SORPTION OF FOMESAFEN IN BRAZILIAN SOILS[1]

Sorção do Fomesafen em Solos Brasileiros

SILVA, G.R.[2], D'ANTONINO, L.[2], FAUSTINO, L.A.[2], SILVA, A.A.[2], FERREIRA, F.A.[2], and TEXEIRA, C.C.[2]

ABSTRACT - The study of the dynamics of a herbicide in the soil focus on the interactions with environmental components to obtain agronomic efficiency, ensuring selectivity to the culture and risk reduction of environmental impact. This study evaluated the sorption process of fomesafen in the Brazilian soils Ultisol, Cambisol, and Organosol. Besides soil, washed sand was used as an inert material for determination of the sorption ratio of fomesafen in the soil. The bioassay method was applied, using *Sorghum vulgare* plants as bio-indicator of herbicide presence. Plant poisoning evaluation and harvest for dry matter determination were carried out 21 days after sorghum sowing. To calculate $C_{50,}$ the nonlinear log-logistic model was applied and sorption ratios of the herbicide were obtained in different soils. The decreasing sorption ratio of formesafen in the soils was: Organosol > Ultisol > Cambisol. It was concluded that the contents of organic matter and clay in the soils were the attributes that most influenced fomesafen sorption.

Keywords: bioassay, *carryover*, environmental impact.

RESUMO - O estudo da dinâmica de um herbicida no solo averigua as suas interações com os componentes do meio tendo em vista a eficiência agronômica, o que garante a seletividade à cultura e a redução dos riscos de impacto ambiental. Neste trabalho avaliou-se o processo de sorção do fomesafen em solos brasileiros: Argissolo Vermelho-Amarelo, Cambissolo e Organossolo. Além dos solos utilizou-se também como substrato a areia lavada como material inerte para determinação das razões de sorção do fomesafen nos solos estudados. Para isso, empregou-se o método de bioensaios, utilizando-se plantas de ***Sorghum vulgare*** *como bioindicadoras da presença do herbicida. Aos 21 dias após a semeadura do sorgo, foram realizadas avaliações de intoxicação das plantas e colheita da parte aérea para determinação da matéria seca. No cálculo do* C_{50} *utilizou-se o modelo log-logístico não linear, obtendo-se a seguir as relações de sorção do herbicida nos diferentes solos. A ordem decrescente da relação de sorção do formesafen nos solos estudados foi: Organossolo > Argissolo Vermelho-Amarelo > Cambissolo. Conclui-se que os teores de matéria orgânica e de argila dos solos foram os atributos que mais afetaram a sorção do fomesafen.*

Palavras-chave: bioensaio, *carryover*, impacto ambiental.

INTRODUCTION

Grain production stands out in Brazilian agriculture, and one of the reasons for its success is the development of weed science. The great advances in the synthesis of new molecules, highly efficient in controlling different species of weeds, enabled productivity gains in various crops, reducing costs. However, some compounds used for weed control are more persistent in the environment, causing poisoning in sensitive plants grown in succession.

One of the main herbicides used in the bean crop is fomesafen (Embrapa, 2012),

[1] Recebido para publicação em 12.12.2012 e aprovado em 19.9.2013.
[2] Universidade Federal de Viçosa, Viçosa, Minas Gerais, Brasil, <gustavo.r.silva@ufv.br>.

isolated or in commercial combination with fluazifop-p-butyl. It is a weak acid with a pKa value of 2.7 (sodium salt), having water solubility considered high for this class of product (50 mg L^{-1} at 20 °C), low vapor pressure (<10^{-4} Pa at 50 °C) and Kow varies according to the pH from 2.9 (pH 1) to -1.2 (pH 7) (Oliveira Júnior & Regitano, 2009; Rodrigues & Almeida, 2011). Fomesafen belongs to the chemical group of diphenylethers, protoporphyrinogen oxidase inhibitors, and is indicated for the control of annual dicots. On the relevance of this herbicide, one must also consider that it presents a great potential for use in sugar cane and eucalyptus – cultures rapidly expanding in Brazil.

Among the parameters that influence the behavior of a herbicide in the soil, sorption is the key process that involves transport, absorption and its bioactivity, affecting the availability to plants and even their selective action (Hermes, 1991).

As fomesafen is still little studied in Brazilian soils, the aim of this study was to evaluate the sorption of this herbicide in three Brazilian soils with different physicochemical characteristics.

MATERIAL AND METHODS

Samples of three soils were collected at a depth of 0 to 20 cm, with no history of herbicide use, in three locations: an Ultisol in Viçosa, MG; a Cambisol in Porto Firme, MG; and an Organosol in the Municipality of Venda Nova do Imigrante, ES.

Soil samples were sieved (4 mm sieve – TFSA) and characterized for physical (Table 1) and chemical (Table 2) properties. Subsequently, all soils were fertilized at a ratio of 1 kg of P_2O_5 per 100 L of soil.

Table 1 - Physical characterization and textural classification of the soil samples used in the experiments

Soil	Sand	Silt	Clay	Textural class
	(dag kg^{-1})			
Ultisol	38	13	49	Sand clay
Cambisol	76	7	17	Sandy loam
Organosol	34	30	36	Clay loam

The method used to estimate the sorption potential of the herbicide from the quantification of fomesafen residues in the soil was bioassay. The species used was sorghum (*Sorghum vulgare*), cultivar BRS655. In tests conducted previously, we determined a higher sensitivity to fomesafen by sorghum plants, compared to the corn plants in increasing doses of the herbicide.

The soils and sand were used as substrates. The sand was preincubated for 72 hours with hydrochloric acid, for removal of organic matter contained in it, washed with water and next incubated with sodium hydroxide for 24 hours in order to raise the pH of the substrate. Then, it was again washed with water until the pH stabilized at 6.5.

After seeding five sorghum seeds in pots of 250 cm^3 of substrate, we applied increasing doses of fomesafen, a FLEX® commercial product, containing 250 g L^{-1} of active ingredient in pre-emergence (Table 3). The containers were internally coated with polyethylene plastic bags, to prevent loss of the herbicide by leaching. The soil was maintained with moisture near field capacity during the experimental period. For this, we used the gravimetric method, replenishing water daily, as needed. On the eighth day after the application, we performed the roughing, leaving two plants per pot, and applied additional fertilizers with solution of 30 mL L^{-1}

Table 2 - Chemical characterization of the soil samples used in the experiments

Soil	pH	P	K	Ca	Mg	Al^{3+}	H+Al	SB	(t)	(T)	V	m	OC
	(H_2O)	(mg dm^{-3})		(cmol$_c$ dm^{-3})							(%)		(dag kg^{-1})
Ultisol	5,8	44,7	165	4,3	0,6	0,0	1,98	5,32	5,32	7,30	73	0	2,9
Cambisol	4,6	2,2	14	0,3	0,1	0,2	1,32	0,44	0,64	1,26	25	7	1,1
Organosol	5,0	18,1	185	5,1	3,0	0,6	26,64	8,57	9,17	34,81	25	31	20,2

Table 3 - Doses of fomesafen (commercial product FLEX® - 250 g L^{-1} i.a. – 25% m/v), used in each substrate: Cambisol, Ultisol, Organosol and washed sand

Substrate			
Cambisol	Ultisol	Organosol	Sand
0	0	0	0
10	50	200	5
15	100	400	10
20	125	600	15
30	150	800	20
40	175	900	30
50	200	1000	40
60	225	1100	50
70	250	1200	60
80	300	1400	70

in water with the fertilizer Nutri Verde®. The experiment was conducted in a randomized block design with four replications.

At 21 days after seeding (DAS), intoxication evaluations were made (visual scale ranging from 0 to 100, where 0 means a plant with no symptoms and 100 represents the death of the indicator plant). The plants were harvested to determine the dry matter of the shoot and put in an oven with forced air circulation at 70 °C to constant weight, and all samples were weighed on a precision electronic scale.

To interpret the results, the dry matter values were compared to the treatment without herbicide (zero dose), and subjected to statistical analysis, using the log-logistic nonlinear model (equation 1) proposed by Seefeldt et al. (1995):

$$y = f(x) = C + \frac{D - C}{1 + \frac{X^b}{C_{50}}} \qquad \text{(eq. 1)}$$

Equation 1: log-logistic nonlinear model

In this model, C and D correspond, respectively, to the maximum and minimum levels of the dose-response curve; b corresponds to the slope of the curve around C_{50}; e C_{50}, to the dose-response for the reduction of 50% of dry matter of the indicator plant's shoot.

From the C_{50} data obtained in soil and sand, equation 2 was used to express the sorption relation (RS) of the soil compared to the response obtained in sand for the indicator species (Souza, 1994). Higher RS values indicate higher sorption capacity of the herbicide in the soil and, therefore, less potential for leaching of the compound in the soil profile.

$$RS = \frac{C_{50}\text{solo} - C_{50}\text{areia}}{C_{50}\text{areia}} \qquad \text{(eq. 2)}$$

Equation 2: equation of sorption ratio between soil and sand

This percentage ratio was used to correct the calculations of fomesafen residues in the soil. For this purpose, the values of dry matter of the shoot were compared to those obtained from the dose-response curve of each soil.

RESULTS AND DISCUSSION

Intoxication caused by the application of fomesafen in the sorghum plants at 21 DAS is shown in Figure 1 [washed sand (A), Cambisol (B)] and Figure 2 [Ultisol (A) and Organosol (B)]. A differential behavior of the herbicide was observed in each substrate, with the degree of toxicity varying with the dose and type of soil. It also has effect on the accumulation of dry matter of the shoot of sorghum plants (Figures 3 and 4).

This differential behavior of the herbicide in each substrate is attributed to interactions between the herbicide molecule and the sorbing sites, whether of organic matter or clay minerals. Thus, the physical and chemical characteristics of soils can cause differential retention of herbicides, which may cause their distinct availability in the soil solution, thus influencing the control of weeds and their leaching to deeper layers (Gerstl, 2000).

According to Oliveira Jr. et al. (2001), Brazilian soil properties which are more correlated with the sorption of basic, acidic and nonionic herbicides are pH and organic matter. In another study, Oliveira Jr. (2009) states that the sorption of herbicides of acidic character, such as fomesafen, is weaker when compared to that of basic and neutral products. When in contact with the soil, such herbicides may be adsorbed by electrostatic forces exerted

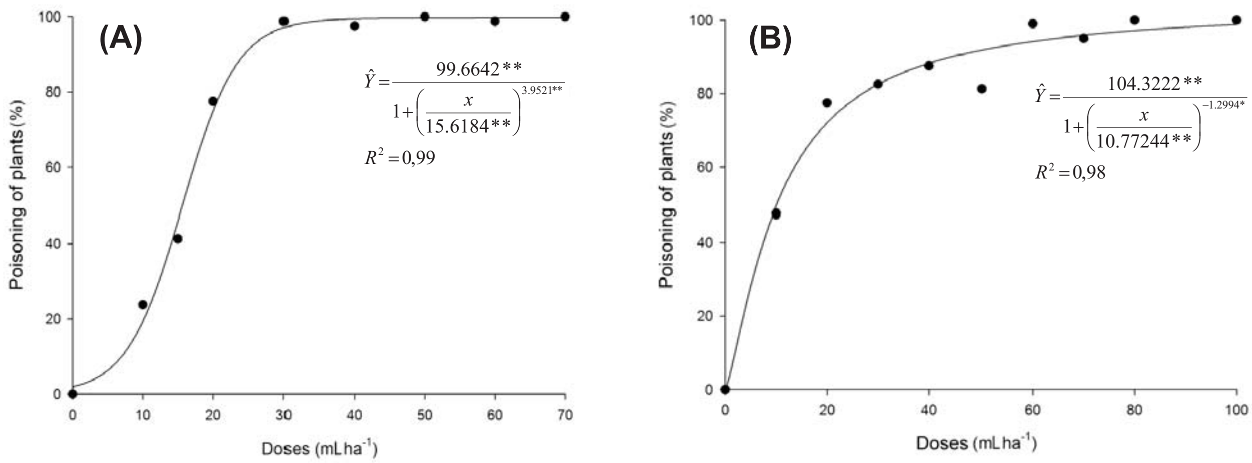

Figure 1 **-** Evaluation of intoxication in sorghum plants in washed sand (A) and Cambisol (B) treated with different doses of fomesafen (commercial product FLEX® - 250 g L^{-1} a.i. - 25% w/v) 21 days after planting.

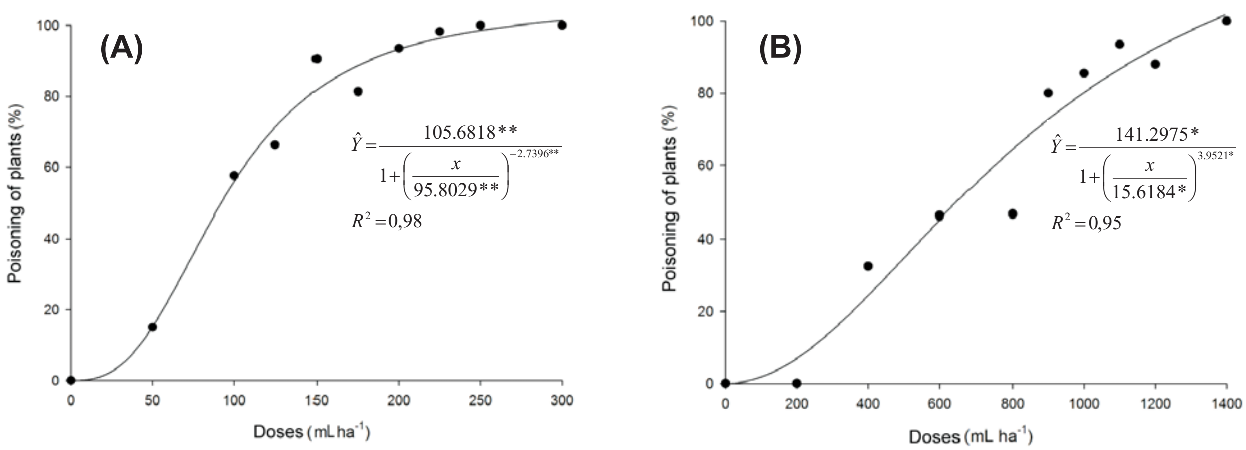

Figure 2 **-** Evaluation of intoxication in sorghum plants in Ultisol (A) and Organosol (B) treated with different doses of fomesafen (commercial product FLEX® - 250 g L^{-1} a.i. - 25% w/v) 21 days after planting.

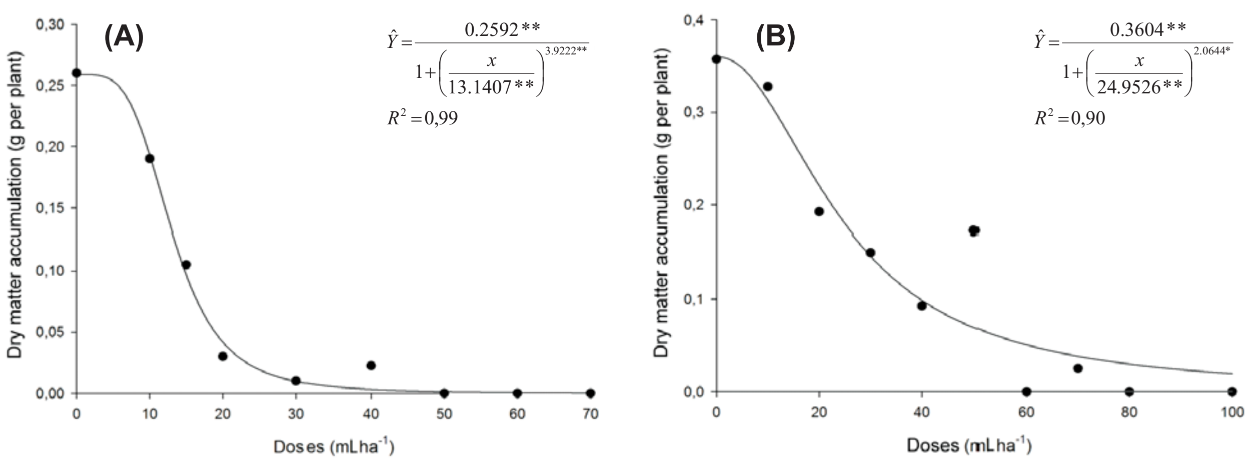

Figure 3 **-** Dry matter accumulation in sorghum plants in washed sand (A) and Cambisol (B) treated with different doses of fomesafen (commercial product FLEX® - 250 g L^{-1} a.i. - 25% w/v) 21 days after planting.

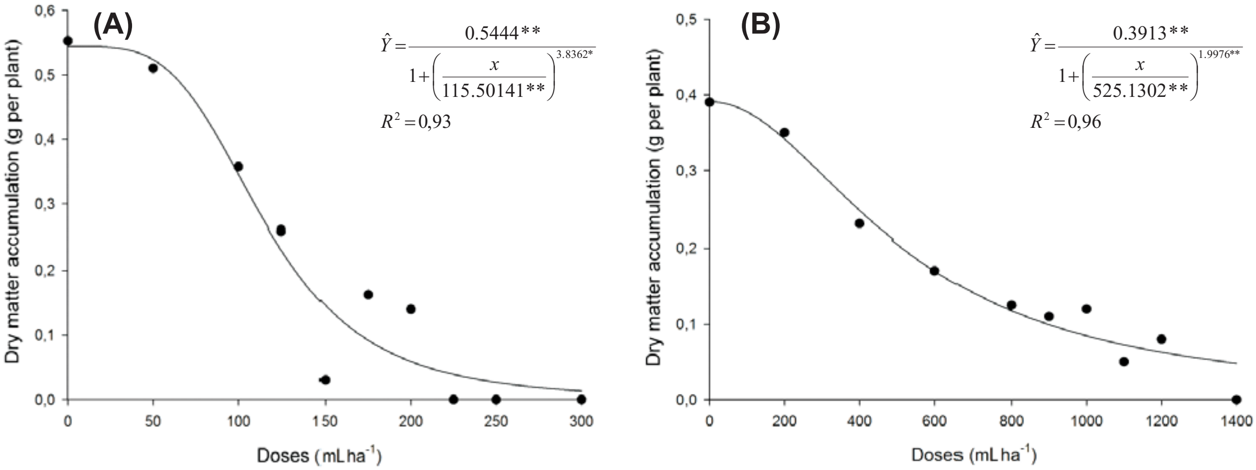

Figure 4 - Dry matter accumulation in sorghum plants in Ultisol (A) and Organosol (B) treated with different doses of fomesafen (commercial product FLEX® - 250 g L^{-1} a.i. - 25% w/v) 21 days after planting.

by soil particles, which involve specific mechanisms for covalent bond, bridges with divalent metallic cations, ligand exchange and hydrophobic partitioning.

Doses of fomesafen (C_{50}), commercial product FLEX®, containing 250 g L^{-1} of the active ingredient 25% m/v, which reduced accumulation of the dry matter of shoots of sorghum plants by 50% at 21 days after seeding (DAS), according to the substrate used, were: washed sand, 13.14 mL ha^{-1}; Cambisol 32.12 mL ha^{-1}; Ultisol, 115.50 mL ha^{-1}; and Organosol, 525.13 mL ha^{-1}. The ratio of sorption in the substrates was calculated with equation 2, being: washed sand, 0; Cambisol, 1.44; Ultisol, 7.79; and Organosol, 38.96. The decreasing ratio of fomesafen sorption in the soils was: Organosol > Ultisol > Cambisol.

Among various factors influencing the soil sorption of a herbicide of acidic character, such as fomesafen, the pH may be the most important (Oliveira et al. 2005; Guo et al. 2003). Oliveira (2011) reports that the pH correlates inversely as K_d, while the organic matter content correlates positively with this coefficient. The decrease of one unit on soil pH doubles the sorption of fomesafen. This herbicide, being separable, have the soil pH as an important factor in their behavior, since this will determine the ionic form that predominates in the soil solution (Oliveira Jr et al., 2009). However, in this study, the pH factor was not as determining in the sorption of the herbicide. This fact can be explained by the different origins of the loads in the soils studied, that is, the greater or lesser dependence of these loads to the soil pH. It is believed that the higher sorption of Organosol over the other soils is due to the high content of organic matter present in it (Table 2). In this soil, increasing the pH causes a slight variation of sorption forces, since most electrostatic forces responsible for fomesafen sorption are pH-independent.

On the other hand, the higher sorption of the Ultisol relative to the Cambisol may be related to its higher clay content (Table 1) and organic matter (Table 2). Being a herbicide derived from a weak acid (Silva et al. 2007), it was expected that fomesafen would be less sorbed in the Ultisol compared to the Cambisol (Figures 3A and 4A). However, the higher content of clay in the Ultisol may have favored this result, besides the higher organic matter content, overriding the effect of pH-dependent loads (Tables 1 and 2).

These results confirm those of Brusseau & Rao (1989), Blumhorst et al. (1990) and Dores & De-Lamonica-Freire (1999), which emphasize that organic matter is the main material that makes many herbicides unavailable in the soil, which has seen sites that work in three-dimensional retention of ionic compounds. Guo et al. (2003) found an increase in the sorptive capacity of fomesafen with the increase of organic matter. Besides its herbicide sorption potential, organic matter is related to the activity of microorganisms, being more abundant in the surface layers of soil. Microorganisms act on the biodegradation processes of the herbicide molecules, and may use them both as substrates and for power supply (metabolism), or even, the microbial action can modify the chemical structure of the product without supplying energy for its growth and co-metabolism (Miller, 1996).

Other studies done with PROTOX inhibitor herbicides show the importance of the soil's organic matter and clay on the sorption of these herbicides. For Passos (2011), the sorption of sulfentrazone is related to organic matter and clay contents. Ferrell et al. (2005) reported that organic matter is the main parameter correlated to flumioxazin sorption. These herbicides show a different behavior with respect to soil pH. Fomesafen, derived from a weak acid, has pKa of 2.7 (Roberts & Adams, 2011). Herbicides with these characteristics are strongly influenced by soil pH. When the pKa is higher than the pH, the herbicide appears more adsorbed (molecular form); when pH is higher than pKa, the herbicide is less adsorbed (dissociated form). Sulfentrazone shows a pKa of 6.5 (Grey et al. 2000) and is derived from a weak base, being more adsorbed when the soil pH is lower than its pKa (dissociated form) and less adsorbed when the pH is higher than the pKa (molecular form). Flumioxazin is a nonionic herbicide (Oliveira et al. 1999), that is, it is unable to dissociate, and therefore not influenced by the pH of the soil (Hatzios, 1998).

We conclude that the levels of organic matter and clay in the soils are attributes of great importance in fomesafen sorption. This explains the higher values of fomesafen sorption obtained in the Organosol, which had the highest content of organic matter among the soils evaluated. Furthermore, even with higher pH, the Ultisol showed higher sorption relative to the Cambisol. The results evidence the importance of knowing the physical and chemical characteristics of the soil and their interaction with fomesafen, in order to place a recommendation to ensure better technical efficiency and lower environmental risk.

LITERATURE CITED

BLUMHORST, M. R.; WEBER, J. B.; SWAIN, L. R. Efficacy of selected herbicides asinfluenced by soil properties. **Weed Technol.**, v. 4, p. 279-283, 1990.

BRUSSEAU, M. L.; RAO, P. S. C. The influence of sorbate-organic matter interactions on sorption nonequilibrium. **Chemosphere**, v. 18, n. 9/10, p. 1691-1706, 1989.

Disponível em: <http://www.agencia.cnptia.embrapa.br/Agencia4/AG01/arvore/AG01_46_1311200215103.html>. Acesso em: 20 fev. 2012.

DORES, E. F. G. C.; DE-LAMONICA-FREIRE, E. M. Contaminação do ambiente aquático por pesticidas: vias de contaminação e dinâmica dos pesticidas no ambiente aquático. **Pesticidas: R. Ecotoxicol. Meio Amb.**, v. 9, n. 1, p. 1-18, 1999.

EMBRAPA ARROZ E FEIJÃO. Herbicidas registrados para a cultura do feijão no Brasil. Circular técnica, 35. 1999

EMBRAPA ARROZ E FEIJÃO. **Manejo de plantas daninhas na cultura do feijão**. Dezembro/2005. Disponível em: <http://sistemasdeproducao.cnptia.embrapa.br/FontesHTML/Feijao/FeijaoPrimSegSafraSulMG/manejo_pdaninhas.htm> Acesso em: 20 fev. 2012.

FERRELL, J. A.; VENCILL, W. K; XIA, K. Sorption and desorption of flumioxazin to soil, clay minerals and ion-exchange resin. **Pest Manag. Sci.**, v. 1, p. 40-46, 2005.

GERSTL, Z. An update on the Koc concept in regard to regional scale management. **Crop Protec.**, v. 19, p. 643-648, 2000.

GREY, T. L. et al. Behavior of sulfentrazone in ionic exchange resins, electrophoresis gels, and cation-saturated soils. **Weed Sci.**, v. 48, p. 239-247, 2000.

GUO, J. et al. Adsorption, desorption and mobility of fomesafen in Chinese soils. **Air, Water Soil Pollut.**, v. 14, n. 8, p. 77-85, 2003.

HATZIOS, K. K. **Herbicide handbook**. 7.ed. Champaign: Weed Science, 1998. 104 p.

HERMES, L. C. **Adsorção e mobilidade dos herbicidas 2,4-D e ametrina em solos do Estado de São Paulo**. 1991. 79 f. Dissertação (Mestrado em produção vegetal) – Escola Superior de Agricultura Luiz de Queiroz, Piracicaba, 1991.

MONTEIRO, R. T. R. Biodegradação de herbicidas. In: EMBRAPA – CNPMA. WORKSHOP SOBRE BIODEGRADAÇÃO, 1996, Campinas. **Anais...** Campinas: 1996. p. 120-128.

OLIVEIRA JÚNIOR, R. S.; REGITANO, J. B. Dinâmica de pesticidas no solo. In: MELO V. F.; ALLEONI, L. R. F. (Ed.). **Química e mineralogia do solo:** parte II, aplicações. Viçosa, MG: Sociedade Brasileira de Ciência do Solo, 2009. p. 187-248.

OLIVEIRA, M. F. et al. Lixiviação de flumioxazin e metribuzin em dois solos em condições de laboratório. **Planta Daninha**, v. 17, n. 2, p. 207-214, 1999.

OLIVEIRA, V. S. **Dinâmica do fomesafen no solo e impacto de tiametoxam e fomesafen sobre três espécies de macrófitas aquáticas.** 2011. 103 f. Tese (Doutorado em fitotecnia) – Universidade Federal de Lavras, Lavras, 2011.

PASSOS, A. B. R. J.; FREITAS, M. A. M.; TORRES, L. G.; SILVA, A. A.; QUEIROZ, M. E. L. R.; LIMA, C. F. Sorption and desorption of sulfentrazone in Brazilian soils. **J. Environ. Sci. Health, Part B, Pestic. Food Contam. Agric. Wastes,** v. 48, p. 646-650, 2013.

RODRIGUES, B. N.; ALMEIDA, F. S. **Guia de herbicidas**. Londrina: Universidade Estadual de Londrina, 2011. 697 p.

SEEFELDT, S.S.; JENSEN, S.E.; FUERST, E.P. Log-logistic analysis of herbicide dose-response relationship. **Weed Technology**, v.9, p.218-227, 1995.

SILVA, A. A. et al. Herbicidas: classificação e mecanismos de ação. In: SILVA, A. A.; SILVA, J. F. (Ed). **Tópicos em manejo de plantas daninhas**. Viçosa, MG: Universidade Federal de Viçosa, 2007. 367 p.

SOUZA, A. P. **Atividade de oxyfluorfen, 2,4-D e glifosate em solos de diferentes texturas na presença e na ausência de composto orgânico**. 1994. 71 f. Dissertação (Mestrado em Fitotecnia) – Universidade Federal de Viçosa, Viçosa-MG, 1994.