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Leaching of 2,4-d and atrazine herbicides in red-yellow latosol

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Abstract: The intensive use of herbicides has increased the possibility of environmental contamination and the accumulation of pesticide residues in soil and water. This work aimed to evaluate the leaching potential of 2,4-D and atrazine herbicides in red-yellow latosol with a clayey texture. The experimental design was entirely randomized, in factorial 5x3 (five doses of each herbicide for three soil depths). The doses used were 1.25, 2.50, 6.25 and 12.50 L ha^{-1} for the 2.4-D herbicide and 2.25, 4.50, 11.25 and 22.50 L ha^{-1} for the atrazine herbicide (plus absolute witnesses). The herbicides were applied in buried pvc tubes to the soil and after accumulated rainfall of 87 mm, cucumber was grown as a bio indicator plant. The plant phytotoxicity, plant height, dry mass accumulation and leaf area where the evaluations were performed at 21 days after the sowing of the cucumber were analyzed. The 2.4-D herbicide didn`t present significant difference between treatments for the plant phytotoxicity variable, however, there was difference between treatments for plant height and dry mass. For leaf area, the difference was observed only for soil depths. Atrazine herbicide also showed no difference between treatments for plant phytotoxicity, but there was a difference between treatments and soil depths for the other variables. Under the conditions evaluated, 2,4-D and atrazine herbicides can leach into clayey soil regardless of the dose used and can reach up to 30 cm depth.
Keywords: depth, doses, cucumber, soil

Introduction

The intensive and sometimes inappropriate use of herbicides in modern agriculture has increased environmental contamination due to the accumulation of pesticide residues in the soil and in the water (Belo et al., 2011). One of the phenomena observed by the deposition of pesticide residues in the soil is leaching, which is one of the main forms of transport of these non-volatile and soluble molecules through the soil profile (Monquero et al., 2010).

When these molecules leach into the soil, physical-chemical processes that regulate the degradation of the molecule in the soil or the contamination of groundwater can occur (Mancuso et al., 2011). The leaching potential of these molecules, as well as subsequent behavior, are related to physical and chemical factors of the soil such as: organic matter content, clay content and type, soil pH, soil structure and texture, in addition to factors such as slope of the land and the water regime of the place.

According to Silva et al. (2011), the residual effect of the herbicide 2,4-D is more apparent in medium to clayey soils, due to the presence of higher levels of organic matter. Such levels have a sorption action of the herbicide 2,4-D, avoiding the availability of part of the molecule for the soil solution. Therefore, organic matter from plant residues from agriculture is an important variable for reducing the leaching of herbicides in the soil (Chirukuri & Atmakuru, 2015).

The molecule of the herbicide atrazine (chloro-ethyll-isopropyl-triazine-diamine) has high soil mobility and high potential for groundwater contamination, and the presence of this molecule in the water table reduces the quality of water intended for agriculture and especially for public supply (Soares et al., 2013). For Silva & Silva (2007), the water demand for urban, industrial and agricultural supply has been increasing in recent years, and on the other hand, few studies have been conducted aiming to find ways to delay the transportation of herbicides by water.

Due to the environmental importance that the studies on herbicide leaching represent, this work aimed to evaluate the leaching potential of the 2,4-D and atrazine herbicides, applied in clayey soil columns grown with cucumber plants as bio indicators due to these have shown to be sensitive to these herbicides that are used to control broadleaf plants (Santos et al., 2013).

Methods

The field experiment was carried out at Fazenda Tropeiro Velho (12º 02 '00" S and 55º 31 '06" W), at an altitude of 384 m and 22 km from Sinop - Mato Grosso. The local climate is classified according to Koppen-Geiger as Am (tropical with dry winter), presenting two well-defined seasons, dry: between May and September and rainy: between October and April. The soil used in the experiment was classified as dystrophic red-yellow latosol (DRYL), with clayey texture following the soil classification parameters in Brazil (EMBRAPA, 2013), Table 1.

Table 1. Chemical and physical analysis of the red yellow latosol (RYL)

Chemical analysis											
Depth	pH H_2O	P	K^+	Ca^{+2}	Mg^{+2}	Al^{+3}	H + Al	Effective CEC	Potential CEl	V	O. M.
cm		-----mg/dm^3-----		-----------------------------cmol/dm^3----------------------------						%	g/dm^3
0 a 10	6.80	11.18	126.00	3.88	2.21	0.00	0.49	6.41	6.90	92.83	18.30
10 a 20	6.70	4.87	32.00	3.90	1.94	0.00	0.83	5.92	6.75	87.71	13.63
20 a 30	6.50	2.37	32.00	4.57	3.09	0.00	2.64	7.74	10.38	74.57	20.45

Physical analysis						
Depth (cm)	Porosity (cm^{-3} L)	Macro Porosity (cm^{-3} L)	Micro Porosity (cm^{-3} L)	Particle Density (g cm^{-3})	Soil Density (g cm^{-3})	Degree of Compaction (MPa)
0-10	50.28	10.4	39.83	2.86	1.11	0.39
10-20	52.11	13.4	39.04	2.78	1.16	0.57
20-30	46.77	5.85	40.93	2.97	1.19	1.22

For the experiment, 40 tubes of pvc (polyvinyl chloride) were used as a soil column in the evaluation of the leaching potential of the two herbicides. The dimensions of the tubes were 10 centimeters in diameter and 30 centimeters in length. The experiment was completely randomized in a 5x3 factorial, with 5 doses of herbicide over three depth ranges (0 to 10, 10 to 20 and 20 to 30 cm).

According to the manufacturer, the recommended dose of the herbicide 2,4-D (2,4-D NORTOX®) for growing cucumbers is 1.25 L ha^{-1}. In view of this information, the treatments used were 1.25, 2.50, 6.25 and 12.50 L ha^{-1} and the absolute control. For the herbicide atrazine (ATRAZINA NORTOX 500 SC®) the recommended dose is 2.25 L ha^{-1}. In the same reasoning, the doses used were 2.25, 4.50, 11.25 and 22.50 L ha^{-1}, in addition to the absolute control.

Each herbicide used had its leaching potential assessed independently, with no interaction between them. For each herbicide dose evaluated, four replications were used. The application of the herbicides in the tubes was carried out by means of syrup with a volume equivalent to 125 L ha-1. Thus, the spray volume applied to the area occupied by the tube was 0.10 mL. In order to better control the volume applied and avoid contamination between doses and between herbicides, the doses were applied using 1 mL disposable syringes.

The precipitation occurring at the experiment site was evaluated with a rain gauge. Between the date of application of the herbicide to the soil until the day of removal of the tubes (9 days), 87 mm of rain precipitated. Then the tubes were taken to the greenhouse for growing cucumber as a bioindicator.

The greenhouse had controlled internal temperature and relative humidity (25ºC with a variation of 2ºC and 80% relative humidity). For the planting of cucumber seeds, the tubes with soils that received the doses of the herbicides were cut in half parallel to the length and the seeds were distributed every 10 cm in depth. Each 10 cm depth received four seeds, two seeds for each side of the tube.

For the irrigation of cucumbers during the growing period, each tube with soil was weighed in a condition of humidity corresponding to the field capacity and, thus, the volume of water added to each tube corresponded to the difference between the weight of the tube in capacity to field and weight at the time of irrigation. To avoid handling the tubes, irrigation was performed on alternate days from planting to the end of the experiment, totaling 21 days. After this period, the data were evaluated for the variables:

Phytotoxicity, whose determination of the effect of treatments on cucumber plants was carried out through the visual assessment of phytotoxicity symptoms, from which scores from 1 (No symptoms) to 9 (Plant death) are attributed according to EWRC (1964).

Plant height, obtained by the distance between the stem of the plant until the first leaf intersection, dry masses of the aerial part and root by weighing after drying the plants in an oven for 48 hours at 105 ºC.

The leaf area was determined using a LI-3100 leaf area meter (Li-Cor).

The data obtained were analyzed by variance using the F test and the means were compared using the Tukey test, at a level of 5% probability. To perform these analyzes, the statistical software SISVAR (Ferreira, 2011) was used.

Results and discussion

There was no difference between treatments for phytotoxicity symptoms presented in cucumber plants grown in soil with 2,4-D herbicide. On the other hand, there were injuries to cucumber plants, such as leaf deformation, partial leaf necrosis and senescence of some plants for all depths evaluated. The same symptoms were reported by Santos et al. (2013) in tomato, cucumber and beet crops, when evaluating different doses of auxinic herbicides, such as 2,4-D and picloram.

The doses of the 2,4-D herbicide used in this study are shown in Tables 2 and 3 in kg. a. e. ha-1 (kilogram of acid equivalent per hectare) to describe the amount of active ingredient in each product used. For each dose of 2,4-D evaluated, the plant height, leaf area and accumulated dry mass of cucumber were different between depths (Table 2).

Table 2. Plant height (cm), leaf area (cm2) and dry mass (g) of common cucumber (*Cucumis sativus*) grown at different depths and doses of 2,4-D, in a dystrophic red-yellow latosol (DRYL) in Sinop, MT , 2018

	Depth (cm)	------------------------------Dosages (kg a. e. ha^{-1})------------------------------				
		0	0.837	1.675	4.187	8.375
Plant height (cm)	0-10	3.63 aAB	3.08 bAB	2.81 bB	3.75 aAB	4.06 abA
	10-20	4.16 aA	3.33 bA	4.33 aA	4.08 aA	4.50 aA
	20-30	4.16 aA	4.41 aA	2.50 bB	4.08 aA	3.36 bAB
	CV (%): 15.46					
	Depth (cm)	------------------------------Dosages (kg a. e. ha^{-1})------------------------------				
		0	0.837	1.675	4.187	8.375
Leaf area (cm^2)	0-10	29.06 aA	22.45 bA	21.91 bA	37.05 abA	36.06 aA
	10-20	40.24 aA	32.04 abA	37.64 aA	31.39 bA	42.21 aA
	20-30	38.22 aA	39.07 aA	33.24 abA	45.44 aA	37.27 aA
	CV (%): 21.84					
	Depth (cm)	------------------------------Dosages (kg e. a. ha^{-1})------------------------------				
		0	0.837	1.675	4.187	8.375
Dry mass (g)	0-10	0.49 aAB	0.37 bB	0.34 bB	0.48 aAB	0.56 aA
	10-20	0.46 aA	0.53 aA	0.60 aA	0.44 aA	0.57 aA
	20-30	0.52 aA	0.54 aA	0.34 bB	0.56 aA	0.49 aAB
	CV (%): 18.78					

Averages followed by the same lowercase letter in the vertical and uppercase letters in the horizontal do not differ statistically from each other at the level of 5% probability by the Tukey test.

For the variable plant height, it was observed that the herbicide was concentrated in the depths of 0 to 10 and 10 to 20 cm for the dose of 0.837 kg. a. e. ha^{-1}. The dose of 1.675 kg e. The. ha-1 decreased plant height at depths of 0 to 10 cm and from 20 to 30 cm, demonstrating the concentration of the herbicide at different depths. Similar results were observed for the dose of 8.375 kg. a. e. ha^{-1}. For the dose of 4,187 kg. a. e. ha^{-1} there was no difference between the depths evaluated. Thus, it is suggested that the 2,4-D herbicide molecule had an irregular behavior in the soil profile regardless of the dose used. These results are different from those reported by Shirvani et al. (2014) who evaluated the mobility of the 2,4-D herbicide in the soil and found leaching at a depth of 20 to 25 cm, causing reduced growth in watercress plants. The organic matter content and clay texture of the soil used in this study may have contributed to the degradation of the herbicide molecule. According to Gomes et al. (2017), herbicides are more absorbed in soils with higher levels of clay and organic matter.

There was a difference in plant height between doses at depths from 0 to 10 and from 20 to 30 cm. At the depth of 0 to 10 cm, the highest plant height received the highest dose, the other doses, including the control, the heights were lower than the highest dose.

This result can be explained by the probability of greater leaching for this dose and / or the degradation of most of the molecules, and thus, the remaining herbicide acted as a growth promoter due to its auxinic origin. At a depth of 20 to 30 cm, the highest plant heights were at doses of 0.837 and 4.177 kg. a. e. ha^{-1}, suggesting an irregular behavior of the herbicide molecule in the soil regardless of the dose used.

These results differed from those reported by Silva et al. (2011), since there was a reduction in the height of soybean plants as the dose of the herbicide 2,4-D increased. Gomes et al. (2017) also found that corn plants grew less at the higher doses of the mixture of glyphosate and 2,4-D herbicides, possibly due to the greater residual effect of these molecules on the soil.

Because the location of the experiment was an area explored by the no-tillage system for several years, the structure of the red yellow latosol may have contributed to the leaching of the herbicide by macroporosity in the profile of this soil. Pinheiro et al. (2011) found the occurrence of leaching of several pesticides, including the herbicide 2,4-D, in soils with a clayey and medium texture, where the depth exceeded 30 cm reaching up to 100 cm.

There was a reduction in leaf areas at a depth of 0 to 10 cm for the doses of 0.837 and 1.675 kg. a. e. ha^{-1} compared to the other depths. For the dose of 4,187 kg. a. e. ha^{-1}, the leaf area was smaller at depths of 0 to 10 and 10 to 20 cm. The highest dose of the herbicide showed no difference between depths. These leaching results are similar to those found at plant height and corroborated the fact that the herbicide may have unexpected behavior in the soil.

The first two doses of the herbicide had a smaller leaf area at a depth of 0 to 10 cm. For the third dose used, the reduction of the leaf area occurred to a depth of 10 to 20 cm, suggesting that the increase in the dose of the product resulted in an increase in the probability of leaching of the molecule in the soil. In the comparison between the herbicide doses, there was no difference for the leaf area, showing irregularity of the herbicide action on the plant. since for plant height there was a difference between doses. Auxinic compounds influence plant growth. One effect is the abnormal growth of certain parts of the plant, such as phloem vessels and adjacent tissues, causing several anomalies, such as epinastia (Deuber, 2003), which may explain the difference for plant height, but not to the leaf area of this experiment.

The analysis of dry mass accumulation showed that for the dose of 0.837 kg. a. e. ha^{-1} there was less accumulation in the depth of 0 to 10 cm compared to the others, corroborating with the results presented for plant height and leaf area for this same dose of the herbicide. This result contrasts with that observed for the dose of 1.675 kg. a. e. ha^{-1}, where the reduction in the dry mass accumulation of the plant occurred at depths of 0 to 10 and 20 to 30 cm. For the other doses of the herbicide, no differences were observed in the accumulation of dry plant mass between depths.

There was no difference between the doses used for the depth of 10 to 20 cm, but there was for the others. At a depth of 0 to 10 cm there was a greater accumulation of dry mass for the highest dose of the herbicide and, for a depth of 20 to 30 cm, the greatest accumulation of dry mass occurred at doses of 0.837 and 4.187 kg. a. e. ha^{-1}, which did not differ from the control. Different results were reported by Santos et al. (2004). The authors observed the sensitivity of cucumbers to increasing doses of herbicides derived from synthetic auxins, such as 2,4-D.

The results obtained for dry mass in cucumber using the herbicide 2,4-D demonstrated that herbicide leaching occurred in the soil regardless of the applied dose. The physical and chemical attributes of the soil can significantly interfere in the behavior of herbicides in soil. Baumgartner et al. (2017) reported that the climate, product characteristics, soil physical-chemical attributes, soil management, among others, interfere with the behavior of the 2.4-D herbicide residual in the soil.

For the herbicide atrazine, there was also no difference between treatments for the phytotoxicity variable. The symptoms observed were similar to those found for the herbicide 2,4-D (leaf deformation, partial leaf necrosis and plant senescence). Because atrazine has mobility in the soil, these symptoms were found in some plants for all depths evaluated. These results are different from those observed by Camargo et al. (2011), who found severe intoxication symptoms, as the dose of the herbicide atrazine was increased using a red latosol with a clay texture.

Atrazine influenced the growth of cucumber plants according to the doses used and depths reached (Table 3).

Analyzing the plant height, it can be observed that the use of the dose of 1,125 kg. a. e. ha^{-1} allowed the herbicide to concentrate at depths of 0 to 10 and 10 to 20 cm in the soil. As the dose increased, the herbicide reached a depth of 20 to 30 cm, as was observed in the doses of 2.250 and

5.625 kg. a. e. ha^{-1}. These results are similar to those reported by Barriuso et al. (1992), Laabs et al. (2000), Cerdeira et al. (2005) and Correia & Langenbach (2006), who found atrazine mobility in depth in the soil profile. Laabs et al. (2000) studied the leaching and degradation of pesticides in the soil under cultivation of corn and beans, and found moderate mobility for atrazine in dystrophic purple latosol. According to these authors, 0.46% of the volume of atrazine was found at a depth of 15 cm from the soil in a period of 28 days after application of the product.

Table 3. Plant height (cm), leaf area (cm2) and dry mass (g) of common cucumber (Cucumis sativus) grown at different depths and doses of atrazine, in a dystrophic red-yellow latosol (DRYL) in Sinop, MT, 2018

	Depth (cm)	Dosages (kg. a. e. ha^{-1})				
		0	1.125	2.250	5.625	11.250
Plant height (cm)	0-10	4.40 aA	4.16 bA	3.85 bA	4.10 aA	4.03 aA
	10-20	3.83 aAB	4.45 bAB	4.78 aA	3.76 aB	4.66 aAB
	20-30	4.45 aA	4.50 aA	3.80 bA	2.58 bB	4.08 aA
	CV (%): 12.08					
	Depth (cm)	Dosages (kg. a. e. ha^{-1})				
		0	1.125	2.250	5.625	11.250
Leaf area (cm^2)	0-10	34.60 bA	35.96 aA	27.75 bA	33.29 aA	33.64 bA
	10-20	27.08 bC	38.35 aAB	30.62 abBC	32.94 aBC	44.58 aA
	20-30	48.74 aA	32.00 aBC	37.96 aAB	25.50 aC	36.17 abBC
	CV (%): 15.98					
	Depth (cm)	Dosages (kg. a. e. ha^{-1})				
		0	1.125	2.250	5.625	11.250
Dry mass (g)	0-10	0.41 bAB	0.50 abA	0.34 bB	0.31 aB	0.50 aA
	10-20	0.38 bB	0.46 bAB	0.48 aAB	0.40 aAB	0.53 aA
	20-30	0.59 aA	0.58 aA	0.52 aA	0.38 aB	0.53 aA
	CV (%): 14.26					

Averages followed by the same lowercase letter in the vertical and uppercase letters in the horizontal do not differ statistically from each other at the level of 5% probability by the Tukey test.

There was no difference for the highest herbicide dose at plant height between depths, this suggests that the herbicide may have been leached to depths greater than 30 cm considering that atrazine has moderate mobility in the soil. (Correia & Langenbach, 2006). Evaluating the dynamics of the distribution and degradation of atrazine in red yellow argisol, under humid tropical climate conditions, he found the presence of the herbicide in up to 50 cm of soil depth in 90 days after application. In the comparison between doses of the herbicide atrazine for the variable plant height, there was no difference for the depth of 0 to 10 cm. For depths of 10 to 20 and 20 to 30 cm, the lowest plant height was observed for the dose of 5.625 kg. a. e. ha^{-1}.

The effects of herbicide doses on the development of cucumber plants, in this case, were observed at depths greater than 10 cm, which indicates the potential for leaching of the molecule in the soil. The properties of atrazine resulted in moderate mobility and high persistence in the soil, thus promoting the accumulation of contaminating levels both on the surface and in the depth of the soil and potentially reaching surface and groundwater (Prosen, 2012).

Assessing the leaf area, there was a difference between depths for the doses of 2.250 and 11.250 kg. a. e. ha^{-1}, being the smallest leaf area at a depth of 0 to 10 cm, suggesting that most of the herbicide was concentrated at this depth. At the other doses, there was no difference in leaf area between depths, except for the control. This result demonstrated an atypical behavior of this herbicide in the soil. In studies on the leaching of atrazine in different soils, Martinazzo et al. (2011) found that the herbicide had an intermediate potential for leaching, indicating the risk of groundwater contamination. Pinheiro et al. (2011) detected the presence of atrazine at a depth of up to 100 cm in humic cambisol in the municipality of Ituporanga - SC, in an area with crop rotations between corn, onions, potatoes, beans and beets.

Comparing the doses of atrazine for the depth of 10 to 20 cm, the lowest values were in the doses of 2.250 and 5.625 kg. a. e. ha^{-1} and, for the depth of 20 to 30 cm, the lowest value was in the dose of 5.625 kg. a. e. ha^{-1}. There was no difference between doses at the depth of 0 to 10 cm for the variables plant height and leaf area, and the differences between doses were observed from the depth of 10 cm. This result suggests that the leaching of the herbicide atrazine occurred, reaching depths greater than 10 cm according to the physical and chemical attributes of the soil. Similar results have been reported in oxidic soils by Barriuso et al. (1992), in a study on the behavior of herbicides in an oxisol. In studies of the behavior of the herbicide atrazine in columns containing samples of eutrophic red latosol, Cerdeira et al. (2005) reported the occurrence of movement of atrazine to a depth of 20 cm, while Correia & Langenbach (2006) found that approximately 15% of the applied atrazine mass was distributed gradually and decreasing to a depth of 25 cm.

The dry mass variable showed the lowest accumulation at a depth of 10 to 20 cm for the dose of 1,125 kg. a. e. ha^{-1} and, for the depth of 0 to 10 cm, for the dose of 2,250 kg. a. e. ha^{-1}. These results showed that the leaching of the herbicide in the soil does not depend on the dose, because, even using the dose of 1.125 kg. a. e. ha^{-1}, which is recommended by the manufacturer, the molecule leached to a depth of 10 to 20 cm. In experiments with undisturbed argisol, Correia et al. (2007) used the 1,500 kg. a. e. ha^{-1}of the herbicide atrazine and observed leaching of approximately 7% of this dose up to 50 cm deep in the soil.

The dry mass evaluation identified lower values for the doses of 2.250 and 5.625 kg. a. e. ha^{-1} at a depth of 0 to 10 cm; doses of 1,125, 2,250 and 5,625 kg. a. e. ha^{-1} at a depth of 10 to 20 cm and; the dose of 5.625 kg. a. e. ha^{-1} at a depth of 20 to 30 cm. The results suggested that despite the imprecise behavior of the herbicide molecule in clayey soil, different doses of the herbicide provided a reduction in the dry mass of the plant. These results corroborate those found by Tibúrcio et al. (2012), who reported a reduction in the dry mass of the aerial part when they evaluated different doses of atrazine on the growth of plants in clayey soil.

The differences observed between the depth and the dose for the variables plant height, leaf area and dry mass, demonstrated that the use of the herbicide atrazine in clayey soil, organic matter content above 1% and after the half-life period of the product, is 10 days. According to the manufacturer, it is possible to identify the occurrence of leaching of the herbicide in the soil under rain.

Conclusion

The 2,4-D herbicide can leach in clayey soil in a no-tillage system, regardless of the applied dose, reaching a depth of 30 cm.

Atrazine can leach in clayey soil under no-till system even using doses recommended by the manufacturer, reaching a depth of 30 cm.

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