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Pesticide Residues Evaluation in Pulp, Juice and Nectar of Fruits

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Abstract

Industrial processing of fruit in order to produce juice and nectar can contribute to over exposure of some contaminants, such as pesticide residues. Thus, this work aimed to check the compliance with the Maximum Residue Levels (MRL). In our research, 162 samples of frozen pulps, 16 of juice and 2 of nectar, were evaluated for pesticide residues, as well as the acceptable dietary intake (ADI). A multi-residue method was employed and almost 140 active ingredients were studied. Positive results were detected only in pulps, corresponding to 40% of the amount of samples. According to the Brazilian and the *Codex Alimentarius* legislation, none of the pesticide residues found were above the MRL. The most frequently found compounds were: pyridaphenthion, azinphos-methyl and carbendazim in peach and endosulfan in strawberry samples. Multiple findings were found in strawberry (29.6%) and peach (7.8%). Chronic dietary intake was not exceeded. The results demonstrated the necessity of pesticide residue control in fruit.

Keywords: pesticide, residue, fruit, pulp, juice, health risk

1. Introduction

In Brazil, the fresh fruit industrial processing to produce pulp, juice and nectar is an important agro-industry activity. Almost 1.6 million tones of juice are exported, being the orange juice the leader in the world trade. Such contribution corresponds to more than 80% of all fruit trading, what places Brazil as the main producer/exporter (Andrigueto, 2008).

Many fruits (tropical and temperate climate) are used in the industrial processing, such as banana, mango, orange, passion fruit, peach, pineapple and strawberry. The pulp has an extensive use in the food industry, especially when it comes to the production of nectar, juice, ice-cream, jelly and other fruit sweet products. Basically, the pulp is the product not fermented, which arose from the edible part of the fruit, after have being submitted to a typical process of cutting, milling and homogenization and preserved by a physical process as freezing. Following the pasteurization process, the pulp could be commercialized and used in juice or other preparations at restaurants, fast food restaurants, hospitals and also for home consumption.

It is important to highlight the fact that during the fruit production, 20 to 30 % is destroyed, especially by pests' activities (IBGE, 2003). Therefore, in order to prevent and control the pests, some techniques including the pesticide usage are frequently applied. According to Garcia et al. (2005) in Brazil there are 367 active substances, which are distributed to 1045 formulated products such as insecticides, fungicides, herbicides, among other categories, comprehending all toxicological classes. Quality controls such as pesticide residues evaluation are parameters that should be verified to guarantee health food for the consumers. The presence of such chemical substances in foodstuffs promotes a health and economic impact

Finally, samples of pulp, juice and nectar were evaluated by pesticide residues contamination as well as their contribution to health risk.

2. Material and Method

2.1 Chemicals and Samples

All organic solvents and reagents were analytical grade from Tedia or Merck. Pesticide standards were from Ultra Scientific, AccuStandard, Dr. Ehrenstorfer and Riedel-de-Haën with around 99% of purity.

The present study evaluated a total of 180 samples: 1. Pulp - acerola (5), apple (3), banana (3), caja (1), coconut (3), graviola (1), guava (4), mango (6), melon (3), papaya (4), passion fruit (16), peach (77), pear (5), pineapple (4) and strawberry (27), 2. Juice - guava (9), lemon (1) and orange (6), 3. Nectar - peach (2).

2.2 Quality Control

The validation study for the multiresidue method employed at Laboratorio de Residuos de Pesticidas (LRP) was accomplished with the criteria for analytical performance established from IUPAC Technical Report, 1999 (Thompson et al., 2002). The LRP participates in proficiency testing schemes on an annual basis with satisfactory performances. The recoveries are generally from 70 to 110%.

The concentrations were calculated using a calibration curve generated from peak area, obtained by the results of standard injections. The quantification limit for organochlorine pesticides were 0.001 mg/kg and 0.01 to 0.05 mg/kg for organophosphorus, carbamates, pyrethroids insecticides some herbicides and fungicides.

2.3. Methodology

The multi-residue method DFG S19 was employed (Specht, 1992 and Modular L.00.00.34) to check the contamination by pesticide residues. Almost 140 active ingredients were evaluated, including organochlorine, organophosphorus, pyrethroids, carbamates and others insecticides, some fungicides and herbicides.

In brief, the samples were committed, homogenized and an aliquot was extracted with acetone. Partitioning was employed with a solvent mixture of cyclohexane + ethyl acetate (1:1). The clean-up was performed using gel permeation chromatography (GPC) with Bio Beads® S-X3 polystyrene gel and an additional clean-up step with silica gel deactivated 1.5% was employed when necessary.

Identification and quantification of pesticides were carried out by GC with electron capture detector (ECD), nitrogen/phosphorus detector (NPD), flame photometric detector (FPD) and HPLC with UV/Vis and fluorescence detectors. All confirmations were carried out by LC/MS/MS.

Dithiocarbamates were determined by the DFG S15 (Specht, 1992), method with a modification using a vertical disulfide reaction system proposed by Caldas et al. (2000). An aliquot of 300 g of sample was heated with a solution of stannous chloride and hydrochloric acid. The carbon disulphide were distilled, purified and collected in an ethanol solution of cupric acetate and diethanolamide. A spectrophotometric method, using the visible range was employed for the determination of dithiocarbamates by CS_2 conversion.

Dithiocarbamates fungicides were analyzed employing the spectrophotometer to determine the CS_2 concentration (Caldas et al., 2001).

Positive results were compared with the Brazilian legislation (ANVISA, 2011) and international MRLs from *Codex Alimentarius* (CODEX, 2011).

Pesticide residue contribution to ADI (acceptable dietary intake) parameter was calculated employing the recommended World Health Organization procedure (GEMS/FOOD, 1997) and the results were calculated in mg/person/day or mg/body weight/day considering the body weight (b.w.) of an adult as 60 kg.

Dietary exposure = $\sum$ concentration of chemical in food ($mg.kg^{-1}$) x food consumption (kg)/ b.w.

The food consumption was evaluated according to data consumption from IBGE (2010) and GEMS/FOOD (2003) to regional diet.

The values from the dietary exposure were compared with the ADI (%ADI <100) and the percentage of pesticide residue contribution was calculated as follows:

% ADI = dietary exposure x 100/ADI

3. Results and Discussion

Positive results were observed only in pulp samples, corresponding to 40% of the total amount of samples. The results according to national and international legislation are presented at Table 1. None of the samples were contaminated by pesticide residues above the Maximum Residue Level (MRL) and pesticide residues below the MRL were found in 3.9% and 12.2%, according to Anvisa (2011) and *Codex Alimentarius* (2011).

The Table 2 presents the pesticide residues found in the samples, the levels and MRL from national and international legislation. The most frequent pesticide/commodity combination was: pyridaphenthion in peach (16), endosulfan in strawberry (15), azinphos-methyl in peach (12) and carbendazim in peach (10). According to the national and international legislation some of those, as azinphos ethyl, bromopropylate, carbaryl, chlorothalonil, dimethoate, endosulfan, pyridaphenthion, simazine and tetradifon have no MRL. Multiple findings were observed in strawberry and peach, 29.6% and 7.8%.

Table 1 Pesticide residues results according to the Brazilian and the *Codex Alimentarius* legislation

Fruit sample	Total sample	>MRL		<MRL		No MRL	
		BR	Codex	BR	Codex	BR	Codex
Acerola	5						
Apple	3			1			1
Banana	1						
Caja	1						
Coconut	3						
Graviola	1						
Guava	4					2	2
Guava	9 (juice)						
Lemon	1 (juice)						
Mango	6						
Melon	3						
Orange	6 (juice)						
Papaya	4						
Passion fruit	16						
Peach	77			1	18	47	30
Peach	2 (nectar)						
Pear	5						
Pineapple	4						
Strawberry	27			5	4	16	17
Total samples	180	0	0	7	22	65	50
Total %	100	0	0	3.9	12.2	36.1	27.8

Table 2. Pesticide residues levels found and the MRL from Brazilian and *Codex Alimentarius* legislation

Pesticide found	≤ 0.01	> 0.01-0.05	>0.05-0.2	>0.2-0.4	>0.4-0.8	> 0.8-1.0	MRL		Commodity
							BR	Codex	
Azinphos-ethyl		6					NPC	NPC	peach
Azinphos-methyl	2	6	4				NPC	2.0	peach
Bifenthrin	2						NPC	1.0	strawberry
Bromopropylate	1						NPC	NPC	strawberry
Captan			1	2	1		NPC	15.0	strawberry
Carbaryl	2	1					NPC	NPC	peach
Carbendazim	9		1				NPC	2.0	peach
		1	1				5.0	NPC	strawberry
Chlorothalonil	2	2					NPC	NPC	strawberry
Chlorpyrifos		1					1.0	NPC	apple
Diazinon			1				NPC	0.1	strawberry
Dimethoate			2	1			NPC	NPC	Guava and peach
Dithiocarbamates			1				2.0	NPC	peach
Endosulfan	7	7	1				NPC	NPC	strawberry
Fenpropathrin	1	1	1	1			2.0	NPC	strawberry
Fluazinam		2	2	1			2.0	NPC	strawberry
Folpet	1						NPC	15.0	strawberry
Iprodione		1	2	3			2.0	10.0	strawberry
Malathion		1	1				1.0	1.0	strawberry
Procymidone	2		4	1		1	3.0	10.0	strawberry
Pyridafenthion	6	10					NPC	NPC	peach
Simazine				1			NPC	NPC	strawberry
Tetradifon	2	2					NPC	NPC	strawberry

The results are very similar to those observed in fruit samples from national data (Gebara et al., 2005a, 2005b, 2008, Cantarutti et al., 2008, Ciscato et al., 2009, PARA, 2001-2009). International data from pesticide monitoring programs (FDA, 2007; EFSA, 2008), presented pesticide residues at or below the MRL (35%), above the MRL (2%) and with no detectable residues (60%).

Caldas and Souza, 2000, observed that some crops as rice, beans, fruit, especially citrus and tomato, were the most important in pesticide residue contamination, as well as the surpassing of the ADI parameter. The authors suggested that the Brazilian legislation does not contemplate the risk assessment during the pesticide registration process. The same scenery was observed by Enes et al. (2005).

The ADI parameter in this study was not exceeded in any samples. The greater value was observed only for azinphos-methyl in one peach sample (26.9%). The other compounds did not contribute more than 4% of ADI and < 0.5% considering the acute reference parameter (dimethoate, carbendazim, chlorpyrifos, endosulfan, folpet, captan, diazinon and malathion). It is worthwhile to point out that their contribution to health risk, even for the more sensible consumers, was not significant.

Jardim and Caldas (2009) attributed the differences in the ADI values between national and international data for some substances, as observed in this study (azinphos-methyl, carbaryl and carbendazim) to the differences in the toxicological criteria employed during the evaluation process by the governmental agencies. A surpass on ADI parameter does not represent pesticide residues above the MRL. In such case, the dietary data of consumption should be revised.

Multiple findings observed in peach and strawberry could contribute to a health risk for the consumers. Boobis et al. (2008) highlighted that the presence of compounds which belong to the same chemical group could contribute to a cumulative effect.

Pesticide residues studies provide an important data about food quality and food production. Currently in Brazil, fruit production is using the Integrated Production of Fruit (IPF), whose pesticide management contributes to reduce the pesticide contamination comparing to conventional agriculture (Andrigueto et al., 2005). Cruz et al. (2006) indicates the good agricultural practices as an important prerequisite in food production, suggesting that pesticide residues data are an input in such project.

4. Conclusion

In spite of the positive results found in the samples, the national and international MRLs were not exceeded. Most of the pesticides found in the samples corresponded to organophosphate group. Peach and strawberry samples were the most important commodities, which were contaminated by pesticide residues.

The ADI parameter evaluated in this study were not surpassed, all results were <100% of ADI. It could be emphasized that the samples did not contribute to a health risk. Some pesticides, according to the national and international legislation, do not have a MRL established to the crop and this result showed the necessity of a continuous evaluation of the pesticide usage, especially to the pulps of guava, peach and strawberry, which are prepared by a simple homogenizing process (peal and flesh).

The goal on fruit production is the continuous effort in quality and safe products for the consumers. Brazil, as a great producer and exporter, should associate this safe parameter in order to obtain sustainable fruit production, so that it can increase its participation on national and international market (Nacheruber et al., 2009; Sansavinf, 2006).

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