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Article

Clomazone Leaching Estimate in Soil Columns Using the Biological Method

Estimativa da Lixiviação do Clomazone em Colunas de Solos Utilizando Método Biológico

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ABSTRACT **-** The chemical control of weed is a necessary practice in large-scale agriculture. However, when herbicides are used in the wrong way, they can remain into soil for long periods and/or be leached in its profile, and they may even contaminate groundwater. In this research, clomazone leaching in soil samples collected from different Brazilian regions was estimated by biological method. To do so, columns containing soils were used, and samples were collected every 5 cm. After preparing columns and applying a 1,500 g a.i. ha^{-1} clomazone dose, rain simulation was performed. Sorghum was used in order to detect the herbicide. More than 60% similarity was found for the studied variables; it was chosen to use only data referring to toxicity percentage. Clomazone did not cause reduction in sorghum cultivated in Organosol, thus indicating a strong herbicide sorption in this soil. Increased pH in Oxisol reduced leaching. More rainfall caused increased herbicide leaching in Oxisol (pH 5.1) and Quartzarenic Neosol. The highest leaching occurred in soils with lower pH and lower organic matter content. It is possible to conclude that, in soils with higher organic matter content, clomazone has lower risks of being leached.

Keywords: herbicide, mobility in soil, environmental impact.

RESUMO **-** *O controle químico das plantas daninhas é prática consolidada na agricultura em larga escala. No entanto, quando os herbicidas são utilizados da forma incorreta, eles podem permanecer no solo por longos períodos e/ou serem lixiviados no seu perfil, podendo contaminar águas subterrâneas. Nesta pesquisa foi estimada, por método biológico, a lixiviação do clomazone em amostras de solos, coletados em diferentes regiões do Brasil. Para isso, foram usadas colunas contendo os solos, seccionadas de 5 em 5 cm. Após o preparo das colunas e aplicação do clomazone na dose de 1.500 g i.a.* ha^{-1}*, foi feita a simulação das chuvas (60 e 90 mm). O sorgo foi utilizado para detecção do herbicida. Similaridade superior a 60% foi constatada nas variáveis em estudo, optando-se por utilizar apenas os dados referentes à porcentagem de intoxicação. O clomazone não causou intoxicação ao sorgo cultivado no Organossolo indicando forte sorção do herbicida nesse solo. O aumento do pH do Latossolo Vermelho-Amarelo reduziu a lixiviação. Maior precipitação causou aumento da lixiviação do herbicida no Latossolo Vermelho-Amarelo (pH 5,1) e no Neossolo Quartzarênico. A maior lixiviação ocorreu em solos com menor pH e menor teor de matéria orgânica. Conclui-se que, em solos com maiores teores de matéria orgânica, o clomazone tem menor risco de ser lixiviado.*

Palavras-chave: herbicida, mobilidade no solo, impacto ambiental.

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INTRODUCTION

Weed management in sugarcane and other cultures in Brazil has been frequently performed with herbicides that persist into soil for a long time (Carbonari et al., 2010). The incorrect and indiscriminate use of these agrochemicals has caused environmental problems, such as the contamination of soil (impeding crop rotation by carryover), groundwater and surface waters (Tanabe et al., 2001). This may be the result of scarce information about herbicide dynamic on different Brazilian soils, which resulted in a single recommendation for different cultivation conditions.

Clomazone [2-(2-chlorobenzyl)-4,4-dimethyl-1,2-oxazolidin-3-one] is an herbicide from the oxazolidinone chemical group and has a wide spectrum for pre- and post-emergence control of monocots and dicots in sugarcane cultures (ANVISA, 2016). In soil solution, it tends to remain in its molecular form because it is a non-ionizable herbicide (Jia et al., 2013). However, non-ionic herbicide behaviors may be influenced by the changes that pH alteration causes in clay mineral complexes and in the organic matter of soil (Silva et al., 2007).

Knowing the processes that interfere in herbicide behavior is fundamental to understand its destination in the environment, especially in relation to the process of leaching into soil (Andrade et al., 2010). This process is characterized as the main herbicide transport way, because of the descending movement of molecules from these products into soil matrix in mass flow, together with soil water. The leaching potential of an herbicide depends on its physical-chemical characteristics and on the edaphoclimatic conditions of culture location (Andrade et al., 2011).

Herbicide mobility is a necessary process in the effective control of weed plant seeds distributed in the soil seed bank (Bachega et al., 2009). However, excessive leaching may contribute to herbicide migration from the place of interest to deeper soil layers, with the possibility of reaching groundwater. Thus, the leaching process is directly related to the effectiveness in controlling weeds and to the risks of environmental contamination by herbicides.

Herbicides are toxic agents that are frequently found in very low soil concentrations, which hinders their detection. In this case, biological tests with vegetal species that present high sensitivity to herbicides have been used in various researches about monitoring herbicides into soil (Pessala et al., 2004). These tests constitute an active form of biomonitoring, because test organisms are used in them, defined as individuals that are standardized and cultivated in a protected environment, which may provide information about the conditions of an ecosystem facing the presence of an environmental impact agent (Raya-Rodriguez, 2000). When the contaminant is an herbicide, plants that are sensitive to the compound of interest have been used to detect its presence. Schreiber et al. (2013) verified that sorghum was very sensitive to clomazone and with the ability to be used in studies about herbicide behavior into soil.

Considering that there are few studies about clomazone behavior in tropical soils, this research was conducted with the goal of determining its leaching potential, by biological method, in five soils with different physical and chemical characteristics, collected in different Brazilian regions.

MATERIAL AND METHODS

Soil samples used in this study were collected in the states of Minas Gerais (cities of Viçosa, Diamantina and Rio Paranaíba) and Espírito Santo (city of Venda Nova do Imigrante). Five experiments were conducted, one for each soil type. Evaluated soils were: Red-Yellow Latosol, in Viçosa, Minas Gerais state; Red Latosol, in Rio Paranaíba, Minas Gerais state; ortic Quartzarenic Neosol, in Diamantina, Minas Gerais state; and Organosol, in Venda Nova do Imigrante, Espírito Santo state. The Red-Yellow Latosol was separated in two samples; one of them was submitted to acid-base titration curve with $CaCO_3$, and its pH was elevated to 6.5.

Soil samples were collected in areas with no herbicide application history, in the superficial layer (0.0 - 0.20 m depth); subsequently, they were buffered, dried in the shade, sieved in a 2 mm mesh and, later, they were chemically and physically characterized (Table 1). As well as the five experiments with each soil type, an experiment in inert substrate was conducted, in completely

Table 1 - Characteristics of chemical and physical analyses of soils that were evaluated in the experiments: Red-Yellow Latosol (LVA) with and without liming, Red Latosol (LVr), Quartzarenic Neosol (Entisol) (NQd) and Organosol (Ov)*

Soil	pH	P	K	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	(t)	V	M	MO
	(H_2O)	(mg dm^{-3})		(cmol$_c$ dm^{-3})					(%)		
LVA(1)	6.5’	0.6	9	0.34	0.15	0.0	2.52	0.79	60.0	0.0	2.07
LVA(2)	5.1	0.6	9	0.04	0.06	1.6	5.30	1.66	2.90	90.7	2.07
LVr	6.0	2.6	39	1.20	0.40	0.0	2.64	1.70	39.0	0.0	2.18
NQd	5.3	10.5	41	0.70	0.20	0.0	1.48	1.00	40.0	0.0	1.55
Ov	5.0	18.1	185	5.10	3.00	0.6	26.64	9.17	25.0	31.0	20.20

	Coarse S.	Fine S.	Silt	Clay	Textural class
	(dag kg^{-1})				
LVAv	11	10	17	62	Very Clayey
LVr	10	33	16	41	Clayey
NQd	44	44	8	4	Sandy
Ov	14	20	30	36	Granitic-clay

* Analyses were conducted in the Laboratório de Análises de Solo Viçosa (Viçosa Soil Analyses Laboratory), according to the Empresa Brasileira de Pesquisa Agropecuária – Embrapa metodology (1997); (t) = effective cation exchange capacity; V = base saturation; m = Al^{+3} saturation; MO = organic matter; (1) Red-Yellow Latosol with liming, (2) Red-Yellow Latosol without liming.

randomized design with four replications. In all experiments, treatments were arranged in 2 x 10 factor scheme; the first factor corresponded to the quantity of simulated precipitation in each soil column (60 and 90 mm) and the second one corresponded to the collection depth of soil samples in columns (0-5, 5-10, 10-15, 15-20, 20-25, 25-30, 30-35, 35-40 and 45-50 cm).

The simulation of soil profile was made in PVC tubes with 10 cm diameter and 50 cm height, which were covered with filter paper on their lower side and, on the inside, paraffin layers were applied, in order to avoid side leaking in soil solution.

Columns were filled with samples from different substrates (soils to be evaluated). After that, soil columns were submitted to capillary irrigation until visible saturation on top of them. After saturation, these columns remained 48 hours in the vertical position for water draining, in order to get closer to field capacity. Subsequently, clomazone (Gamit®) was applied using a high-precision sprayer, in the 1,500 g a.i. ha^{-1} dose, on top of the columns. In order to avoid drifting, applications were made at a room temperature around 25 °C and 70% relative humidity. During rain simulation, the water volume reaching each column was monitored by rain gauges; subsequently, columns were kept at rest for 72 hours to drain the remaining excess water.

After this period of time, columns were placed in the horizontal position and opened to collect substrate samples every 0.5 cm depth (10 depths). Samples were transferred to planters with 260 cm^3 capacity; in each one of them five BR 007 sorghum (*Sorghum bicolor*) seeds were planted, at 0.015 m depth.

On day 7, 14 and 21 after sorghum plants germination, the visual evaluation of plant intoxication percentage was performed, giving grades that varied from 0 (no intoxication) to 100 (plant death).

On day 21 after germination, the experiment harvest was performed, which was constituted by cutting the aerial part of plants close to the substrate surface and removing roots in running water. Later, all this material was dried in a forced air ventilation oven (70 ± 2 °C) until reaching constant mass. The determination of aerial part dry matter, root and total indicator plants was performed with a 0.001 g precision scale.

All these variables were statistically analyzed, with the goal of selecting groups that could be discriminated and represented by a single evaluation. To do so, a similarity percentage multivariate analysis among variables was performed for each substrate and it was based on the absolute correlation among variables. These analyses were performed using Minitab® 16.2.1 statistical software. After that, averages were presented with their respective standard-deviations to observe the ability of retaining clomazone by the different soil samples.

RESULTS AND DISCUSSION

Based on the observed results, it was noticed that clomazone is highly absorbed by Organosol. In this substrate, regardless of the applied rain volume, no intoxication symptom was observed in sorghum plants that were cultivated in samples collected in the different column depths. This also indicates that, in case this dose is applied for pre-emergence weed control, it would be totally ineffective. For this reason, the proposed statistical analysis were not conducted in this substrate. These results may be explained by the polarity of the studied compound (clomazone) and by the levels of organic matters found in Organosol (20.20%).

Generally speaking, the connection of the herbicide with soil colloids occurs by adsorption with the surface, through hydrogen connections and van der Waals interactions, connecting to hydroxyl and carboxyl groups (Liao et al., 2014). The sorption of non-ionic molecules, like clomazone, is quite influenced by the percentage of organic matter (Benoit et al., 2008); it is the probable cause of the absence of intoxication symptoms, causing herbicide unavailability in soil solution to plants.

In the other substrates, similarity percentage multivariate analyses among variables were similar in the four soils (Figure 1). In these substrates, indices were higher than 60%, which represents high similarity among variables. For this reason, all variables were framed in the same group and represented by the same variable: intoxication of sorghum plants that were evaluated 21 days after emergence.

Intoxication symptoms were characterized by whitening of young tissues and later necrosis, and, in some cases, plant death occurred. These symptoms are evident and characteristic because clomazone acts on the inhibition of carotenoid biosynthesis, reducing the ability of

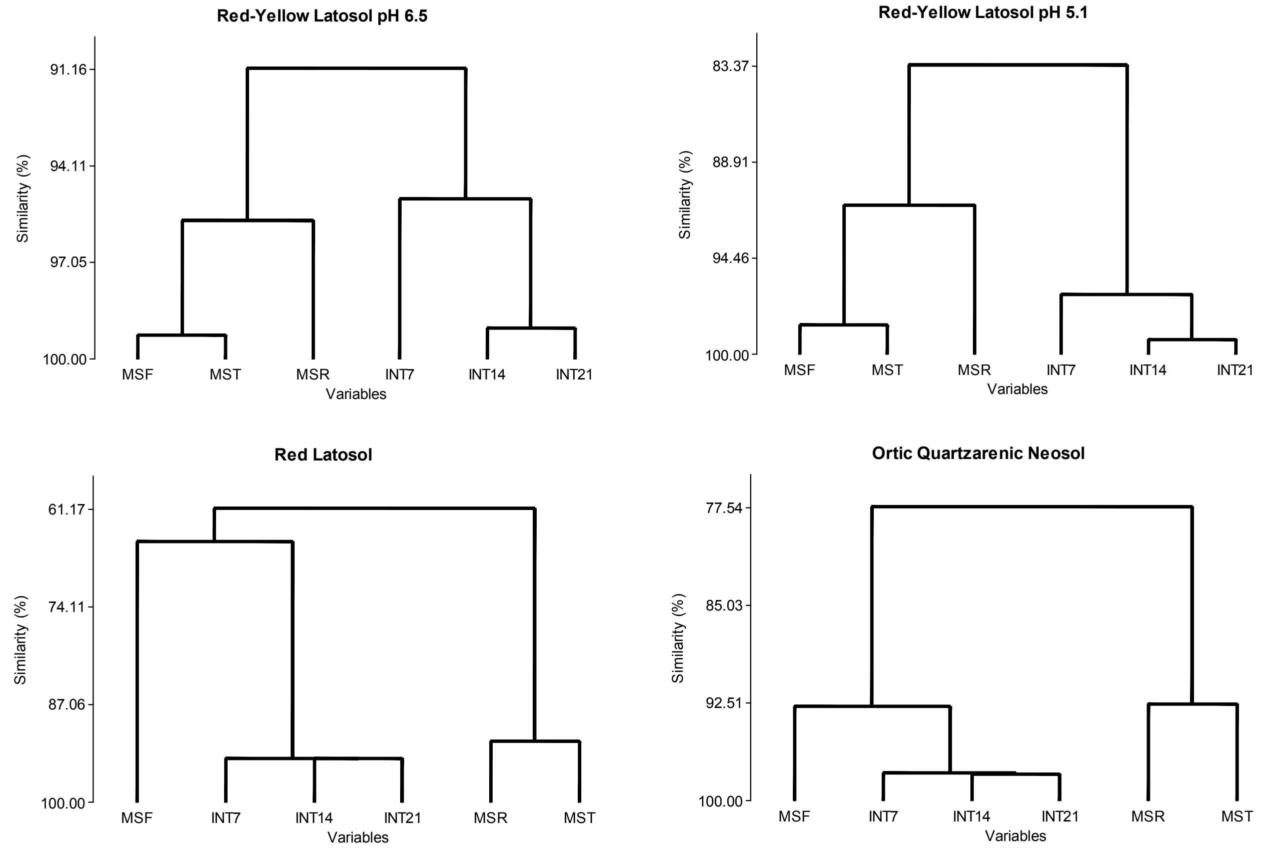

Figure 1 - Similarity percentage among variables: sorghum intoxications on day 7 (INT 7), 14 (INT 14) and 21 (INT 21) after emergence and aerial part dry matter (MSF), root (MSR) and total (MST) for each studied substrate (Red-Yellow Latosol, Red Latosol and ortic Quartzarenic Neosol), established according to absolute correlations among variables.

these compounds to dissipate the excess of energy in the aerial part of plants (Dayan et al., 2007). Dan Hess (2000) reports that these pigments are essential in energy dissipation and, when excessive, they may cause the destruction of chlorophyll molecules by oxidation reactions.

In Red-Yellow Latosol with pH correction (6.5), sorghum intoxication values (Figure 2A) indicated that clomazone was leached until 15 to 20 and 20 to 25 cm depths, in the 60 and 90 mm precipitation simulations, respectively. In this same substrate with no pH correction (5.1), there was no difference in herbicide leaching compared to the substrate with pH correction, in the 60 mm precipitation (Figure 2B). However, in the simulation of 90 mm rain precipitation, higher herbicide leaching occurred; symptoms were observed on plants that were cultivated in samples collected up to the 30 to 35 cm layer.

The highest clomazone leaching in the lowest pH value and under 90 mm rain simulation is probably due to the strong interaction between clomazone and organic matter in soils. This interaction may be influenced by conformational changes caused by organic matter molecules, when there is pH variation of the medium; they can influence the herbicide adsorption ability (Gennari et al., 1998; El Madani et al., 2003).

Clomazone was leached until the 20 to 25 cm layer in Red Latosol, regardless of the applied rain volume (Figure 2C). The possible explanation to this behavior is based in the small herbicide proportion absorbed, due to lower organic matter content and the average clay content of this substrate (Table 1). However, in the simulation of 90 mm rain precipitation, higher herbicide leaching occurred; symptoms were observed on plants that were cultivated in samples collected up to the 10 to 15 cm layer, under 60 mm rain precipitation simulation. When 90 mm rain was applied, these symptoms were visible in sorghum samples collected up to 30 to 35 cm depths.

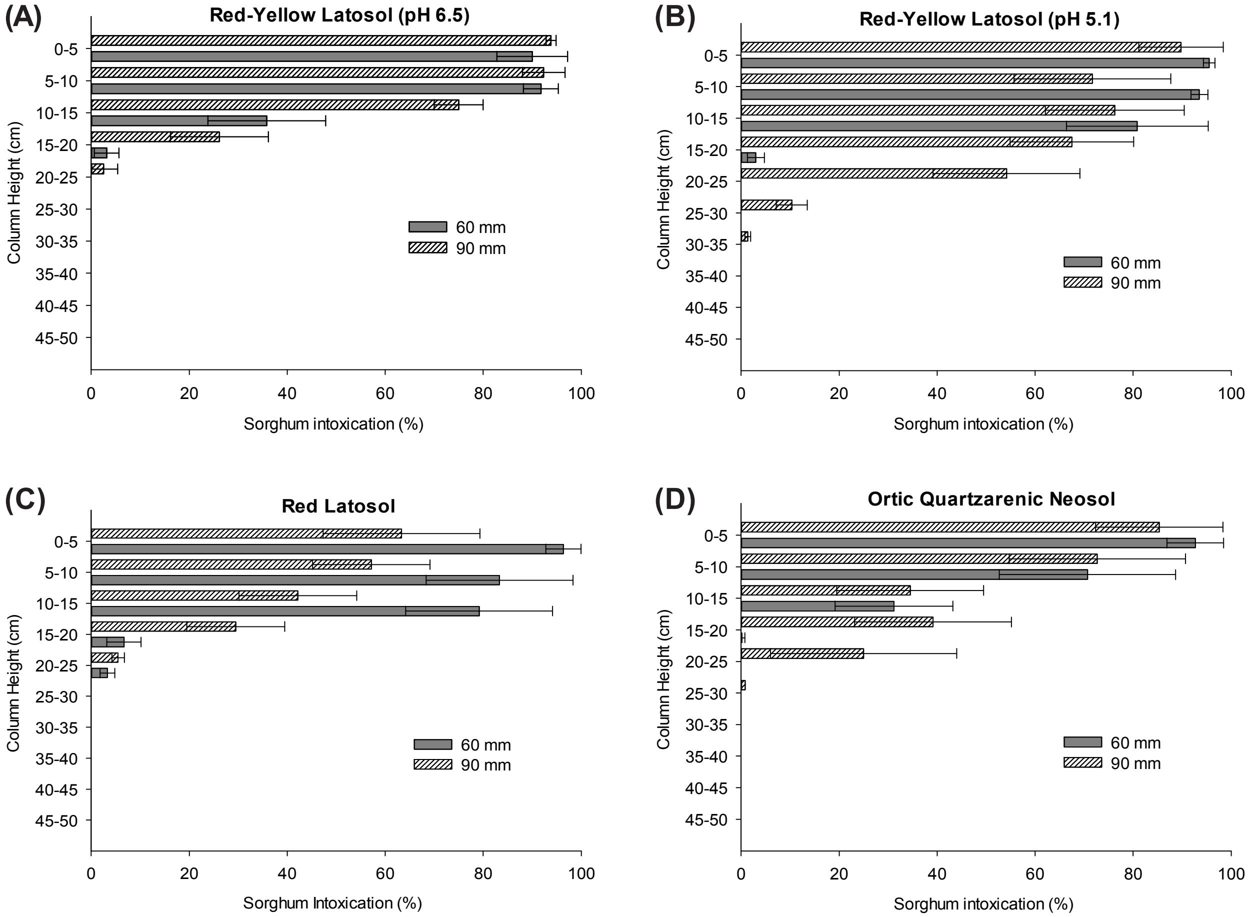

Figure 2 - Sorghum plant intoxication after clomazone leaching in columns that were filled with Red-Yellow Latosol (pH 6.5 and 5.1), Red Latosol and ortic Quartzarenic Neosol and submitted to 60 and 90 mm rains, evaluated on day 21 after emergence.

Clomazone leaching in soils with sandy texture, similar to Neosol, is due to the low organic matter content (1.55%) and to low herbicide sorption to colloids in this substrate, as well as its mineralogy. Consequently, higher herbicide quantities remained in soil solution and were taken to lower depths, mainly under greater rain and/or irrigation intensity, as observed by Cumming et al. (2002).

The varied behaviors observed in the studied substrates may change the effectiveness in weed control when herbicide application is performed in pre-emergence. Higher clomazone quantities may be lost due to leaching in some soils. In these cases, despite the fact that, at first, the herbicide has a greater chance of controlling propagules of soil seed bank at lower depth, it may promote ineffective control of plants whose seeds are in the upper layer of soil profile. According to Buhler et al. (1997), more than 90% weeds that germinate in an agricultural area had seed origin distributed up to 10.0 cm depth. Moreover, greater clomazone transport in soil profile may cause higher water contamination.

Agrochemical leaching in soil profile has direct implications in the contamination potential of water resources in the subsoil, because once it has percolated in the upper soil layer (where there are higher organic matter contents and microbial activity), its persistence in the environment may be intensively prolonged (Sarmah et al., 1998; Prata et al., 2001). Some studies using clomazone in different soils over the world have related its sorption with soil organic matter contents (Gunasekara et al., 2009; Umiljendiæ et al., 2013), which explains symptom absence in Organosol, with lower herbicide leaching. In the other substrates that presented lower organic matter levels, the other attribute that must be considered is clay content, as reported by Monquero et al. (2008). These authors concluded that, the lower the contents of organic matter and clay in the studied soils, the higher the risk of clomazone leaching.

It is possible to conclude that, in soils with higher organic matter content, clomazone has lower probabilities of being leached. However, in soils with lower percentages of this attribute, such as most latosols and neosols, there is great risk for this herbicide to be leached through the soil profile. Knowing this leaching ability in soil before its application may determine the selectivity and/or effectiveness of weed control, as well as the risk of groundwater contamination.

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