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# Effect of thermal processing on the degradation of pesticides in a banana jam partially formulated with banana peel flour

Magnólia Carneiro de Oliveira<sup>a</sup>, John Kelvyn de Oliveira<sup>a</sup>, Joselito Brilhante Silva<sup>a</sup>, Luana Guabiraba Mendes<sup>a</sup>, Felipe Sousa da Silva<sup>b</sup>, Mairlane da Silva Alencar<sup>b</sup>, Crisiana de Andrade Nobre<sup>b</sup>, Mayra Garcia Maia Costa<sup>b</sup>, Micael de Andrade Lima<sup>c</sup>, Maria Aparecida Liberato Milhome<sup>a,\*</sup>

<sup>a</sup> Federal Institute of Education, Science and Technology of Ceará (IFCE), Post-Graduate in Food Technology, Rua Estevão Remígio de Freitas, 1145, Monsenhor Otávio, CEP: 62930-000, Limoeiro do Norte, Ceará, Brazil

<sup>b</sup> Nucleus of Technology and Industrial Quality of Ceará (NUTEC), Fortaleza, Ceará, Brazil

<sup>c</sup> Natural Resources Institute (NRI), University of Greenwich, Medway Campus, United Kingdom

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#### ABSTRACT

Bananas are one of the most widely consumed fruits in Brazil and across the world. However, the intensive use of pesticides in these and other crops can negatively impact human and animal health due to the possibility of pesticide residues persisting in derived products, even after industrial processing. Therefore, this study evaluated the effect of thermal processing on the degradation of the pesticides azoxystrobin, bifenthrin, difenoconazole, and simazine in samples of caramelized banana jam added of banana peel flour (4% w/w) in partial replacement of the fruit pulp. QuEChERS (quick, easy, cheap, effective, rugged, and safe) method and gas chromatography coupled to mass spectrometry (GC-MS) wa used to analyze the above compounds. The method was validated following the standard procedures of the European Commission and ANVISA. Samples of banana pulp were spiked with the pesticides at different concentrations (0.1, 0.5 and 1.0 mg.Kg<sup>-1</sup>) in order to observe their degradation following thermal processing. Degradation percentages ranged between 28 and 60 %, and these were potentially influenced by the physicochemical properties of each compound, as well as the characteristics of the food matrix. The thermal processing provided partial degradations of pesticide residues, some at levels below the MRLs (Maximum Residual Levels) established for bananas. Currently, there is no specific legislation in Brazil and in many other countries for controlling pesticides in processed foods, such as fruit jams. Therefore, this research highlights the need for the creation of new food laws by government agencies to this end to ensure the provision of safe food to the wide population.

#### 1. Introduction

Banana (*Musa* sp.) is a fruit consisting of a sweet and soft pulp, containing a high energy value, and that is widely employed as a raw material for the production of different types of food products. These include fruit purees, nectars, syrups, liqueur, flours, flakes, chips, other freeze-dried products, jams and jellies, juices, wine, and vinegar (Kraithong & Issara, 2021). The crop is grown throughout the entirety of the Brazilian land, with an estimated production of 7 M tons in 2021. The Brazilian states of São Paulo (1 M tons), followed by Bahia, Minas Gerais, Santa Catarina, Pernambuco, Pará, Espírito Santo, and Ceará are

the greatest banana producers, both in harvested area and in production per hectare (IBGE, 2021).

The presence of pesticide residues in a wide array of fruits has been reported in several studies, a consequence of the heavy use of these chemicals in agricultural crops, which has long been associated with increased productivity (Pszczolinska et al., 2022). However, their continuous and excessive use can compromise human and animal life, in view of their permanence in food products, even after the stages of production, processing, storage, transport and commercialization. Therefore, the monitoring of such substances in foods ready for consumption becomes paramount (Rodríguez-Ramos et al., 2023).

\* Corresponding author. *E-mail address:* maria.milhome@ifce.edu.br (M.A.L. Milhome).

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Available online 9 July 2024 2772-5022/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC license (http://creativecommons.org/licenses/by-nc/4.0/). Additionally, their indiscriminate use has led to pest resistance and promoted soil and water contamination (Reyes-Avila et al., 2023). In Brazil, the monitoring of pesticide residues in foods of plant origin is performed by the National Health Surveillance Agency (ANVISA) through the Program for the Analysis of Pesticide Residues in Food (PARA), implemented in 2001. However, the program does not encompass the analysis of pesticide residues in processed foods.

Jam consists of a semi-solid food product prepared by cooking sugar with fruit or vegetable pulp and other ingredients until an appropriate consistency is obtained. The jam must contain 65 % or more TSS and at least 45 % pulp (Awulachew, 2021). Products that have a high sugar content in their formulation, as well as low moisture content, are considered complex matrices for the determination and quantification of pesticides (Reichert et al., 2015). Inedible parts of fruits after processing constitute about 10 to 60 % of the total weight of the product. The skin and peel are the main constituents of these residues, representing more than 50 % (Kraithong & Issara, 2021). Therefore, the content of pesticide residues in foods containing fruit peel flour must be monitored (Nguyenet al, 2020)

Recent studies point out the importance of food processing in the degradation and reduction of various types of pesticides in fruits and vegetables, which promotes a safer consumption of these foods (Naman et al., 2022; Heredia et al., 2023; Munir et al., 2024). Cámara et al. (2020) suggests that the operations of washing, cutting, sealing, squeezing, cooking, pasteurizing, and canning of fruits and vegetables lead to a decrease in pesticide residues in these matrices which varies in magnitude according to the applied techniques, as some of which have proved more efficient than others (Cámara et al., 2020). The use of high temperatures, such as those used in bleaching, frying, drying, cooking and canning, have been shown to promote good levels of degradation of these substances in food (Hrynko et al., 2023). However, depending on the type of pesticide, its physicochemical characteristics (solubility, partition coefficient, and vapor pressure) and its concentration levels, a high amount of residues may still remain in the final products even after their processing.

Chromatographic techniques coupled to mass spectrometry are the most widely employed methods for multi-residue analyses of food matrices, due to the possibility of analyzing a vast number of active principles, in addition to their inherent high sensitivity and selectivity. The QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction method, developed by Anastassiades et al. (2003), has been widely used associated with such chromatographic techniques, ensuring the efficiency of these multiresidue methods (Pszczolinska et al., 2022).

Castricini et al. (2021), for example, carried out a study to monitor bifenthrin residues in washed and unwashed bananas in tanks via GC-MS. For this, protective bags impregnated with 1.0 g.Kg<sup>-1</sup> of the substance were used in banana bunches to protect them against pests and diseases. These were removed after harvesting, with some of the fruits being washed while others remained unwashed. For the extraction of the analyte from the samples of banana peel, pulp, and peel + pulp, a modified QuEChERS extraction method was used. From the data obtained, it was verified that the washing process reduced the bifenthrin residue in the fruit peel at the point of harvest. In addition, in ripe fruits, the compound under study was only present at quantifiable levels in the unwashed fruits.

Thus being, the objective of this work was to evaluate the effect of thermal processing on the degradation of four relevant pesticides (azoxystrobin, bifenthrin, difenoconazole and simazine) in a fruit jam added of banana peel flour at 4% w/w that partially replaced the fruit pulp for waste valorization purposes. The residue degradation was monitored via gas chromatography coupled to mass spectrometry (GC-MS). The selection of pesticides used in this study was based on the chemicals commonly employed in Irrigated Perimeter of the Jaguaribe Region (Apodi, Ceará, Brazil) for banana cultivation (Silva et al., 2019), as well as the compounds allowed by ANVISA (2024) for use in this crop (azoxystrobin, bifenthrin, difenoconazole and simazine).

#### 2. Materials and methods

#### 2.1. Reagents

Analyses were performed using the following reagents: acetone 99.9 % UV/HPLC/Spectroscopic grade (Vetec); acetonitrile, 99.9 % UV/HPLC/Spectroscopic grade (Vetec); acetonitrile, 99.9 % UV/HPLC/Spectroscopic grade (Vetec); primary secondary amine (PSA) with a particle size of 40  $\mu$ m (Supelcobonded Silica Supelcoclean); C-18; tribasic sodium citrate, 99 % P.A. (Vetec); sodium chloride, 99 % P.A. (Vetec); sodium hydrogen citrate sesquihydrate, 99 % P.A. (SIGMA-Aldrich); anhydrous magnesium sulfate, 98 % P.A. (Vetec); sodium hydroxide; 5 % formic acid solution; GCB sorbent (ENVI-carb); 99.999 % helium gas (White Martins, Brazil); ultrapure water purified using a Milli-Q Direct UV3® system (18.2 M $\Omega$  cm resistivity); analytical standards of azoxystrobin (Supelco, >99 %), bifenthrin (Sigma-Aldrich >99 %), difenoconazole (Sigma-Aldrich >99 %) and simazine (Supelco, >99 %).

#### 2.2. Sample preparation

For the manufacture of the fruit jam with the addition of ripe banana peel flour, a formulation was developed with 4 % (w/w) of peel flour, as shown in Table 1. The product was prepared and processed at the Pilot Plant for Fruit and Vegetables of the IFCE (Federal Institute of Ceara), Limoeiro do Norte Campus, following the methodology of Oliveira et al. (2018).

For the development of the fruit jam, the banana peel flour and the hot banana pulp was initially prepared (Fig. 1). The bananas were selected, washed in running water and subsequently subjected to a cleaning and sanitization stage, using a sodium hypochlorite solution (2.5 % active chlorine) for 15 min. They were then rinsed for subsequent peeling. The peels were placed in stainless steel trays and subjected to oven drying at 60 °C for 48 h, ground in a domestic blender, and sieved to obtain a fine flour.

Subsequently, the flour was packaged in hermetically sealed glass jars to avoid exposure to air. The peeled bananas were then subjected to a heat treatment at 70  $^{\circ}$ C for 15 min at a ratio of 1 Kg of banana to 1.0 L of water, with the aim deactivating the browning enzymes peroxidase and polyphenol oxidase. Following this step, the bananas were pulped in an industrial blender to disintegrate and homogenize of the fruit mass.

#### 2.3. QuEChERS method

Samples of the banana pulp and the jam formulation (4% w/w peel flour) were subjected to extraction procedures by an adapted QuEChERS method to obtain extracts for chromatographic analysis (Anastassiades et al., 2003).

Initially, 5.0 g of the sample were weighed in a Teflon tube, diluted in 10 mL of water, and thoroughly homogenized. Then, 10.0 mL of acetonitrile were added to the previous solution and this, stirred for 1 min on a vortex shaker. Sequentially, 4.0 g of anhydrous magnesium sulfate, 1.0 g of tribasic sodium citrate, 1.0 g of sodium chloride and 0.5 g of sodium hydrogen citrate sesquihydrate were added, followed by vortexing for 1 min, and centrifugation for 5 min at 1594 rcf. For the cleanup stage, performed by a dispersive solid phase extraction (D-SPE), an aliquot of 4.0 mL of the supernatant, 0.6 g of magnesium sulfate, 0.1 g of PSA solvent, 0.1 g of C-18, and 0.05 g of GCB were mixed together,

Table 1			
Formulations of banana jam	(w/w) added	of banana	peel flour.

Ingredients	Formulation (%)
Banana pulp	46.0
Sugar	48.0
Banana peel flour	4.0
High Methoxy Pectin	2.0



Fig. 1. Flow chart of the production of banana peel flour (a), pulp (b) and jam (c).

vortexed for 30 s, and centrifuged for 5 min. A final aliquot of 1.0 mL was removed and transferred to a 2-mL vial for analysis in the GC-MS.

#### 2.4. Chromatographic conditions

The multiresidue analyses were performed using a gas chromatograph coupled to a single quadrupole mass spectrometer (GC-Q/MS, model DSQII, Thermo, USA). The separation of the pesticides was performed using an RTX-5MS (30 m, 0.25 mm, 0.25  $\mu$ m) capillary column and helium carrier gas (99.99 %), at a constant flow of 1 mL.min<sup>-1</sup>. The injection temperature was 250 °C, with a volume of 1  $\mu$ L injected in splitless mode (1 min). The oven temperature program consisted of an initial temperature of 100 °C (1 min), a 15 °C ramp (1 min) to 180 °C, and a 4 °C ramp (1 min) to 280 °C, which was held for 14 min, (21 min total run time).

The mass spectrometer conditions included: electron impact ionization (EI) mode, 70 eV, ion source temperature: 270 °C, and transfer line temperature: 270 °C. The quantitative analysis was performed in the Selected Ion Monitoring- SIM mode, based on the use of one quantitative and two qualitative fragments (Table 2).

#### Table 2

Retention	time and	fragments	of the	compounds	analyzed

Compound	Retention time (min.)	Fragmer	nts ( <i>m/z</i> )	
Azoxystrobin	34.90	388	345	_
Bifenthrin	21.66	181	165	166
Difenoconazole	33.17	323	267	-
Simazine	10.03	201	186	173

#### 2.5. Method validation

The chromatographic method was validated by the determination of its selectivity, linearity, Limits of Detection (LOD) and Quantification (LOQ), as well as precision and accuracy, according to the Guidance SANTE 11,312/2021 and ANVISA (EU, 2021; ANVISA, 2017).

The selectivity of the method was evaluated from the chromatograms obtained through the previously spiked samples of food matrix. Linearity was determined through the analytical curves of the analyte standards (0.1; 0.25, 0.5; 0.75; 1.0 mg.Kg<sup>-1</sup>) and based on the determination coefficients ( $R^2$ ). The linearity range was also evaluated

according to the Guidance SANTE 11,312/2021 and ANVISA (EU, 2021; ANVISA, 2017).

The limits of detection (LOD) and quantification (LOQ) were determined by the signal/noise ratio (three times the value obtained for the detection/quantification limit), which were compared with the maximum residue limits (MRL) allowed by FAO (2021) and ANVISA (2024). Accuracy and precision were verified through the recovery rate of the spiked jam samples at 3 concentration levels: low (0.1 mg.Kg<sup>-1</sup>), medium (0.5 mg.Kg<sup>-1</sup>) and high (1.0 mg.Kg<sup>-1</sup>). The precision of the method was calculated and expressed by the relative standard deviation-RSD (%).

#### 3. Results and discussion

#### 3.1. Method validation

Initially, the selectivity of the method was evaluated, so we could ensure that the response peak is exclusively associated with the analyte of interest (Costa et al., 2023). The selectivity proved to be satisfactory in the analyses of the spiked extract of samples of jam added of banana peel flour, considering that the peaks in the chromatogram are indeed associated with a single analyte (Fig. 2), thus guaranteeing the absence of interferences.

The linearity of the compounds under study, as well as the application range used in the analyses, their accuracy, precision, Limits of Detection (LOD) and Quantification (LOQ) are all presented in Table 3. For the calibration curves, five concentrations were established (0.1; 0.25, 0.5; 0.75; 1.0 mg.Kg<sup>-1</sup>), with key parameters being evaluated in accordance with the Guidance SANTE 11,312/2021 and ANVISA which recommend a coefficient of determination (R<sup>2</sup>) greater than 0.99 (EU, 2021; ANVISA, 2017). The method was able to reach the low values within the working range used (0.1–1.0 mg.Kg<sup>-1</sup>). The LOQs values were below the MRLs established by FAO (2021), and are therefore satisfactory for the study at hand. Also, ANVISA establishes recovery rate limits of 70 % to 120 % (ANVISA, 2017). Therefore, the compounds analyzed in the samples are within the reference values established by current legislation, and the average values for recovery rates (71 to 78 %), within the standards required by legislation.

With regards to the analysis of the jam added of banana residue, the values obtained in this study for the coefficient of variation (CV%) in the fortified extract samples ranged from 4.3 % to 9.7 %, confirming satisfactory results that are within the recommended limit by ANVISA (<20%) (ANVISA, 2017).

In the studies by Carneiro et al. (2013), satisfactory values were also found for the validation parameters (selectivity, linearity, accuracy, precision, LOD, LOQ) of a multiresidue method used to determine 128 pesticides (including azoxystrobin, bifenthrin and difenoconazole) in bananas using a modified QuEChERS and UHPLCMS/MS extraction, which demonstrated the good applicability of the method. According to the study, selectivity reached acceptable levels, as the method proved to be interference-free, and the calibration curves showed significant linearity, according to the coefficient of determination  $(R^2)$ . LODs and LOQs were also satisfactory for the pesticides under study, reaching concentrations of 5 µg.Kg<sup>-1</sup> and 10 µg.Kg<sup>-1</sup>, respectively, except for the compounds phenamiphos and mevinphos. The recovery test values were between 70 and 120 %, except for methamidophos, which showed a recovery rate of 67.5 %, and the coefficient of variation for most of the results was below 10 % for all the concentration levels used (10.0, 25.0, 50.0 and 100 µg.Kg<sup>-1</sup>) (Carneiro et al., 2013).



Fig. 2. Chromatograms and mass spectra of the compounds analyzed: (1) simazine, (2) bifenthrin, (3) difenoconazole, and (4) azoxystobin.

#### Table 3

Validation of the analy	vtical method for	the banana ja	am added of ripe	e banana peel	flour and MRLs.
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Compounds	MRLs	(mg.Kg <sup>-1</sup> )	LOD (mg.Kg <sup>-1</sup> )	LOQ (mg.Kg <sup>-1</sup> )	Linearity (mg.Kg <sup>-1</sup> )	Coefficients			Accuracy (%)	Precision (RSD%)
	FAO	ANVISA				Angular	Linear	R <sup>2</sup>		
Azoxystrobin	2.0	15.0	0.01	0.1	0.1 – 1.0	5,097,881	-76,453	0.9951	71	6.0
Bifenthrin	0.1	0.02	0.01	0.1	0.1 - 1.0	39,068,607	-1,270,080	0.9968	78	5.4
Difenoconazole	0.1	0.5	0.01	0.1	0.1 - 1.0	6,995,649	-165,922	0.9954	71	4.3
Simazine	-	0.02	0.01	0.1	0.1 - 1.0	6,594,591	-29,803	0.9961	78	9.7

Table 4

MRL - Maximum Residue Limit; LOD - Limit of Detection; LOQ - Limit of Quantification.

## 3.2. Effect of processing on the degradation of pesticides in jam added of banana peel flour

The results of the degradation of the analyzed compounds (azoxystrobin, bifenthrin, difenoconazole and simazine) in the jam added of banana peel flour are described in Fig. 3. Based on these, a considerable degradation of all compounds can be seen in the jam samples (Table 4). The degradations can be associated to the thermal instability of these analytes at high temperatures (Naman et al., 2022).

From the graph in Fig. 3, it can be noted that the degradation of the relevant analytes occurred in all concentration ranges used in this study (0.1 mg.Kg<sup>-1</sup>, 0.5 mg.Kg<sup>-1</sup> and 1.0 mg.Kg<sup>-1</sup>). Degradation percentages varied from 28 to 60 %, as shown in Fig. 3. The data also shows that although processing provokes a reduction in compound concentrations in the matrix, complete degradations were not achieved.

Furthermore, it was observed that the thermal degradation rates were different for the different compounds analyzed. Azoxystrobin showed reduction percentages of 40 % (0.1 mg.Kg<sup>-1</sup>), 58 % (0.5 mg.Kg<sup>-1</sup>) and 31 % (1.0 mg.Kg<sup>-1</sup>), the most significant reduction being that observed at the midpoint concentration. It is also important to highlight that the thermal processing promoted the degradation of this analyte to acceptable values at all concentrations investigated (MRL = 15 mg.Kg<sup>-1</sup>). Fig. 4 shows the chromatograms obtained from the degradation of azoxystrobin under the 3 concentration levels studied (0.1 mg.Kg<sup>-1</sup>, 0.5 mg.Kg<sup>-1</sup> and 1.0 mg.Kg<sup>-1</sup>).

The compound bifenthrin, on the other hand, showed lower dissipation compared to azoxystrobin. The most significant degradation was observed at the concentrations of 0.5 mg.Kg<sup>-1</sup> (51 %) and 1.0 mg.Kg<sup>-1</sup> (44 %), followed by 1.0 mg.Kg<sup>-1</sup> (28 %), as shown in Fig. 3. It is also

Concentration of the compounds Azoxystrobin, Bifenthrin, Difenoconazole, and Simazine (mg.Kg $^{-1}$ ) before and after the processing of banana jam added of banana peel flour.

Compound	bound 0.1 mg.Kg <sup>-1</sup> 0.5 mg.Kg <sup>-1</sup>		1.0 mg.Kg <sup>-1</sup>			
	BP (mg. Kg <sup>-1</sup> )	AP (mg. Kg <sup>-1</sup> )	BP (mg. Kg <sup>-1</sup> )	AP (mg. Kg <sup>-1</sup> )	BP (mg. Kg <sup>-1</sup> )	AP (mg. Kg <sup>-1</sup> )
Azoxystrobin	0.05	0.03	0.38	0.16	0.65	0.45
Bifenthrin	0.09	0.05	0.47	0.23	0.83	0.6
Difenoconazole	0.05	0.02	0.45	0.19	0.81	0.55
Simazine	0.07	0.04	0.46	0.2	0.96	0.55

BP: Before processing; AP: After processing.

worth mentioning that the thermal processing was unable to promote the degradation of bifenthrin to values acceptable by the current national legislation, considering that the MRL for this substance is 0.02 mg. Kg<sup>-1</sup>and that relatively higher values than these were observed in all concentrations analyzed. Therefore, it can be inferred that the thermal processing used promotes the degradation of the pesticide, but not below the permitted levels if the initial concentration of the compound in the food is very high. Bifenthrin is commonly used to combat mites and ants, as well as to control different insects on crops (Table 2). Its application in banana cultivation is performed in a localized manner, with safety intervals not determined due to the type of use. This substance belongs to the pyrethroid group and is considered highly toxic for humans and very dangerous for the environment (ANVISA, 2024).

The compound that showed the highest degradation rates in this







Fig. 3. Degradation (%) of the compounds Azoxystrobin, Bifenthrin, Difenoconazole and Simazine after processing the jam added of banana peel flour (thermal processing: 75 °C to 85 °C, 35 min; triplicate).



Fig. 4. Overlaid chromatograms of the degradation of the compound azoxystrobin at 3 concentration levels (0.1 mg.Kg<sup>-1</sup>, 0.5 mg.Kg<sup>-1</sup> and 1.0 mg.Kg<sup>-1</sup>).

study was difenoconazole, i.e., 60, 68 and 32 %, at the concentrations of 0.1 mg.Kg<sup>-1</sup>, 0.5 mg.Kg<sup>-1</sup> and 1.0 mg.Kg<sup>-1</sup>, respectively (Fig. 3). It is worth noting that in all concentrations studied, difenoconazole was successfully degraded down to the MRL established by legislation for this analyte (MRL = 0.5 mg.Kg<sup>-1</sup>), implying that the use of high temperatures promotes sufficient degradation of the compound.

Finally, simazine presented similar dissipation values in the ranges of 0.1 mg.Kg<sup>-1</sup> and 1.0 mg.Kg<sup>-1</sup>, with an average degradation value of 43 %. The higher percentage of degradation occurred at the concentration 0.5 mg.Kg<sup>-1</sup>, i.e., 57 % (Fig. 3). However, it is important to highlight that even after the thermal processing, simazine presented concentrations higher than the MRL permitted by the current legislation for this compound (MRL =  $0.02 \text{ mg.Kg}^{-1}$ ), in all concentrations under study. Thus, even though the analyte is degraded by the high temperatures applied in the process, these are not capable of promoting the degradation of the analyte to conditions acceptable for consumption. Simazine is considered a product unlikely to cause acute damage (class V), but it dangerous to the environment (class III), and its control is of fundamental importance to minimize the contamination of natural resources (Table 5). Simazine is used to control weed growth in agricultural production, for example, with the application in banana cultivation carried out pre- or post-emergence (ANVISA, 2024). The characteristics of the compounds under study are listed in Table 5 below.

According to Hrynko et al. (2023), some physicochemical properties of pesticides, such as solubility, partition coefficient, and vapor pressure, lead to differences in the elimination of these compounds in fruits and vegetables that are subjected to processing, which justifies the differences found in this study. Difenoconazole has greater solubility in water than the other pesticides analyzed and a low pka value (1.07), which facilitates its dissociation in the food matrix (Milhome et al., 2009). Thus, thermal processing showed a partial degradation of the studied components during the preparation of banana jelly.

#### 4. Conclusion

The results obtained in the analyses carried out corroborate that the thermal processing employed provides a partial removal of the pesticide residues present in the food matrix. Difenoconazole showed higher degradation rates. The efficiency of removal of these analytes depends on their physical-chemical properties, as well as the characteristics of the food matrix under study. Thus, the results corroborates the importance of monitoring pesticide residues in complex processed products, such as fruit jam. Therefore, it is suggested that future research work be focused at a wider array of pesticides, in addition to analyzing other types of processed and ultra-processed foods.

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#### Table 5

Classification of the compounds azoxystrobin, bifenthrin, difenoconazole and simazine.

Parameters	Azoxystrobin	Bifenthrin	Difenoconazole	Simazine
Chemical formula Structural formula	C <sub>22</sub> H <sub>17</sub> N <sub>3</sub> O <sub>5</sub>	C <sub>23</sub> H <sub>22</sub> CIF <sub>3</sub> O <sub>2</sub>	C <sub>19</sub> H <sub>17</sub> Cl <sub>2</sub> N <sub>3</sub> O <sub>3</sub>	C7H12CIN5
Chemical group Class MRL mg.Kg <sup>-1</sup> (for bananas) Solubility in water at 20 °C (mg.L <sup>-1</sup> ) Dissociation constant (pKa) at 25 °C Log Kow Vapour pressure at 20 °C (mPa) Boiling point ( °C) Acceptable Daily Intake (ADI) mg.Kg <sup>-1</sup> b.w <sup>-1</sup> Toxicological classification	Strobilurin F 15.00 6.7 N.A. $3.16 \times 10^{02}$ $1.10 \times 10^{-07}$ 360 0.02 IV	Pyrethroid I 0.02 0.001 N.A. $3.98 \times 10^{-06}$ $1.78 \times 10^{-02}$ Decomposes before boiling 0.02 II	Triazole F 0.50 15.0 1.07 2.29 $\times$ 10 <sup>-04</sup> 3.33 $\times$ 10 <sup>-05</sup> 101 0.6 IV	Triazine H 0.02 5.0 1.62 2.00 $\times$ 10 <sup>-02</sup> 8,10 $\times$ 10 <sup>-04</sup> Decomposes before boiling 0.006 V

MRL - Maximum Residue Limit. F- Fungicide; I- Insecticide; H- Herbicide; N.A- Not applicable (No dissociation). \*Toxicological classification: I - Extremely toxic; II - Highly toxic product; III - Moderately toxic product; IV - Slightly toxic product; V- Product unlikely to cause acute damage; \*\*Environmental Classification: I - Highly Dangerous to the Environment; II - Very Dangerous to the Environment; III - Dangerous to the Environment; IV - Slightly Dangerous to the Environment; V - Low Risk to the Environment. Source: Brasil (2023); PPDB, pesticide (2023).

#### Ethical statement - Studies in humans and animals

This article does not contain any studies with human or animal subjects.

#### CRediT authorship contribution statement

Magnólia Carneiro de Oliveira: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Supervision, Validation, Visualization, Writing – original draft. John Kelvyn de Oliveira: Formal analysis, Methodology. Joselito Brilhante Silva: Supervision. Luana Guabiraba Mendes: Conceptualization, Formal analysis, Investigation, Supervision, Validation. Felipe Sousa da Silva: Formal analysis, Methodology. Mairlane da Silva Alencar: Formal analysis, Methodology. Validation. Crisiana de Andrade Nobre: Project administration, Supervision, Validation. Mayra Garcia Maia Costa: Project administration, Supervision. Micael de Andrade Lima: Conceptualization, Formal analysis, Project administration, Supervision. Maria Aparecida Liberato Milhome: Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.afres.2024.100445.

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