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Pesticide residues in stored wheat and their action on *Sitophilus oryzae* and *Rhyzopertha dominica*

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Abstract

The concern over supplying safe foods and discarding food lots with agrochemical residues over the legal limits has been the target of alerts from various agencies. Products derived from wheat are widely consumed in Brazil, and thus studies that aim at detecting agrochemical residues in this cereal grain and their risks are of utmost importance. The aims of this study were to evaluate the presence of agrochemical residues in wheat stored in a silo in Rio Grande do Sul and verify if there was residual action of the insecticides detected in the wheat. The first experiment consisted of multiresidue analyses of agrochemicals over a period of 10 months of storage. The second consisted of infesting samples from the previous experiment with *Sitophilus oryzae* and *Rhyzopertha dominica* to evaluate mortality. Nine agrochemicals were detected in the wheat, of which six were below the maximum limit of residues and three were above, according to Brazilian legislation. There was 100% mortality of *Sitophilus oryzae* after 96 h of exposure of this insect to the grain in all the samples evaluated, indicating that the residues of insecticide were still active even after the withholding period. No mortality was observed for *Rhyzopertha dominica* in the samples analyzed.

Keywords: *Triticum aestivum* L.; food safety; insecticides; fungicides; herbicides.

Practical Applications: Monitoring pesticide residues in stored wheat can contribute to the consumption of safer products, as well as to the detection of problems related to the withholding period of products applied in food production and storage.

1 INTRODUCTION

Wheat is grown in three regions in Brazil: the South of Brazil (Rio Grande do Sul, Santa Catarina, and southern Paraná), South Central Brazil (other regions of Paraná, Mato Grosso do Sul, and São Paulo), and Central Brazil (Distrito Federal, Goiás, Minas Gerais, Mato Grosso, and Bahia) (Cunha et al., 2016). Production in the 2022 wheat crop was 10.5 million tons, concentrated for the most part in the three states of the South of Brazil, which represented more than 92.0% of national production (Conab, 2023b).

According to De Mori (2016), wheat is widely used in the human diet, but it is also used in non-food products, as well as in animal feed. Data from Conab (2023a) show that Brazilian wheat production in the 2022 crop provided for 85.2% of national consumption, which was estimated at 12.4 million tons.

This information indicates the importance of the wheat crop in Brazil and, as a result, the need to use available technologies so as to maximize production, ensuring the quality and conservation of the product.

From the perspective of plant health of the crop, the use of agrochemicals (i.e., pesticides) constitutes one of the management strategies (chemical control) used to minimize the risks of quantitative and qualitative losses of wheat. The Brazilian Wheat and Triticale Research Commission guides the use of agrochemicals registered in the Brazilian Ministry of Agriculture and Livestock (MAPA) for control of pests, diseases, and weeds that may occur in the wheat crop (Reunião da Comissão Brasileira de Pesquisa de Trigo e Triticale, 2023).

According to Belitz and Grosch (1997), contamination of foods of plant origin may occur directly through treatment of the products, in their storage, and in transport. Contamination may also be indirect, through exposure to pesticide residues in the soil, from agrochemicals that were applied on a previous crop and that can be taken up by the subsequent crop, through the atmosphere, through displacement of agrochemicals from nearby crops (drift – when the chemical product is deposited outside of the intended target), or through storage in locations previously treated with pesticides. In this respect, it is important to establish limits for pesticide use on wheat.

The maximum residue limit (MRL) was defined in Brazil (2019b) as the maximum quantity of agrochemical residue or associated substance officially permitted in/on the food as a result of adequate application in a specific phase, from its production up to consumption, expressed in parts (in weight)

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of the agrochemical, associated substance, or their residues by parts per million of food (in weight, ppm or mg/kg).

To certify the quality of foods and monitor the levels of pesticide residues, MAPA has the National Program of Contaminant Residues in Products of Plant Origin (PNCRC) (Brasil, 2022), and the Ministry of Health through the Brazilian Health Regulatory Agency (Anvisa) coordinates the Food Agrochemical Residue Analysis Program (PARA) (Anvisa, 2023b).

Abuse in the use of agrochemicals, without following stated instructions, as well as disregard for the withholding period, can also result in food contamination. According to Brasil (2002), the withholding period in the application of agrochemicals or associated substances can be defined as follows:

- before harvest: the time interval between the last application and harvest;
- post-harvest: the time interval between the last application and commercialization of the treated product, among other situations.

According to the Wheat Technical Regulation, instituted by Normative Instruction nº 38 — IN nº 38 (Brasil, 2010), MAPA can carry out analyses of harmful substances related to risk to human health, and the product will be declassified when the presence of substances is found at limits above the maximum established in specific legislation, or furthermore, when the presence of substances not authorized for the product is found.

The measures to be adopted, which were established by Brazilian legislation, in the case of confirmation of non-conformity (contamination by agrochemicals), are declassification of the lot, suspension of its sale, and a summons of the technician responsible for the product to present an alternative aiming at its compliance with the levels permitted of the hygiene-health factors or a proposal for its final destination (Brasil, 2013). If it is impossible to bring the product into conformity with the health and hygiene conditions required by legislation in effect, the contaminated product may be disposed of, which constitutes loss of the food.

Considering that agrochemicals are used in the wheat crop (in the field and during post-harvest) to avoid losses brought about by biotic factors (pests, diseases, and weeds), the aim of this study was to evaluate if agrochemical residues are present in the mass of wheat grain stored for 10 months in a commercial metal silo in Rio Grande do Sul. An additional aim was to check for the persistence of residual action of the insecticides used in the storage of this grain on the insect pests *Sitophilus oryzae* (*S. oryzae*) and *Rhyzopertha dominica* (*R. dominica*).

2 MATERIALS AND METHODS

The commercial wheat used in the evaluations of this study was produced in the 2017 crop season in the Southern region of Brazil. First, the wheat was received from growers in a storage facility in the state of Paraná. Before filling the silo structure with grain, it was treated with the insecticides pirimiphos-methyl and deltamethrin. After that, the grain was treated with the insecticide phosphine at the beginning of storage and in the days it was aerated. After complete filling this silo, the wheat was taken to a concrete silo, which is also located in Paraná, where a preventive treatment with phosphine was applied.

After around 3 months in this storage facility, 1,650 tons of this wheat were transported for storage in a metallic silo in the state of Rio Grande do Sul.

In that silo, recommended procedures were performed for integrated pest management for the stored grain before storage, such as general cleaning of the inner part of the empty silo (on January 23, 2018) and application of diatomaceous earth (on January 24, 2018) through the silo exhaust system, so as to control insect pests of stored grains that could be infesting the silo structure.

During storage in the metal silo, the following chemical treatments were performed in the wheat grain mass:

- the insecticides bifenthrin and pirimiphos-methyl at the dose of 16.97 ml/ton of grain for preventive treatment of insect pests (from January 30, 2018 to February 7, 2018) applied during filling of the silo through application in the conveyor;
- curative treatment (expurgation) with phosphine (a total dose of 13.0 kg), for control of *R. dominica* and *Sitophilus* spp. (on February 26, 2018).

Two more applications of phosphine were made (August 9, 2018 and September 19, 2018) using a pneumatic probe, and on November 1, 2018, the upper layer of the grain mass was dusted with diatomaceous earth.

The wheat remained in storage in that silo for 10 months (from January 30, 2018 to December 5, 2018). During that period, samples were taken through two systems: dynamic collection, with displacement of the grain, according to IN nº 38 (Brasil, 2010), and static collection, with a pneumatic probe, near the grain temperature monitoring cables and at different points and depths of the silo. For static collection, the silo was divided into 36 sampling units (Figure 1), and in each collection, three points were sampled (considered as repetitions), at random, obtained by drawing lots, among the 36 sampling units.

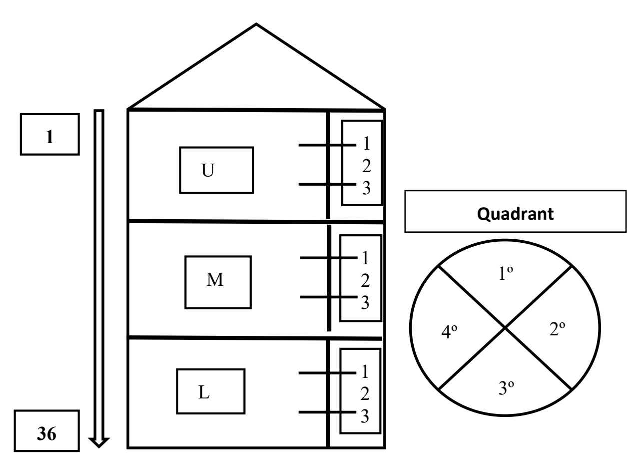

Figure 1. Representation of the sampling points for static collection of grain in the metal storage silo, including three different heights (upper: U, middle: M, and lower: L), subdivided into four quadrants.

A total of six sample collections were made with three repetitions: the first upon filling the silo was a dynamic collection (it was made from January 30, 2018 to February 7, 2018); the four subsequent collections were static (they were made with a pneumatic probe, on March 9, 2018, May 4, 2018, August 3, 2018, and October 26, 2018); and the last collection was dynamic and it was made upon emptying the silo (on December 5, 2018). The weight of each sample (experimental unit) was 30 kg, for each repetition.

The samples collected over the study period were packaged, identified, and sent to Embrapa Trigo, Passo Fundo, RS, where they were homogenized, splintered, and separated into subsamples for the evaluations made in two experiments presented below (Sections 2.1 and 2.2).

2.1 Analysis of agrochemical residues in stored wheat

The wheat grain samples for the purpose of tracing agrochemical residues were sent to the Laboratório Agrosafety Monitoramento Agrícola Ltda., Piracicaba, SP. Selection of the active ingredients to be traced (a total of 203) was based on IN nº 17 (Brasil, 2014), PARA (Anvisa, 2016), the Codex Alimentarius (1993), and the list of active ingredients cited in the publication of the Reunião da Comissão Brasileira de Pesquisa de Trigo e Triticale (2018).

The methods used in the multiresidue analyses of the different groups of active ingredients traced were proposed by Zoonen (1996), Anastassiades et al. (2003), and Horwitz and Latimer (2007).

2.2 Residual activity of insecticides on **Sitophilus oryzae** *and* **Rhyzopertha dominica**

Two sets of wheat samples drawn from the 18 sample collections made in the silo were placed in Petri dishes (experimental unit containing 30 g of grain), in quadruplicate, as well as the control composed of wheat grain of known origin without agrochemicals. One set of samples received 10 adults of *S. oryzae* per Petri dish, and the other received 10 adults of *R. dominica* per Petri dish; the insects were around 7 days of age and not sexed. In the controls, 10 adults of each one of the species of insects were inserted in the dishes.

The Petri dishes containing the treatments infested with the insects were placed in a growth chamber (22 ± 1°C and 12 h photophase) for 4 days. At 24-h intervals, the dishes were removed from the chamber to evaluate the number of dead insects, which were discarded after counting. After that, the dishes were returned to the chamber. This procedure was carried out at 24, 48, 72, and 96 h.

3 RESULTS AND DISCUSSION

3.1 Analysis of agrochemical residues in stored wheat

Tables 1 and 2 show the active ingredients detected in the multiresidue analyses of agrochemicals from the wheat samples taken from the metal silo.

Table 1. Active ingredients detected in multiresidue analyses of agrochemicals in wheat samples collected from a metal silo in Rio Grande do Sul that had some values above the maximum residue limit (MRL, mg/kg), established by Brazilian legislation.

Collection identification[1]/ time in days[2]	Sample identification[3]	Active ingredients detected (mg/kg)		
		Glyphosate	Fenitrothion	Pirimiphos-methyl
First dynamic/71	1R	ND	1.747	0.515
	2R	0.231	1.749	0.657
	3R	5.206	1.656	0.445
First static/84	6 (2QU2)	ND	0.995	12.340
	4 (4QU1)	ND	1.437	12.360
	23 (3QM3)	ND	0.164	6.050
Second static/133	26 (2QL1)	ND	0.722	9.778
	24 (4QM3)	ND	0.803	11.310
	2 (2QU1)	ND	1.331	8.539
Third static/229	33 (1QL3)	ND	1.992	7.498
	25 (1QL1)	ND	ND	12.350
	16 (4QM1)	0.443	0.078	9.637
Fourth static/281	22 (2QM2)	ND	0.071	11.260
	1 (1QU1)	ND	1.577	9.650
	15 (3QM1)	ND	0.127	9.409
Second dynamic/308	1R	0.05	0.978	3.883
	2R	0.106	0.651	3.313
	3R	0.070	0.927	3.772
Quantification limit (QL), mg/kg		0.05	0.05	0.01
Maximum residue limit, mg/kg[5]		0.05	1.00	5.00
Withdrawal period per modality of use, in days[4]		Application in post-emergence of infested plants: Not determined Pre-harvest desiccation: Use not authorized	Product stored: 120	Product stored: 45

[1]Dynamic collection: performed at filling and emptying of the wheat and according to IN nº 38 (Brasil, 2010); static collection: performed with a pneumatic probe, without grain movement; [2]The time was calculated from the end of filling the silo (on February 7, 2018) up to carrying out analyses of residues; [3]R: repetition, Q: quadrant, U: upper, M: middle, L: lower; [4]According to registration in Anvisa (2023a); ND: not detected.

Table 2. Active ingredients detected in the multiresidue analyses of agrochemicals in wheat samples collected in a metal silo in Rio Grande do Sul that had values below the maximum residue limit (MRL, mg/kg) established by Brazilian legislation.

Collection identification[1]/time in days[2]	Sample identification[3]	Active ingredient (mg/kg)					
		Bifenthrin	Chlorpyrifos ethyl	Deltamethrin	Dithiocarbamates	Phosphine	Triflumuron
First dynamic/71	1R	< QL	ND	0.061	< QL	0.014	ND
	2R	< QL	ND	0.122	< QL	0.031	ND
	3R	< QL	ND	0.062	< QL	0.014	ND
First static/84	6 (2QU2)	0.402	ND	0.100	ND	ND	ND
	4 (4QU1)	0.372	ND	0.124	ND	< QL	ND
	23 (3QM3)	0.417	0.01	ND	ND	0.017	ND
Second static/133	26 (2QL1)	0.292	ND	0.015	ND	< QL	ND
	24 (4QM3)	0.258	ND	0.030	ND	0.019	ND
	2 (2QU1)	0.228	ND	0.044	< QL	ND	ND
Third static/229	33 (1QL3)	0.438	ND	0.227	ND	< QL	0.032
	25 (1QL1)	0.597	ND	ND	ND	< QL	ND
	16 (4QM1)	0.630	ND	0.017	ND	< QL	ND
Fourth static/281	22 (2QM2)	0.313	ND	ND	ND	0.038	ND
	1 (1QU1)	0.263	ND	0.187	ND	0.027	ND
	15 (3QM1)	0.286	ND	0.023	ND	0.059	ND
Second dynamic/308	1R	0.682	ND	0.086	< QL	ND	0.030
	2R	0.631	ND	0.083	< QL	ND	0.060
	3R	0.679	ND	0.087	< QL	ND	0.048
Quantification limit (QL), mg/kg		0.01	0.01	0.01	0.05	0.01	0.01
Maximum residue limit, mg/kg		0.7	0.2	1	1	0.1	0.5
Withholding period per modality of use, in days[4]		Seeds: Not determined Leaf: 7 Stored product: 30	Leaf: 21	Leaf: 14 Stored product: 3	Leaf: 32	Stored product: 4	Leaf: 14

[1]Dynamic collection: performed at filling and emptying of the wheat and according to IN nº 38 (Brasil, 2010); static collection: performed with a pneumatic probe, without grain movement; [2]The time was calculated from the end of filling the silo (on February 7, 2018) up to carrying out analyses of residues; [3]R: repetition, Q: quadrant, U: upper, M: middle, L: lower; [4]According to registration in Anvisa (2023a); ND: not detected.

Residues of nine active ingredients of pesticides were detected from the samples collected in the silo. The insecticides fenitrothion (in 7 samples) and pirimiphos-methyl (in 12 samples) and the herbicide glyphosate (in 5 samples) were found at a concentration above the LMR according to the limits established in the corresponding monographs published by Anvisa (2023a) (Table 1). Six active ingredients had values below the LMR – the fungicide of the dithiocarbamate chemical group and the insecticides bifenthrin, chlorpyrifos-ethyl, deltamethrin, phosphine, and triflumuron (Table 2).

Given that the period of application of pirimiphos-methyl was from January 30, 2018 to February 7, 2018, the LMR for this active ingredient remained high for various months, exceeding the 45-day withholding period (Table 1), as published in its monograph (Anvisa, 2023a).

In relation to fenitrothion, there had been no report on the use of that active ingredient in pest management in wheat by any of the technicians responsible for the Paraná and Rio Grande do Sul storage facilities. Nevertheless, observing the data presented in Table 1, which show the presence of this active ingredient already in the three repetitions of the first dynamic collection, it is clear that this product was applied at some time prior to transport of the wheat grain from the storage facility of the state of Paraná to the metal silo of Rio Grande do Sul. Results indicate that the values of residues found in this insecticide remained high in various samples, even after having gone beyond the withholding period of 120 days established for this active ingredient, as published in its monograph (Anvisa, 2023a). This indicates the need for stricter control in recording all the agrochemicals used during the entire wheat production process, passing through storage, until arriving at the final destination, the consumer. With stricter control of all the activities related to the use of agrochemicals, in the field and in storage, all the links of the wheat production chain can be traced. When necessary, this will allow making decisions that can eliminate or reduce the contaminants of wheat grain and its derivatives.

The herbicide glyphosate, detected above the LMR in 5 of the 18 samples analyzed (Table 1), was quite likely applied in pre-harvest desiccation in wheat by farmer(s) that delivered the wheat to the storage facility in Paraná. It is nearly impossible that the results found may have come from application of the glyphosate for control of weeds infesting the wheat crop because its application is recommended from 20 days up to 1 day before sowing the wheat, that is, the wheat crop would not have been established yet. An additional consideration is the long period of time from sowing up to harvest of the wheat.

The other active ingredients detected in the wheat grain below the LMR, except for dithiocarbamates (fungicides) and chlorpyrifos-ethyl and triflumuron (insecticides), have agricultural use authorized by Anvisa for pest control, both for control of pests in the field and for those in storage (Table 2). The insecticide deltamethrin was used in disinfestation of the storage facility in Paraná before receiving the wheat grain, and the insecticide bifenthrin was used during the filling of the metal silo in Rio Grande do Sul. Therefore, these are likely the origin of these residues, although we cannot rule out the hypothesis that the residues detected by these two insecticides arose from applications of these active ingredients in the wheat fields. The insecticide phosphine was used in the storage facilities of Paraná and in the metal silo of Rio Grande do Sul in different steps of storage for control of insect pests. As the product is recommended for that purpose, the origin of the residues is thus well characterized.

In the most updated report that considers a wheat derivative, the "Report of analyses of samples monitored in the period from 2013 to 2015," published by Anvisa (2016), results of multiresidue analyses of agrochemicals in 506 samples of wheat flour were presented. Of these, 468 samples were considered satisfactory; specifically, 248 samples did not show residues of the agrochemicals researched and 220 had residues at concentrations less than or equal to the LMR. A total of 17 active ingredients of agrochemicals were also detected (all at concentrations below the LMR established by Brazilian legislation). Among the 110 active ingredients researched, those that had the largest number of detections in the samples analyzed were pirimiphos-methyl (in 135 samples), bifenthrin (87), fenitrothion (31), and chlorpyrifos-ethyl (31). These four active ingredients were also detected in this study at different concentrations, per sample, and in some, with values greater than the LMR allowed by Brazilian legislation (Tables 1 and 2).

In the table of violations of legislation detected in samples of Brazilian wheat analyzed by the PNCRC/Vegetal, the herbicide glyphosate and fungicide folpet were found in the 2016 and 2017 crop years, respectively (Brasil, 2019a), as well as the insecticide permethrin, in wheat, and glyphosate, in wheat flour, in the 2019 crop year (Brasil, 2021). Except for glyphosate, the active ingredients reported in the PNCRC/Vegetal were not found in this study. This means that the evaluations of residues of agrochemicals in samples of wheat and wheat flour should be continuous, with analyses that allow tracing the largest possible number of active ingredients, as the residues of these pesticides vary (they depend on the plant health management practices adopted in the fields and in storage — post-harvest, the withholding period, the degradability of the active ingredients according to the storage period and storage conditions, temperature conditions, moisture, etc.). Routine evaluation of the residues of agrochemicals can contribute to food safety as it will allow the detection of the problem and the adoption of measures for prevention, control, or reduction of the contaminants.

3.2 Residual action of insecticides on **Sitophilus oryzae** *and* **Rhyzopertha dominica**

There was no mortality of adults of *R. dominica* when exposed to the grain collected in the silo at the 18 sampling points evaluated, even after 96 h of evaluation of the experiment. The absence of mortality of the insects when exposed to the grain obtained from the silo may be related to the fact that the active ingredients registered in MAPA for control of this species, such as bifenthrin, deltamethrin, and phosphine (Brasil, 2023) present in the samples of wheat grain, were at very low doses (Table 2).

The percentages of mortality of adults of *S. oryzae* as a function of time of exposure of the insects to the wheat grain collected at 18 sampling points containing residues of active ingredients are shown in Table 3. At the end of 96 h of exposure, 100% mortality was observed in all the collections. In the control (grain free of agrochemicals), there was no mortality.

The mortality of *S. oryzae* was likely brought about by residues of the insecticides fenitrothion and pirimiphos-methyl, as, in most of the samples collected from the silo, these active ingredients were at doses near or higher than the LMR, in contrast with the other insecticide active ingredients, which had residual values below the LMR (Tables 1, 2, and 3).

The results found in this study indicate that the withholding period established for fenitrothion (120 days) and pirimiphos-methyl (45 days) was not sufficient to degrade/deactivate the active ingredients of the insecticides.

Results similar to those found in this study were also obtained by Vásquez-Castro (2006). This author treated wheat grain with fenitrothion and evaluated the dosages of the residues and the residual activity of this insecticide on insect pests over 12 months of storage. The author found a residue of this active ingredient in the wheat grain after the withholding period of 120 days three times greater than the LMR established by Brazilian legislation, which is 1 mg/kg, even having obtained treatment of the grain with 62% of the dosage recommended by the manufacturer (10 mg/kg). In addition, the author found 100% mortality of adults of *S. oryzae* when exposed to the grain treated with the insecticide in the first few months after the treatment and nearly 90% mortality at 8 months after treatment of the grain with the active ingredient, results that were similar to those obtained in this study for this same species of insect.

Sgarbiero (2001), in turn, treated wheat grain with pirimiphos-methyl and evaluated the dose of the residue up to 240 days over storage, as well as the residual activity on adults of *Sitophilus* spp. up to 360 days after treatment of the grain. The author found that the dose of the residue declined over storage, but the amounts present in the grain were sufficient to cause 100% mortality in insects up to 210 days, and from 94 to 100% mortality up to 360 days after treatment of the grain. Similar results were observed in this study for *S. oryzae*. Alleoni and Ferreira (2006) treated wheat grain with pirimiphos-methyl at doses that ranged from 2 to 16 g of the active ingredient (a.i.)/ton of grain and evaluated the mortality of adults of *S. oryzae* and *S. zeamais* over 240 days after application of the insecticide. For *S. oryzae* at the lowest dose of 2 g of

Table 3. Percentage of mortality of *Sitophilus oryzae* that occurred at different periods of exposure of the species to the presence of wheat grain with residues of active ingredients used in the control of insect pests in wheat samples collected in a metal silo in Rio Grande do Sul.

Collection identification[1]/ time in days[2]. Statistical data	**Sample identification[3]**	**Insecticide residues (mg/kg)**					**Percentage of mortality per exposure period (h)**			
		Bifenthrin	**Deltamethrin**	**Fenitrothion**	**Phosphine**	**Pirimiphos-methyl**	**24**	**48**	**72**	**96**
	1R	< QL	0.061	**1.747**	0.014	0.515	5.0	40.0	30.0	25.0
First dynamic/71	2R	< QL	0.122	**1.749**	0.031	0.657	7.5	40.0	42.5	10.0
	3R	< QL	0.062	**1.656**	0.014	0.445	2.5	47.5	42.5	7.5
Mean		–	**0.082**	**1.717**	**0.020**	**0.539**	**5.0**	**42.5**	**38.3**	**14.2**
Standard deviation		–	**0.035**	**0.053**	**0.010**	**0.108**	**2.5**	**4.33**	**7.2**	**9.5**
	6 (2QU2)	0.402	0.100	0.995	ND	**12.340**	85.0	15.0	0.0	0.0
First static/84	4 (4QU1)	0.372	0.124	**1.437**	< QL	**12.360**	62.5	35.0	2.5	0.0
	23 (3QM3)	0.417	ND	0.164	0.017	**6.050**	37.5	60.0	2.5	0.0
Mean		**0.397**	**0.112**	**0.865**	**0.017**	**10.250**	**61.7**	**36.7**	**1.7**	**0.0**
Standard deviation		**0.023**	**0.017**	**0.646**	–	**3.637**	**23.8**	**22.6**	**1.4**	**0.0**
	26 (2QL1)	0.292	0.015	0.722	< QL	**9.778**	15.0	70.0	15.0	0.0
Second static/133	24 (4QM3)	0.258	0.030	0.803	0.019	**11.310**	32.5	60.0	7.5	0.0
	2 (2QU1)	0.228	0.044	**1.331**	ND	**8.539**	35.0	6.0	0.0	0.0
Mean		**0.259**	**0.030**	**0.952**	**0.019**	**9.876**	**27.5**	**65.0**	**7.5**	**0.0**
Standard deviation		**0.032**	**0.015**	**0.331**	–	**1.388**	**10.9**	**5.0**	**7.5**	**0.0**
	33 (1QL3)	0.438	0.227	**1.992**	< QL	**7.498**	10.0	75.0	12.5	2.5
Third static/229	25 (1QL1)	0.597	ND	ND	< QL	**12.350**	25.0	70.0	5.0	0.0
	16 (4QM1)	0.63	0.017	0.078	< QL	**9.637**	25.0	70.0	5.0	0.0
Mean		**0.555**	**0.122**	**1.035**	–	**9.828**	**20.0**	**71.7**	**7.5**	**0.8**
Standard deviation		**0.103**	**0.148**	**1.353**	–	**2.432**	**8.7**	**2.9**	**4.3**	**1.4**
	22 (2QM2)	0.313	ND	0.071	0.038	**11.260**	25.0	75.0	0.0	0.0
Fourth static/281	1 (1QU1)	0.263	0.187	**1.577**	0.027	**9.650**	27.5	72.5	0.0	0.0
	15 (3QM1)	0.286	0.023	0.127	0.059	**9.409**	17.5	67.5	12.5	2.5
Mean		**0.287**	**0.105**	**0.592**	**0.041**	**10.106**	**23.3**	**71.7**	**4.2**	**0.8**
Standard deviation		**0.025**	**0.116**	**0.854**	**0.016**	**1.006**	**5.2**	**3.8**	**7.2**	**1.4**
	1R	0.682	0.086	0.978	ND	3.883	42.5	55.0	2.5	0.0
Second dynamic/308	2R	0.631	0.083	0.651	ND	3.313	12.5	85.0	2.5	0.0
	3R	0.679	0.087	0.927	ND	3.772	32.5	65.0	2.5	0.0
Mean		**0.664**	**0.085**	**0.852**	–	**3.656**	**29.2**	**68.3**	**2.5**	**0.0**
Standard deviation		**0.029**	**0.002**	**0.176**	–	**0.302**	**15.3**	**15.3**	**0.0**	**0.0**
Quantification limit (QL), mg/kg		0.01	0.01	0.05	0.01	0.01				
Maximum residue limit, mg/kg		0.7	1.0	1.0	0.1	5.0				
Withholding period per modality of use, in days[4]		Seeds: Not determined Leaf: 14 Stored product: 30	Leaf: 14 Stored product: 30	Stored product: 120	Stored product: 4	Stored product: 45				

[1]Dynamic collection: performed at filling and emptying of the wheat and according to IN nº 38 (Brasil, 2010); static collection: performed with a pneumatic probe, without grain movement; [2]The time was calculated from the end of filling the silo (on February 7, 2018) up to carrying out analyses of residues; [3]R: repetition, Q: quadrant, U: upper, M: middle, L: lower; [4]According to registration in Anvisa (2023a); ND: not detected.

the a.i./ton, the mortality was from 86% to 96% up to 60 days after application, achieving 71% mortality at 240 days after application. At the dose of 4 g of the a.i./ton, they obtained from 91% to 100% mortality throughout the period evaluated. Therefore, these authors obtained high mortality rates, even at the lowest doses evaluated, and even after various months of treatment of the grain with the insecticide, similar to the results observed in this study for *S. oryzae*.

4 CONCLUSION

In the grain stored in the metal silo in Rio Grande do Sul, residues of nine active ingredients of pesticides were detected, of which three had values higher than the LMR. This indicated that some active ingredients did not degrade even after the passage of the withholding period foreseen in the monographs of Anvisa. This may indicate the need for reevaluation and updating of their withholding periods, suggesting stricter control for registration of the agrochemicals to be used in the wheat production and storage process.

From another perspective, whereas the long residual period of the insecticides allowed more prolonged protection of the grain against infestation by insects (100% mortality of *S. oryzae* in all the grain samples collected, although, for *R. dominica,* there was no mortality under the same exposure conditions), it nevertheless compromised the quality of the stored product to the extent that some of the active ingredients detected exceeded the LMR permitted. This can occur in occasions in which the wheat is stored for a shorter time than what is necessary for the degradation of the residues to levels lower than the LMR established by Brazilian legislation.

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REFERENCES

Agência Nacional de Vigilância Sanitária (Anvisa) (2016). *Programa de Análise de Resíduos de Agrotóxicos em Alimentos (PARA)*. Relatório das análises de amostras monitoradas no período de 2013 a 2015. ANVISA. Retrieved from https://www.gov.br/anvisa/pt-br/assuntos/agrotoxicos/programa-de-analise-de-residuos-em-alimentos/arquivos/3778json-file-1

Agência Nacional de Vigilância Sanitária (Anvisa) (2023a). *Monografias de agrotóxicos*. ANVISA. Retrieved from https://www.gov.br/anvisa/pt-br/setorregulado/regularizacao/agrotoxicos/monografias

Agência Nacional de Vigilância Sanitária (Anvisa) (2023b). *Programa de Análise de Resíduos de Agrotóxicos em Alimentos (PARA)*. ANVISA. Retrieved from https://www.gov.br/anvisa/pt-br/assuntos/agrotoxicos/programa-de-analise-de-residuos-em-alimentos

Alleoni, B., & Ferreira, W. (2006). Control of *Sitophilus zeamais* Mots., 1958 and *Sitophilus oryzae* (L., 1763) weevils (Coleoptera, Curculionidae) in stored wheat (*Triticum aestivum* L) with insecticide pirimiphos methyl (Actellic 500 ce). In *Proceedings of the 9th International Working Conference on Stored Product Protection*, Campinas, Brazil.

Anastassiades, M., Lehotay, S. J., Štajnbaher, D., & Schenck, F. J. (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *Journal of AOAC International*, *86*(2), 412-431. https://doi.org/10.1093/jaoac/86.2.412

Belitz, H. D., & Grosch, W. (1997). *Química de los alimentos* (2. ed.). Acribia.

Brasil (2002). Presidência da República. Dispõe sobre a pesquisa, a experimentação, a produção, a embalagem e rotulagem, o transporte, o armazenamento, a comercialização, a propaganda comercial, a utilização, a importação, a exportação, o destino final dos resíduos e embalagens, o registro, a classificação, o controle, a inspeção e a fiscalização de agrotóxicos, seus componentes e afins, e dá outras providências (Decreto nº 4.074, de 04 de janeiro de 2002). *Diário Oficial da República Federativa do Brasil*. Retrieved from http://www.planalto.gov.br/ccivil_03/decreto/2002/d4074.htm

Brasil (2010). Ministério da Agricultura, Pecuária e Abastecimento. Estabelece o Regulamento Técnico do Trigo, definindo o seu padrão oficial de classificação, com os requisitos de identidade e qualidade, a amostragem, o modo de apresentação e a marcação ou rotulagem, nos aspectos referentes à classificação do produto. (Instrução Normativa nº 38, de 30 de novembro de 2010). *Diário Oficial da República Federativa do Brasil*. Retrieved from http://sistemasweb.agricultura.gov.br/sislegis/action/detalhaAto.do?method=visualizarAtoPortalMapa&chave=358389789

Brasil (2013). Ministério da Agricultura, Pecuária e Abastecimento. Estabelece os procedimentos a serem adotados no âmbito do Ministério da Agricultura, Pecuária e Abastecimento, na constatação de resíduos de agrotóxicos e contaminantes químicos, físicos e biológicos, conforme estabelecido em legislação específica da ANVISA, em produtos vegetais, seus subprodutos e resíduos de valor econômico, padronizados (Instrução Normativa nº 31, de 15 de agosto de 2013). *Diário Oficial da República Federativa do Brasil*. Retrieved from https://sistemasweb.agricultura.gov.br/sislegis/action/detalhaAto.do?method=imprimirAto&tipo=INM&numeroAto=00000031&seqAto=000&valorAno=2013&orgao=MAPA&codTipo=&desItem=&desItemFim=

Brasil (2014). Ministério da Agricultura, Pecuária e Abastecimento. Define o Plano Nacional de Controle de Resíduos e Contaminantes em Produtos de Origem Vegetal - PNCRC/Vegetal para o Ano-Safra 2014-2015 (Instrução Normativa nº- 17, de 31 de julho de 2014). *Diário Oficial da República Federativa do Brasil*. Retrieved from https://sistemasweb.agricultura.gov.br/sislegis/action/detalhaAto.do?method=imprimirAto&tipo=INM&numeroAto=00000017&seqAto=000&valorAno=2014&orgao=SDA/MAPA&codTipo=&desItem=&desItemFim=

Brasil (2019a). Ministério da Agricultura, Pecuária e Abastecimento. Publicar os resultados do Programa Nacional de Controle de Resíduos e Contaminantes nas culturas agrícolas de abacaxi, alface, alho, amêndoa (amêndoa de cacau, Prunus dulcis), amendoim, arroz, avelã (Corylus avellana), banana, batata, beterraba, café, castanha de caju, castanha do Brasil, cebola, cenoura, cevada malteada, farelo de soja, feijão, goiaba, kiwi, laranja, limão, maçã, mamão, manga, melão, milho, morango, pêra, pimenta do reino, pimentão, pistache (Pistacia vera), soja, suco de uva, tomate, trigo, uva, vinho e de que trata o Plano Nacional de Controle de Resíduos e Contaminantes em Produtos de Origem Vegetal - PNCRC/Vegetal, no 2º semestre de 2015 (2015.2), no ano de 2016, no ano de 2017 e no ano de 2018, na forma dos Anexos à presente Portaria (Instrução Normativa Nº 267, de 11 de dezembro de 2019). *Diário Oficial da República Federativa do Brasil*.

Brasil (2019b). Ministério da Saúde. Agência Nacional de Vigilância Sanitária. Dispõe sobre os critérios para avaliação do risco dietético decorrente da exposição humana a resíduos de agrotóxicos, no âmbito da Anvisa, e dá outras providências (Resolução da Diretoria Colegiada - RDC nº 295, de 29 de julho de 2019). *Diário Oficial da República Federativa do Brasil*. Retrieved from http://antigo.anvisa.gov.br/legislacao#/visualizar/403291

Brasil (2021). Ministério da Agricultura, Pecuária e Abastecimento. Torna público os resultados do Programa Nacional de Controle de Resíduos e Contaminantes nas culturas agrícolas de abacaxi, alface, alho, amêndoa (Prunus dulcis), amêndoa de cacau, amendoim, arroz, avelã (Corylus avellana), banana, batata-inglesa, beterraba, café, castanha de caju, castanha do brasil, cebola, cenoura, cevada malteada, citros, farinha de trigo, feijão, goiaba, kiwi, maçã, mamão, manga, melão, milho, morango, pera, pimenta do reino, pimentão, soja, tomate, trigo, uva e de que trata o Plano Nacional de Controle de Resíduos e Contaminantes em produtos de origem vegetal - PNCRC/Vegetal, no ano de 2019 e no ano de 2020, na forma dos anexos à presente portaria (Instrução Normativa nº 448, de 17 de novembro de 2021). *Diário Oficial da República Federativa do Brasil*.

Brasil (2022). Ministério da Agricultura, Pecuária e Abastecimento. Institui o Programa Nacional de Controle de Resíduos e Contaminantes em Produtos de Origem Vegetal (PNCRC/Vegetal), definindo o alcance, os objetivos, os critérios e os procedimentos para a realização dos controles oficiais (Portaria SDA Nº 574, de 9 de maio de 2022). *Diário Oficial da República Federativa do Brasil*. Retrieved from https://sistemasweb.agricultura.gov.br/sislegis/action/detalhaAto.do?method=imprimirAto&tipo=POR&numeroAto=00000574&seqAto=000&valorAno=2022&orgao=SDA/MAPA&codTipo=&desItem=&desItemFim=

Brasil (2023). Ministério da Agricultura, Pecuária e Abastecimento. *Agrofit: sistema de agrotóxicos fitossanitários*. Retrieved from https://agrofit.agricultura.gov.br/agrofit_cons/principal_agrofit_cons

Codex Alimentarius (1993). *Pesticides residues in food* (2. ed.). FAO. Retrieved from www.fao.org/input/download/standards/41/CXA_004_1993e.pdf

Companhia Nacional de Abastecimento (Conab) (2023a). *Acompanhamento da safra brasileira de grãos – safra 2022/23. 10*(10). Companhia Nacional de Abastecimento. Retrieved from https://www.conab.gov.br/component/k2/item/download/48137_6239e58c7fc01900f76618eb4ca2bb01

Companhia Nacional de Abastecimento (Conab) (2023b). *Trigo – safras 2022 e 2023: Comparativo de área, produtividade e produção*. Companhia Nacional de Abastecimento. Retrieved from https://www.conab.gov.br/component/k2/item/download/48631_7bd0e4f83fe9c70724f7f735e0a74bbf

Cunha, G. R. da, Pasinato, A., Pires, J. L. F., Dalmago, G. A., Santi, A., Gouvêa, J. A. de (2016). Bioclimatologia e zoneamento agrícola. In C. De Mori, J. M. Antunes, G. S. Faé, & A. da S. Acosta (Eds.), *Trigo: o produtor pergunta, a Embrapa responde* (p. 39). Embrapa.

De Mori, C. (2016). Aspectos comerciais e econômicos do trigo. In C. De Mori, J. M. Antunes, G. S. Faé, & A. da S. Acosta (Eds.), *Trigo: o produtor pergunta, a Embrapa responde* (p. 299). Embrapa.

Horwitz, W., & Latimer, G. W. (Eds.). (2007). *Official methods of analysis of AOAC International* (18. ed.). AOAC International.

Reunião da Comissão Brasileira de Pesquisa de Trigo e Triticale (2018). *Informações técnicas para trigo e triticale – safra 2018*. Coodetec.

Reunião da Comissão Brasileira de Pesquisa de Trigo e Triticale (2023). *Informações técnicas para trigo e triticale – safra 2023*. Embrapa. Retrieved from https://www.conferencebr.com/conteudo/arquivo/informacoestecnicastrigotriticalesafra2023-1683736866.pdf

Sgarbiero, E. (2001). *Resíduos de pirimifós-metil em grãos de trigo, milho e milho pipoca, em alguns de seus produtos processados e ação residual desse inseticida sobre Sitophilus spp. (Coleoptera, Curculionidae)*. (Master Dissertation). Escola Superior de Agricultura "Luiz de Queiroz" da Universidade de São Paulo, Piracicaba.

Vásquez-Castro, J. A. (2006). *Resíduos de fenitrotion e esfenvalerato em grãos de milho e trigo, em alguns de seus produtos processados e sua ação residual sobre Sitophilus oryzae (L., 1763), Sitophilus zeamais Motsch., 1855 (Coleoptera: Curculionidae) e Rhyzopertha dominica (Fabr., 1792) (Coleoptera: Bostrichidae)*. (Doctorate Thesis). Escola Superior de Agricultura "Luiz de Queiroz" da Universidade de São Paulo, Piracicaba.

Zoonen, P. Van (Ed.). (1996). *Analytical methods for pesticides residues in foodstuffs* (6. ed.). Ministery of Public Health Welfare and Sports, General Inspectorate for Health Protection.