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Article

Transport of Atrazine Via Leaching in Agricultural Soil with Mineral Oil Addition

Transporte de Atrazine Via Lixiviação em Solo Agricultável com Adição de Óleo Mineral

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ABSTRACT - Adjuvants, such as mineral oils, are widely used in the application of herbicides by reducing the drift and evaporation of the droplets and by increasing herbicide uptake by the plant. However, little is known about how mineral oil behaves when in contact with the soil. Thus, the objective of this research was to evaluate the transport of atrazine via leaching with the addition of mineral oil in a soil agricultural under laboratory conditions. To quantify the concentration of the herbicide along the profile of the very clay soil column (30 cm), ^{14}C-atrazine (ring-U-^{14}C) was used with 16,667 Bq of radioactivity per column in volume of 200 mL solution and 0 (control), 1, and 2% mineral oil (v/v) was added in the application volume. Atrazine was applied at the highest commercial dose recommended for sugarcane (4 kg ha^{-1}). After simulation of a precipitation of 200 mm for 48 h, each column was sectioned into six parts of 5 cm and the analytes of each soil sample and the leachate were quantified by liquid scintillation spectrometry. The atrazine remained in the superficial layer of the soil, between 0 and 10 cm of depth, independent of the addition of mineral oil. No atrazine residues were detected in the leachate solution (> 30 cm) in any evaluated treatment. The addition of mineral oil at the time of application of pre-emergence atrazine did not interfere with the transport of this herbicide in the soil profile agricultural via leaching; therefore, the adjuvant may have positive effect only in the herbicide-plant relationship.

Keywords: adjuvant, mobile herbicide, triazine group, leachate.

RESUMO - Os adjuvantes, como os óleos minerais, são amplamente utilizados na aplicação de herbicidas por reduzir a deriva e a evaporação das gotas, bem como por aumentar a absorção do herbicida pela planta. Contudo, pouco se sabe como o óleo mineral se comporta quando em contato com o solo. Assim, o objetivo desta pesquisa foi avaliar o transporte de atrazine via lixiviação com adição de óleo mineral em um solo agricultável sob condições de laboratório. Para quantificar a concentração do herbicida ao longo do perfil da coluna de solo de textura muito argilosa (30 cm), foi utilizada a ^{14}C-atrazine (ring-U-^{14}C) com 16.667 Bq de radioatividade por coluna em volume de 200 μL de solução e adicionado 0 (controle), 1% e 2% de óleo mineral (v/v) no volume de calda de aplicação. A atrazine foi aplicada na maior dose comercial recomendada para a cultura de cana-de-açúcar (4 kg ha^{-1}). Após a simulação de uma precipitação de 200 mm durante 48 horas, cada coluna foi seccionada em seis partes de 5 cm, e os analitos de cada amostra de solo e do lixiviado foram quantificados por espectrometria de cintilação em meio líquido. A atrazine permaneceu na camada superficial do solo, entre 0 e 10 cm de profundidade, independentemente da adição de óleo mineral. Não foram detectados resíduos de atrazine na solução lixiviada (> 30 cm) em

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nenhum tratamento avaliado. A adição de óleo mineral no momento da aplicação de atrazine em pré-emergência não interferiu no transporte deste herbicida no perfil do solo agricultável via lixiviação; portanto, o adjuvante pode ter efeito positivo apenas na relação herbicida-planta.

Palavras-chave: adjuvante, herbicida móvel, grupo das triazinas, lixiviado.

INTRODUCTION

Atrazine (6-chloro-*N*2-ethyl-*N*4-isopropyl-1,3,5-triazine-2.4-diamine) is a selective and systemic herbicide that acts on the inhibition of photosystem II, interfering in the Hill reaction, and its non-cyclic photophosphorylation is associated with the photosynthetic process (Shimabukuro and Swanson, 1969). In Brazil, this herbicide is widely used in agriculture, mainly in sugarcane and maize crops for the control of Eudicotyledonous weeds. In 2016, the country commercialized almost 29,000 ton of the active ingredient, making atrazine the fourth most sold pesticide (IBAMA, 2018). Although widely used here, atrazine has already been banned in nine countries plus the European Union, which is comprised of 28 member countries (Pesticide Action Network International, 2017).

Due to its physicochemical properties, such as low volatility, high leaching potential and moderate persistence in the soil, the atrazine has high potential as a polluter of water and several toxic effects to organisms (Ghosh and Philip, 2006). Moreira et al. (2012) detected the atrazine to surface waters, groundwater (wells) and rain water at levels higher than the maximum established by the National Council of the Environment – CONAMA (Brazil, 2008), which is 2 $\mu g\ L^{-1}$.

The atrazine can be applied in both pre- and post-emergence. In post-emergence, the use of adjuvants of additive type (e.g., mineral and vegetable oil) aims to increase the absorption, distribution and persistence of herbicide in plants (Vargas and Roman, 2006). Adjuvants help expressing your herbicides activity and effectiveness of control, being dependent on their physical-chemical properties. Silva and Weda (1986) found that atrazine mixture with soybean oil in early post-emergence showed greater efficiency in the control of alexandergrass (*Urochloa plantaginea*) when used in isolation, but Mendes et al. (2018) reported that the addition of oil in mixture oxyfluorfen + flumioxazin had not interfered on weed population in comparison with the mixture without mineral oil.

In order to reduce drift and avoid evaporation of the product, the adjuvants began to be used also in pre-emergence in crops, such as sugarcane (Almeida et al., 2017). However, before using this composition, it is necessary to evaluate the behavior of the active ingredients, together, in the soil. Understanding the leaching potential is one of the extremely important factors both from the agronomic and environmental point of view, since the deeper layer percolation reduces the herbicide efficacy and increases the risks of water contamination (Oliveira and Brighenti, 2011).

Studies conducted by Bachega et al. (2009) in Brazil showed that mineral oil maintained amicarbazone in the most superficial layer of the soil but did not present a differentiated effect of sulfentrazone leaching. In Poland, Kucharski and Sadowski (2009) reported that the addition of adjuvants, especially the oil, caused a reduction in the leaching of phenmedipham in the soil profile. Therefore, adjuvants can be integrated into the concentration of herbicide residues in the plant and soil.

Thus, the objective of this research was to evaluate the transport of atrazine via leaching with the addition of mineral oil in an agricultural soil under laboratory conditions.

MATERIAL AND METHODS

Experimental design

The study was installed in a completely randomized design with three replications, in a 3 x 7 factorial scheme. The factors were composed of three concentrations of mineral oil [0%, 1% and 2% (v/v)] in the volume of application of atrazine and six soil depths (0–5; 5–10; 10–15; 15–20; 20–25, and 25–30 cm) plus the leached solution.

Soil sample

Soil was classified as Oxisol (clay texture) and was collected in the municipality of Rio Paranaíba, MG, Brazil. After removal of the vegetation debris, a soil sample of the superficial layer (0–10 cm depth) was collected. The soil was air dry, sifted into 2 mm mesh, and stored at room temperature. The physicochemical characteristics of the soil are shown in Table 1.

Table 1 **-** Physicochemical characteristics of the soil used in this study. Rio Paranaíba, MG, Brazil

pH	OC	P	K	Ca	Mg	H+Al	BS	CEC	V	Clay	Silt	Sand
($CaCl_2$)	(%)	(mg dm^{-3})	(mmol$_c$ dm^{-3})						(%)	(g kg^{-1})		
5.5	2.15	73	1.8	37	10	25	48.8	73.8	66	744	133	123

pH = hydrogen potential; OC = organic carbon; P = phosphorus; K = potassium; CA = calcium; Mg = magnesium; H + Al: potential acidity; BS = base saturation; CEC = cation exchange capacity; V = base saturation levels. Source: Soil science departament of ESALQ/USP, Piracicaba, SP, Brazil.

Preparing the soil columns

Glass columns with 35 cm in height and 5 cm in diameter were placed with the soil samples. The bottom was closed with glass wool and sand and filled with dry soil until it reached the height of 30 cm, with 696.2 ± 8.3 g per column. After filling, the columns were placed in test tubes of 2 L with $CaCl_2$ solution 0.01 mol L^{-1}, until the saturation by capillarity. Subsequently, the columns of soil were removed from the test tubes, stuck in vertical brackets and drained until cease the flow of solution, lasting approximately 1 hour. After that, it was placed below each column of soil a Schott bottle for collection of leachate.

Herbicide and mineral oil

Atrazine was applied at the highest recommended commercial dose for the sugarcane crop (4 kg ha^{-1}). We used the standard atrazine (non-radiolabelled) (chemical purity = 98.9%), acquired at Chem Service, Inc., West Chester, PA, USA. As a radiolabelled product, ^{14}C-atrazine (ring-U-^{14}C) was used with specific activity of 3.2 MBq mg^{-1} (radiochemical purity = 95%), acquired at Ciba Geigy, Delhi, India. The radioactivity of 16,667 Bq was used per soil column. For each soil column, an aliquot of 200 µL of the working solution (atrazine radiolabelled + non-radiolabelled) was used for the application, in order to achieve the recommended dose of the herbicide, and in treatments with 1% and 2% of mineral oil (v/v), 2 and 4 µL of Nimbus mineral oil (Syngenta) were added to each aliquot, respectively.

The products were applied directly on the soil surface of each column, with the aid of a micropipette. After herbicide application, a thin and circular glass wool was placed in each column to avoid the formation of preferential flow of water, and, above the glass wool, an inverted funnel was added to fit the hose that connects to the peristaltic pump in order to simulate rainfall.

Leaching study

The study was carried out in a room with low luminosity and temperature between 18 °C and 25 °C, according to the recommendations of the Organisation for Economic Co-operation and Development-312 “Leaching in Soil Columns” (OECD, 2002). By means of a calibrated peristaltic pump, the rainfall simulation was initiated with $CaCl_2$ 0.01 mol L^{-1}, with an intensity of 8 mL h^{-1}, for 48 hours, totaling approximately 200 mm. The leachate was collected and its volume was measured at the end of the simulation, with three aliquots of 1 mL each of the solution being collected by column. In each aliquot we added 10 mL of liquid scintillator solution (Insta-Gel®), and radioactivity readings were performed by the Liquid Scintillator Spectrometer (LSS) (Tri-Carb® 2910 TR LSA, PerkinElmer).

After the simulated rain ended, the soil was removed from the glass columns by forced air injection at the tip of the spine. Each soil column was divided equally into six sections (5 cm each), which were air-dried, weighed, and homogenized in a mechanical mill. Three subsamples (0.2 g each) of each soil layer were removed, which were oxidized by the biological oxidizer (OX–500, R.J. Harvey Instrument Corporation) for further quantification of total radioactivity by extrapolation of soil mass in its respective layer. The $^{14}CO_2$-shaped radioactivity from the herbicide ^{14}C was measured by the LSS.

Statistical analysis

The data were subjected to analysis of variance (ANOVA) to verify the interaction between the factors (mineral oil concentration and soil depth plus leachate solution), and, when significant by the F test, the averages were compared by the Tukey test (p<0.05). The figure was plotted using the Sigma Plot (version 10.0 for Windows, Systat Software Inc., Point Richmond, CA, USA).

RESULTS AND DISCUSSION

Mass balance

The average of the total atrazine recovered (detected in the soil profile + leachate) was 95%, 103%, and 90% for the columns without the addition of mineral oil, with 1% and 2% mineral oil, respectively. The mass balance is within acceptable limits recommended by OECD (2002), which is between 90% and 110%. So, the reported data of leaching of atrazine in the soil profile were reliable.

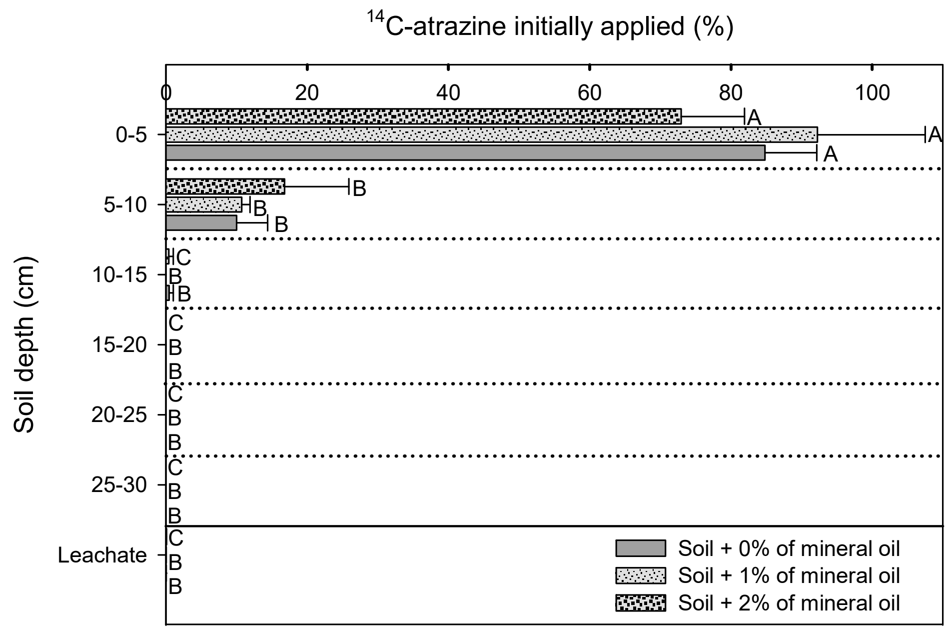
Leaching of atrazine in soil profile with addition of mineral oil

Figure 1 shows the results of atrazine leaching after application of simulated rainfall in the soil columns. The interaction between the use of mineral oil and the leaching of atrazine in the soil profile was not significant (F=0.2114, p>0.05). Moreover, there was no difference between the doses of mineral oil in the application syrup (F=0.6080, p>0.05), i.e. the transport of atrazine was similar in the soil, regardless of the dose of mineral oil added in the syrup. Bachega et al. (2009), when using sorghum (*Sorghum bicolor*) as a bioindicator plant to study sulfentrazone leaching, found that after precipitation of 106 mm, the addition of mineral oil also did not interfere with the herbicide behavior in soil profile.

The significance of the data occurred only in the soil depth factor (F=248.508; p>0.05), the highest amount of the herbicide (> 73%) remained in the superficial layer of 0–5 cm, regardless of the addition of mineral oil (Figure 1). According to Oliveira and Brighenti (2011), this small leaching is interesting, since the weeds present in the seed bank with the highest germination potential are found in this layer. In addition, small amounts of atrazine were found in the layers of 5–10 cm in the treatments without mineral oil (~ 10%) and with 1% of the adjuvant (~ 11%), but there was no difference between these quantities of the herbicide and the other depths of 10–30 cm of the soil profile (Figure 1).

The low percolation of the herbicide is due to the OC content (2.15%) and the soil textural class, which was clay (Table 1). Dick et al. (2010) analyzed an Oxisol of clay texture and found that, despite the low OC content (2.3%), this was responsible for the highest quantity (74%) of atrazine sorbed, followed by the inorganic fraction deferrified, with 22%, and by iron oxides, with 4%. When analyzing the effect between atrazine sorption capacity and soil mineralogical composition, Huang et al. (2015) found that clayey soils had higher sorption capacity and lower herbicide desorption capacity when compared to sandy soils.

Soil clay fraction, although present less sorption capacity of the OC, is crucial in the potential leaching of atrazine in the soil profile. Souza (2017) used the cucumber (*Cucumis sativus*) as species bioindicador to evaluate the percolation of atrazine (0.5 kg ha^{-1}) in a Oxisol loam sand texture (71% of sand) and noted that, two days after a simulated precipitation 60 mm, the atrazine had percolated up to the depth of 25 cm.



Horizontal columns are represented by mean ± standard deviation of mean (n = 3). The same letter at the end of column does not differ among themselves by Tukey test ($p < 0.05$). Least Significant Difference - LSD (soil depth): 15.76. Coefficient of Variation - CV: 35.10%. Rio Paranaíba, MG, Brazil.

Figure 1 - Percentage of ^{14}C-atrazine in agricultural soil columns of clay texture with mineral oil addition, after simulated 200 mm of rainfall.

The fact that much of the atrazine in the arable soil layer remain, coupled with moderate persistence and moderate sorption of herbicide (PPDB, 2019), one must be aware of the cultures in succession to avoid possible carryover. Guimarães (2017) applied the atrazine (2 kg ha^{-1}) in a field of corn, which was later succeeded by cultivation of potato (*Solanum tuberosum*) and, subsequently, by the beet (*Beta vulgaris*). After eight months of application of atrazine, it was found that the residual effect of the herbicide reduced, on average, 8.3 ton of sugar per hectare. In the study by Furlan et al. (2016), the residual effect of atrazine (up to 0.25 kg ha^{-1}) has not impacted the percentage of emergency nor the commercial pattern of the carrot.

As can be seen in Figure 1, there was no detection of atrazine in leachate solution, regardless of the addition of mineral oil, which is a result consistent with the estimate made by Andrade et al. (2011). Based on climatic conditions of Rio Paranaíba, MG, and in information obtained in previous research, the authors estimated 1.02 x 10^{3}% losses of atrazine by leaching in a clay texture Oxisol with 80 cm depth. In practice, the intense mechanization, common in agricultural soils, further reduces the porosity of clay soil, creating a layer of compression (20–30 cm), which complicates the possibility of contamination of atrazine in groundwater even more (Souza and Lobato, 2018).

However, the low leaching of atrazine observed in this study may lead to high concentrations of the herbicide in water from runoff. In research conducted by Aquino et al. (2013), the use of atrazine in an irrigation channel area promoted the transport of the herbicide to the lower areas. Ludovice et al. (2003) have recommended the use of filter in order to prevent the draining of atrazine, since the use of filter strips of 5 and 10 m was able to reduce herbicide concentration in the solution was drained in 73.8% and 89.7%, respectively.

Atrazine was unmovable in the agricultural soil profile, remaining in the superficial layer (0–10 cm), and it showed no potential for contamination of the groundwater, probably because the soil has high organic carbon content and has a clay texture. The importance of having a crop planning in succession to the application of atrazine in pre-emergence to avoid problems with carryover, especially in soils with low potential for loss of herbicides by leaching, should be emphasized. The addition of mineral oil at the time of atrazine application did not interfere in the transport of this herbicide in the soil profile via leaching; therefore, the adjuvant may have positive effects only in the herbicide-plant ratio.

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