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Pesticide residues in strawberries cultivated in the state of Rio Grande do Sul, Brazil

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ABSTRACT: Strawberries are of high social and economic importance and the crop is mainly produced at small family enterprises. Strawberries are repetitively amongst products in which unauthorized pesticide residues are determined. The PARA program launched in Brazil by ANVISA has disclosed that many samples have residues above the maximum residue limit (MRL). The present study appraised the pesticide residues detected in strawberries produced in the state of Rio Grande do Sul and marketed at the CEASA / RS. Along the harvesting seasons of 2018 and 2019, 62 strawberry samples were collected at the CEASA-pavilion destined for growers from the state of Rio Grande do Sul. Each sample was tested for 238 active ingredients of pesticides. Of the 62 samples retrieved, 40% were considered satisfactory and 60% resulted as unsatisfactory. Of the 25 satisfactory samples, three samples did not present any residues, and 22 had residues below the MRL. Of the 37 samples with an unsatisfactory outcome, 11 had active ingredients not allowed (NA) for use on strawberries, 13 presented active ingredients above the MRL and 13 reports presented the sum of both: residues above the MRL and NA. Thirty five different active ingredients were detected in the samples summing up to a total of 303 detection events. The active ingredients detected most frequently were procymidone (66.13%); carbendazim (53.22%) and difenoconazole (50%).

Key words: Fragaria x ananassa, agrochemicals, chemical contamination, food safety.

Resíduos de agrotóxicos em morangos produzidos no estado do Rio Grande do Sul, Brasil

RESUMO: A cultura do morangueiro tem grande participação econômica e social no estado do Rio Grande do Sul, especialmente devido a sua importância na agricultura familiar. No entanto, o morango está constantemente entre as principais culturas com resíduos de agrotóxicos não autorizados ou acima do limite máximo de resíduos no principal Programa de Análise de Resíduos de Agrotóxicos em Alimentos (PARA) do Brasil. O presente estudo teve por objetivo avaliar os resíduos de agrotóxicos encontrados em morangos produzidos no estado do Rio Grande do Sul comercializados na CEASA/RS. Nos anos de 2018 e 2019 foram coletadas 62 amostras de morangos no pavilhão destinado aos produtores gaúchos desta central de abastecimento. Cada amostra foi analisada para presença de 238 ingredientes ativos de agrotóxicos. Das 62 amostras, 40% foram consideradas satisfatórias e 60% apresentaram resultado insatisfatório. Das 25 amostras satisfatórias, três amostras não continham resíduos de agrotóxicos e 22 apresentaram resíduos abaixo do limite máximo de resíduos (LMR) estipulado pela ANVISA. Dos 37 casos de amostras insatisfatórias, 11 foram por ingrediente ativo não permitido para a cultura (NPC), 13 por ingrediente ativo acima do LMR e 13 laudos apresentaram o somatório de resíduos acima do LMR e NPC. Foram encontrados 35 diferentes ingredientes ativos nas 62 amostras de morango, totalizando 303 eventos de detecção. Os ingredientes ativos detectados com maior frequência nas 62 amostras de morango foram procimidona (66,13%); carbendazim (53,22%) e difenoconazol (50%).

Palavras-chave: Fragaria x ananassa, agroquímicos, contaminação química, alimento seguro.

INTRODUCTION

Global strawberry production doubled in an eighteen-year period: from 2001 up to 2019, the total 4.5 million metric tons (t) increased to 8.9 million t of fruit. Increments in the area of production fields were in the range of 21%, which means that average yields augmented from 13.7 t \cdot ha⁻¹ to 22.4 t \cdot ha⁻¹ (FAO, 2018).

Strawberry production is of high economic and social significance in Brazil. Most of the

strawberry fields are family operated enterprises (ANTUNES et al., 2016). The crop is very sensitive to pest and pathogen infestations and requires controls and cultural practices from start until the postharvest stages. The investment to establish a strawberry field is high and as such, the growers need constant vigilance to warrant an economic return of the activity. Therefore, the use of agrochemicals has become more common to secure yields, nonetheless, agrochemical sprays occur with insufficient precautions and adequate technically recommended procedures are

scarcer. These circumstances have inconveniences because of possible residue presence in fruit aside from the potential environmental impacts, effects on consumer health and, most importantly, the risks to growers directly exposed to agrochemicals (EMBRAPA, 2006).

The National Sanitary Vigilance Agency (ANVISA) of the Ministry of Health launched programs in Brazil to evaluate and divulge results of agrochemical residue analyses on horticultural crops to, mainly, improve unambiguousness and confidence in residue analyses. The PARA program (program of agrochemical residue analyses in food), since its start in 2001, has analyzed more than 35 thousand samples of 28 different vegetable crops (ANVISA, 2019).

The last PARA report in which strawberry samples were analyzed for residue presence was released in 2016. The samples are from the sampling period of 2013, 2014 and 2015, but only in 2014 strawberries were collected: 157 samples at national level. Of that total amount of samples, 110 samples presented agrochemical residues of non-authorized molecules for use in strawberry production and 41 samples had residues of active ingredients above the maximum residue limit (MRL) indicated by the legislation for strawberries. The overall outcome is that 72.61% of the samples had unsatisfactory results (ANVISA, 2016).

In the year of 2012, a Term of Conduct Adjustment (TAC) was settled in between the CEASA/RS (Central Supply Market of Porto Alegre) and the Ministério Público (MP = Public Ministry) to run residue analyses of produce commercialized only at the CEASA/RS premises. The MP took responsibility to act in response to media news and public concerns on the presence of agrochemical residues on produce marketed at the CEASA/RS. In the TAC, collected produce samples were analyzed at the Central Laboratory of Public Health (LACEN) of the state of Rio Grande do Sul. However, because of lack of personnel, financial resources and infrastructure the LACEN discontinued analyses in 2016.

From 2017 and onwards samples were directed to an accredited private laboratory. The costs of retrieval and analyses were covered by a partnership in between the CEASA/RS (carrying 30% of the costs) and Sebrae/RS (Brazilian Micro and Small Enterprises Support Service carrying 70% of the costs).

Therefore, the research scrutinized the agrochemical residue reports handed over by the accredited laboratory of strawberry samples commercialized at the CEASA/RS covered by the

TAC. The appraisal of the residue reports is intended to get hold of data on the main active ingredients used in strawberry fields in the state of Rio Grande do Sul and discuss the outcomes with all (growers, CEASA/RS personnel, MP, EMATER/State Extension Service, State Secretary of Agriculture, Supply and Rural Development, Ministry of Agriculture and University) to warrant lower percentages of unsatisfactory outcomes of pesticide residue analyses in the state of Rio Grande do Sul.

MATERIALS AND METHODS

The strawberry samples were retrieved at the CEASA-pavilion destined to growers from the state of Rio Grande do Sul, the southernmost state in Brazil. In that premises, which is exclusive for growers of the state, approximately 2,200 smallholders commercialize their crops (CEASA, 2019). That area was chosen to collect samples because of the characteristic of direct trade between growers and consumers reducing intermediaries in the postharvest handling chain that could interfere in the residue analyses.

A total of 62 strawberry samples were collected from August to November in two years: 39 samples in 2018 and 23 in 2019. In the last year of sampling, growers that had unsatisfactory results in the previous year were selected preferably to retrieve samples. All these growers had to attest that they had taken part in a training course in good agricultural practices offered by the state of Rio Grande do Sul extension service (Emater/RS) to continue commercialize at the CEASA-pavilion.

The collected samples at the CEASA-pavilion were transported under controlled temperature to the laboratory responsible for the agrochemical residues analyses. The whole process of retrieving samples, analyses and re-analyses followed standard operational procedures (POP) for agrochemical residue analyses established by ANVISA in 2008 and published in 2013 by the Brazilian Ministry of Agriculture, Livestock and Supply (MAPA) in the Manual to Collect Samples of the National Plan for the Control of Residues and Contaminants in Vegetable Crops.

The samples were prepared at the accredited laboratory and residues determined by High Performance Liquid Chromatography coupled to Mass Spectrometry (HPLC-MS) and Gas Chromatography coupled to Mass Spectrometry (GC-MS) based on standard operational procedures of the Official AOAC 2007-1 method. Every strawberry

sample was analyzed for the presence of 238 distinct active ingredients and their concentration is expressed either in ppm (parts per million) or mg kg⁻¹.

For the analysis of the reports from the 62 collected strawberry samples, electronic spreadsheets were generated as displayed in figure 1. These spreadsheets assist in the organization of the data and facilitate to recover information and standardization of the analysis of the data.

The data for the origin of the sample (county), day of sample retrieval and return of the residue report, presence, frequencies, and concentrations of identified active ingredients were organized and used to elaborate the present paper. Moreover, the system was conceived to homogenize the conferral and examination of the analytical reports. Data were disclosed to all involved in the process of residue analyses with the intention to perfect the system and to reduce the likelihood of human error in the different steps from sample retrieval up until disclosure of the results.

The analyses of the results were based on a descriptive statistical analysis involving organization, summarizing, and outlining of the data. The tools for that organization included frequency tables, graphs, relative amounts, and comparison of indicators used in pesticide residue analysis in food.

Figure 1 - Electronic spreadsheet elaborated for data transcription.

RESULTS

All the 238 active ingredients determined by the analyses are listed in table 1. The table also contains the minimal quantification limit (MLQ) of the analytical method and the maximum residue limit (MRL) for every active ingredient for strawberries in the regulation published February of 2020 by the National Health and Sanitary Surveillance Agency (ANVISA, 2019) of the Brazilian Ministry of Health. In the situation of a not established MRL for a specific crop, the active ingredient is considered unauthorized (NA) for that crop or, furthermore, with commercialization prohibited at a national level.

The analysis of the pesticide residue reports points towards several distinct results: satisfactory reports without pesticide residues or satisfactory reports with residues below de MRL. In the reports in which unsatisfactory results are indicated, the reasons for that outcome are: MRL beyond the maximum limit authorized for that crop, active ingredient not registered for use in that specific crop or active ingredient with its use prohibited in Brazil. And there is still the possibility of having more than one motive for an unsatisfactory outcome such as residues with a MRL higher than the authorized limit together with the presence of residues of active ingredients

*	REPOR	TS TRANS	CRIPTION	SPREADSHEET	7	
	KEI OK	IJ IIIAIIJ	CIVII HOIV			
REPORT				SAMPLE DATE		
GROWER				REPORT DATE		
CULTURE			REVISER			
COUNTY				REVIEW DATE		
			RESULTS			
ACTIVE IN	IGREDIENT	MLQ	(mg/kg)	MRL (mg/kg	5)	RESULT (mg/kg)
			·			•
•	•					
•	•		·			
			·			
SATISFACTORY	WITHOUT RESIDUES			WITH RESIDU	ES	
NSATISFACTORY	MRL		NA	P	ROHIBIDO	
MLQ = MINIMAL LIMIT OF	QUANTIFICATION	MRL = MAXIMI	UM RESIDUE LIMIT	NA = ACTIVE INGREDIEN	T NOT ALLOWE	D FOR THE CULTURE

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Table 1 - List of not-allowed active ingredients analyzed in 62 strawberry samples collected at the CEASA growers-pavilion in the years of 2018 and 2019 as regulated by ANVISA in February/2020.

2,4D	Clomazone	Fenamidone	Metalaxyl-M	Quizalofpop-P-Ethy
Acephate	Clothianidin	Fenamiphos	Metamitron	Rotenone
Acetamiprid	Coumaphos	Fenarimol	Methidathion	Simazine
Acibenzolar-S-Methyl	Cyanofenphos	Fenbuconazole	Methiocarb	Spinosad
Alachlor	Cyazofamid	Fenhexamid	Methomyl	Spirodiclofen
Allethrin	Cyfluthrin	Fenitrothion	Methoxyfenozide	Spiromesifen
Ametryn	Cyfluthrin beta	Fenothrin	Metribuzin	Spiroxamine
Aminocarb	Cymoxanil	Fenoxycarb	Monuron	Sulfentrazone
Asulan	Cypermethrin	Fenpropimorph	Myclobutanil	Sulfometuron methy
Atrazine	Cyproconazole	Fenvarelate	Neburon	Sulfosulfuron
Azaconazole	Cyromazine	Fipronil	Nitempyram	Sulfotep
Azinphos-Methyl	Dazomet	Flazasulforon	Nuarimol	Tebufenozide
Benalaxyl	Deltamethrin	Fluazifop-P-buthyl	Oxifluorfen	Tebufenpyrad
Bendiocarb	Diafenthiuron	Flufenoxuron	Paclobutrazol	Tebuthiuron
Bifenthrin	Diallate	Fluquinconazole	Paraoxon methyl	Temephos
Bioalethrin 1 & 2	Diazinon	Flusilazol	Penconazole	Terbufos
Bromacyl	Dichlofluanid	Flutriafol	Pencycuron	Tetraconazole
Bromuconazole	Dichlorvos	Folpet	Pendimenthalin	Tetradifon
Bupirimate	Dieldrin	Fonophos	Permethrin	Thiabendazole
Buprofezin	Diflubenzuron	Forchlorfenuron	Phosmet	Thiacloprid
Cadusafos	Dimethoate	Fostiazate	Picloran	Thiobencarb
Captan	Dimethomorph	Halosulfuron methyl	Picoxystrobin	Thiodicarb
Carbaryl	Diniconazole	Heptenophos	Pirimicarb	Thionazin
Carbosulfan	Disulfoton	Hexachlorobenzene	Pirimiphos ethyl	Tralkoxydim
Carboxin	Diuron	Hexazinone	Pirimiphos methyl	Triadimefon
Chlordane	Dodecachlor	Hexythiazox	Profenophos	Triazophos
Chlorfluazuron	Dodemorph	Imazalil	Prometryn	Trifloxisulfuron
Chlorimuron ethyl	Epoxiconazole	Imidacloprid	Propamocarb	Triflumizole
Chlorotalonyl	Esfenvarelate	Indoxacarb	Propiconazole	Trifluralin
Chlorpyrifos	Ethephon	Iprovalicarb	Propoxur	Zoxamide
Chlorpyriphos Methyl	Ethoprophos	Linuron	Pyraclostrobin	
Chlorthiophos	Etofenprox	Lufenuron	Pyriproxyfem	
Clethodin	Famoxadone	Malaoxon	Quintozene	

not authorized for use in a specific crop. The overall results of satisfactory and unsatisfactory reports in both 2018 and 2019 have some similarity (Figure 2).

Nonetheless, in a more detailed observation of the outcomes, two significant changes are noteworthy: the percentages of unsatisfactory results due to not-allowed active ingredients and the maximum residue limits beyond the concentration indicated in the regulation of the Agrofit/Ministry of Agriculture, Livestock and Supply (BRASIL, 2003). The reports with unsatisfactory results for not allowed active ingredients (NA) have decreased from 23% of the samples in 2018 to 9% of the samples in 2019, which is a very positive outcome. Conversely,

though, as a negative result is the increase from 13% to 35% of the reports in which samples presented residues above the maximum residue limit (>MRL). For conclusive results on the persistence of increases and decreases of percentages, more years of sampling for residue analyses need to be evaluated.

According to ANTUNES et al. (2007), the strawberry production system has migrated from open field production systems to production in protected environments. YURI et al. (2012) indicated that the use of plastic mulching was adopted in the early stages of strawberry production to reduce contact of aerial parts of the plant, including the fruit, with soils and to reduce hand labor to remove weeds.

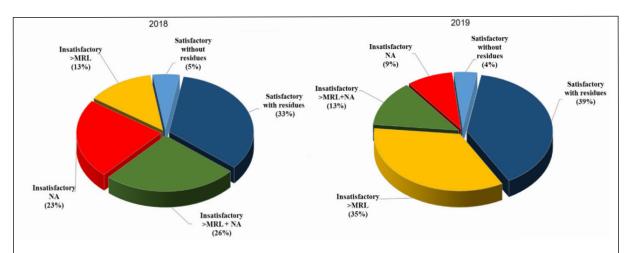


Figure 2 - Compilation of results of residue analyses reports of 2018 and 2019. Percentages of different outcomes of 39 samples collected in the first year (left panel) and out of 23 samples collected in 2019 (right panel).

Important to point out is that in many different trials a longer persistence of active ingredients has been demonstrated in protected cultivation systems. That observation could explain, in part, the fact that in the present report analyses, increments in active ingredient concentrations were determined even when the grace period and the concentration of the pesticide were abided according to the technical recommendations.

FRANK et al. (1987) in field experiments along two harvesting seasons with tomatoes were able to correlate the falloff of the active ingredient captan with the amount of rainfall in a period of 15 days. In opposition, the authors did not observe any reduction in captan residues in tomatoes cultivated in a protected environment in the first year of trials and; furthermore, in the second year of trials an increase in captan residue was determined in the tomatoes cultivated under protection. These results are also documented by SANTOS et al. (2002) with coffee plants submitted to artificial rainfall and a reduction in the active ingredient mancozeb, an important fungicide of the dithiocarbamate group, was determined.

According to CHAVARRIA & SANTOS (2013) in vineyards, precautions are necessary with the use of agrochemicals in protected cultivation systems. A 33% higher residue was detected in grapes growing under plastic covers. The conclusion of the authors pointed to less degradation of the molecules by incident radiation in comparison to open field systems. Additionally, there is also less

rain wash-off of the agrochemicals on aerial parts under plastic cover affecting, concurrently, the winemaking processes.

Even though the presence of residues of agrochemicals could be envisioned as a positive effect towards phytosanitary control of diseases and pests, these residues may enlarge considerably the waiting period (= grace period) of active ingredients considering the manufacturers' specifications in the labeling of the commercial formulation of the pesticide. In the shift to under plastic cover production systems, the growers might become as not conforming in residue analyses reports according to the guidelines on maximum residue limits. That likelihood arises from the aforementioned influence of the production system on decomposing elements of active ingredients enlarging the grace period for pesticides in crops growing in a protected environment. Consequently, the policies have to consider those circumstances to reduce the risks for growers and, ultimately, for consumers.

Amongst the 238 active ingredients tested in every strawberry sample, only 35 active ingredients were detected in the samples. These figures indicated that 303 detection events occurred in the 62 analyses reports, which end out with 4.89 active ingredients in every sample. When only unsatisfactory reports are dissected, then 221 detection events were observed in 37 reports rendering 5.97 active ingredients per sample. On contrary, looking into the reports with a satisfactory outcome an average of 3.28 active ingredients are present in every sample: 82 detections in 25 reports.

The active ingredients procymidone, carbendazim and difeconazole are the most frequent molecules detected in strawberry samples. All of them are fungicides and are present in 50% or more of reports. The most frequent insecticide was thiamethoxam present in 40.32% of the reports (Table 2). Also needs to be emphasized that the active ingredient carbendazim does not have a calculated MRL in the ANVISA monographs, only

the precursor of the molecule: thiophanate methyl for which a MRL of 0.5 ppm and waiting period of three days is indicated.

The ANVISA report of the year 2015 indicated that 48 different active ingredients were detected in 157 strawberry samples. Carbendazim was the most frequent (59%) active ingredient followed by azoxystrobin (50%) and difeconazole (38%). These same active ingredients are amongst

Table 2 - List of prohibited and authorized active ingredients as for 2020 ANVISA/panel of monographies in 62 strawberry samples collected at the CEASA growers-pavilion in the years of 2018 and 2019 with the minimal limit of quantification (MLQ expressed in mg kg⁻¹) and the maximum residue limit (MRL expressed in mg kg⁻¹). The panel of ANVISA/monographies on pesticides is continuously updated for online consulting.

Active Ingredient	MLQ	MRL	Active ingredient	MLQ	MRL
Abamectin	0.01	0.02	Iprodione	0.01	2
Aldicarb	0.01	Prohibited	Kresoxim methyl	0.01	1
Aldrin	0.01	Prohibited	Lambda cyhalothrin	0.05	0.5
Azinphos-Ethyl	0.01	Prohibited	Malathion	0.01	1
Azoxistrobin	0.01	0.3	Metconazole	0.01	0.1
Bitertanol	0.01	Prohibited	Methamidophos	0.01	Prohibited
Boscalid	0.01	5	Methoxychlor	0.05	Prohibited
Bromopropylate	0.01	Prohibited	Metolachlor	0.01	Prohibited
Carbendazim	0.01	0.5	Mevinphos	0.01	Prohibited
Carbofuran	0.01	Prohibited	Monocrotophos	0.01	Prohibite
Carbophenothion	0.01	Prohibited	Oxadixyl	0.01	Prohibite
Chlorfenapyr	0.01	2	Oxamyl	0.01	Prohibite
Chlorfenvinphos	0.01	Prohibited	Parathion ethyl	0.01	Prohibite
Clofentezine	0.01	Prohibited	Parathion methyl	0.01	Prohibite
Cyanazine	0.01	Prohibited	Phenthoate	0.01	Prohibite
Cyprodinil	0.01	1	Phorate	0.01	Prohibite
DDT	0.01	Prohibited	Phosalone	0.01	Prohibite
Demeton-S-methyl	0.01	Prohibited	Phosphamidon	0.01	Prohibite
Dicofol	0.05	Prohibited	Prochloraz	0.01	Prohibite
Dicrotophos	0.01	Prohibited	Procymidone	0.01	3
Difenoconazole	0.01	0.5	Propargite	0.01	0.5
Dithiocarbamates	0.07	0.2	Prothiophos	0.01	Prohibite
Endosulfan	0.01	Prohibited	Pyrazophos	0.01	Prohibite
Endrin	0.01	Prohibited	Pyridaben	0.01	0.1
Ethiofencarb	0.01	Prohibited	Pyridaphenthion	0.01	Prohibite
Ethion	0.01	Prohibited	Pyrifenox	0.01	Prohibite
Etrimfos	0.01	Prohibited	Pyrimethanil	0.01	2
Fenazaquim	0.01	Prohibited	Tebuconazole	0.01	0.7
Fenpropathrin	0.01	2	Teflubenzuron	0.01	1
Fenpyroximate	0.01	0.01	Thiamethoxam	0.01	0.1
Fenthion	0.01	Prohibited	Thiophanate methyl	0.01	0.5
Furathiocarb	0.01	Prohibited	Tolyfluanid	0.01	Prohibite
Heptachlor	0.01	Prohibited	Trichlorfon	0.01	Prohibite
Hexachlorocyclohexane	0.01	Prohibited	Trifloxystrobin	0.01	0.3
Hexaconazole	0.01	Prohibited	Vamidathion	0.01	Prohibite
Imibenconazole	0.01	0.5	Vinclozolin	0.01	Prohibite

the five most frequent of the present survey (ANVISA, 2016).

Another important aspect in the analysis of the data is the amplitude of residue concentrations detected in the samples (Table 3). In the table are detailed data on active ingredients with a satisfactory or not satisfactory outcome of the 62 strawberry samples collected.

Examining the data in table 4 it becomes evident that the active ingredient procymidone is

not only the most frequent active ingredient in the residue analyses report but also the chemical that presented the highest variation in concentrations: 0.02 ppm up to 12.35 ppm. Considering the MRL of 3 ppm for procymidone in strawberries reported in the ANVISA panel of monographs in 2020, the maximum concentration determined (12.35 ppm) is 312% higher than the maximum limit established by the residue legislation. However, out of the 41 detections of procymidone residues, 32 samples were

Table 3 - List of active ingredients, class of pesticide, number of detections and frequency in 62 strawberry samples retrieved from the Central Supply Market (CEASA Porto Alegre) in 2018 and 2019.

Active Ingredient	Class of pesticide	Detections	Frequency (%)		
Procymidone	Fungicide	41	66.1		
Carbendazim	Fungicide	33	53.2		
Difenoconazole	Fungicide	31	50.0		
Thiamethoxam	Insecticide	25	40.3		
Azoxystrobin	Fungicide	19	30.6		
Dithiocarbamate	Acaricide/Fungicide	18	29.0		
Boscalid	Fungicide	17	27.4		
Metalaxyl-M	Fungicide	12	19.4		
Pyrimethanil	Fungicide	10	16.1		
Fenpropathrin	Acaricide/Insecticide	9	14.5		
Kresoxim methyl	Fungicide	8	12.9		
Acetamiprid	Insecticide	7	11.3		
Lambda Cyhalothrin	Insecticide	7	11.3		
Propargite	Acaricide	7	11.3		
Tebuconazole	Fungicide	7	11.3		
Thiophanate methyl	Fungicide	7	11.3		
Teflubenzuron	Insecticide	6	9.7		
Fenpyroximate	Acaricide	5	8.1		
Pyraclostrobin	Fungicide	5	8.1		
Chlorfenapyr	Acaricide/Insecticide	4	6.4		
Pyridaben	Acaricide/Insecticide	4	6.4		
Cypermethrin	Insecticide	3	4.8		
Clothianidin	Insecticide	3	4.8		
2,4D	Herbicide	2	3.2		
Imidacloprid	Insecticide	2	3.2		
Trifloxystrobin	Fungicide	2	3.2		
Abamectin	Acaricide/Insecticide	1	1.6		
Chlorothalonyl	Fungicide	1	1.6		
Deltamethrin	Insecticide	1	1.6		
Spiromesifen	Acaricide/Insecticide	1	1.6		
Phosmet	Acaricide/Insecticide	1	1.6		
Metconazole	Fungicide	1	1.6		
Pyriproxyfen	Insecticide	1	1.6		
Propamocarb	Fungicide	1	1.6		
Triazophos	Acaricide/Insecticide	1	1.6		

^{*}MRL = maximum residue limit; ** NA – not allowed.

Table 4 - Occurrence and frequency of active ingredients detected in 62 strawberry samples collected at the Central Supply Market (CEASA-Porto Alegre) in the years of 2018 and 2019 for presence of pesticide residues. Number and percentage of satisfactory (Sat) and unsatisfactory (Ins) outcomes; lowest detected concentration (Cmin) and the maximum concentration (Cmax) of the active ingredient and the ratio Cmax/MRL

Active Ingredient	Sat (N)	Sat (%)	Ins (N)	Ins (%)	Total (%)	MRL* (ppm)	Cmin (ppm)	Cmax (ppm)	Cmax / MRL
Procymidone	32	78.0	9	21.9	66.1	3	0.02	12.35	4.12
Carbendazim	29	87.9	4	12.1	53.2	0,5	< 0.01	0.96	1.92
Difenoconazole	29	93.6	2	6.4	50.0	0,5	< 0.01	0.55	1.10
Thiamethoxam	18	72.0	7	28.0	40.3	0,1	< 0.01	0.8	8.00
Azoxystrobin	10	52.6	9	47.4	30.6	0,3	< 0.01	1.88	6.27
Dithiocarbamate	16	88.9	2	11.1	29.0	0,2	< 0.07	1.59	7.95
Boscalid	17	100	0	0.00	27.4	5	< 0.01	1.94	0.39
Metalaxyl-M	0	0.00	12	100	19.4	NA**	< 0.01	0.36	NA
Pyrimethanil	10	100	0	0.00	16.1	2	0.01	0.7	0.35
Fenpropathrin	9	100	0	0.00	14.5	2	0.01	1.92	0.96
Kresoxim methyl	8	100	0	0.00	12.9	1	0.02	0.13	0.13
Acetamiprid	0	0.00	7	100	11.3	NA	< 0.01	0.82	NA
Lambda Cyhalothrin	6	85.7	1	14.3	11.3	0,5	0.15	1.19	2.38
Propargite	7	100	0	0.00	11.3	0,5	< 0.01	0.3	0.60
Tebuconazole	7	100	0	0.00	11.3	0,7	< 0.01	0.18	0.26
Thiophanate methyl	6	85.7	1	14.3	11.3	0,5	< 0.01	1.41	2.82
Teflubenzuron	6	100	0	0.00	9.7	1	0.01	0.36	0.36
Fenpyroximate	3	60.0	2	40.0	8.1	0,01	< 0.01	0.17	17.0
Pyraclostrobin	0	000	5	100	8.1	NA	< 0.01	0.02	NA
Chlorfenapyr	3	75.0	1	25.0	6.4	2	0.12	2.22	1.11
Pyridaben	1	25.0	3	75.0	6.4	0,1	0.02	0.7	7.00
Cypermethrin	0	0.00	3	100	4.8	NA	0.02	0.69	NA
Clothianidin	0	0.00	3	100	4.8	NA	0.01	0.02	NA
2,4D	0	0.00	2	100	3.2	NA	< 0.01	< 0.01	NA
Imidacloprid	0	0.00	2	100	3.2	NA	< 0.01	0.34	NA
Trifloxystrobin	2	100	0	0.00	3.2	0,3	< 0.01	0.18	0.6
Abamectin	1	100	0	0.00	1.6	0,02	0.02	0.02	1.0
Chlorothalonyl	0	0.00	1	100	1.6	NA	1.7	1.7	NA
Deltamethrin	0	0.00	1	100	1.6	NA	0.04	0.04	NA
Spiromesifen	0	0.00	1	100	1.6	NA	0.58	0.58	NA
Phosmet	0	0.00	1	100	1.6	NA	< 0.01	< 0.01	NA
Metconazole	1	100	0	0.00	1.6	0,1	< 0.01	< 0.01	NA
Pyriproxyfen	0	0.00	1	100	1.6	NA	< 0.01	< 0.01	NA
Propamocarb	0	0.00	1	100	1.6	NA	0.04	0.04	NA
Triazophos	0	0.00	1	100	1.6	NA	< 0.01	< 0.01	NA

considered satisfactory, *i. e.*, with a residue limit below the maximum indicated by the legislation.

The active ingredient metalaxyl-M is not allowed for use in strawberry production, but the Agrofit/MAPA lists mixtures of that active ingredient in formulations with other active ingredients, also fungicides, for use in several other horticultural crops (BRASIL, 2020). Therefore, the technical orientation by

the extension service and private consultants is important to instruct growers on the correct use of pesticides.

The fungicide procymidone has by far reached the highest concentration in absolute figures amongst all the other active ingredients. In spite of that, the acaricide fenpyroximate surpassed by 1,600% the MRL authorized for strawberries. Likewise, thiamethoxam, the dithiocarbamates,

pyridaben, and azoxystrobin exceeded by more than 500% de MRL indicated by the ANVISA regulation.

The European Food Safety Authority (EFSA) through the European Union Commission of the *Codex Alimentarius* has established the maximum limit for fenpyroximate residues 30 times higher than the Brazilian regulation for that pesticide. Conversely, the fungicide thiophanate methyl has in Europe a MRL of 0.1 ppm, which is five times lower than the Brazilian legislation (0.5 ppm). The continual evaluation of data and toxicological tests in many countries might result in divergences such as those pointed out.

Aside the MRL, the waiting period has also significant disagreements. The active ingredient thiophanate methyl had its waiting period for strawberries reduced from 14 to three days via resolution RE number 1.141 of May 3rd 2018. Even for apples and also tomatoes and grapes the waiting period was not altered from the original 7 and 14 days, respectively. An unquestionable evidence of the inevitability of constant alertness on new regulatory releases.

CONCLUSION

Amongst the classes of pesticides, the fungicides represent 64.3% of detected residues. Insectides and herbicides are present in 35% and 0.7% of the collected samples, respectively. The active ingredients azoxystrobin, fenpyroximate, and pyridaben are the most frequent molecules with unsatisfactory outcomes for maximum residue limits in strawberries.

The official pesticide monitoring programs such as the program of residue analysis in food (PARA) provide data in order to lessen the likelihood of residue presence in produce such as strawberries and to assist the rural extension service to be more assertive in policies to reduce the risks for growers and, ultimately, to consumers.

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