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Article

Extraction Method for Determining Florpyrauxifen-benzyl Herbicide in Soil

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Florpyrauxifen-benzyl is the new active ingredient authorized by Brazilian legislation, which acts as herbicide and may be used to control weeds in rice cultivation, but studies on toxicity to humans and the environment are still under review. Due to recent insertion in the world pesticide market, there are still few studies related to the extraction and detection methodologies of this compound. Therefore, this study aimed to optimize and validate solid-liquid extraction with low temperature purification (SLE-LTP) for determining florpyrauxifen-benzyl in soil using high-performance liquid chromatography coupled to a diode array detection (HPLC-DAD). The results showed that the best conditions were achieved using Poroshell column, a temperature of 30 °C, mobile phase composition of acetonitrile:water (85:15 v/v) acidified with formic acid 0.1% (v/v), a flow rate of 0.3 mL min^{-1}, and 243 nm as the wavelength. The best extracting phase was acetonitrile acidified with formic acid 0.1% (v/v) which achieved a recovery rate ca. 100% and relative standard deviation (RSD) less than 3.9%. The methodology was precise, accurate, linear and selective, with a limit of quantification of 20 μg kg^{-1}. The stability study of this compound in soil showed that approximately 17.5 days is the half-life of florpyrauxifen-benzyl in soil.

Keywords: florpyrauxifen-benzyl, SLE-LTP, arylpicolinate herbicide

Introduction

Florpyrauxifen-benzyl is a potent herbicide of the chemical group arylpicolinate, being selective and post-emergent for weeds, which mainly act in rice cultivation.[1-4] The chemical structure of this compound may be seen in Figure 1.[5]

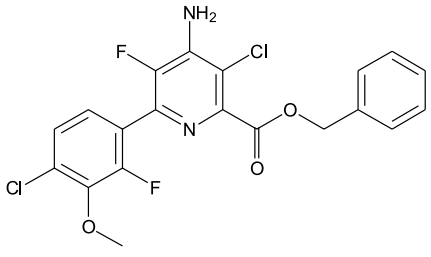

Figure 1. Chemical structure of the florpyrauxifen-benzyl molecule.

This active principle may be applied to weed shoots, being absorbed by the leaves and later metabolized to the active form. The herbicide moves through the phloem and accumulates in growing regions, acting as a systemic and post-emergent herbicide. This herbicide was authorized in Brazil in 2019[2] to be used to combat weeds in rice crops, but also in other crops such as soybeans, cotton, corn, sorghum and sunflower, which may generally be cultivated after rice is harvested.[6-9]

The toxicity of this compound to humans and the environment has been the objective of studies in Brazil and in other countries.[10-12] Therefore, the insertion of this active ingredient in the environment must be monitored in detail, as the use of this product may cause episodes of environmental and human contamination, and its impacts are still poorly studied.[10-12]

This herbicide has low water solubility (< 0.015 mg L^{-1}) and high affinity for nonpolar organic solvents.[5,10,13,14] These characteristics are very favorable for contamination and accumulation in soils, plants, as well as entering the food chain, since some rice varieties have been cultivated in highly irrigated soils.[8] Therefore, with this broad study, we intend to optimize and validate methodologies for extracting florpyrauxifen-benzyl in soil.

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Due to its recent insertion in agriculture, reports on the extraction method for determining this herbicide in soil samples are rare. To the best of our knowledge, only the quick, easy, cheap, effective, ruged and safe (QuEChERS) method was optimized and validated for this compound.[4] Although this methodology has proven to be very efficient, it is desirable to develop other methodologies which may be simpler, easier to execute, more efficient and cheaper. In this sense, previous works[15,16] have shown that solid-liquid extraction coupled with low-temperature purification (SLE-LTP) has met these characteristics when applied to other environmental contaminants. One of the main advantages of this methodology is the extraction and cleaning in a single step.

Therefore, herein we intend to optimize and validate the SLE-LTP methodology for determining florpyrauxifen-benzyl in soil samples using high-performance liquid chromatography coupled to a diode array detection (HPLC-DAD).

Experimental

Reagents and solutions

HPLC-grade acetonitrile was purchased from Sigma-Aldrich (St. Louis, USA). P.A. solvents including ethyl acetate were purchased from Dinâmica (Indaiatuba, Brazil), acetonitrile from Êxodo Científica (Sumaré, Brazil), formic acid (FA) from Sigma-Aldrich (St. Louis, USA) and hydrochloric acid from Anidrol (Diadema, Brazil). All solvents were filtered on 0.22 μm pore polytetrafluoroethylene (PTFE) membrane which was purchased from Filtrilo (Colombo, Brazil). Standard solutions of florpyrauxifen-benzyl were purchased from LGC Dr. Ehrenstorfer (Augsburg, Germany). Standard stock solutions were prepared at a concentration of 20 mg L^{-1} and working solutions were prepared at a concentration of 5 mg L^{-1}. All solutions were stored at −20 °C.

Equipment

The equipment used in this study included a vortex from Scilogex (Rocky Hill, USA), a vacuum pump from Prismatec (Itu, Brazil), an analytical balance from Shimadzu (Barueri, Brazil), and an ultraviolet and visible (UV-Vis) Cary 50 spectrophotometer from Agilent Technologies (St. Clair, USA).

Chromatographic analyzes

The chromatographic analyzes were performed in a HPLC-DAD, model 1290, Agilent Technologies (St. Clair, USA). The injection volume was 10 μL for the Poroshell column (St. Clair, USA) and 20 μL for the Kinetex column (Torrance, USA). The optimized chromatographic conditions may be seen in the Table 1.

Table 1. Optimized chromatographic conditions

Parameter	
Wavelength (λ) / nm	210
	243
	260
Chromatographic column	Kinetex (C18) (100A, 150 mm × 4.60 mm, 5 μm, Phenomenex)
	Poroshell 120 EC-C18 (50 mm × 4.60 mm, 2.7 μm, Agilent)
Mobile phase composition in the isocratic mode	acetonitrile:water 100:0 (v/v)
	acetonitrile:water acidified with formic acid 0.1% (v/v)[a]
Flow rate / (mL min^{-1})	0.3
	0.4
	0.5
	1.0
Column temperature / ºC	30
	35

[a]100:0; 90:10; 85:15; 80:20; 75:25 and 70:30 (v/v).

SLE-LTP optimization

The SLE-LTP was optimized by evaluating six extracting phase compositions (Table 2). This extraction method is based on adding 4.0 g of soil into glass vials (22 mL) and 72 μL of working solution containing florpyrauxifen-benzyl at a concentration of 5 mg L^{-1}. The mixture was maintained at rest for 1 h to allow complete integration of the analyte with the matrix. Next, 4 mL of water and 8 mL of extracting mixture were added and the system was homogenized in a vortex for 30 s, and maintained at −20 °C for one hour for

Table 2. Extracting phase compositions evaluated in the extracting method optimization step

Assay	Extracting phases		Proportion / mL
A	ACN	H_2O	8:4
B	ACN + FA	H_2O	8:4
C	ACN	H_2O + FA	8:4
D	ACN + FA	H_2O + FA	8:4
E	ACN + EtOAc	H_2O	6.5 + 1.5:4
F	ACN + HCl	H_2O + HCl	8:4

ACN: acetonitrile; EtOAc: ethyl acetate; FA: formic acid solution 0.1% (v/v); HCl: hydrochloric acid solution 0.1% (v/v).

complete freezing of the aqueous-phase. Then, 3 mL of the obtained extract were completely evaporated, resuspended in 400 µL of acetonitrile acidified with formic acid at 0.1% (v/v) and stored at −20 °C until analysis by HPLC-DAD. The extraction rate was evaluated by the *t*-test ($P < 0.05$).

Methodology validation

The methodology validation was performed through selectivity, limit of detection (LOD), limit of quantification (LOQ), precision, accuracy, linearity range, and matrix effect.[17] Selectivity was investigated by comparing chromatograms of extracts of the spiked soil matrix and the blank (florpyrauxifen-benzyl-free matrix extract), in six independent replicates.

The LOD and LOQ were determined by spiked soil samples with the lowest possible amount of florpyrauxifen-benzyl which may be detected and quantified using the optimized SLE-LTP conditions. The LOD and LOQ were considered three and ten times the baseline noise signal of analyte-free samples (blank), respectively.

Accuracy was evaluated through experiments that recover analyte from the spiked matrix using three concentration levels of 20.0, 90.0 and 160.0 µg kg^{-1}, with three replicates each. Precision was determined under repeatability conditions, through experiments that recover analyte from the spiked matrix using a concentration level of 90.0 µg kg^{-1}, with seven replicates. Accuracy was analyzed by the recovery of analytes, in which values between 70 and 120% were considered acceptable. Precision was evaluated by the relative standard deviation (RSD) of replicates, with RSD less than 20% being the acceptability criterion.[17]

Linearity range was evaluated through analytical curves of the spiked matrix in six concentration levels of: 20.0; 55.0; 90.0; 125.0; 160.0 and 195.0 µg kg^{-1}, with three independent replicates for each level. The linear regression parameters were estimated by the least squares method and based on the regression residues analysis, with maximum exclusion of 22.2% of data (Jackknife test). Linear regression residues were evaluated by normality parameters (Ryan and Joiner test), homoscedasticity (Brown and Forsythe test) and independence (Durbin and Watson test). Analysis of variance (ANOVA) was applied to the analytical curves to verify how much the regression line explains the values that were used to fit the linearity.[18,19]

The matrix effect was evaluated by two analytical curves, with the first in solvent (acetonitrile) and the second in spiked soil matrix extract, both containing the florpyrauxifen-benzyl at the concentrations of: 20.0; 55.0; 90.0; 125.0; 160.0 and 195.0 µg kg^{-1}, in triplicate. The two analytical curves were evaluated according to the linearity procedure, as previously described. The matrix effect was determined by equation 1.

$$\text{Matrix effect rate}(\%) = \frac{\text{Slope}_{\text{matrix}} - \text{Slope}_{\text{solvent}}}{\text{Slope}_{\text{solvent}}} \times 100 \quad (1)$$

In which: $\text{Slope}_{\text{matrix}}$ = slope of the analytical curve in spiked soil extract; $\text{Slope}_{\text{solvent}}$ = slope of the analytical curve in solvent (acetonitrile).

Values between −20% and +20% were interpreted as low matrix effect, between −20% and −50% or between +20% and +50% as medium matrix effect, and values below −50% or above +50% as high matrix effect.[20,21]

Study on the stability of florpyrauxifen-benzyl in soil

An experiment was prepared in this study to evaluate the stability of florpyrauxifen-benzyl in soil by simulating environmental conditions. First, 4.0 g of florpyrauxifen-benzyl free-soil sample was added into a 22.0 mL glass flask. Then, each soil samples were spiked with florpyrauxifen-benzyl, obtaining an initial concentration of 195.0 µg kg^{-1}. The flasks were kept open under sunlight for 1, 5, 10, 15, and 20 days. After each day, the samples were submitted to SLE-LTP followed by HPLC-DAD analysis to determine the florpyrauxifen-benzyl concentration present in the soil. All experiments were performed in triplicate.

Results and Discussion

Optimization of the chromatographic conditions

The first step of the study was to define the best wavelength for determining the florpyrauxifen-benzyl. The absorption spectrum may be seen in Figure S1 (Supplementary Information (SI) section).

The obtained spectrum revealed that the highest absorbances were observed at 210, 243 and 260 nm. These wavelengths were evaluated on HPLC-DAD and the chromatograms obtained may be observed in Figure S2 (SI section).

The results showed that the signal of the compound at 210 nm was not adequately separated, as shown in Figure S2a. On the other hand, 260 nm was selective but the signal reduced considerably in intensity, as shown in Figure S2c. Therefore, 243 nm was defined as a suitable wavelength for determining this herbicide (Figure S2b). Similarly, a previous study reported that florpyrauxifen-benzyl showed higher absorbance at 212 and 245 nm in acidic and neutral solutions, respectively.[6]

Next, the mobile phase flow was evaluated at four levels (Table 1). The chromatograms obtained are shown in Figure S3 (SI section). The chromatogram obtained using a flow 0.3 mL min^{-1} resulted in a sharper signal, separated from the interference signal. Therefore, 0.3 mL min^{-1} was defined for the next stages of this study. This same flow value was used by a previous study.[4]

In sequence, two analysis temperatures were evaluated to better separate the target analyte signal from interferer signal. The chromatograms obtained may be observed in Figure S4 (SI section). The results revealed that the increase in temperature promotes an approximation of the interfering signal to the analyte signal, therefore the temperature of 30 °C was defined for this study.

Next, two chromatographic columns were evaluated to determine florpyrauxifen-benzyl (Table 1). The results obtained may be observed in the chromatograms of the Figure S5 (SI section). The chromatograms of the florpyrauxifen-benzyl solution in the two columns present a narrow and sharp chromatographic signal, however the signal in the Poroshell column (120 EC-C18) presented a shorter retention time (1.52 min), higher intensity and chromatographic area. Therefore, this column was defined for the next stages of this study.

Different mobile phase compositions were evaluated in this study, as may be observed in Table 1, and the chromatograms obtained in each condition are shown in Figures S6 and S7 (SI section). The use of the mobile phase acidified with formic acid did not change the signal intensity compared to formic acid-free conditions (see Figures S6a and S6b). However, the use of formic acid in the mobile phase composition improved the method selectivity for the soil matrix compared to the mobile phase without formic acid (see Figure S7).

The mobile phase consisting of 85% acetonitrile:15% water acidified with 0.1% formic acid resulted in a chromatogram with an interference-free florpyrauxifen-benzyl signal along with greater intensity and chromatographic area, as may be seen in Figure 2. Therefore, this condition was defined for this study. A similar mobile phase was used in a previous study using acetonitrile and 0.1% (v/v) formic acid aqueous solution (60:40, v/v).[4]

After optimizing the chromatographic conditions for determining florpyrauxifen-benzyl by HPLC-DAD, the extracting conditions of the SLE-LTP methodology were optimized.

Optimization of extracting conditions by SLE-LTP

A previous work[22] carried out with this herbicide showed the use of extractor phases consisting of acetonitrile acidified with formic acid or hydrochloric acid. Therefore, in this study we evaluated six different extractor phases, as may be seen in Table 2. The recovery rates obtained in each extractor phase are shown in Figure 3.

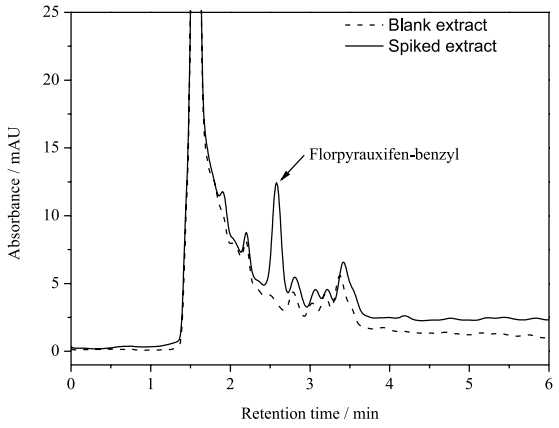

Figure 2. Chromatograms of spiked extract with florpyrauxifen-benzyl at 90 μg L^{-1}. Chromatographic conditions: Poroshell column, injection volume = 10 μL, flow rate = 0.3 mL min^{-1}, temperature (T) = 30 °C, λ = 243 nm and mobile phase (85% acetonitrile:15% water) acidified with 0.1% (v/v) formic acid.

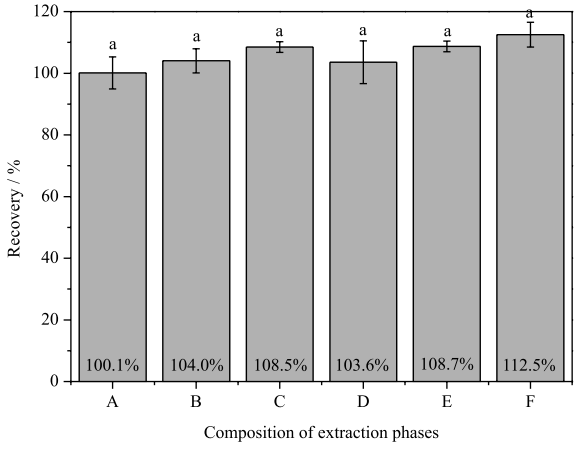

Figure 3. Recovery rate of florpyrauxifen-benzyl in the six different extraction phase compositions. Bars followed by the same letter do not differ statistically from each other by the Tukey's test at a 5% significance level. A: acetonitrile:water (8:4 v/v); B: acetonitrile acidified with formic acid:water (8:4 v/v); C: acetonitrile:water acidified with formic acid (8:4 v/v); D: (acetonitrile:water) acidified with formic acid (8:4 v/v); E: acetonitrile + ethyl acetate:water (6.5 + 1.5:4 v/v); F: (acetonitrile:water) acidified with hydrochloric acid (8:4 v/v).

The results revealed that the recovery rate of the six extracting phases were within the range of 100.1 and 112.5%, with a relative standard deviation below 6.9%. However, the chromatogram with the lowest number of interferents was obtained using acetonitrile acidified with formic acid and water (Figure S8b, SI section). Therefore, this extractor phase composition was defined for this study. Acetonitrile was also used as an extracting phase in a previous study,[4] however, without the addition

of formic acid. An analytical validation of the optimized methodology was subsequently performed after completing this optimization step of the extracting conditions.

Validation

The validation of the optimized methodology was carried out through the six figures of merit, namely: selectivity, LOD and LOQ, linearity range, precision, accuracy and matrix effect.

Selectivity

The selectivity of the optimized methodology was confirmed by analyzing the chromatograms of the blank extract (analyte-free soil matrix extract) and spiked soil matrix extract. The chromatograms obtained may be seen in Figure 4.

Peaks attributed to interference in the retention time of the florpyrauxifen-benzyl peak characterizing the method selectivity were not observed in the chromatogram of the blank extract.

Limits of quantification and detection

The LOD and LOQ values achieved for the optimized methodology were 5 and 20 μg kg^{-1}, as may be observed in Table 3, respectively. These values are within the concentration range found in previous works.[10,11] The maximum residual limits (MRL) for florpyrauxifen-benzyl in soil samples has not yet been defined by Brazilian legislation. Thus, we chose the MRL of other pesticides to compare with the LOQ of the method proposed in this study. Dichloro-diphenyl-trichloroethane (DDT), dieldrin and endrin in the soil have MRLs in the range of 200 to 5000 μg kg^{-1} according to CONAMA (Conselho Nacional do Meio Ambiente) Resolution No. 420 of 2009.[23] Therefore, the LOQ found for florpyrauxifen-benzyl is lower than that established for other pesticides, which demonstrates the potential of this method for monitoring florpyrauxifen-benzyl in soil. Although the study carried out by Zhou *et al.*[4] reached an LOD of approximately 1 μg kg^{-1} using the QuEChERS method, the matrix was different (i.e., it was paddy soil).

Precision and accuracy

The precision and accuracy were simultaneously confirmed by fortification and recovery experiments. The results in Table 3 showed that the RSD values were less than 20% and recovery rates were between 70 to 120%. These values ensure the precision and accuracy of the optimized method according to the SANTE guidelines.[17]

Linearity range

The linearity range of the optimized method was determined through six equidistant concentration levels with three independent replicates for each level for the LOQ value, with the first level of the analytical curves in soil matrix extract, as may be observed in Figure S9a (SI section). Thus, the linearity range included the

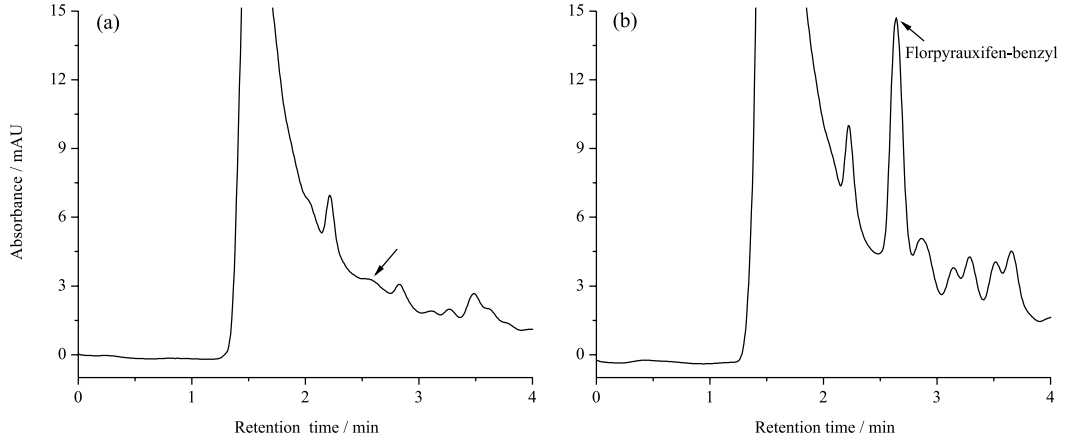

Figure 4. Chromatograms of analyte-free soil matrix extract (blank extract) (a) and spiked soil matrix extract with florpyrauxifen-benzyl at 90 μg kg^{-1} (b).

Table 3. Results of the analytical validation study

Linearity range / (μg kg^{-1})	Linear equation	R^2	Recovery ± RSD / %			LOD / (μg kg^{-1})	LOQ / (μg kg^{-1})
			20.0 μg kg^{-1} [a]	90.0 μg kg^{-1} [b]	195.0 μg kg^{-1} [a]		
20.0-195.0	$y = 91420.3x - 452846.3$	0.9973	108.8 ± 9.30	108.3 ± 2.25	109.1 ± 1.86	5.0	20.0

[a]Mean of 3 replicates [b]mean of 7 replicates; R^2: determination coefficient; RSD: relative standard deviation; LOD: limit of detection; LOQ: limit of quantification.

LOQ concentration value (20.0 μg kg^{-1}), and the sample fortification concentration (90.0 μg kg^{-1}).

The linear regression parameters were estimated by the ordinary least squares method (OLSM), thus obtaining the slope, intersection and determination coefficient (R^2) values as may be seen in Table 3. The Jackknife test was applied to regression residuals and no extreme values were found (Figure S9b). The R^2 value was greater than 0.99, indicating the variability of collected data explained by the regression model. Then, the normality, homoscedasticity and independence of regression residues were evaluated.

The normality of regression residuals was evaluated by the Ryan-Joiner test (i.e., a graph showing the normal probability of regression residuals was constructed) (Figure S9c). The correlation coefficients found in the graphs were higher than the critical correlation coefficient ($R = 0.9622 > R_{crit} = 0.9461$) obtained by polynomial interpolation. Therefore, it could be concluded that the residuals followed normal distribution (significance level of 0.05), thus allowing the use of hypothesis tests that follow this type of distribution.

The homoscedasticity of regression residuals was investigated by the Brown-Forsythe test which determines the existence of differences between residual variances through an adaptation of the Levene test. The distribution of regression residuals along the concentration levels studied was homogeneous, thus confirming homoscedasticity, as may be seen in Figure S9b.

The independence of regression residuals was analyzed by the Durbin-Watson test and no autocorrelation was observed at the significance level of 0.05. A graphical representation of data was performed to confirm this result, and a random distribution of residuals in the four quadrants was obtained demonstrating their independence, as may be seen in Figure S9d.

The data were fitted to the linear model throughout the assessed range from 20.0 to 195.0 μg kg^{-1} (Table 3), in which significant regression and non-significant linearity deviation were observed at the significance level of 0.05. Therefore, it could be concluded that the OLSM was adequate for the data studied. All linearity assessments followed procedures proposed by de Souza and Junqueira[18] and Bazilio *et al.*[19]

Matrix effect

The matrix effect was determined by comparing the angular coefficients obtained from the analytical curves in the matrix extract and acetonitrile (Figure S9a), obtaining a value of –3.34%. Therefore, the proportional systematic error was not significant. However, it is noted that there is a matrix effect with constant systematic error. This result was considered a low matrix effect, considering that soil is a complex matrix that contains several compounds, which may interfere in the analyte signal. A previous study[15] carried out for dioxins and furans in soil found significant differences in the chromatographic response of the two analytes when prepared in solvent and in the soil matrix extract obtained after SLE-LTP, which corroborates the previous statement.

Study on the stability of florpyrauxifen-benzyl in soil

The initial florpyrauxifen-benzyl concentration in the soil sample was 195.0 μg kg^{-1}, which is the highest concentration in the linearity range of the methodology validated in this study. The results obtained in the experiments to study the stability of florpyrauxifen-benzyl in soil are shown in Figure 5.

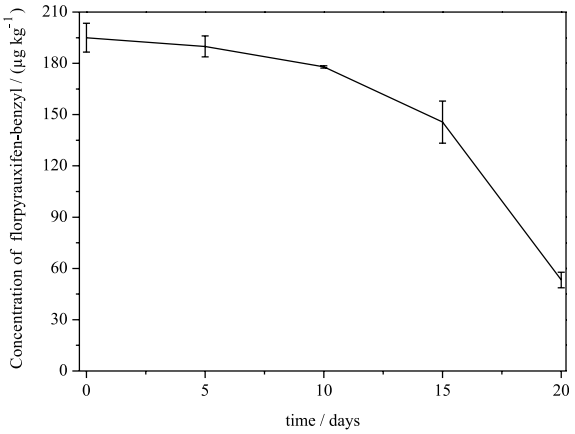

Figure 5. Mean concentration of florpyrauxifen-benzyl in soil samples for 20 days.

The results indicate that the half-life of florpyrauxifen-benzyl in soil was approximately 17.5 days. During this period, the average concentration of the compound decreased from 195.0 to 97.5 μg kg^{-1}. A previous study[24] showed a half-life of 8-10 days, however, for flooded soil,[11] and half-life for water of near 3.3 days, indicating that the shortest half-life for flooded soil is due to presence of water in the soil.

Conclusions

The SLE-LTP followed by HPLC-DAD analysis was optimized and validated for determining florpyrauxifen-benzyl in soil samples. This methodology proved to be easy to execute, fast, sensitive, and effective with high recovery rates and a low matrix effect. The limit of quantification reached was lower than the maximum acceptable by Brazilian legislation for other pesticides in soil. For all of these reasons, this methodology may be considered a promising alternative for monitoring florpyrauxifen-benzyl in soil samples. Finally, the stability study of this compound

in soil showed that approximately 17.5 days is the half-life of florpyrauxifen-benzyl in soil.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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