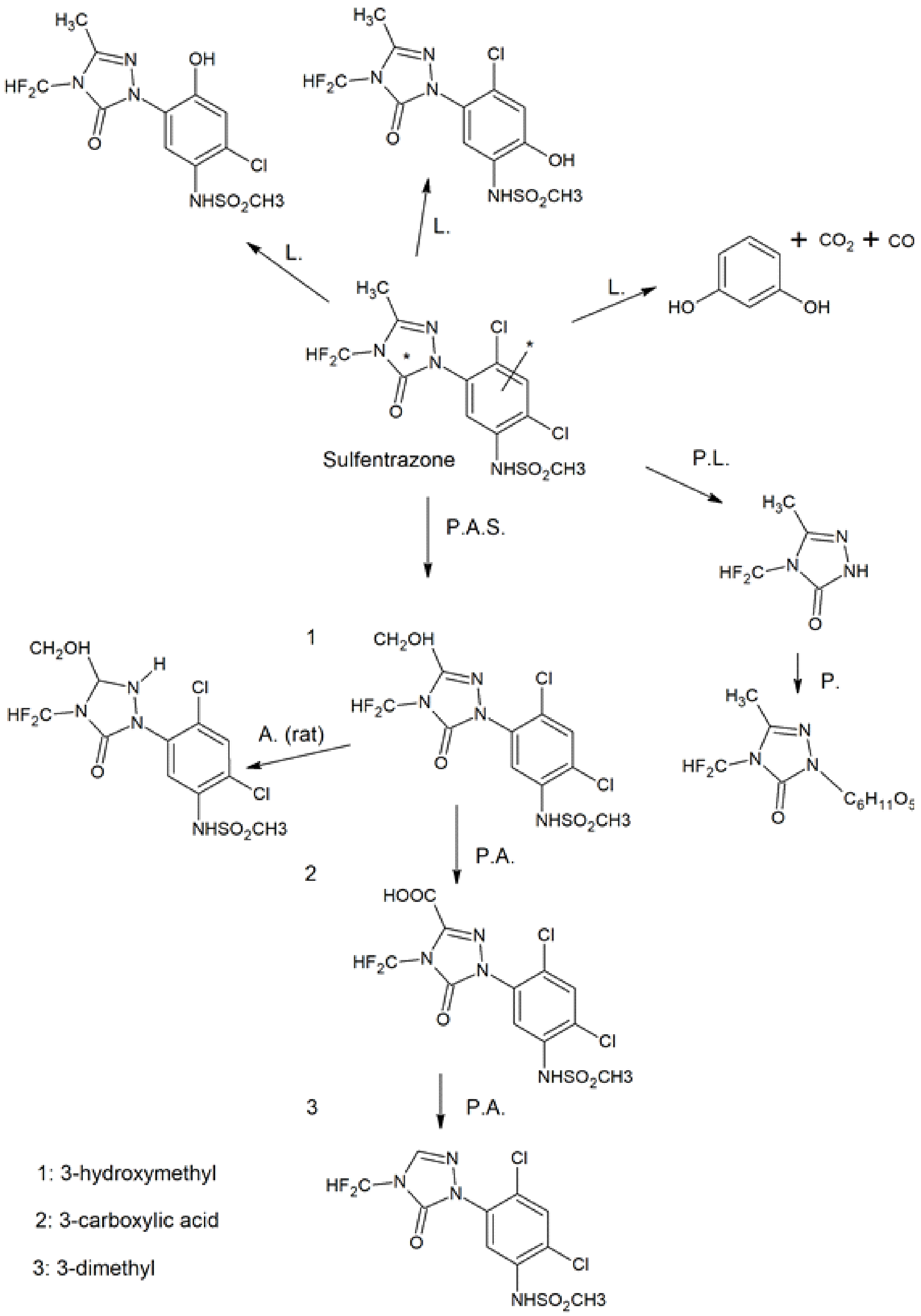


Figure 1 - Metabolism and degradation of sulfentrazone in plants (P), rats, goats and chickens (A), soil (S), and light (L). Adapted from Aizawa and Brown (1999).

a situation in which absorption occurs by the roots, where sulfentrazone can be metabolized. This added to the lower translocation, leads to a low amount of herbicide reaching the chloroplasts.

In soybean cultivation, the choice of cultivar has an impact on the tolerance to sulfentrazone (Swantek et al., 1998; Taylor-Lovell et al., 2001; Reiling et al., 2006). According to Dayan et al. (1997), this is due to the differential tolerance to the peroxidative stress intrinsic to each cultivar. However, there is a lack of information about the tolerance of soybean cultivars available in the Brazilian market, and the most recent work was that of Gazziero et al. (2005); it is important to emphasize that the cultivars evaluated in that work are not commercialized anymore. This gap can be solved using rapid methodologies, like the measurement of growth parameters (Li et al., 1999; Gazziero et al., 2005) and conductivity of the cellular extravasation (Li et al., 2000a) of seedlings submitted to different doses of sulfentrazone during the germination test.

Symptomatology

Susceptible plants after emerging on soils in which sulfentrazone was applied become necrotic and die after exposure to the sun (FMC, 2004; Fisher et al., 2006). This occurs due to the need for light to react with protoporphyrin and oxygen in chloroplasts and to form reactive species (Matringe et al., 1989).

Other noticeable symptoms include twisting and, in extreme situations, hypocotyl abortion, formation callus on the stem at the surface of the soil, necrotic spots on leaf tissue, and growth and leaf area reduction (Swantek et al., 1998; Hulting et al., 2001; Taylor-Lovell et al., 2001).

Protox is present in the route of chlorophyll synthesis; thus, its inhibition reduces the production of chlorophyll causing chlorosis in the leaves of plants exposed to sulfentrazone (Dayan et al., 1996).

Toxicology

The consumption of agricultural products treated with sulfentrazone does not pose a risk in human health, as well as other herbicides inhibitors of the Protox (Duke and Rebeiz, 1994). When ingested, sulfentrazone is either not absorbed by the digestive system or it is metabolized and subsequently eliminated from the body.

Leung et al. (1991) demonstrated that the elimination of sulfentrazone occurs in the form of the metabolites 3-hydroxymethyl (88-95%) and 3-carboxylic acid (0,3-5%) in the urine of rats and goats and in the excrement of chickens (Figure 1).

It should be emphasized that exposure to sulfentrazone may cause problems in the gestational phase of mammals (EPA, 2015). By exposing gestational rats to this herbicide, Castro et al. (2007) observed developmental disorders and reproductive and motor problems.

Environmental dynamics

Sorption in soil

Sorption of herbicides in soil has a direct effect on weed control, biodegradation, leaching, and contamination of soil and water (Harper, 1994). The specific chemical-physical characteristics of each soil can explain different behaviors of sulfentrazone, including the availability in the solution attributed to soil texture, pH, organic matter, iron oxide content, and cation exchange capacity (CEC). These can still vary according to environmental factors like temperature, humidity, rainfall, and others.

The sulfentrazone molecule is a weak acid (pka = 6.56); thus, its dynamics differs in alkaline and acidic soils. In soils with pH> 7, the anionic form of sulfentrazone predominates whereas at pH <6, the neutral is the most prominent form. In the neutral form, this herbicide can behave like a zwitterionic ion, which presents negative and positive potential distributed around the molecule that promotes the potential for polar bonds in the soil (Grey et al., 2000b).

In soils with low pH, sulfentrazone tends to be highly adsorbed in organic matter and mineral clays (Reddy and Locke, 1998; Grey et al., 2000b; Ohmes and Mueller, 2007) through London-van der Waals forces or other weak interactions (Grey et al., 2000b). On the other hand, in alkaline soils, solubility increases and sorption is very low, practically negligible (Grey et al., 2000b; Katz and Mishael, 2013). In these soils, the organic matter content becomes the control factor of the process of sulfentrazone sorption (Grey et al., 2004; Reiling et al., 2006; Szmigielski et al., 2009; 2012; Carbonari et al., 2016b) since its molecule is in dissociated form with negative charge and thus repelled by other negative charges, mainly from the organic matter.

CEC favors sorption of sulfentrazone to colloids regardless of soil pH. In this context, Kerr et al. (2004) related the effect of soil pH and CEC with phytotoxicity caused by sulfentrazone in sunflower plants. These authors observed that the change in pH had little effect on phytotoxicity; however, CEC reduction from 23.3 cmol kg^{-1} to 8.2 cmol kg^{-1} increased the phytotoxicity by 34%.

Iron oxides and hydroxides, found in several Brazilian soils also affect the sorption of sulfentrazone to soil (Alves et al., 2004). When evaluating the efficiency of sulfentrazone in the control of *Cyperus rotundus,* Alves et al. (2004) observed that this decreases according to the increase of iron oxides in the soil and that the organic matter and clay contents in the soil did not interfere in the efficiency. Iron oxides in acid medium adsorb hydrogens in the silanol group and present positive charges on the surface of soil colloids (Araujo et al., 2012), which favor sorption of sulfentrazone to these minerals.

Higher rainfall and soil moisture levels cause increased sulfentrazone availability in the soil solution, and some situations increase the phytotoxic effect on the plants (Alves et al., 2004; Reiling et al., 2006). The availability of sulfentrazone increases significantly in saturated soils; however, the opposite is observed when sulfentrazone is applied in dry soils, where there is a reduction in its availability in soil solution and control efficiency, and an increase in its persistence (Rizzi, 2003; Lourenço and Carvalho, 2015).

Persistence in the environment

Sulfentrazone is relatively persistent in soil, with an average half-life of 150 days ranging from 121 to 302 days (Shaner, 2014) depending on weather conditions and soils (Table 2). In many cases, the high persistence of sulfentrazone may become a restriction factor for substitute crops (Ohmes et al., 2000; Main et al., 2004; Garcia Blanco et al., 2010; Pekarek et al., 2010).

After applying sulfentrazone, its residues may extend to the next crop. Periods of safety are recommended for sowing new crop, for example, three months for barley, wheat, rye, oats, triticale, maize, rice and sorghum; 10 months for millet and teosinte; 12 months for sweet potatoes; 18 months for cotton and sweet corn; and 24 months for canola and sugar beet (FMC, 2004; Shaner, 2014). However, these periods may vary according to soil characteristics and climatic conditions.

Rainfall has ambiguous effects on the degradation of sulfentrazone. Depending on the intensity and frequency, it leads to increased degradation of the herbicide due to increased availability or less degradation due to leaching since microbial activity tends to be reduced at greater depths. In this context, Shaner (2012) evaluated the time required for 50% dissipation of the sulfentrazone in soil (DT_{50}) under field conditions in two years. In the first year, the author observed the first rainfall of 52 mm on the first day after applying the herbicide and in the second year, the first rainfall was of 71 mm, between the 10-12 days after the application; the DT_{50} observed was 30 and 14 days, respectively. Another study on leaching found that sulfentrazone was leached to the soil layer of 7.5-22.5 cm, thus reducing the degradation capacity of the herbicide since its higher biodegradation occurs in the superficial layer of the soil (0-10 cm); thus, intense rains tend to reduce the dissipation of sulfentrazone in the soil. (Ohmes et al., 2000).

The soil moisture content has a complex effect on the degradation of sulfentrazone. For example, in the work of Martinez et al. (2008a,b; 2010), the degradation rate did not differ between the levels of 30%, 70%, and 100% of the field capacity in Latosol and Red Argisol. Brum et al. (2013) observed a complex interaction between temperature, humidity, and soil

Table 2 - The half-life of the herbicide sulfentrazone in soil influenced by edaphic factors and environmental conditions

Condition			Half-life (days)	Reference
Soil	Temperature °C	Humidity		
Sandy soil	27	70% CC(4)	172.4(1)	Martinez et al. (2008a)
Red Latosol	40	70% CC(4)	91.6(1)	Martinez et al. (2010)
Latossolo distrófico		Dry	182(3)	Lourenço and Carvalho (2015)
Clayey Soil			70.8(2)	Mueller et al. (2014)
pH= 6.6 OM=2.6 pH= 8,0 OM=1.3			111(1) 21(1)	Szmigielski et al. (2012)
Sterilized Non-sterilized 0-10 cm Non-sterilized 30-40 cm Rainfalls above average			198(1) 93(1) 102(1) 24(2)	Ohmes et al. (2000)
Red Latosol	30º	80% CC(4)	60(1)	Brum et al. (2013)
Quartzarenic Neosol	30º 30º 40º	50% CC(4) 80% CC(4) 80% CC(4)	116(1) 77(1) 49(1)	
Clay-loam soil	52 mm 1 DAA(5) 71mm 12 DAA(5)		30(2) 14(2)	Shaner (2012)

(1) Laboratory; (2) Field; (3) Bioindicator; (4) Field Capacity; (5) Days after application.

characteristics, with degradation rates higher at 80% field capacity than at 30%, and the temperature at 40 °C favoring degradation in comparison to 30 °C. The temperature affects the persistence of sulfentrazone due to the stimulation of the metabolism of the microorganisms responsible for the degradation (Martinez et al., 2008a).

In periods of drought or low soil moisture, the persistence of sulfentrazone in the soil is greater and the half-life can be extended to 180 days (Lourenço and Carvalho, 2015) as a consequence of the higher soil sorption of the herbicide (Rizzi, 2003). The slow desorption of sulfentrazone from the soil particles reduces its availability in the soil solution, and consequently, the dissipation processes are reduced (Reddy and Locke, 1998; Ohmes and Mueller, 2007).

Soil management also influences the persistence of sulfentrazone. Reddy and Locke (1998) reported that sulfentrazone mineralization in prepared soils was 2.1%. In no-till it was 1.7% with the straw adversely affecting the degradation. In a previous study, Reddy et al. (1995) reported a larger population of microorganisms and higher enzymatic activity of the soil with direct sowing; therefore, the reduction of mineralization is probably due to the higher sorption of the herbicide to the organic carbon, or the need of adaptation of the microorganisms.

Transport

The volatilization of sulfentrazone is considered negligible (Shaner, 2014), and thus this process has little importance in studies of environmental fate (EPA, 2015). Due to the low vapor pressure (1.07 x 10^{-7}), with an estimated Henry's Law constant of 6.45 Pa m^{-3} mole^{-1}, this molecule has a low tendency to volatilize.

Herbicide leaching interferes both in the agronomic efficiency and in its environmental impact. Low leaching in the soil surface layer is important for its efficiency; however, excessive leaching values may cause contamination of groundwater.

The physicochemical characteristics of sulfentrazone (high solubility and low value of the organic carbon partition coefficient (K_{oc})), indicate a high leaching potential for its molecule (Table 1). However, this behavior is hardly observed (Grey et al., 2000b) except in situations of sandy soils, which are favored by the increasing rainfall events (Bachega et al., 2009; Melo et al., 2010).

Leaching is limited in soils with a clayey texture and hardly exceeds the depth of 10 cm, except in conditions with high rainfall or in soils with low organic matter content (Vivian et al., 2006; Bachega et al., 2009; Melo et al., 2010). In soils with a sandy texture, sulfentrazone leachates tend to reach depths of 20-30cm and may even exceed this depth (Table 3).

Table 3 **-** Leaching of the herbicide sulfentrazone in different soils

Soil/Texture	Depth$^{(1)}$	Reference
Argissolo Vermelho-Amarelo	0-10 cm	Vivian et al. (2006)
Dark-Red Latosol	0-10 cm	Bachega et al. (2009)
Chernosol (sandy)	Up to 30 cm	Rossi et al. (2003)
Red Latosol (clayey)	2.5 cm	Brum et al. (2013)
Clay-loam soil (sandy)	22.5 cm	Melo et al. (2010)
Clayey soil (OM=4.4 dag kg^{-1})	25 cm	Melo et al. (2010)
Clayey soil (OM=9.0 dag kg^{-1})	17.5 cm	Melo et al. (2010)
Red Latosol	30 cm	Scorza Jr and Franco (2014)

(1) Depth of leaching observed.

Leaching is directly dependent on soil sorption since the herbicide must be available in the soil solution for leaching to occur. Thus, soil texture, pH, organic matter content, and CEC impact the sulfentrazone leaching process. In addition to sandy soils, soils with low organic matter content are predisposed to the higher sulfentrazone leaching (Melo et al., 2010; Shaner, 2012) due to lower soil sorption (Szmigielski et al., 2009; 2012).

Rainfall does not affect clay soils and/or high organic matter content, which is justified by the high soil sorption rate (Grey et al., 2000b). However, the effect of rains on sandy soils where sorption is reduced is clear where increased leaching is observed along with increased rainfall (Bachega et al., 2009).

Transformations

Sulfentrazone is not susceptible to photodegradation when applied to soil (Shaner, 2014) with stable hydrolysis in the pH range of 5-9 (Aizawa and Brown, 1999; FMC, 2004). However, it becomes extremely susceptible to photolysis in water (FMC, 2004; EPA, 2015) and is accentuated at alkaline pH.

The half-life of sulfentrazone in water determined at pH 7 and 9 was one hour and at pH 5 the extrapolated half-life was 12 hours (Willut et al., 1997). Photolysis of the sulfentrazone molecule in water produces dechlorinated and hydroxylated compounds and in continuous exposure causes the cleavage of the aromatic and triazole rings (Figure 1) (Aizawa and Brown, 1999).

Microbial degradation is the main route of sulfentrazone dissipation in soil (FMC, 2004; Shaner, 2014). However, Reddy and Locke (1998) observed a low rate of mineralization in the soil without a historic of application of sulfentrazone, where at 77 days after incubation, this was 2.1% in conventional tillage and 1.7% in direct sowing. Further research has demonstrated the need for an initial adaptation period of microorganisms (lag phase) with subsequent degradation. For example, a study by Martinez et al. (2010) detected the formation of the 3-hydroxymethyl metabolite (first product of biodegradation, Figure 1) after the average period around 60 days from incubation varyied according to temperature and humidity.

The temperature has a direct effect on sulfentrazone degradation, with the range of 30-40 °C proper to biodegradation (Martinez et al., 2008b). This environmental parameter directly affects the proliferation, population dynamics, and metabolism of microorganisms (Martinez et al., 2008a).

The dissipation of sulfentrazone is faster when rainfall is higher (Ohmes and Mueller, 2007; Mueller et al., 2014). However, the results of Martinez et al. (2008a,b, 2010) did not show significant differences in the biodegradation of sulfentrazone under conditions of 30%, 70%, and 100% field capacity.

Biodegradation occurs via aerobic and facultative microorganisms, which use it as a source of carbon and energy (Martinez et al., 2010). Microorganisms have the potential for degradation depending on the soil type: *Rhizobium radiobacter*, *Ralstonia pickettii*, *Methylobacterium radiotolerans*, *Cladosporium* sp., *Eupenicillium* sp., *Paecilomyces* sp., *Metarhizium* sp., *Chrysosporium* sp., *Nocardia brasiliensis*, sp., and *Acinetobacter calcoaceticus* are able to degrade sulfentrazone in tropical soils (Martinez et al., 2008a,b; 2010) .

Environmental contamination

Air

Sulfentrazone is a compound with negligible volatility (Shaner, 2014). Its ability to become gas becomes limited and the air contamination by this herbicide is reduced. The particles are removed by dry and wet deposition and their estimated half-life in the atmosphere is low: 15.7 hours at 5×10^5 (FMC, 2004; TOXNET, 2015).

Water

The high persistence and low adsorption in some soils give sulfentrazone a potential risk for contamination of water springs (Passos et al., 2013). Although leaching is not as significant in most soils (Table 3), sulfentrazone residues can be detected in watercourses, which are generally attributed to drift in applications and surface runoff (Canada, 2011; EPA, 2015).

The estimated GUS coefficient of sulfentrazone is 6.48, characterizing it as a herbicide with high leaching potential (Santos et al., 2015). This coefficient estimates the leaching potential of the pesticide, considering its half-life and K_{oc}); values higher than 2.8 show a high leaching potential of the pesticide (Gustafson, 1989). However, it is worth mentioning that the results of some studies have shown that the leaching of sulfentrazone in the superficial layer is low (Vivian et al., 2006; Bachega et al., 2009), except in sandy soil conditions (Melo et al., 2010).

After surveying the amount of sulfentrazone used in the Corumbataí River basin in the São Paulo State, Brazil, Armas et al. (2005) related the amount used in the region with the GUS coefficient and the LEACH Index of the herbicide noting that sulfentrazone is a potential contaminant of the water sources of the region. Through water sampling in springs and artesian wells in the region of Córrego-Rico in Jaboticabal, São Paulo State, Brazil, Santos et al. (2015) detected sulfentrazone residues with concentration reaching up to 0.6 ppb, in 15.4-30% of the springs and 21.9-34.4% in artesian wells, varying according to time of sampling.

Since sulfentrazone may be a potential contaminant of water resources, alternatives to decontamination are necessary. One of these alternatives uses filters and/or columns composed of montmorillonite as this mineral has a high capacity to retain sulfentrazone (Polubesova et al., 2003; Ziv and Mishael, 2008). Based on this principle, Nir et al. (2012) developed a column composed of sand and montmorillonite mycelia with the capacity to retain more than 90% of the sulfentrazone contained in a solution of 75 ppm.

Another alternative for the mitigation of sulfentrazone contamination in water was demonstrated by Lima et al. (2010), through the electro-oxidation processes and the electro-Fenton method with Mohr's salt. In this work, the authors verified that the electro-oxidation process is not efficient and causes the formation of more toxic by-products. However, the use of the electro-Fenton process is capable of mineralizing 60% of the molecule since this process produces hydroxyl radicals ($^{\bullet}$OH) capable of simultaneously attacking several groups of the sulfentrazone molecule and consequently producing smaller and less toxic by-products.

Food

Food contamination by sulfentrazone has not been reported in the literature. It is probably related to its use in pre-emergence for some previously studied crops (FMC, 2004; Shaner, 2014; Brasil, 2018). Another fact to be considered is the rapid sulfentrazone metabolization in tolerant crops, which reduce herbicide activity and leave no residue on grains (Leung et al., 1991; Dayan et al., 1998).

Tao et al. (2014) developed a method for the rapid detection of triazolinone herbicides through high-performance liquid chromatography (HPLC). During the validation step, the authors carried out analyzes on samples of rice, corn, soybean, and wheat grains marketed for human consumption, which could potentially have residues; however, no sample showed positive results for sulfentrazone contamination.

Soil

The high persistence of sulfentrazone in the soil, besides been a restriction factor in rotation systems, can also have a strong environmental impact as commented above in the item Persistence in the environment. The use of the bioremediation technique is one of the possible alternatives to avoid contamination of sulfentrazone in the soil. Plants like the brown hemp, jack bean, pigeon pea, sunflower, lablab-bean, and peanut are good options for the reduction of sulfentrazone residues in soil (Madalão et al., 2012; Belo et al., 2016).

In addition to persistence, sulfentrazone may adversely affect the soil microbiota (Vivian et al., 2006). Silva et al. (2014) observed that sulfentrazone was harmful to the microbial biomass, mycorrhizal colonization, and organic phosphate solubilizing microorganisms in soils cultivated with eucalyptus. Also, nodulation and fixation of nitrogen can be partially impaired by the application of sulfentrazone (Arruda et al., 2001).

FINAL REMARKS

Sulfentrazone is a good option for management of difficult to control and resistant weeds. The tolerance of crops to sulfentrazone depends on a set of factors formed by lower absorption and translocation, rapid metabolization, and ability to tolerate oxidative stress. There is a need for more information on the tolerance of soybean cultivars in the Brazilian market.

Sulfentrazone sorption is correlated to pH, soil texture, and organic matter. These three factors determine the herbicide availability in the soil, transport processes, dissipation, and weed control efficiency. Sulfentrazone has moderate to long persistence in the soil with a potential of contaminating groundwater when used in sandy soils. This long residual herbicide may cause toxicity to the crops used in succession and/or rotation. Biodegradation is apparently the primary route of dissipation in the environment.

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