

EVALUATION OF ORGANOHALOGENATE PESTICIDE RESIDUES IN COMMERCIALY AVAILABLE ORANGES IN BRAZIL

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INTRODUCTION

Citrus crops are highly susceptible to pests and diseases. The organohalogenate pesticides correspond to one of the most important groups of pesticides used in Brazil and has been found in various cultures. The improper use of these chemicals may lead to occupational, environmental and food safety risks. Brazilian legislation allows the use of 61 pesticide active ingredients for citrus¹. Fruits destined for consumption should present only residues of authorized pesticides and be within the maximum residue limits (MRLs)².

OBJECTIVES

The work had as objective to determine organohalogenate pesticides residues in samples of “Pera” oranges, a sweet variety of oranges, predominant in Brazil, commercialized in São Paulo, as well as to estimate the contribution of risk to health of the consumer population.

MATERIALS AND METHODS

Were collected 57 samples of “Pera” oranges (2 Kg each) at consumption points in the regions: North, South, East, West and Central of São Paulo City during the period from August to December 2010. Sampling was according to FAO/WHO Codex Alimentarius Commission³. The method of analysis was the Analytical Methods for Pesticide Residues in Foodstuffs, Ministry of Health of Netherlands, with adaptations⁴. Sample (30g) previously ground was homogenized in Ultra-Turrax mixer with 30 ml of acetone for 1min. Next, added 60mL of dichloromethane: n-hexane (1:1) and agitated again in Ultra-Turrax mixer for 1min. The mixture was centrifuged and the supernatant was filtered with PTFE membrane of 0.45 µm and 0.2 ml was concentrated under nitrogen flow to dryness. The volume was completed to 1 mL with n-hexane and analyzed by gas chromatography. Agilent CG6890, detector µECD, column 5% phenyl 95% dimethylsiloxane). Results confirmed in Thermo Scientific TRACE GC Ultra, ECD detector, column 35% phenyl 65% phenyl dimethylsiloxane. The risk of organohalogenate pesticides intake was calculated, for adult population (60Kg) and children (15Kg), based on comparison of the highest values found in this work and the per capita food intake of 4.404 Kg/person/year (Instituto Brasileiro de Geografia e Estatística (IBGE POF-2008)⁵, with their respective ADIs.

RESULTS AND DISCUSSION

Were investigated 36 active ingredients of organohalogenate pesticides (3432 determinations), including isomers and metabolites compounds. Pesticide residues were found in 8 (14%) of the samples, including 3 from the east, 2 of the south, 1 of the west, one of north of São Paulo City and 1 of the central area, at levels ranging from 0.06 to 2.92 mg/Kg (Table 1). Of these, 2 (3.5%) samples were considered unsatisfactory,

because one contained a residue of bifenthrin (2.92 mg/Kg) above the MRL and the other in having the active ingredient myclobutanil (1.64 mg/Kg) of unauthorized use. Fenpropathrin and dicofol residues found in this study were also detected in the National Sanitary Control Agency's (ANVISA) - Program for Analysis of Pesticide Residues in Food (PARA)⁶ - in 2009 (N = 147) and in 2007 (N = 149), all within MRLs (Table 1).

Table 1. Pesticide residues in "Pera"orange (N = 57), LOD, LOQ, MRLs. Comparison of results with those of PARA 2007 (N = 149) and PARA 2009 (N = 147). 2008 data were not available.

Pesticides	LOD mg/kg	LOQ mg/kg	MRL mg/kg	Total samples >LQ	Results Min-Max mg/kg	PARA 2009 Total samples detected	PARA 2007 Total samples detected
Alachlor	0.03	0.06	NA	-	-		
Aldrin	0.005	0.01	NA	-	-		
Allethrin	0.1	0.2	NA	-	-		
Azoxystrobin	0.2	0.4	0.5	-	-		
Bifenthrin	0.03	0.06	0.07	2 (3.5%)	0.06-2.92	0	0
Cyfluthrin	0.2	0.4	NA	-	-		
Cypermethrin	0.2	0.4	NA	-	-		
Clofentezine	0.05	0.1	0.2	2 (3.5%)	0.1-0.2	Nan	Nan
Chlorfenapyr	0.005	0.01	0.5	-	-		
Chlorothalonil.	0.02	0.04	0.5	-	-		
Chlorpyrifos metil	0.01	0.02	NA	-	-		
DDT total	0.01	0.02	NA	-	-		
Deltamethrin	0.02	0.04	0.1	-	-		
Dicofol	0.01	0.02	5	2 (3.5%)	0.06	10 (6.8%)	18 (12.0%)
Dieldrin	0.005	0.01	NA	-	-		
Difenoconazole	0.3	0.5	0.5	-	-		
Endosulfan	0.005	0.01	NA	-	-		
Esfenvalerate	0.1	0.2	0.05	-	-		
Fenpropathrin	0.01	0.02	1	1 (1.7%)	0.1	1 (0.7%)	3 (2.0%)
Fenarimol	0.02	0.04	NA	-	-		
Folpete	0.1	0.2	10	-	-		
HCB	0.005	0.01	NA	-	-		
HCH total	0.03	0.06	NA	-	-		
Heptaclor	0.005	0.01	NA	-	-		
Heptachlor epoxide	0.005	0.01	NA	-	-		
Iprodione	0.2	0.4	NA	-	-		
Lambda-cyhalothrin	0.1	0.2	1	-	-		
Myclobutanil	0.2	0.4	NA	1 (1.7%)	1.64	0	0
Mirex	0.005	0.01	NA	-	-		
Oxyfluorfen	0.005	0.01	0.05	-	-		
Permethrin	0.1	0.2	NA	-	-		
Procimidone	0.01	0.02	NA	-	-		
Propiconazole	0.4	0.8	NA	-	-		
Tolyfuanid	0.01	0.02	NA	-	-		
Trifluralin	0.1	0.2	0.05	-	-		
Vinclozolin	0.005	0.01	NA	-	-		

LOD: Limit of Detection; LOQ: Limit of Quantification; MRL (Maximum Residue Limit)²; NA (not authorized); ND: Not detected (below of Limit of Detection); Nan: Not analyzed; PARA: Program for Analysis of Pesticide Residues in Food⁶

Unsatisfactory results indicate necessity of better application of Good Agricultural Practice and greater control in trade and use of formulated products. Bifenthrin, myclobutanil, dicofol, fenpropathrin and clofentezine residues showed percentages of risk estimates (Table 2), in decreasing order, in orange samples of studied regions, with greatest impact on children population. Consumption of fruits and vegetables has been encouraged, which may contribute to risk, by consumption increasing. The other organohalogenate results pose no risk to consumer population.

Table 2. Estimative of risk to health of the consumer population by “Pera” orange intake: children and adult population.

Organohalogenated Pesticides	Reference ADI* µg/kg bw/day	Highest residue found mg/kg	Estimated intake** µg/kg bw***day	Population	Estimated risk (% ADI)
Bifenthrin	20	2,92	0,587	Children	11.7
				Adults	2.9
Clofentezine	20	0,20	0,040	Children	0.8
				Adults	0.2
Dicofol	2	0,06	0,012	Children	2.4
				Adults	0.6
Fempropathrin	30	0,01	0,020	Children	0.3
				Adults	0.1
Myclobutanil	30	1,64	0,329	Children	4.4
				Adults	1.1

*ADI: Acceptable Daily Intake, according Codex Alimentarius (FAO/WHO)³ or ANVISA²

** Estimated intake, according IBGE-POF and the highest residues found mg/kg in this study;

*** bw: body weight - 60kg for adults and 15kg for children

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