

## ATRAZINE LEACHING IN SOIL SUBMITTED OF SWINE WASTEWATER APPLICATION

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### 1 ABSTRACT

In this study, swine wastewater (SW) effects on atrazine leaching were evaluated. The experiment was conducted in laboratory in Cascavel, Paraná, Brazil, where soil columns filled with samples of a Rhodic Hapludox soil received the application of 2.5 kg ha<sup>-1</sup> of atrazine mass and were incubated for seven days according to the following treatments: T1 (Sterile soil + SW), T2 (Sterile soil + distilled water), T3 (Non sterile soil + SW) and T4 (Non sterile soil + distilled water). In T1 and T3 treatments SW, corresponding to 435 m<sup>3</sup> ha<sup>-1</sup>, was applied, while in T2 and T4 treatments, 421 m<sup>3</sup> ha<sup>-1</sup> of distilled water was applied. Atrazine leaching tests were conducted for each treatment and the results showed that the application of SW in the soil increased the atrazine leaching in the soil profile, and consequently the risk of contamination of groundwater.

**Keywords:** herbicide, swine slurry, transport.

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RESIDUÁRIA DA SUINOCULTURA

### 2 RESUMO

Neste estudo foram avaliados os efeitos da aplicação de água residuária da suinocultura (ARS) na lixiviação de atrazina. O experimento foi conduzido em laboratório em Cascavel, Paraná, Brasil, onde colunas de solo preenchidas com amostras de Latossolo Vermelho distroférico, receberam a aplicação de 2,5 kg ha<sup>-1</sup> de massa de atrazina e foram incubadas durante sete dias de acordo com os seguintes tratamentos: T1 (Solo estéril + ARS); T2 (Solo estéril + água destilada); T3 (Solo não estéril + ARS) e T4 (Solo não estéril + água destilada). Nos tratamentos T1 e T3 foi adicionada ARS, correspondente a 435 m<sup>3</sup> ha<sup>-1</sup>, e nos tratamentos T2 e T4, foram adicionados 421 m<sup>3</sup> ha<sup>-1</sup> de água destilada. Foram conduzidos ensaios de lixiviação da atrazina para cada tratamento, e os resultados demonstraram que a aplicação de ARS ao solo proporcionou o aumento da lixiviação de atrazina no perfil do solo, e consequentemente a possibilidade de contaminação de águas subterrâneas.

**Palavras-chave:** herbicida, dejetos suíno, transporte.

### 3 INTRODUCTION

Leaching is the transport of solutes to subsurface layers and is responsible for the transport of pesticides and other elements of agricultural areas. Therefore, it is a fundamental process in the soil, whereby the constituents (solubles and suspended particles) are transported by water seepage.

Atrazine is a triazine herbicide widely used in agriculture to control weeds in crops of maize and sugarcane. However, atrazine is considered a moderate persistent pesticide in the environment and it has been found in groundwater (HAMILTON & MILLER, 2002; ARRAES, BARRETO & ARAÚJO, 2008; GUERIT et al., 2008).

In last ten years, public attention focused on the risks of contamination of water resources, work has been conducted to evaluate the sorption and transport of atrazine in the soil profile. Researchers evaluated the atrazine distribution dynamic in red-yellow ultisol under conditions of humid tropical climate, and found, in a field experiment that atrazine was found at 50 cm depth after 90 days of experiment, may have reached greater depths not studied in work (CORREIA & LANGENBACH, 2006).

The reuse of treated wastewater on crops fertigation is a widespread practice worldwide. However, there are environmental concerns about the effects of wastewater application on the transport of pesticides in soil. Soil and wastewater characteristics that may affect the movement of pesticides include pH, electrolyte composition and the presence of dissolved organic matter (SEOL & LEE, 2001; ARIAS-ESTÉVEZ et al., 2008; WILDE et al., 2009).

Traditionally, the transport of pesticide has been viewed as a simple process of two phases, where the dissolved phase is transported by leaching and sorbed phase acts as a process delay. Sorptive interactions between organic matter and stationary phase remove the contaminant from the soil solution and may even form bound residues, thus slowing its motion. However, a high degree of interaction between dissolved organic carbon and organic contaminant can accelerate the process of facilitated transport (SILVA & FAY, 2004). In this context, the potential for formation of pesticides complexes with dissolved organic matter can increase the mobility of pesticides in soils irrigated with wastewater (PRATA & LAVORENTI, 2000; SEOL & LEE, 2001; MÜLLER, MAGESAN & BOLAN, 2007).

Whereas there are few studies that investigated the handling pesticides due to the addition of organic residues in subtropical soils, this study aimed to evaluate the effects of applying swine wastewater (SW) on the leaching of atrazine in samples of a Rhodic Hapludox soil.

### 4 MATERIAL AND METHODS

Samples of a Rhodic Hapludox soil, from clay texture, were collected in a place with no history of atrazine application and vegetation composed of grasses, sampled at a depth of 0-30 cm. The soil was air dried and passed through a sieve of 2 mm mesh size. Was performed soil physico-chemical analysis (Table 1), according to methods described by Embrapa (1997) and Tedesco et al. (1995).

**Table 1.** Characterization of the soil used in the experiment.

Parameter	Value
Sand (g kg <sup>-1</sup> )	150.00
Silt (g kg <sup>-1</sup> )	250.00
Clay (g kg <sup>-1</sup> )	600.00
pH (H <sub>2</sub> O)	5.70
Nitrogen (mg kg <sup>-1</sup> )	3.09
Carbon (g kg <sup>-1</sup> )	13.26
Cation Exchange Capacity (cmol <sub>c</sub> kg <sup>-1</sup> )	11.11
Organic matter (g kg <sup>-1</sup> )	22.81
Particle density (kg m <sup>-3</sup> )	2554.00
Apparent density (kg m <sup>-3</sup> )	1056.00

Source: own authorship.

The swine wastewater collected was treated in an integrated biosystem constituted by digester, sedimentation tank, two stabilization ponds, algae tank and fish tank. The sample was collected at the exit of the second stabilization pond, and characterized (Table 2), according to the methodology described by American Public Health Association (2012).

**Table 2.** Characterization of swine wastewater.

Parameter	Value
BOD (mg L <sup>-1</sup> )	1333.30
COD (mg L <sup>-1</sup> )	2500.00
COD filtrated (mg L <sup>-1</sup> )	1595.93
Nitrogen (mg L <sup>-1</sup> )	1052.80
Total solids (mg L <sup>-1</sup> )	2649.50
Fixed solids (mg L <sup>-1</sup> )	1573.00
Volatile solids (mg L <sup>-1</sup> )	1076.50
pH	7.60

BOD: biochemical oxygen demand; COD: chemical oxygen demand.

Source: own authorship.

For the evaluation of miscible displacement of atrazine in the soil treated with SW tests were conducted in soil columns deformed. The soil was placed in acrylic columns with 5.5 cm diameter and 30 cm in length.

Were considered four treatments of soil in columns: T1 (Sterile soil + SW); T2 (Sterile soil + distilled water); T3 (Nonsterile soil + SW) and T4 (Nonsterile soil + distilled water). In treatments T1 and T3 was added SW in the dose of 435 m<sup>3</sup> ha<sup>-1</sup> and in the treatments T2 and T4, was added 421 m<sup>3</sup> ha<sup>-1</sup> of distilled water, uniformly distributed at the top of the column. In the treatments T1 and T2 the soil passed by sterilization in autoclave and in all treatments was applied the atrazine mass recommended for the corn crop, equivalent to 2.5 kg per hectare. The columns were incubated vertically at a temperature of 23 °C for a period of seven days.

After expiry of the incubation period, the columns were fixed by metal brackets vertically in a universal support. Aiming to expel the air contained in the micropores of the soil, was realized saturation of the columns from passage of a low-flow ascendant of solution 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub>, with the finality of avoid eventual destabilization of the soil.

Saturated columns and proven condition of constant flow of 5 mL min<sup>-1</sup> maintained using a peristaltic pump was started passing water downward flow. Experiments in columns in

which, after the soil contamination, is applied a constant flow rate of water, can better simulate the real field conditions of rainfall and irrigation (ZHAO et al., 2009).

The monitoring of leachate began with the first drop leached from column, being collected 20 mL every four minutes test, making a total of four pore volumes. The samples were collected with the aid of a fraction collector in tubes of 25 mL and packaged in plastic bottles with sequential numbering and stored in a freezer for later determination of atrazine in the leachate. After leaching tests, the soil column was air dried and stored in paper boxes for determination of extractable residues of atrazine.

The atrazine concentration in leachate samples was determined from high-performance liquid chromatography (HPLC) techniques. First of all the samples were filtered through filter unit with 0.45  $\mu\text{m}$  pore membrane and injected inside of the chromatograph with the follow conditions: C-18 (150 x 4.6 mm), mobile phase methanol:water (50:50, v/v), detector UV – 230 nm, continuous-flow rate of 1.0 ml min<sup>-1</sup>, oven temperature at 35°C, run time of 15 minutes and injection volume of 20  $\mu\text{L}$ .

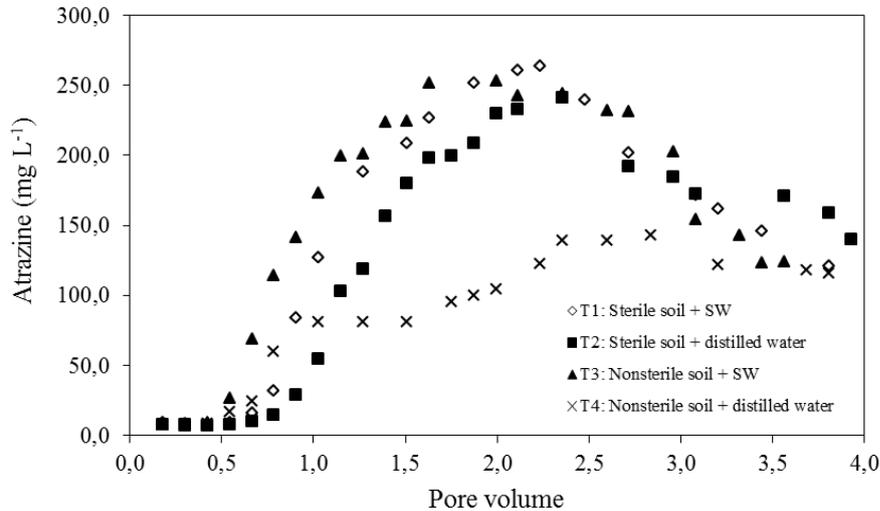
With atrazine concentration values in the leachate samples, were constructed pesticide elution curves for each considered treatment. Relating the relative concentration accumulated of atrazine ( $C/C_0$ ) and volume leachate, got the regression line equations for each treatment, which was applied the statistical tests of lines comparison at the 5% significance level, with finality of check if the lines are similar.

## 5 RESULTS AND DISCUSSION

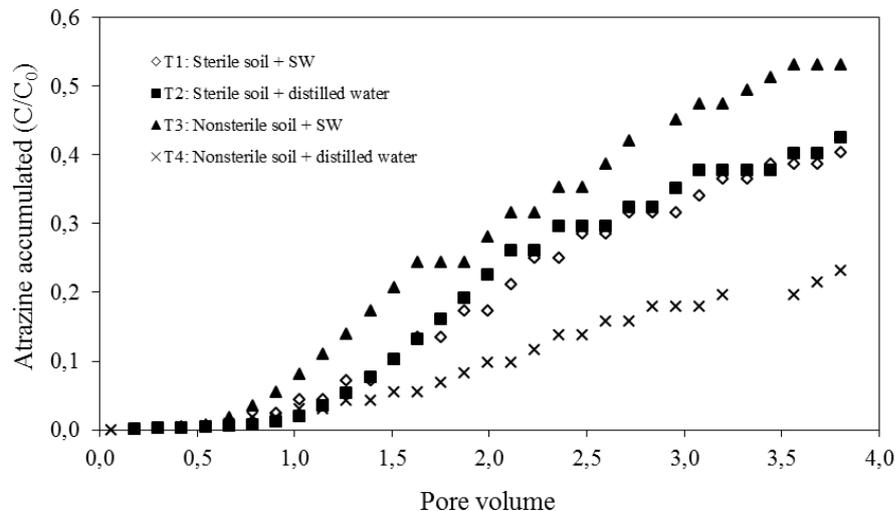
In Figure 1 are showed the elution curves of atrazine (breakthrough curve and accumulative) for the treatments utilizing water as percolate solution.

**Figure 1.** Elution curves for atrazine. Breakthrough curves (A) and Accumulative (B).  $C_0$  is the initial concentration of atrazine applied;  $C$  is the atrazine concentration in the leachate.

A



B



**Source:** own authorship.

The atrazine was released constantly since the start of leaching and the breakpoint occurred in the same time for all treatments. Therefore, the breakthrough curves for the T1, T2 and T3 treatments have an atrazine concentration peak more elevated when compared with the T4 treatment curve (Figure 1A). The atrazine total concentration ( $C/C_0$ ) raised from 0.231 in T4 treatment to 0.404, 0.423 and 0.531 in the T1, T2 and T3 treatments respectively (Figure 1B), indicating leaching raise of atrazine in this treatments.

In treatments without SW addition (T2 and T4), the non-sterile soil (T4) showed more atrazine retention, where possibly there was interaction of herbicide with the soil organic matter and the clay particles, decreasing the leaching (Figure 1B). The procedure of adsorption include as the sorption in the solid-liquid interface (clay mineral surface) as the sorption inside of a

sorbent matrix (into of organic matter), decreasing the mobility of organic molecules in soil (SILVA & FAY, 2004).

In the T2 treatment, with sterile soil and addition of distill water, the atrazine displacement was more elevated than the T4 treatment (without sterilization), resembling the dealing observed in soils that received SW. This fact possibly occur due to the sterilization process in autoclave, whereby passed the T2 treatment soil. Nakagawa and Andréa (1997) cite that one way of further the release of herbicide linked residues in the soil is by mugginess, due to temperature effect over the organic matter structure. The authors cite Schnitzer and Khan (1972) who found that the humic material that compose the soil forming a polymeric structure with hydrogen bridges from different molecular sizes, originating a molecular sieve able to imprison organic molecules, such as the herbicides. Thus, the elevated temperature can weaken the organic matter structure present in the soil, allowing more atrazine leaching.

The T1 and T3 treatments, with SW addition, presented values more elevated of atrazine concentration in the leachate. Studies revealed that addition of dissolved organic matter to soils can facilitate the pesticides leaching (SEOL & LEE, 2001; SONG, CHEN & YANG, 2008; THEVENOT et al., 2008). In fact, the SW applied to the soil columns in this research work, possessed dissolved organic matter by soil sorptive sites can contribute to leaching increase (LI, XING & WILLIAN, 2005; COX et al., 2007). Therefore, with the increase in the concentration of dissolved organic matter, the desorption rate also increase, resulting in elevated leaching (SONG, CHEN & YANG, 2008). Drori, Aizenshtat and Chefetz (2005) evaluated the dissolved organic matter influence in the atrazine behavior in soil, and viewed less herbicide sorption and more desorption in soils with swine wastewater irrigated. The authors concluded that the dissolved organic matter added to soil by wastewater modified the sorption sites available to the atrazine.

In Table 3 are presented the got results for the statistical test of lines comparison for the atrazine leached accumulated.

**Table 3.** Test comparison of linear and angular coefficients of the straight lines of the treatments at 5% significance.

Tr	Angular Coeff. (b)	Linear Coeff. (a)	QME	Test F QME	Test T (b)	Test T (a)
T1	0.131	- 0.0717	0.00053	$\left  \frac{0.57_{Fc}}{1.85_{Ft}} \right  <$	$\left  1.26_{Tc} \right  < 2.00_{Tt}$	$\left  \frac{0.09_{Tc}}{2.00_{Tt}} \right  <$
T2	0.139	- 0.0775	0.00092	$QME_{T1} =$ $QME_{T2}$	$B_{T1} = b_{T2}$	$A_{T1} = a_{T2}$
T1	0.131	- 0.0717	0.00053	$\left  \frac{1.06_{Fc}}{1.87_{Ft}} \right  <$	$\left  7.08_{Tc} \right  > 2.01_{Tt}$	-
T3	0.169	- 0.0661	0.0005	$QME_{T1} =$ $QME_{T3}$	$B_{T1} \neq b_{T3}$	-
T1	0.131	- 0.0717	0.00053	$\left  \frac{3.53_{Fc}}{1.88_{Ft}} \right  >$	-	-
T4	0.0692	- 0.0366	0.00015	$QME_{T1} \neq$ $QME_{T4}$	-	-
T2	0.139	- 0.0775	0.00092	$\left  \frac{0.54_{Fc}}{1.85_{Ft}} \right  <$	$\left  4.75_{Tc} \right  > 2.00_{Tt}$	-
T3	0.169	- 0.0661	0.0005	$QME_{T2} =$ $QME_{T3}$	$B_{T2} \neq b_{T3}$	-
T2	0.139	- 0.0775	0.00092	$\left  \frac{0.16_{Fc}}{1.85_{Ft}} \right  <$	$\left  \frac{12.29_{Tc}}{2.00_{Tt}} \right  >$	-
T4	0.0692	- 0.0366	0.00015	$QME_{T2} =$ $QME_{T4}$	$B_{T2} \neq b_{T4}$	-
T3	0.169	- 0.0661	0.0005	$\left  0.3_{Fc} \right  < 1.85_{Ft}$	$\left  \frac{22.60_{Tc}}{Tt} \right  > 2.00$	-
T4	0.0692	- 0.0366	0.00015	$QME_{T3} =$ $QME_{T4}$	$B_{T3} \neq b_{T4}$	-

Tr: treatments; Coeff.: coefficient; QME: mean square residual; b: angular coefficient; a: linear coefficient; Fc: F value calculated; Ft: critical point of the table F-Snedecor; Tc: T value calculated; Tt: critical value of the table t-Student two-tailed.

Source: own authorship.

Notes that the variances for the T1 and T4 treatments are different and, therefore, the test does not apply, being the comparison concluded. The T1 and T2 treatments showed sameness, because the two lines have intercepts and slope equal, being that in the other comparisons, the treatments presented difference between them at 5% significance.

## 6 CONCLUSIONS

The swine wastewater application in Rhodic Hapludox in dose of 435 m<sup>3</sup> ha<sup>-1</sup>, provided increase of atrazine leaching in the soil profile.

## 7 ACKNOWLEDGMENT

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