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Dissipation of fenitrothion and esfenvalerate in wheat grains, bran and flour

Disipación de fenitrotion y esfenvalerato en granos de trigo, salvado y harina

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Abstract

Chemical insecticides are commonly used to control insect pests in stored wheat. However, the presence of insecticide residues in food may endanger consumers. We studied the degradation and persistence of two insecticides, fenitrothion and esfenvalerate, in wheat grain, bran, and flour. The application system was calibrated to treat grain at theoretical concentrations of 10 and 0.5 mg kg^{-1} of fenitrothion and esfenvalerate, respectively. Samples treated with the insecticide mixture were collected at 0, 15, 30, 60, 90, 120, 180, 240, and 360 days after treatment. Samples were analyzed quantitatively by gas chromatography with an electron capture detector (ECD, Ni63). The experimental design was completely randomized with three replicates. Esfenvalerate was more persistent than fenitrothion, with the residues of both insecticides concentrated mainly in the bran, and with least amounts in the flour. The concentrations of fenitrothion residues during the 120-day preharvest interval exceeded the maximum residue limit (MRL) of 1 mg kg^{-1} set by Brazilian legislation. We discuss the factors that influence the degradation/persistence of fenitrothion and esfenvalerate.

Key words: *Degradation, persistence, chromatography, maximum residue limit, preharvest interval.*

Resumen

Debido a los problemas causados por los insectos en el trigo almacenado, insecticidas químicos son utilizados para el control de esas plagas, existiendo la posibilidad de colocar en riesgo la salud de los consumidores debido a los residuos de estas substancias en los alimentos. El objetivo de este trabajo fue estudiar la degradación/persistencia de los insecticidas Fenitrotion y Esfenvalerato en granos de trigo y en algunos de sus derivados (salvado y harina). El sistema de aplicación fue calibrado para el tratamiento de los granos en las concentraciones teóricas de 10 y 0,5 mg kg^{-1} de Fenitrotion y Esfenvalerato, respectivamente. Las muestras tratadas con la mezcla insecticida fueron colectadas a los cero, 15, 30, 60, 90, 120, 180, 240 y 360 días después del tratamiento. La determinación cuantitativa se hizo mediante técnica de cromatografía en fase gaseosa, utilizándose cromatógrafo equipado con detector de captura de electrones (ECD, Ni^{63}). El diseño experimental fue enteramente al azar, con tres repeticiones. El Esfenvalerato fue más persistente que el Fenitrotion. Los residuos de ambos insecticidas en los granos de trigo se concentraron principalmente en el salvado y en menores cantidades en la harina. El residuo de Fenitrotion en el periodo de carencia de 120 días fue superior al Límite Máximo de Residuo (LMR) de 1 mg kg^{-1} permitido por la legislación brasileña, la misma que resultó inadecuada en la reglamentación de ese insecticida. Los factores que influyeron en la degradación/persistencia del Fenitrotion y Esfenvalerato son discutidos en el presente trabajo.

Palabras clave: *Degradación, persistencia, cromatografía, limite máximo de residuo, periodo de carencia.*

Introduction

Chemical insecticides are one of the most important inputs in modern agricultural production systems, as they are the principal method of pest control. Thus, to avoid consuming food with dangerous levels of these substances, every registered insecticide has a maximum residue limit (MRL) and a preharvest interval allowed by law. However, the improper use of the insecticides in stored products may change the residue levels so that they surpass their MRL,

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thus putting consumers' health at risk (Dordevic & Durovic-Pejcev, 2016; Watanabe et al., 2018). The persistence of the insecticide in stored products depends on several factors, including the physico-chemical characteristics of the pesticides, and the environmental conditions (e.g., humidity and temperature) of the warehouse in which the grain is stored (Farha et al., 2016). In general, pyrethroid insecticides are much more persistent than the organophosphorus ones (Afridi et al., 2001), although both groups of insecticides are more stable at lower humidity levels (Samson et al., 1988). With regards to warehouse temperature, insecticides generally degrade faster at higher temperatures (Arthur et al., 1991).

Insecticides residues may be present not only in stored grains, but also in their by-products, although insecticide residue concentrations generally diminish relative to that in the whole grain (Barbosa, 2004). Therefore, it is important to measure the changes in residues levels that occur during the processing of grains, and these changes must be considered in determining the MRL and preharvest interval for each substrate.

In Brazil, the list of preventive insecticides currently registered for wheat grain treatment in warehouses is as follows: fenitrothion, malathion, pirimiphos-methyl, bifenthrin, deltamethrin, esfenvalerate, and permethrin (Agência Nacional De Vigilância Sanitária [ANVISA], 2019). It should be noted that ministerial resolution No. 165 of the 29th of August 2003, which regulates the use of fenitrothion, has been modified by resolution No 347 of the 22nd of November 2004 (Resolução RE n⁰ 347, 2004). In this resolution, the MRL and preharvest interval values for fenitrothion on stored wheat grain were modified from 10 mg kg^{-1} and 14 days, respectively, to 1 mg kg^{-1} and 120 days, respectively. There are efforts worldwide to eliminate highly toxic insecticides on stored grains. However, the Alimentarius Codex of the Food and Agriculture Organization of the United Nations (FAO) and WHO does not have registry entries for fenitrothion or esfenvalerate applied to stored wheat; there is only an MRL for esfenvalerate used for preharvest treatments: 0.05 mg kg^{-1} (FAO, 2019). Similarly, an MRL for fenitrothion on wheat gluten has been registered with the US Environmental Protection Agency (EPA, 2012).

The presence of insecticide residues in foods constitutes a serious risk for consumers, but the scientific evidence regarding this subject is shallow (Valcke et al. 2017). Moreover, there are some serious inconsistencies between the Brazilian legislation and insecticide manufacturers; some of the MRLs issued by the former are higher than what would be expected based on the dose recommended by the latter, thus allowing the immediate consumption of grain after treatment (Trevizan & Baptista, 2000). On an international level, legislation on pesticide residues in foods has sometimes been used as a mechanism to raise trade barriers. Therefore, it is important to study the fate of insecticide residues in stored grains under Brazilian conditions to provide reliable information in crafting adequate legislation.

The objective of this work is to study the dissipation of fenitrothion and esfenvalerate in wheat grains, flour, and bran.

Materials and Methods

The research was conducted at the Pesticide Residues Analysis Laboratory (LARP) of the Agricultural Superior School "Luiz de Queiroz" at the São Paulo University (USP), Piracicaba, São Paulo (22°42′47″ S, 47°37′40″ O), Brazil.

Treatment of the grains

The wheat cultivar "BRS 208", developed by the Brazilian Agricultural Research Corporation (Embrapa), was used. To treat the grains, a mobile application system equipped with a double-jet hydraulic fan nozzle (model TJ- 8002EVS, Spraying Systems Co., Illinois, USA) was used. The nozzle was operated at 200 KPa and installed 0.5 m above the grain mass. The application system was calibrated to treat the grains at theoretical concentrations of 10 mg kg^{-1} of fenitrothion and 0.5 mg kg^{-1} of esfenvalerate. The commercial product Sumigranplus® (containing 500 g L^{-1} of fenitrothion + 25 g L^{-1} of esfenvalerate) was used. The mobile system moved at a speed of 2.2 km h^{-1} over the mass of grains. Under these operational conditions, the volume of mix equivalent to 5 L of insecticide emulsion was applied per ton of grain (0.4% of commercial product). For the control, the same procedure was performed, except only water was used. The experiment consisted of three replicates. The temperature and relative humidity during treatment applications ranged 16°C –18°C and 72%–79%, respectively. After applications, the grains were placed in plastic bags and stored in the laboratory, where temperature and relative humidity were not controlled. The moisture content of the grains during the storage period was measured by the oven drying method at 105 ± 3°C for 24 h, according to the Rules for Seed Analysis–RAS (Brazil, 1992).

Sampling

The grain samples were collected at 0, 15, 30, 60, 90, 120, 180, 240, and 360 days after the treatments. Wheat grain processing to produce flour and bran was done at the Quality Control Laboratory of the Cargill Alimentos company, located in the municipality of Tatuí, São Paulo, Brazil.

Analytical procedure

The analytical method of Vásquez-Castro et al. (2007) was used to analyze the residues on the grains and their by-products. The procedure starts with the extraction of the residues with ethyl acetate, followed by separation by silica gel-column chromatography, and then quantitative determination through gas chromatography (GC) with an electron capture detector (ECD, Ni63), Thermoquest Trace model (Milan, Italy).

Analytical method validation

The analytical method was validated by spiking samples (grain, bran and flour) with 0.05 and 0.5 mg kg^{-1} of fenitrothion and esfenvalerate, respectively. Three replicates were performed for each dose. Recovery rates of between 70%–120% were considered acceptable.

Statistical analysis

The data for each insecticide and substrate were analyzed by linear regression, using the following model:

$$y = \alpha + \beta x + e,$$

Where "y" is the natural logarithm of the observed value of the insecticide residue; "α" is the logarithm of the insecticide initial value; "β" is the degradation constant; "x" is the time after the insecticide application; and "e" is the random error, which is assumed to be independent and randomly distributed.

The above model requires values of the half-life of each insecticide in each substrate, which were calculated using the following formula:

$$\text{half-life} = \frac{-Ln(2)}{\beta} = \frac{-0.693147}{\beta}$$

Linear regressions were analyzed using the General Linear Models test in SAS software (1999), Raleigh, USA.

Results and discussion

The recovery rates of the insecticides in different substrates ranged between 70% and 120%, thus validating the analytical method. In the control, none of the insecticides were recovered, that is, all substrates were free of contamination by these compounds. The amounts of fenitrothion and esfenvalerate recovered on day 0 were 6.24 and 0.35 mg kg^{-1}, respectively (Tables 1 and 2), which represent 62% and 70% of the theoretical concentrations of the organophosphorus and pyrethroid insecticide, respectively.

Several studies, conducted under both laboratory and storage conditions, have reported on the dissipation of insecticides from treated grains, with a large degrees of variation in the amounts of insecticide lost over the storage period (Arthur et al., 1991; Sgarbiero et al., 2003). Warehouses usually use conical-jet nozzles to apply residual insecticides because they are easier to operate, in contrast to fan-jet nozzles (Miike et al., 2002). However, conical-jet nozzles require a high level of hydraulic pressure to produce droplets and operating them at such high pressures produce fine drops (Sumner, 2012). In Brazil, the high interior temperature of warehouses may cause the evaporation of fine drops, thus leading to the loss of insecticides during their application. In contrast, continuous flow fan-jet nozzles operate at relatively low pressures, generating larger drops, and distribute droplets in a more uniform, transverse pattern, compared to their conical counterparts. Therefore, continuous flow fan-jet nozzles have several advantages for the treatment of stored grains. However, this type of nozzle requires greater care in their calibration (Vásquez-Castro, et al., 2012)

Table 1. Fenitrothion residues (mg kg^{-1}) in wheat grains treated with the insecticide mixture fenitrothion + esfenvalerate.

DAA	Residues (mean ± SD)	Degradation index	Accumulated degradation index
0	6.24 ± 0.10	-	-
15	3.89 ± 0.26	1.60	1.60
30	4.08 ±0.26	0.95	1.53
60	3.65 ± 0.05	1.12	1.71
90	3.34 ± 0.10	1.09	1.87
120	3.19 ± 0.16	1.05	1.96
180	0.88 ± 0.02	3.64	7.11
240	0.76 ± 0.03	1.15	8.21
360	0.54 ± 0.02	1.40	11.48

DAA: Days after application.

Table 2. Esfenvalerate residues (mg kg^{-1}) in wheat grains treated with the insecticide mixture fenitrothion + esfenvalerate.

DAA	Residues (mean ± SD)	Degradation index	Accumulated degradation index
0	0.35 ± 0.04	-	-
15	0.31 ± 0.02	1.12	1.12
30	0.37 ± 0.01	0.85	0.95
60	0.26 ± 0.02	1.41	1.33
90	0.26 ± 0.04	1.00	1.33
120	0.28 ± 0.04	0.93	1.24
180	0.23 ± 0.01	1.23	1.52
240	0.25 ± 0.02	0.91	1.38
360	0.25 ± 0.02	1.00	1.38

DAA: Days after application.

Although grain should be treated uniformly, some studies have shown the efficacy of insecticides in controlling pests when applied non-uniformly (Arthur, 1992). For example, Minett & Williams (1976) proposed mixing non-treated grains with overly treated grains as a method for controlling insect pests. However, this method is legally problematic; for example, the highly inconsistent distribution of insecticide residues in the grain mass may include areas with higher residue concentrations than that allowed by the MRLs, resulting in consequential economic impacts to the producer.

The degradation index values presented in the tables are indicators of the amount of the reduction in insecticide residues during the period between successive measurements. That is, these values show the degradation of the insecticides in different time intervals. The accumulated degradation index represents the degradation of insecticides throughout the evaluation period.

The moisture content of the grains during the experiment ranged between 10% and 11%, that is, the storage conditions were optimal for the preservation of the grains.

The values and adjusted regressions of fenitrothion and esfenvalerate residues in grains treated with the Sumigranplus® formulation are shown in Figs. 1 and 2. The regression of fenitrothion follows a steeper slope, indicating a higher degradation rate in contrast to that of esfenvalerate.

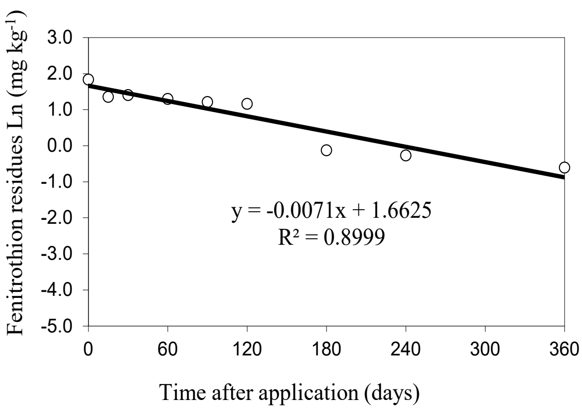

Figure 1. Mean values of fenitrothion residues through time after treating wheat grains with the Sumigranplus® formulation. Values have been logarithmically transformed and the regression has been adjusted.

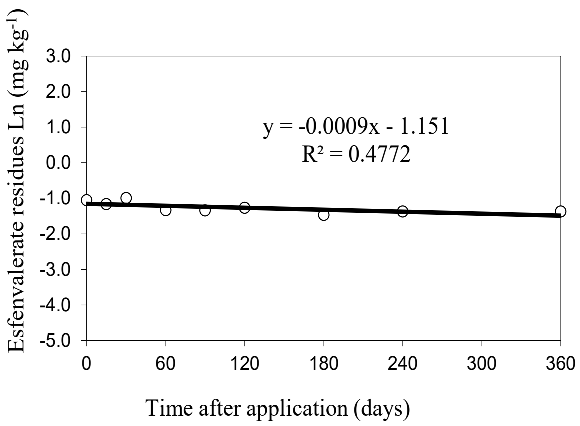

Figure 2. Mean values of esfenvalerate residues through time after treating wheat grains with the Sumigranplus® formulation. The values have been logarithmically transformed and the regression has been adjusted.

Table 3. Fenitrothion and esfenvalerate residues in treated wheat grains, bran, and flour, estimates of the parameter β of the degradation regression, and the mean half-life of the active ingredient based on β.

Substrate	Initial residue (mg kg^{-1})	$-\hat{\beta} \times 10^3$	Linear regression (Pr > F)	Half-life (days)	Confidence interval (95%) of half-life
Fenitrothion					
Grain	5.272	7.05	<0.0001	98	87–113
Bran	8.478	3.06	<0.0001	226	186–288
Flour	2.650	6.52	<0.0001	106	98–116
Esfenvalerate					
Grain	0.316	0.92	<0.0001	747	499–1482
Bran	0.547	1.87	<0.0001	369	242–774
Flour	0.256	1.40	0.0002	494	334–953

Table 3 shows the insecticide residues, β parameter estimates, descriptive level of the probability values of the F-test of the regression analysis, and the estimated half-life of the insecticides. The insecticide deposit was calculated as the exponent of α. Even though there were some low coefficients of determination, the p-values ($P < 0.05$) of the linear regressions indicate significantly linear relationships, mainly for esfenvalerate. We also calculated the standard deviation from regressions, and results indicate that no condition affected the regressions significantly ($P > 0.05$). The degradation rate of esfenvalerate was low, as reflected by a half-life of 747 days in wheat grains and wide confidence intervals. Hence, longer-term experiments that evaluate esfenvalerate for more than 360 days should be performed to corroborate our results.

In the case of fenitrothion, the half-life values range from 98 days for grain, to 226 days for bran, confirming the longer persistence of this insecticide in bran.

The stability of esfenvalerate and fenitrothion depends on the following physico-chemical factors: vapor pressure (with values of $2.0\ 10^{-7}$ and $1.8\ 10^{-2}$ Pa, respectively), n-octanol-water partition coefficient (K_{ow}) (with logarithmic values of 6.22 and 3.43), solubility in water (with values of 0.002 and 21 mg L^{-1}, respectively), and molecular weight (with values of 419.9 and 277.2, respectively) (Tomlin, 1995).

The pesticides become more volatile as the vapor pressure increase, which explains the higher amount of fenitrothion loss during the storage of grains. Lower log K_{ow} values indicate a higher degree of hydrophilicity, and the more water-soluble insecticide penetrates grains more easily, thus increasing the degradation rate. In terms of molecular weight, the general rule is that big molecules are less soluble than smaller ones (Seiber, 1999). Thus, fenitrothion is more soluble than esfenvalerate.

Various studies have shown that pyrethroids are more stable than organophosphorus in liquid applications (Afridi et al., 2001). However, in solid formulations that do not require dilution in water (dust formulations), the two groups of insecticides have similar dissipation rates (Yu et al., 2014). Among the organophosphorus insecticides used to protect stored grains, fenitrothion is considered highly unstable (Gragasin, et al., 1994; Rumbos et al., 2018), whereas among pyrethroids, esfenvalerate is considered more persistent (Joia et al., 1985).

The processes of volatilization, hydrolysis, and oxidation are known to assist in the postharvest degradation of insecticides (Holland et al., 1994). In particular, volatilization and photolytic decomposition are the most important mechanisms involved in the degradation of the organophosphorus components of insecticides (Gragasin et al., 1994; González-Curbelo et al., 2017).

The results of the analysis of wheat bran and flour are shown in Tables 4 and 5. Insecticide residues were not recovered from the control samples, confirming that the materials we used were insecticide-free.

The degradation rates of the insecticides varied among the different substrates. The cumulative degradation indexes of fenitrothion in wheat grains, flour, and bran are 11.48 (Table 1), 9.59, and 4.10 (Table 4), respectively. These results indicate that fenitrothion is most persistent in bran and least persistent in grains. For esfenvalerate, the degradation indexes in wheat grains, flour and bran are 1.38 (Table 2), 1.60, and 3.51 (Table 5), respectively, indicating that esfenvalerate is most persistent in grains and least persistent in bran. In contrast to our observations, Papadopoulou-Mourkidou and Tomazou (1991) reported that the pyrethroid permethrin is more persistent in bran than in grains. Moreover, at the end of our experiment (360 days after treatments), of the original residues present in wheat grains, flour, and bran, 9%, 11%, and 24% of the fenitrothion residues remained, respectively; whereas 71%, 61%, and 28% of the esfenvalerate residues remained, respectively. These results demonstrate that esfenvalerate is more stable than fenitrothion.

Both insecticides tended to concentrate in the pericarp and embryo, which are external and oily parts of the grain; and to a lesser extent in the amylaceous endosperm. The quantity of insecticide residue varied according to the type of substrate, i.e., the highest levels were in bran, followed by grains, then flour. Similar results have been reported in other studies conducted in different countries (Trevizan & Baptista, 2000; Sgarbiero et al., 2003; Bajwa & Sandhu, 2014). Typically, a grain of wheat is composed of 82% endosperm, 3% embryo, and 15% pericarp (Rowlands, 1971). Therefore, insecticides concentrate in a small portion of the grain, which explains the presence of high and low quantities of residues in the bran and flour, respectively.

An insecticide's penetration rate affects its metabolic route and its persistence, that is, insecticides that penetrate the grain quickly will also be degraded rapidly. In general, hydrophilic compounds have a higher rate of penetration than lipophilic compounds, although the latter penetrates grains more easily as the water content decreases (Rowlands, 1967). There is limited information on the fate of esfenvalerate in storage grains, and only a few studies have been conducted on its predecessor, fenvalerate (Joia et al., 1985).

The amount of fenitrothion residues found in wheat grains with a preharvest interval of 120 days was three times higher than the MRL (1 mg kg^{-1}) set by Brazilian legislation, despite having been applied at less than (i.e., 62%) the manufacturer's recommended dose of 10 mg kg^{-1}. Even in the wheat by-products from grains with a preharvest interval of 120 days, the levels of fenitrothion residues were higher than the MRL established for grains. Among these by-products, bran deserves special attention because of its high affinity for pesticides due to its high oil content; consequently, after 120 days of treatment, the level of fenitrothion residues on bran was 450% higher than the MRL for grains. Many people believe that wheat bran is a healthy food, without knowing about the health risks involved in the consuming bran that may not meet the required standards.

The amount of insecticide residues found on wheat grains treated with 0.5 mg kg^{-1} of esfenvalerate was clearly lower than the MRL of 1 mg kg^{-1} for stored grains. If the only basis for evaluation is the comparison between the agronomic value (0.5 mg kg^{-1}) and the MRL (1 mg kg^{-1}), then grains may be immediately consumed after insecticide application. Therefore, it is necessary to modify legislation to be more consistent with the appropriate use of insecticides. This issue was raised by Trevizan and Baptista (2000) in relation to deltamethrin, and Sgarbiero et al. (2003) in relation to pirimiphos-methyl. Additionally, the Alimentarius Codex of the FAO has established an MRL of 0.5 mg kg^{-1} for esfenvalerate in wheat grains (FAO, 2019). Thus, the preharvest interval for this insecticide should last more than one year, making its postharvest use questionable. These results reveal the importance of conducting studies on pesticide dissipation to establish MRL values consistent with how these substances are actually used.

This study demonstrates the necessity of conducting further studies on pesticide dissipation, to provide the regulators with the relevant information to craft suitable pesticide legislation that is appropriate for each country, with the goal of protecting the health of consumers.

Based on our findings, we recommend modifying the preharvest interval for fenitrothion to 180 days, to be consistent with the MRL of 1 mg kg^{-1}. Likewise, we

Table 4. Fenitrothion residues (mg kg^{-1}) in wheat flour and bran.

Substrate	DAA	Residues (mean ± SD)	Degradation index	Accumulated degradation index
Flour	0	2.65 ± 0.34		
	15	2.65 ± 0.48	1.00	1.00
	30	1.89 ± 0.28	1.40	1.41
	60	2.08 ± 0.33	0.91	1.28
	90	1.47 ± 0.10	1.41	1.80
	120	1.37 ± 0.06	1.07	1.93
	180	0.63 ± 0.05	2.17	4.19
	240	0.54 ± 0.03	1.17	4.88
	360	0.28 ± 0.02	1.96	9.59
Bran	0	12.34 ± 2.29		
	15	7.93 ± 0.96	1.56	1.56
	30	6.92 ± 0.34	1.14	1.78
	60	6.60 ± 0.54	1.05	1.87
	90	6.35 ± 0.59	1.04	1.94
	120	4.52 ± 0.34	1.41	2.73
	180	4.60 ± 0.71	0.98	2.68
	240	4.62 ± 0.30	1.00	2.67
	360	3.01 ± 0.36	1.53	4.10

DAA: Days after application.

Table 5. Esfenvalerate residues (mg kg−1) in wheat flour and bran.

Substrate	DAA	Residues (mean ± SD)	Degradation index	Accumulated degradation index
Flour	0	0.23 ± 0.03		
	15	0.23 ± 0.05	0.99	0.99
	30	0.21 ± 0.03	1.11	1.10
	60	0.33 ± 0.12	0.64	0.70
	90	0.24 ± 0.02	1.36	0.96
	120	0.25 ± 0.01	0.97	0.93
	180	0.19 ± 0.01	1.30	1.21
	240	0.19 ± 0.02	1.00	1.21
	360	0.14 ± 0.02	1.33	1.60
Bran	0	1.10 ± 0.14		
	15	0.46 ± 0.03	2.41	2.41
	30	0.45 ± 0.01	1.01	2.43
	60	0.36 ± 0.02	1.26	3.06
	90	0.42 ± 0.04	0.85	2.60
	120	0.38 ± 0.01	1.11	2.89
	180	0.37 ± 0.06	1.04	3.00
	240	0.38 ± 0.00	0.96	2.89
	360	0.31 ± 0.03	1.21	3.51

DAA: Days after application.

recommend modifying the MRL of esfenvalerate to 0.35 mg kg^{-1}, which is consistent with the required preharvest interval of 15 days.

Conclusions

Esfenvalerate is more persistent than fenitrothion in wheat grain, flour, and bran. Maximum and minimum concentrations of both insecticides occur in bran and flour, respectively.

Current Brazilian regulations of the usage of fenitrothion and esfenvalerate in stored wheat are not consistent with measured dissipation rates.

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