ENVIROMENTAL BEHAVIOR OF SULFENTRAZONE AND FIPRONIL IN A BRAZILIAN CLAYEY LATOSOL: FIELD EXPERIMENT AND SIMULATION

Comportamento ambiental do sulfentrazone e fipronil em um Latossolo argiloso brasileiro: experimentação à campo e simulação

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ABSTRACT

There has been an urgent need to assess pesticide environmental behavior under Brazilian field conditions and to evaluate the risks associated to its use in agriculture. Besides a qualitative and quantitative interpretation of field experiments to acquire understanding about pesticide environmental behaviour, field experiments are important to test pesticide fate models. Environmental behaviour of fipronil and sulfentrazone in a sugarcane area in Dourados, MS, was evaluated until 257 days after application. Moreover, the PEARL model was tested to simulate the fate of these two pesticides in the field. Soil samples for pesticide residue quantification and water content were taken at 0-10, 10-30, 30-50, 50-70 and 70-100 cm depth. There was a fast dissipation of both pesticides at soil surface within 15 days after application and their leaching was not beyond 30 cm depth. Dissipation and leaching satisfactory simulations for both pesticides were achieved only after calibration of half-life values or using a reduced initial dose. This study shows that fast dissipation of pesticides in the field can be an important process to consider when assessing the environmental behavior of pesticides in Brazil.

Index terms: Leaching, dissipation, PEARL, risk assessment.

RESUMO

Existe uma necessidade urgente para se avaliar o comportamento ambiental de agrotóxicos nas condições brasileiras de campo e para se avaliar os riscos associados com seu uso na agricultura. Além das interpretações qualitativas e quantitativas dos experimentos de campo para se adquirir entendimento sobre o comportamento ambiental de agrotóxicos, experimentos de campo são importantes para se testar modelos para simular o destino de agrotóxicos. O comportamento ambiental do fipronil e sulfentrazone em uma área com cana-de-açúcar em Dourados, MS, foi avaliado até 257 dias após aplicação. Mais ainda, o modelo PEARL foi testado para simular o destino desses dois agrotóxicos no campo. Amostras de solo para a quantificação dos resíduos dos agrotóxicos e do teor de água foram coletadas nas profundidades de 0-10, 10-30, 30-50, 50-70 e 70-100 cm. Houve uma rápida dissipação de ambos os agrotóxicos na superfície do solo em 15 dias após aplicação e suas lixiviações não foram além de 30 cm de profundidade. Simulações satisfatórias da dissipação e lixiviação para ambos os agrotóxicos foram obtidas somente após calibração dos valores de meia-vida ou utilizando a dose inicial reduzida. Nste trabalho, mostra-se que a rápida dissipação de agrotóxicos no campo pode ser um processo importante a ser considerado na avaliação do comportamento ambiental de agrotóxicos no Brasil.

Termos para indexação: Lixiviação, dissipação, PEARL, avaliação de risco.

INTRODUCTION

During recent years, there has been a growing concern about pesticides used in agriculture and their impacts on natural resources. Because of that, agricultural production systems should not only maximize yields but also evaluate any risks of negative impacts on natural resources. After pesticide application on crops and subsequently soil deposition, many transport processes can occur that need to be characterized and identified by field studies. The magnitude of these processes vary according to soil type, prevailing soil and crop conditions, land topography and climate conditions. Carter (2000) reports that soil surface losses due to pesticide volatilization can be as high as 90% of the applied amount and for leaching and runoff not more than 5%. However, the fate of pesticides in tropical agroecosystems are not well understood as in temperate regions. There has been some evidences that pesticides sprayed in tropical regions can dissipate faster than in temperate regions because, for example, of increased volatility and enhanced degradation rates (Laabs et al., 2002; Moreira et al., 2012).

Assessment of pesticide fate under field conditions and associated environmental risks of its use is time-and money-consuming. A great number of field experiments would be necessary to assess pesticide fate under Brazilian conditions given the diversity of soils, climate, crops and pesticides. To overcome this, environmental fate modeling

of pesticides has become an important and efficient tool to assess pesticide fate considering the diversity of environmental scenarios. Nowadays, environmental fate modeling of pesticides plays a major role in assessing risks and decision in pesticides registration at the European Union level (Boesten, 2000). In Brazil, authorities recently started to use some models for pesticide risk assessment under Brazilian conditions but only a few studies have been carried out aiming to test some models (Castro et al., 2006; Vasconcelos et al., 2013). Therefore, the validation status of pesticide fate models under Brazilian scenarios is quite low.

Due to a rapid increase on sugarcane cultivated area in Mato Grosso do Sul State and its specific soil and climate conditions, it is urgent to assess the environmental risks of pesticides used for this crop. Fipronil is a soil and foliar broad-spectrum insecticide used in sugarcane areas of Mato Grosso do Sul State to control termites. Due to its low water solubility of 19 mg L^{-1} and sorption coefficients (K_{OC}) between 396 and 825 L kg^{-1}, it is expected very high sorption of fipronil on soil (Shuai; Chen; Ray, 2012). Masutti and Mermut (2007) stated that either organic and mineral particles can influence the sorption of fipronil and its degradation products on tropical soils. Another widely used pesticide in sugarcane plantations of Mato Grosso do Sul State is the herbicide sulfentrazone that has shown moderate to high persistence (Brum; Franco; Scorza Júnior, 2013) and low sorption in tropical soils (Passos et al., 2013). This work had the aim to evaluate the field behavior of fipronil and sulfentrazone after application insugarcane in Dourados, Mato Grosso do Sul State and also to test the PEARL model (Boesten, 2007) to simulate the fate of these two pesticides.

MATERIAL AND METHODS

The field experiment was carried out in an area of 0.09 ha (30 x 30 m) located at Embrapa Western Agriculture in Dourados, Mato Grosso do Sul State (22°17'12" S; 54°48'23" W; 408 m above sea level). This area had been previously used for soybean cultivation in summer and wheat or oat cultivation in autumn/winter following the good agricultural practices in the region. The experimental area was divided into four plots containing 25 subplots of 3 x 3m. The soil is classified as a typical distroferric Red Latossol, which represents about 75% of the main soil type at Dourados river watershed. (Oliveira, Urchei; Fietz, 2000). Soil attributes are summarized in table 1. Undisturbed soil cores for the determination of soil water retention curves and dry bulk densitywere taken in triplicates at five different depths (i.e. 0-10, 10-30, 30-50, 50-70, 70-100 cm) in only one pit at the experimental field. Additionally, in-situ measurements of saturated hydraulic conductivities were also carried out in this pit for all five depths using a permeameter of Guelph-type. Meteorological data were obtained from an automatic meteorological station at Embrapa Western Agriculture, which is located about 500 m from the experimental field.

The experimental period was carried out between December 3rd, 2009 and August 8th, 2010. Sugarcane was sown on November 19th, 2009. Fiproniland sulfentrazone, at rates of 0.8 kg a.i. ha^{-1} and 1.6 kg a.i. ha^{-1} respectively, were sprayed separately on December 3rd, 2009 with a tractor-mounted boom sprayer and using 250 L ha^{-1} of water (Andrei, 2005). These rates were two times greater than the label application rate to ensure that pesticides residues in soil during the experimental period were above the analytical quantification limit of the method. Soil profile samples for pesticide residue quantification and water content were taken at 0-10, 10-30, 30-50, 50-70 and 70-100 cm depth at 0, 15, 32, 55, 88, 138, and 257 days after fipronil and sulfentrazone application. Four subplots were randomly selected and pits excavated till 100 cm depth on each sampling date. About 500g of soil for each sampling date and depth in each subplot were stored in plastic bags at -20°C until pesticide residue analysis. For determination of soil water content, soil samples of about 50g were dried at 105°C for 24h.

Table 1 – Soil chemical and physical attributes.

Depth (cm)	Sand (g kg^{-1})	Clay (g kg^{-1})	OM[1] (g kg^{-1})	pH (CaCl$_2$)	BD[2] (g cm^{-3})
0-10	245	630	33.4	4.9	1.13
10-30	229	663	29.6	4.3	1.25
30-50	212	697	22.7	5.1	1.12
50-70	195	713	16.9	5.3	1.09
70-100	195	713	11.3	5.3	1.07

[1]Organic matter content; [2] Dry bulk density.

The methods of fipronil and sulfentrazone quantification in soil are described in more details in Brum, Franco and Scorza Júnior (2013) and Scorza Júnior and Franco (2013). Fipronil and sulfentrazone were extracted by shaking 50 g of moist soil with 100 mL of methanol HPLC grade for 2 hours in a shaking table at 216 rpm and 25°C. After decantation for 1 hour, 50 mL of the supernatant was completely evaporated at 40°C in a rotary evaporator under vacuum and the final residue concentrated in 10 mL of acetonitrile HPLC grade. Thereafter, this aliquot of 10 mL was centrifuged at 2500 rpm for 30 minutes at 15°C. The final extract was filtered through a 0.22 μm membrane of regenerated cellulose directly in a 2-mL vial and stored at -20°C until HPLC analysis. Quantification of both pesticides were carried out using a HPLC-PAD model Varian LC-920 operating at 207 nm for sulfentrazone and at 220 nm for fipronil and separation in a C_{18} column (Polaris Varian 250 mm x 4.6 mm i.d. x 5 μm) at 35°C. For fipronil, the elution phase was: acetonitrile:water at 50:50% (v/v) for 10 minutes; 100%acetonitrile from 10 to 21 minutes and acetonitrile:water at 50:50% (v/v) from 21 to 32 minutes. For sulfentrazone, the elution phase was: acetonitrile: water (acidified with 0.1% of orthophosphoric acid) at 50:50% (v/v) for 10 minutes; 100% acetonitrile from 10 to 21 minutes and acetonitrile:water at 50:50% (v/v) from 21 to 30 minutes. The injection volume was 20 μL and the flow rate of 1 mL minute^{-1} for both pesticides. The extraction efficiencies of the method were on average 98% for fipronil and 101% for sulfentrazone. The limits of quantification for fipronil and sulfentrazone in soil were 0.8 and 0.2 μg g^{-1}, respectively.

Simulations of moisture profiles and pesticide behaviour (leaching and amount remaining in soil profile) were carried out using PEARL model version 4.4.4, which is described in detail elsewhere (Boesten, 2007). Briefly, PEARL is a one-dimensional, dynamic, multi-layer model for simulating pesticide leaching through soil. It uses SWAP model for simulating soil water flow and soil temperature, which is described in detail by Van Dam et al., (2008). SWAP describes water flow using Darcy equation combined with the mass conservation equation, which results in the well-known Richards equation. Moreover, SWAP uses the Van Genuchten functions (Equation 1) (Van Genuchten, 1980) to describe soil water content and soil hydraulic conductivity as a function of the soil water pressure head given by:

$$\theta(h) = \theta_r + \frac{\theta_s - \theta_r}{\left(1 + |\alpha h|^n\right)^{-n}} \quad \text{and}$$

$$K(h) = K_S \frac{\left(\left(1 + |\alpha h|^n\right)^{1 - 1/n} - |\alpha h|^{n-1}\right)^2}{\left(1 + |\alpha h|^n\right)^{(1 - 1/n)(\lambda + 2)}} \tag{1}$$

in which θ is the soil water content (cm^3 cm^{-3}), θ_r is the residual soil water content (cm^3 cm^{-3}), θ_S is the saturated soil water content (cm^3 cm^{-3}), K_S is the saturated soil hydraulic conductivity (cm day^{-1}), and α (cm^{-1}), λ (-) and n (-) are fitting parameters. All input parameters of van Genuchten functions used in the simulations are shown in table 2. In PEARL, the mass conservation equation of pesticide in soil is (Equation 2) given by:

$$\frac{\partial C^*}{\partial t} = \frac{\partial}{\partial z}\left(q.C_L - D_L \frac{\partial C_L}{\partial z} - D_G \frac{\partial C_G}{\partial z}\right) - R_T - R_U \tag{2}$$

in which C^* is the total concentration of pesticide in soil (mg dm^{-3}), t is time (day), z is depth (cm), q is the flux of water in soil (cm day^{-1}), C_L is the concentration of pesticide in the liquid phase (mg dm^{-3}), D_L is the hydrodynamic dispersion coefficient (cm^2 day^{-1}), D_G is the gas diffusion coefficient (cm^2 day^{-1}), C_G is the concentration of pesticide in the gas phase (mg dm^{-3}), RT is the transformation rate of pesticides in soil (mg dm^{-3} day^{-1}), R_U is the pesticide uptake by plants (mg dm^{-3} day^{-1}). R_T is (Equation 3) given by:

$$R_T = \left(f_T.f_\theta.f_Z.\frac{0.693}{DT_{50}}\right)\theta.C^* \tag{3}$$

in which f_T, f_θ and f_z are reduction factors to account for the influence of temperature, soil water content and depth, respectively, and DT_{50} is the pesticide half-life Pesticide sorption is described with the Freundlich isotherm.

For simulations, the soil profile was divided into six layers (0-10, 10-30, 30-50, 50-70, and 70-100 cm depth). The application rates of fipronil and sulfentrazone used in the simulations were 0.63 and 1.71 kg ha^{-1}, respectively, which correspond to the average amount recovered just after application at 0-5 cm depth. Pesticide input parameters were

derived from laboratory studies (Brum; Franco; Scorza Júnior 2013; Scorza Júnior; Franco, 2013). Input DT_{50} values for fipronil and sulfentrazone were 38 and 79 days, respectively. The Freundlich sorption coefficients and the Freundlich exponents were, respectively, 5.4 L kg^{-1} and 1.1 for fipronil and 4.9 L kg^{-1} and 0.9 for sulfentrazone. The bottom boundary condition used in the simulations was set to free drainage.

A stepwise approach (Vanclooster et al., 2000) was used for the testing of the PEARL model, in which each submodel was separately and sequentially evaluated. The package PEST (Doherty, 2000) was used for calibration of moisture profiles and the pesticide remaining amounts in the soil profile.

RESULTS AND DISCUSSION

Cumulative values of precipitation and potential evapotranspiration obtained throughout the experimental period were 1,052 and 807 mm, respectively. The greatest variations in soil moisture profiles for all sampling dates were observed between 0-30 cm depth (Figure 1). Below this layer, soil water contents were greater than 0.3 cm^3 cm^{-3} for all sampling dates. Probably, these variations of soil water contents at soil surface are mainly due to high demand by water from atmosphere and crop uptake. Uncalibrated simulations of soil moisture profiles were slightly overestimated for some sampling dates (Figure 1). For example, simulated soil water contents between 0-10 and 10-30 cm at day 55 were about 0.30 and 0.38 cm^3 cm^{-3}, respectively, where as their corresponding measured values were about 0.23 and 0.33 cm^3 cm^{-3}. These results indicate that soil water retention curves measured in the laboratory were not representative for the experimental field. This lack of representative ness may have been caused by inadequate handling of spatial variability inasmuch as only two samples were taken from only one pit in the 0.09 ha experimental field. Van Alphen, Booltink and Bouma (2001) states that input values of soil water retention curves based on a few measurements in the field should be used only as initial guesses for a calibration procedure when

simulating moisture profiles. Thus, in compliance with this recommendation, we performed calibration of moisture profiles by optimizing θ_r, n and α parameters as recommended by Scorza, Silva and Rigitano (2010). After optimization of these parameters, there was an improvement in the simulation of moisture profiles with these values within the range of measured ones for almost all depths and sampling dates (Figure 1). In general, the optimization of θ_r, α and n parameters (Table 2) resulted in decreasing water retention capacity for all soil layers. Figure 2 shows this decrease in water retention capacity for two representative soil layers.

The average recovered mass of fipronil in the soil profile just after application (Day 0) was 0.63±0.08 kg ha^{-1}, which is about 89% of the nominal applied amount of 0.71 kg ha^{-1} (Figure 3A). For sulfentrazone, this recovered mass was 1.71±0.14 kg ha^{-1}, which is about 120% of the nominal applied dose of 1.43 kg ha^{-1} (Figure 3B). For the following sampling dates, we observed a fast decline in the remaining amounts for both pesticides in the soil profile with values below 4% of applied dose for fipronil and 11% for sulfentrazone. The cumulative precipitation within the period of 24h after application was 63 mm. This amount was sufficient to incorporate both pesticides within the first soil surface layers. However, this small incorporation was not sufficient to avoid the fast dissipation just after application that was probably due to volatilization. Some authors (laabs et al., 2002; Nogueira et al., 2012) have also reported evidences of pesticide volatilization in Brazilian agricultural scenarios based on the detection of its residues in rainfall samples. However, we did not find in literature flux measurements of pesticides losses due to volatilization in Brazilian soils and the influence of meteorological conditionson this process. Rice, Nochetto and Zara (2002) and Prueger et al. (2005) carried out field-scale studies in USA to quantify pesticide volatilization fluxes and the influence of meteorological conditions and soil water content on this process. For both studies, peak volatilization of pesticides from soil did occur during the first 24h after

Table 2 – Uncalibrated and calibrated input parameters for van Genuchten functions.

Depth (cm)	θ_r (cm^3 cm^{-3})	θ_s (cm^3 cm^{-3})	α (cm^{-1})	n (-)	K_s (m day^{-1})
0-10	0.25 (0.22)[1]	0.37	0.01 (0.024)[1]	1.80 (1.99)[1]	7.34
10-30	0.25 (0.30)	0.47	0.01 (0.037)	1.80 (1.88)	3.64
30-50	0.32 (0.29)	0.57	0.01 (0.058)	1.80 (1.32)	2.77
50-70	0.32 (0.11)	0.55	0.01 (0.026)	1.80 (1.24)	2.27
70-100	0.32 (0.15)	0.51	0.01 (0.012)	1.80 (1.37)	1.21

θ_r = residual soil water content; θ_s= saturated soil water content; α and n are parameters; K_s= saturated soil hydraulic conductivity.
[1] calibrated values.

application and was associated with wet soil surface conditions and warm air temperatures. The combination of these factors can enhance soil water evaporation and therefore pesticide volatilization. Thus, we hypothesize that the fast dissipation of fipronil and sulfentrazone observed in our study just after application might be associated with intense volatilization losses favored by high rates of soil water evaporation. Spencer and Cliath (1973) reported that volatilization rate of pesticides in soil is controlled by water loss from soil. Volatilization rate of some pesticides increased by a factor between 2 and 5 after re-wetting of soil surface (Spencer; Cliath, 1973; Spencer; Farmer; Jury, 1982).
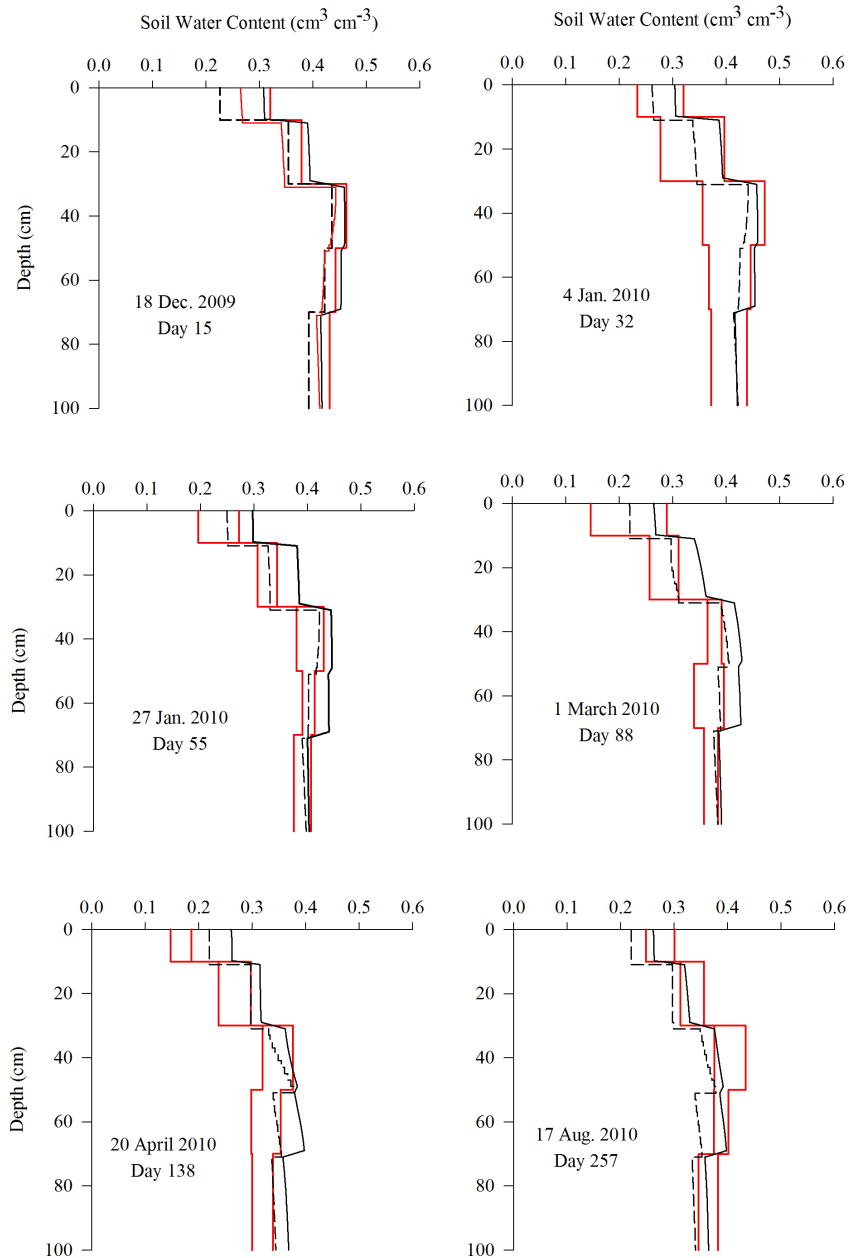

Figure 1 – Measured and simulated moisture profiles in Dourados, MS. The area within the red lines is the range of measured values plus or minus two times the standard error. The solid and dashed black lines are uncalibrated and calibrated simulations.
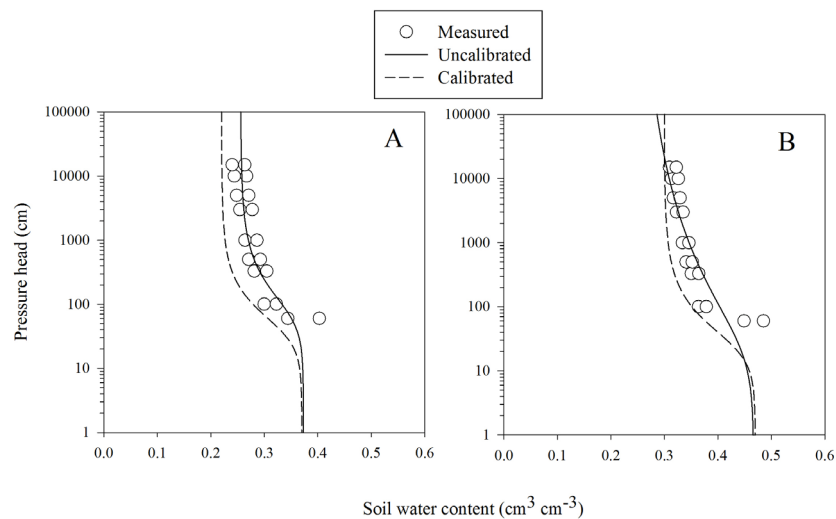
Figure 2 – Soil water retention curves for 0-10 cm (A) and 10-30 cm (B) layers.
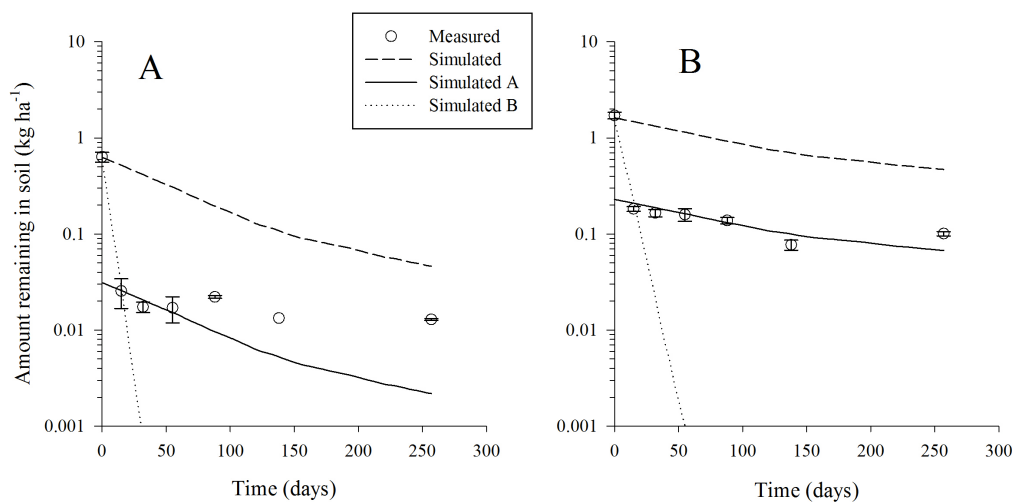

Figure 3 – Measured and simulated (uncalibrated) remaining amount of fipronil (A) and sulfentrazone (B) in the soil profile (0-100 cm) as a function of time. Simulated A = reduced the initial applied dose and uncalibrated DT_{50}; Simulated B = calibrated DT_{50} values without reduction in the initial applied dose.

A few concentration profiles of fipronil and sulfentrazone that represent almost the full range of all sampling dates are shown in figures 4 and 5. Overall, the leaching of fipronil and sulfentrazone was not beyond 30 cm depth for all sampling dates. Concentration profiles of fipronil indicated that its residues were restricted to 0-10 cm depth and the range of concentrations were between 0.013 and 0.025 mg dm^{-3} for all sampling dates (Figure 4). For sulfentrazone, concentration profiles indicated that residues were restricted to 0-30 cm depth and the

range of concentrations were between 0.130 and 0.016 mg dm^{-3} (Figure 5). Our results indicate a deeper leaching of sulfentrazone than fipronil. This is consistent with K_{OC} and DT_{50} values observed for these pesticides in laboratory studies (Table 2). The smaller K_{OC} value of sulfentrazone than fipronil indicates less soil retention for sulfentrazone and therefore more potential for leaching. Moreover, greater DT_{50} value of sulfentrazone than fipronil indicates that sulfentrazone is more persistent and may represent a continuous source in the topsoil for leaching.
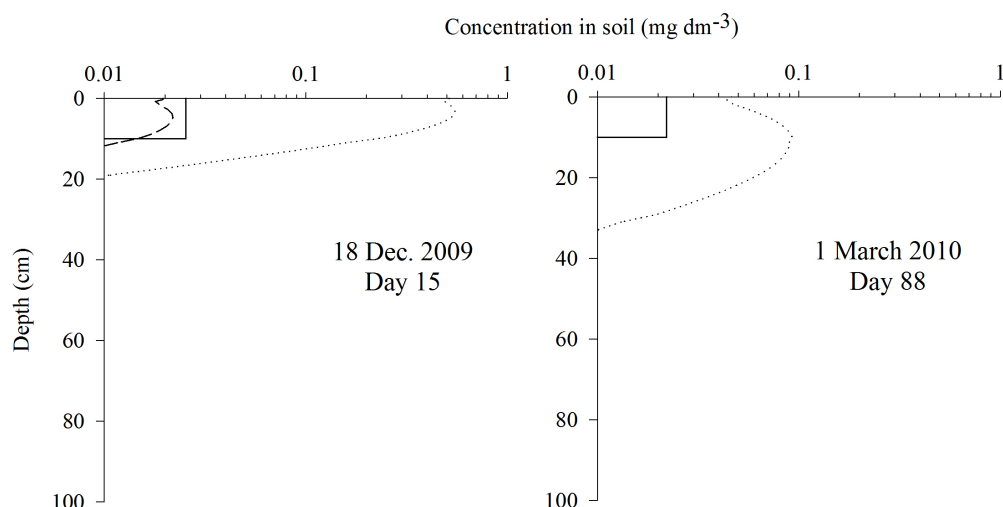
Concentration in soil (mg dm⁻³)

Figure 4 – The solid line is the average of measured fipronil concentrations. Dotted line for uncalibrated simulation and dashed line for calibrated simulation using reduced initial applied dose as input.
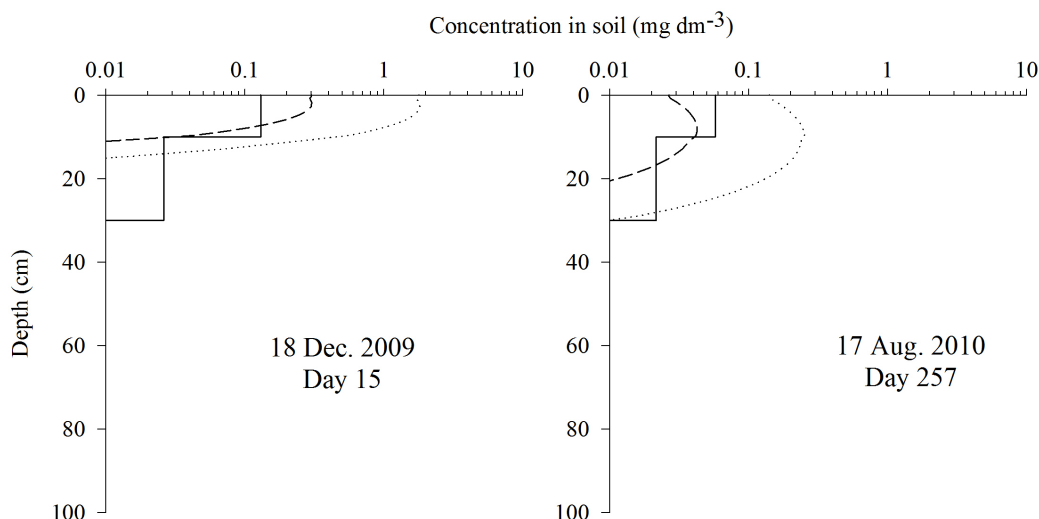
Concentration in soil (mg dm⁻³)

Figure 5 – The solid line is the average of measured sulfentrazone concentrations. Dotted line for uncalibrated simulation and dashed line for calibrated simulation using reduced initial applied dose as input.

The simulations of fipronil and sulfentrazone remaining amounts as a function of time in the soil profile were overestimated at all dates (Figure 3). This discrepancy between measurements and simulations for both pesticides occurs because of PEARL model was not able to simulate the fast dissipation as observed in the field just a few days after application. In the current version of PEARL model, volatilization can only be simulated by diffusion of pesticide vapor in soil gas phase, which is adequate to simulate pesticides that are injected or incorporated into the soil. However, this type of volatilization cannot mimic the fast dissipation of soil surface sprayed pesticides as observed in our study. For a better simulation, it would be necessary to consider film volatilization. As a next step, we carried out additional simulations to investigate if calibrating or changing some input parameters (i.e. initial applied dose and DT_{50}), the PEARL model would be able to describe this fast dissipation. After reduction of initial applied dose for fipronil (95%) and sulfentrazone (86%) as input for PEARL, there was a good simulation of remaining

amounts as a function of time in the soilprofile until 55 days for fipronil and at all dates for sulfentrazone (Figure 3). After 55 days, PEARL overestimated these remaining amounts as a function of time in the soil profile for fipronil (Figure 3A). The calibration of DT_{50} values resulted in good agreement between measurements and simulations of remaining amounts in the soil for both pesticides only at Day 15 (Figure 3). However, this calibration procedure resulted in unrealistic DT_{50} values of 2.3 days for fipronil and 3.7 days for sulfentrazone.Because of these unrealistic DT_{50} values, we consider hereafter calibrated simulations with reduced initial applied dose for both pesticides.

Uncalibrated simulations of fipronil and sulfentrazone concentration profiles overestimated concentration levels for all dates although good representation was obtained for the bulk leaching (Figures 4 and 5). Calibrated simulations of fipronil concentration profiles were similar to measured ones between 0-10 cm depth at Day 15 but much lowerat Day 88, for the same depth. For sulfentrazone, calibrated simulations of concentration profiles resulted in values slightly greater than the measured ones between 0-10 cm depth and much lower ones between 10-30 cm depth at Day 15. However, at Day 257, simulated values were similar to measured ones for 0-10 cm and 10-30 cm depth.

Overall, if Brazilian authorities intend to use pesticide fate models as tools for risk and exposure assessment, it seems crucial that these tools consider the fast dissipation of pesticides by volatilization, for example. However, modeling pesticide volatilization from soil surface just after application is still a challenge because the knowledge of the rate-determining processes is either insufficient or demand very detailed input data.

CONCLUSIONS

There was a fast dissipation of fipronil and sulfentrazone applied to soil in a few days after application. Leaching of both pesticides was not beyond 0.3 m depth. Good simulations of moisture profiles using PEARL were achieved after calibration of soil water retention curves. PEARL was able to simulate the remaining amount of both pesticides in soil as a function of time after using a reduced initial dose as input to mimic the fast dissipation after application. This study shows that fast dissipation of pesticides in the field should be consideredas important process when assessing the environmental behavior of pesticides in Brazil.

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