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Liming on picloram leaching in dystrophic Red Yellow Latosol

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ABSTRACT: The practice of liming may influence the leaching of herbicides in soils, especially those with weak acid character, such as picloram. The study on leaching, preserving soil structure, is an important factor when one intends to understand the dynamics of herbicides and environmental impacts. Thus, the effect of liming on picloram leaching in a dystrophic Red Yellow Latosol under field conditions was studied using a bioindicator plant. The experiment was set up in a completely randomized design (CRD), in split-plot scheme, with factorial in the plot. The factors of the plot corresponded to two soil conditions (presence and absence of liming) and 5 picloram concentrations (0; 384; 768; 1152; 1536 g ha^{-1}), and the factor of the subplot was 5 soil depths (0-8, 8-16, 16-24, 24-32 and 32-40 cm), with four replicates. Pipes were introduced into the soil and, in part of the treatments, limestone was applied superficially. After ninety days, the different doses of picloram were applied on the surface of each pipe and these pipes were withdrawn after an accumulated rainfall of 128 mm, to perform the bioassay using cucumber plants (*Cucumis sativus*). Evaluations of plant development (phytotoxicity and shoot biomass) were carried out 21 days after sowing. It was concluded that picloram showed high leaching rate under all studied conditions and liming increased picloram leaching at doses lower than 768 g ha^{-1}.

Key words: *Cucumis sativus*, herbicide dynamics, soil pH

Calagem na lixiviação do picloram em Latossolo Vermelho Amarelo distrófico

RESUMO: A prática da calagem pode influenciar a lixiviação de herbicidas nos solos, especialmente os com caráter ácido fraco, como é o caso do picloram. O estudo da lixiviação mantendo-se a estrutura do solo é um fator importante quando se busca compreender a dinâmica de herbicidas e possíveis impactos ambientais. Assim, objetivou-se avaliar o efeito da calagem na lixiviação do picloram em um Latossolo Vermelho Amarelo distrófico, em condições de campo, a partir de planta bioindicadora. O experimento foi organizado em delineamento inteiramente casualizado (DIC), no esquema de parcela subdividida, com fatorial na parcela. Os fatores da parcela corresponderam a duas condições de solo (sem e com calagem) e 5 concentrações do picloram (0; 384; 768; 1152; 1536 g ha^{-1}), e o fator da subparcela foram 5 profundidades do solo (0-8, 8-16, 16-24, 24-32 e 32-40 cm), com quatro repetições. Tubos foram introduzidos no solo, onde, em parte dos tratamentos, aplicou-se calcário superficialmente. Após noventa dias, as diferentes doses do picloram foram aplicadas na superfície de cada tubo e os mesmos foram retirados após um acúmulo de 128 mm de chuva, para realização do bioensaio, com plantas de pepino (*Cucumis sativus*). Foram realizadas avaliações do desenvolvimento das plantas (fitointoxicação e biomassa da parte aérea) 21 dias após a semeadura. Concluiu-se que o picloram apresentou alta taxa de lixiviação em todas as condições estudadas e a calagem aumentou a lixiviação do picloram em doses inferiores a 768 g ha^{-1}.

Palavras-chave: *Cucumis sativus*, dinâmica de herbicida, pH do solo

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Introduction

The use of herbicides to control weeds has been fundamental in the cultivation of large agricultural areas (Silva et al., 2012). In pastures, the herbicide picloram (4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid) stands out, being highly active in dicotyledons (Rodrigues & Almeida, 2011).

Picloram has persistence in the environment of up to 360 days (Santos et al., 2006), which may cause toxicity in sensitive species cultivated in succession (Barros et al., 2014; Franco et al., 2016). Additionally, it has high potential for leaching and contamination of underground waters (Inoue et al., 2003; Assis et al., 2011).

Leaching is the main form of transport in the soil of non-volatile and water-soluble molecules (Monquero et al., 2010). This process depends on herbicide characteristics, soil attributes and climatic conditions (D'Antonino et al., 2009).

Soil acidity correction in the direct planting system is carried out by means of liming application on the surface without incorporation (Rodrighero et al., 2015). Soil pH stands out among the soil attributes which influence the behavior from herbicides with ionic character to organic and mineral colloids (Silva et al., 2007). Thus, liming may eventually alter picloram availability in the soil in a significant manner (D'Antonino et al., 2012), possibly intensifying its leaching.

In studies on herbicide activity in soils, researchers have used the bioassay. This technique consists in using plants that are sensitive to the products tested, so that the residues of herbicides present in the soil can be evidenced by the alteration in the agronomic characteristics of the test plants (Melo et al., 2010).

Thus, this study aimed to evaluate the influence of liming on picloram leaching in a dystrophic Red Yellow Latosol, using a bioindicator plant.

Material and Methods

The experiment was carried out in the 2016/2017 season at the Federal University of Mato Grosso, Sinop Campus, located at geographic coordinates 11° 52' 00" S and 55° 28' 52" W. The first phase of the study was set up and conducted under field conditions in a dystrophic Red Yellow Latosol (LVA), according to the classification of EMBRAPA (2013). Soil chemical and granulometric analyses were performed using samples collected in the 0-5 cm layer (Silva, 2009), before the experiment was set up and after the first phase of the study. The results of soil chemical and granulometric analyses before the experiment was set up, in the 0-5 cm layer, were: P (resin): 1.33 mg dm^{-3}, OM: 35.83 g dm^{-3}, pH ($CaCl^2$): 4.3, K: 0.08 $cmol_c$ dm^{-3}, Ca: 1.15 $cmol_c$ dm^{-3}, Mg: 0.29 $cmol_c$ dm^{-3}, H+Al: 7.83 $cmol_c$ dm^{-3}. Fe: 148 mg dm^{-3}, Sand: 335 g dm^{-3}, Silt: 167 g dm^{-3}, Clay: 498 g dm^{-3}.

The characterization performed after the first phase of the study, in the 0-5 cm layer, showed: P (resin): 0.043 $cmol_c$ dm^{-3}, OM: 31.92 g dm^{-3}, pH ($CaCl^2$): 4.8, K: 17 mg dm^{-3}, Ca: 2.34 $cmol_c$ dm^{-3}, Mg: 1.51 $cmol_c$ dm^{-3}, H+Al: 5.74 $cmol_c$ dm^{-3}, Fe: 77 mg dm^{-3}, Sand: 262 g dm^{-3}, Silt: 229 g dm^{-3}, Clay: 509 g dm^{-3}.

The experiment was conducted in a completely randomized design (CRD), in split-plot scheme, with factorial in the plot. The factors of the plot corresponded to 2 soil conditions (presence and absence liming) and 5 picloram concentrations (0; 384; 768; 1152; 1536 g ha^{-1}), whereas the factor of the subplot was 5 soil depths (0-8, 8-16, 16-24, 24-32 and 32-40 cm), with four replicates.

To study picloram leaching, 40 PVC pipes (15 cm diameter and 40 cm length) were inserted in the soil. To evaluate the influence of limestone on the leaching process, magnesium limestone (RNV 99%) was applied on the surface of the pipes in an amount corresponding to 0.93 Mg ha^{-1}, calculated based on the results of soil chemical analysis in the 0-10 cm layer. The experiment remained in the field for 3 months for a complete reaction of limestone in the soil, and a rainfall of 816 mm accumulated during this period.

Three months after soil correction, the 5 picloram doses were applied on the surface of each pipe, with the mixture volume calibrated to 400 L ha^{-1}. After application, the pipes were withdrawn from the soil with an accumulated natural rainfall of 128 mm, which occurred within a period of 40 h. The accumulated rainfall was measured by a rain gauge installed in the experimental area.

Twenty four hours after the last rainfall, the pipes were withdrawn from the soil, maintaining their original integrity. Then, they were taken to a greenhouse, longitudinally cut and separated into two parts for the bioassay, which consisted in the second phase of the study.

In each longitudinal half of the PVC pipes and at each depth evaluated (0-8, 8-16, 16-24, 24-32 and 32-40 cm), 4 seeds of the bioindicator species, cucumber (*Cucumis sativus*), were sown, two in each one of the halves, and the mean of four plants corresponded to a replicate. Cucumber development (phytotoxicity and shoot dry matter) was evaluated at 21 days after sowing.

Phytotoxicity in cucumber plants was evaluated by assigning grades from 0 (plants with absence of symptoms) to 10 (plant death) (EWRC, 1964). Cucumber plants were cut at the collar to separate the shoots. This material was dried in a forced-air oven at 75 °C until constant weight. Then, it was weighed on a precision scale to obtain the dry matter.

The means of the evaluations of the controls (picloram dose of 0 in each treatment), except those of phytotoxicity, were converted to 100%. Then, the means of the treatments with picloram doses were transformed to percentage, in relation to the mean of the control.

The data obtained in the bioassay were subjected to analysis of variance by F test and, when significant, treatment means were compared by Scott-Knott test at 0.05 probability, and means of the doses were subjected to regression analysis. The statistical analysis was conducted using the software program SISVAR (Ferreira, 2011).

Results and Discussion

Higher doses of picloram in the soil, regardless of liming, caused phytotoxicity in cucumber plants cultivated at all depths evaluated, as shown in Figure 1.

Among the symptoms of phytotoxicity, it was possible to observe crinkled leaves, twisted stem, alterations of height

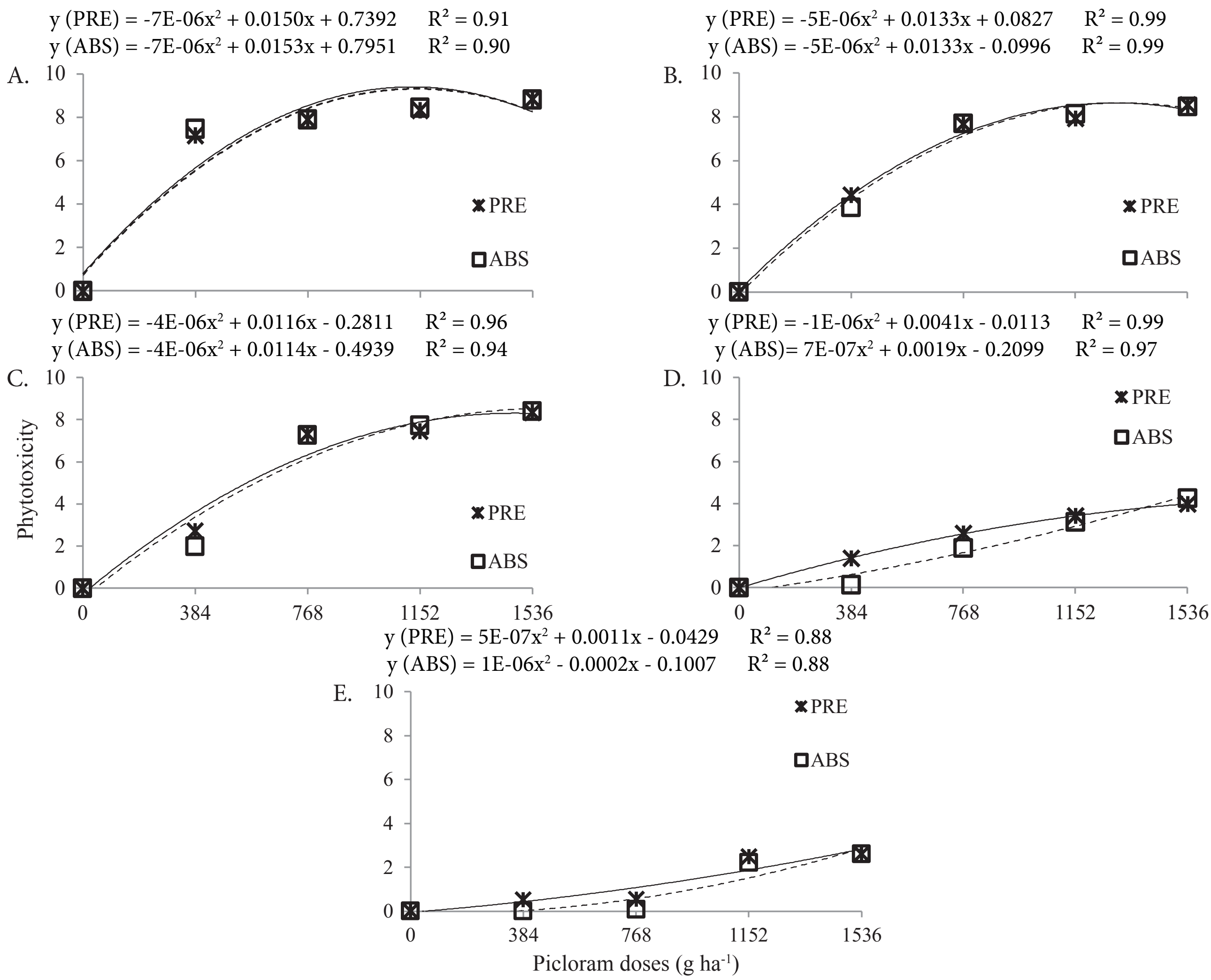

Figure 1. Phytotoxicity in cucumber plants (*Cucumis sativus*) cultivated at depths of 0-8 cm (A); 8-16 cm (B); 16-24 cm (C); 24-32 cm (D) and 32-40 cm (E) in a dystrophic Red Yellow Latosol (LVAd), subjected to doses of the herbicide picloram, in the presence (PRE) and absence (ABS) of limestone

and reduced growth of true leaves, especially at the highest doses and shallowest depths studied, indicating the presence of picloram.

Santos et al. (2013), studying doses of auxinic herbicides, including picloram, on bioindicator plants, reported the same symptoms found here and highlighted that visual phytotoxicity was the most adequate variable to detect low levels of picloram residues.

The results of phytotoxicity in cucumber plants, for each dose of picloram, and the influence of limestone on leaching, are presented in Table 1. For all doses of picloram and values of pH studied, there was a reduction in the phytotoxicity of plants as soil depth increased.

These results are similar to those observed by D'Antonino et al. (2009), who studied picloram leaching in a Red Yellow Latosol with pH of 4.9, followed by a simulated rain of 40 mm, and observed high intensity of the symptoms in cucumber plants cultivated in the upper part of the column, and this intensity decreased up to 35 cm depth.

Limestone influenced the phytotoxicity of plants at the lowest doses of picloram (Table 1). With limestone application on soil surface, the phytotoxicity was greater at 8-16 cm depth

Table 1. Means of phytotoxicity of cucumber plants (*Cucumis sativus*) cultivated at different depths and doses of picloram, in a dystrophic Red Yellow Latosol (LVAd) in the presence (PRE) and absence (ABS) of limestone

Depth (cm)	Doses (g ha^{-1})									
	0		384		768		1152		1536	
	Limestone									
	PRE	ABS	PRE	ABS	PRE	ABS	PRE	ABS	PRE	ABS
0-8	0	0	7.2 aA	7.5 aA	7.9 aA	7.9 aA	8.3 aA	8.4 aA	8.9 aA	8.8 aA
8-16	0	0	4.4 bA	3.9 bB	7.7 aA	7.7 aA	7.9 aA	8.1 aA	8.6 bA	8.5 aA
16-24	0	0	2.7 cA	2.0 cB	7.3 bA	7.3 bA	7.5 bA	7.7 bA	8.4 bA	8.4 aA
24-32	0	0	1.4 dA	0.1 dB	2.6 cA	1.9 cB	3.4 cA	3.1 cA	4.0 cA	4.3 bA
32-40	0	0	0.5 eA	0.0 dB	0.6 dA	0.1 dB	2.5 dA	2.2 dA	2.6 dA	2.6 cA
CV 1 (%)	7.99									
CV 2 (%)	6.90									

Means followed by the same uppercase letter for each dose in the row and lowercase letter in the column do not differ by Scott-Knott test at 0.05 probability level for the dose of 384 g ha^{-1} and at 24-32 cm depth for the dose of 768 g ha^{-1}, compared with the means in the treatment without liming. These results suggest that the superficial application of limestone influenced picloram leaching at doses lower than 768 g ha^{-1}.

In Latosols, kaolinite, which is the main mineral of these soils, has pH-dependent charges. The increase in pH causes this mineral to become negatively charged due to the deprotonation of hydroxyls (Oliveira & Brighenti, 2011). This same effect occurs with picloram molecules, which also become negatively charged because they have weak acid character (pKa ~ 2.3) (Rodrigues & Almeida, 2011).

As limestone application elevated the pH in the surface soil layer, this may have left clays and picloram with a greater amount of negative charges, which led to a repulsion between them, resulting in a smaller sorption of the herbicide, and consequently causing its leaching (Silva et al., 2007).

For the highest doses of the herbicide (1152 and 1536 g ha^{-1}), limestone application did not influence the phytotoxicity of the plants, showing no difference from the condition without limestone. However, higher levels of phytotoxicity were observed in the entire column. This indicates that, at high doses of picloram, the effect of liming, with the consequent increase in pH, is no longer an important factor in the herbicide leaching.

Shoot dry matter decreased as the applied doses of picloram increased, in both absence and presence of limestone (Figure 2).

The reductions of dry matter compared with the control reached 74% at the depth of 0-8 cm and 62% at 8-16 cm. Similar results were also reported by Santos et al. (2013), who observed that the picloram dose of 656.8 g ha^{-1} reduced by 50% the total dry matter of cucumber plants cultivated in soil with pH of 5.3.

At depth 16-24 cm, in the absence of limestone application, there were reductions in shoot dry matter as increasing doses of picloram were used. The same occurred for the soil under limestone application, but with higher intensity (Figure 2).

Studies conducted in soils, through the collection of water percolated in lysimeters, demonstrated that picloram was found at depth of 109 cm (Berisford et al., 2006). Studies of this nature are an important contribution to evaluate the environmental impacts of these products and their future effects.

It is possible to observe in Table 2 that there was influence of limestone on picloram leaching at all doses of this herbicide. At dose of 384 g ha^{-1}, limestone reduced shoot dry matter from

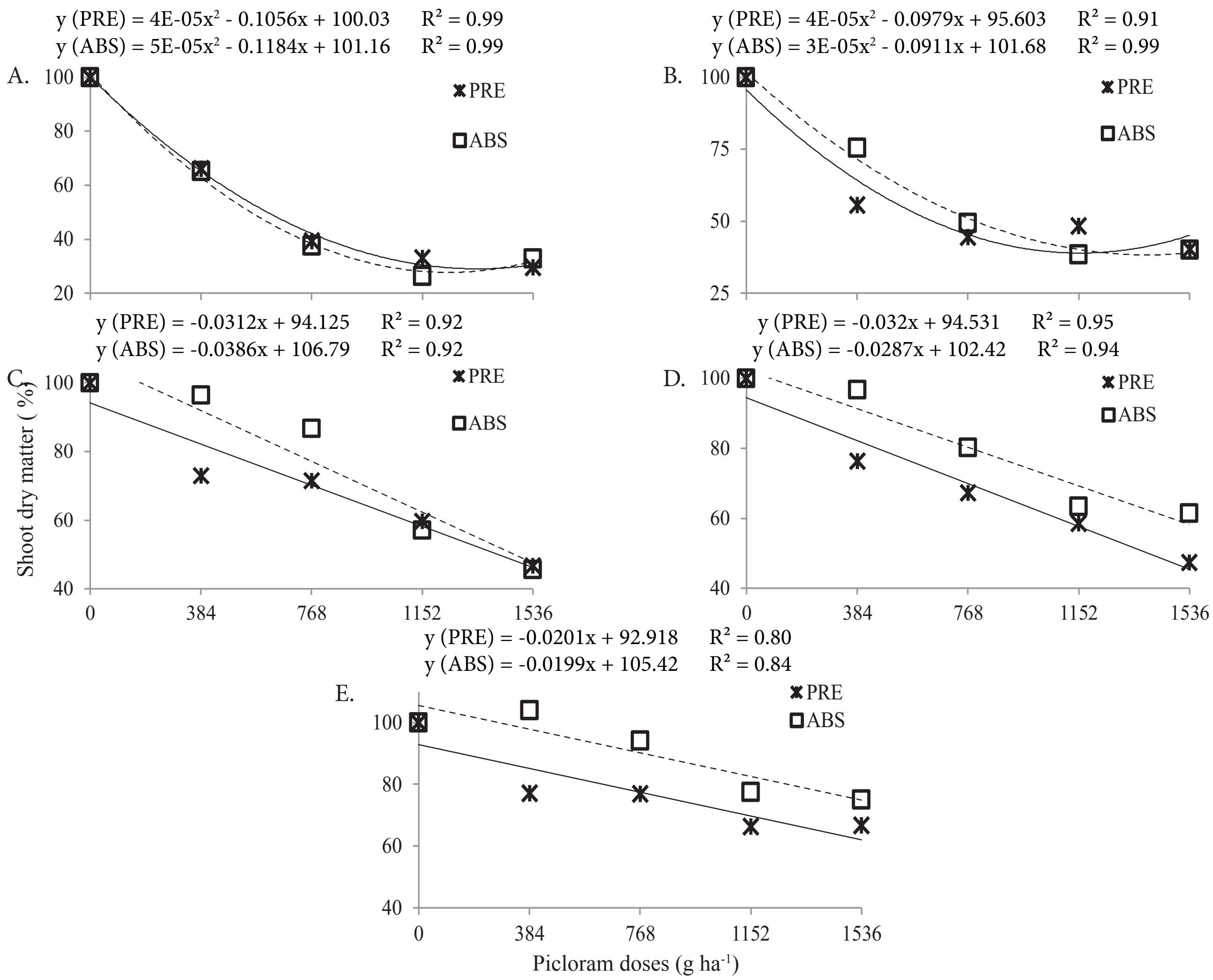

Figure 2. Shoot dry matter of cucumber plants (*Cucumis sativus*) cultivated at the depths of 0-8 cm (A); 8-16 cm (B); 16-24 cm (C); 24-32 cm (D) and 32-40 cm (E) of a dystrophic Red Yellow Latosol (LVAd), subjected to doses of the herbicide picloram, in the presence (PRE) and absence (ABS) of limestone

Table 2. Means of shoot dry matter percentage in cucumber plants (*Cucumis sativus*) cultivated at different depths and doses of picloram, in a dystrophic Red Yellow Latosol (LVAd) in the presence (PRE) and absence (ABS) of limestone

Depth (cm)	Doses (g ha^{-1})									
	0		384		768		1152		1536	
	Limestone									
	PRE	ABS	PRE	ABS	PRE	ABS	PRE	ABS	PRE	ABS
0-8	100	100	66.2 aAaA	65.3 aA	39.5 aA	37.7 aA	33.1 aA	26.5 aA	29.6 aA	32.9 aA
8-16	100	100	55.7 aAaA	75.5 aB	44.6 aA	49.4 aA	48.5 bA	38.5 aA	40.4 aA	40.2 aA
16-24	100	100	72.9 bAbA	96.4 bB	71.5 bA	86.8 bB	59.6 cA	57.0 bA	46.7 aA	45.5 aA
24-32	100	100	76.4 bAbA	96.7 bB	67.4 bA	80.2 bB	58.6 cA	63.4 bA	47.5 aA	61.5 bA
32-40	100	100	77.5 bAbA	104.0 bB	76.9 bA	94.2 bB	66.4 cA	77.5 cA	66.8 bA	75.1 bA
CV 1 (%)						23.83				
CV 2 (%)						15.38				

Means followed by the same uppercase letter for each dose in the row and lowercase letter in the column do not differ by Scott-Knott test at 0.05 probability level

the 8 cm depth and, at dose of 768 g ha^{-1}, from the 16 cm depth. However, no effect was observed at higher doses.

These results reinforce the responses observed for phytotoxicity, evidencing that liming does not interfere with picloram leaching at doses of 1152 and 1536 g ha^{-1}. Possibly, the quantity of charges present in the soil was not able to adsorb the large amount of molecules of this herbicide, keeping it more available in the soil solution and allowing greater leaching to occur.

At dose 384 g ha^{-1}, limestone caused a reduction in shoot dry matter compared with the control. However, without limestone application, from the 16 cm depth, the shoot dry matter of the plants varied between 96 and 104% of that found in the control, which indicates little or no leaching of picloram under these conditions. At doses between 768 and 1536 g ha^{-1}, regardless of liming, there was a reduction in the shoot dry matter of the plants at all depths, indicating leaching of picloram in the entire soil profile.

According to Silva et al. (2007), in soils with pH higher than the herbicide's pKa, there is greater release of the herbicide to soil solution, thus becoming more available to the medium. D'Antonino et al. (2009) concluded that picloram has high leaching potential in Red Yellow Argisol and in Red Yellow Latosol, and that the pH of these soils was decisive in its movement.

Picloram leaching was influenced by liming and by the herbicide dose used. These factors must be taken into account to provide adequate technical recommendations because more acid soils under lower doses of picloram pose lower risk of leaching of this product.

Conclusions

1. There was leaching of the herbicide picloram in dystrophic Red Yellow Latosol (LVAd) and its leaching intensity decreased along the soil profile, regardless of limestone application.

2. Limestone application on surface increases picloram leaching at doses lower than 768 g ha^{-1}, in dystrophic Red Yellow Latosol (LVAd).

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