

# **SURVEY OF ECD/GC ANALYZED PESTICIDE RESIDUES IN ORANGES AND APPLES AND ITS CONTRIBUTION TO PREVENTION HUMAN HEALTH RISKS OF CONSUMERS IN BRAZIL**

Maria Celeste CARDEAL DE OLIVEIRA, Viviane Emi NAKANO, Iracema de A. KIMURA, Tereza Atsuko KUSSUMI, Sonia Bio ROCHA, Vera Regina Rossi LEMES, Kennia Cristian WALDHLM, Reinaldo A RIBEIRO, Ana L. FARIA, Janete ALABURDA

Instituto Adolfo Lutz, São Paulo State Health Secretary, São Paulo, SP – Brazil  
Avenida Dr. Arnaldo, 355, CEP 01246-, São Paulo-SP, Brazil  
moliveir@ial.sp.gov.br; celestecardeal@yahoo.com.br

## **INTRODUCTION**

Fruits crops are highly susceptible to pests and diseases. Organochlorine, pyrethroids, pyrethrins, and triazoles pesticides correspond to important groups of pesticides used in Brazil and have been found in various cultures. The improper use of these chemicals may lead to occupational, environmental and food safety risks. Fruits destined for consumption should present residues of only authorized pesticides and be within the maximum residue limits (MRLs)<sup>1</sup>. This study was conducted to determine these pesticide residues by gas chromatography analyzes (GC) with micro- electron capture detection ( $\mu$ -ECD) in oranges and apples, basic fruits in Brazilian eating habits, and to estimate the risk to public health .

## **OBJECTIVES**

The work had as objective to determine these pesticides residues in samples of “Pera” oranges and apples samples (Gala and Fuji varieties) commercialized in São Paulo City, as well as to estimate the contribution of risk to health of the consumer population.

## **MATERIAL AND METHODS**

Were collected 57 “Pera” oranges and 108 apples samples Gala (N=54) and Fuji (N=54) varieties at consumption points in the regions: North, South, East, West and Central of São Paulo City during the period 2010 and 2011. Sampling was according to FAO/WHO Codex Alimentarius Commission<sup>2</sup>. The method was the Analytical Methods for Pesticide Residues in Foodstuffs, Ministry of Health Netherlands, with adaptations<sup>3</sup>. Sample (30g) previously ground was homogenized in Ultra-Turrax mixer with 30 ml of acetone during 1min. Added 60mL of dichloromethane: n-hexane (1:1) and agitated again in Ultra-Turrax mixer during 1min. The mixture was centrifuged and supernatant was filtered with PTFE membrane of 0.45  $\mu$ m and 0.2 ml was concentrated under nitrogen flow to dryness. Volume was completed to 1 mL with 1 mL of n-hexane and analyzed by gas chromatography. Agilent CG6890, detector  $\mu$ ECD, column 5% phenyl 95% dimethylsiloxane). Results were confirmed in Thermo Scientific TRACE GC Ultra, ECD detector, column 35% phenyl 65% phenyl dimethylsiloxane. The risk of pesticides intake was calculated, for adult population (60Kg) and children (15Kg), based on comparison of the highest values found in this work in oranges and apples and the per capita oranges intake of 4.404 Kg/person/year and apples intake of 2.375 Kg/person/year.(IBGE POF-2008)<sup>4</sup>, with their respective acceptable daily intakes (ADIs)

## RESULTS AND DISCUSSION

Were investigated 57 pesticide active ingredients in oranges and apples samples, 9405 determination results of ECD/GC analyzed pesticide residues, including isomers and metabolites compounds.(Table 1)

### [Table 1]

Pesticide residues were found in 8 (14%) of orange 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 nationwide ANVISA monitoring program – Program Analysis of Pesticide Residues in Food (PARA)<sup>5</sup> (N=147) and 2007 (N=149), all within MRLs (Table 1). In apples samples surveyed, pesticide residues were found in 7 (13.0%) of Gala apple samples and in 10 (18.5%) of Fuji apple samples at levels ranging from 0.01 to 8.16 mg/Kg. Four samples (3.7%) were considered unsuitable for consumption, from these three (2.8%) were Gala apples, 2 due to residues above the MRL and 1 with dieldrin which use is not allowed in the country and one Fuji apple sample (0.9%), with cypermethrin residue of unauthorized use (Table 1).

The estimated health risks by exposure to pesticides through oranges and apple intake are in Table 2 and Table 3.

### [Table 2]

### [Table 3]

Bifenthrin, myclobutanil, dicofol, fenpropathrin and clofentezine residues showed percentages of risk estimates in orange samples of studied regions, with greatest impact on children population (Table 2). The other results pose no risk to consumer population. The estimated health risks by exposure to pesticides through apple intake considering the highest residues values found and consumption data (POF-IBGE)<sup>4</sup> for adult and children population, were: cypermethrin (7.1% and 1.8%), dieldrin (4.3% and 1.1%), folpet (1.4 % and 0.3%), chlorothalonil (1.2% and 0.3%), and dicofol (0.4% and 0.1%), deltamethrin (0.3% and 0.07%), procymidone (0.08% and 0.02%) and difenoconazole (0.05% and 0.01%) (Table 3). Unsatisfactory results indicate necessity of better application of Good Agricultural Practice and greater control in trade and use of formulated products. The other compounds results pose no risk to consumers

## REFERENCES

1. Brasil. Ministério da Saúde. Agência Nacional de Vigilância Sanitária. Resolução RE nº. 165, de 29 de agosto de 2003. Determina a publicação do “Índice das monografias dos ingredientes ativos de agrotóxicos, domissanitários e preservantes de madeira”, Anexo I. Diário Oficial [da] Republica Federativa do Brasil, Brasília DF, 02 de set 2003. p.48-50 e atualizações. Available in [<http://www.anvisa.gov.br/toxicologia/index.htm>].
- 2 Food and Agriculture Organization of the United Nations. World Health Organization. Food Standards Programme. Codex Alimentarius Commission. Pesticide Residues in food. Methods of Analyses and Sampling. 2<sup>a</sup> ed. 2000; 2(A), Part.1.

- Instituto Adolfo Lutz (São Paulo – Brasil). Métodos físico-químicos para análise de alimentos. Capítulo XX – Resíduos de Pesticidas. 4ª ed. Brasília (DF): ANVISA; 2005: 683-701.
- Instituto Brasileiro de Geografia e Estatística (IBGE). Pesquisa de Orçamentos Familiares 2008. Sistema IBGE de Recuperação Automática-SIDRA. Available in [http://www.sidra.ibge.gov.br]. [Accessed in 07 April 2011].
- Agência Nacional de Vigilância Sanitária (Brasília – Brasil). Programa de Análise de Resíduos de Agrotóxicos em Alimentos (PARA). Relatórios de Atividades de 2008 e 2009. Gerência Geral de Toxicologia. Brasília (DF): ANVISA; 2009, 2010. Available in [http://www.anvisa.gov.br]. [Accessed in April. 2011].

**Table 1.** Pesticide residues in orange pear (N = 57), apples (N = 54 Gala and N = 54 Fuji), LOD, LOQ, MRLs, and results.

Pesticides	ORANGES					APPLES						
	LOD mg/Kg	LOQ mg/Kg	MRL mg/Kg	Total samples >LOQ	Results Min-Max mg/Kg	LOD mg/Kg	LOQ mg/Kg	MRL mg/Kg	Total samples >LOQ		Results Min-Max mg/Kg	
									Gala	Fuji	Gala	Fuji
Alachlor	0.03	0.06	NA	-	-	0.03	0.06	NA	-	-	-	-
Aldrin	0.005	0.01	NA	-	-	0.005	0.01	NA	-	-	-	-
Allethrin	0.1	0.2	NA	-	-	0.1	0.2	NA	-	-	-	-
Azoxystrobin	0.2	0.4	0.5	-	-	0.2	0.4	NA	-	-	-	-
Bifenthrin	0.03	0.06	0.07	2 (3.5%)	0.06-2.92	0.03	0.06	NA	-	-	-	-
Cyfluthrin	0.2	0.4	NA	-	-	0.2	0.4	NA	-	-	-	-
Cypermethrin	0.2	0.4	NA	-	-	0.2	0.4	NA	-	1	-	8.16
Clofentezine	0.05	0.1	0.2	2 (3.5%)	0.1-0.2	0.05	0.1	0.1	-	-	-	-
Chlorfenapyr	0.005	0.01	0.5	-	-	0.005	0.01	NA	-	-	-	-
Chlorothalonil	0.02	0.04	0.5	-	-	0.02	0.04	1	6	4	0.02-0.48	0.02-0.27
Chlorpyrifos metil	0.01	0.02	NA	-	-	-	-	-	-	-	-	-
DDT total	0.01	0.02	NA	-	-	0.08	0.08	NA	-	-	-	-
Deltamethrin	0.02	0.04	0.1	-	-	0.01	0.02	0.02	1	-	0.06	-
Dicofol	0.01	0.02	5	2 (3.5%)	0.06	0.01	0.02	5	-	-	-	-
Dieldrin	0.005	0.01	NA	-	-	0.005	0.01	NA	1	-	0.01	-
Difenoconazole	0.3	0.5	0.5	-	-	0.3	0.5	0.5	1	-	0.63	-
Endosulfan	0.005	0.01	NA	-	-	0.01	0.03	NA	-	-	-	-
Esfenvalerate	0.1	0.2	0.05	-	-	0.1	0.2	NA	-	-	-	-
Fenpropathrin	0.01	0.02	1	1 (1.7%)	0.1	0.01	0.02	1	-	-	-	-
Fenarimol	0.02	0.04	NA	-	-	0.02	0.04	0,05	-	-	-	-
Folpete	0.1	0.2	10	-	-	0.1	0.2	10	8	11	0.10-0.83	0.02-3.19
HCB	0.005	0.01	NA	-	-	0.005	0.01	NA	-	-	-	-
HCH total	0.03	0.06	NA	-	-	0.05	0.10	NA	-	-	-	-
Heptaclor	0.005	0.01	NA	-	-	0.005	0.01	NA	-	-	-	-
Heptachlor epoxide	0.005	0.01	NA	-	-	0.01	0.02	NA	-	-	-	-
Iprodione	0.2	0.4	NA	-	-	0.2	0.4	5	1	-	0.35	-
Lambda-cyhalothrin	0.1	0.2	1	-	-	0.1	0.2	NA	-	-	-	-
Myclobutanil	0.2	0.4	NA	1 (1.7%)	1.64	0.2	0.4	0.1	-	-	-	-
Mirex	0.005	0.01	NA	-	-	0.005	0.01	NA	-	-	-	-
Oxyfluorfen	0.005	0.01	0.05	-	-	0.005	0.01	NA	-	-	-	-
Permethrin	0.1	0.2	NA	-	-	0.1	0.2	NA	-	-	-	-
Procimidone	0.01	0.02	NA	-	-	0.01	0.02	2	-	1	-	0.19
Propiconazole	0.4	0.8	NA	-	-	0.4	0.8	NA	-	-	-	-
Tolyfluanid	0.01	0.02	NA	-	-	0.01	0.02	NA	-	-	-	-
Trifluralin	0.1	0.2	0.05	-	-	0.1	0.2	NA	-	-	-	-
Vinclozolin	0.005	0.01	NA	-	-	0.005	0.01	NA	-	-	-	-

LOD: Limit of Detection; LOQ: Limit of Quantification; MRL (Maximum Residue Limit); NA (not authorized)

**Table 2.** Pesticide residues in oranges surveyed (N = 57), ADI results and % risk

Pesticides	Reference ADI $\mu\text{g}/\text{Kg}/\text{bw}$	Highest residue found $\text{mg}/\text{Kg}$	Population	Estimated ADI $\mu\text{g}/\text{Kg}/\text{bw}$	
				Children	Adults
Bifenthrin	20	2.9	Children	0.587	11.7
			Adults		2.9
Clofentezine	20	0.2	Children	0.040	0.8
			Adults		0.2
Dicofol	2	0.06	Children	0.012	2.4
			Adults		0.6
Fempropathrin	30	0.1	Children	0.020	0.3
			Adults		0.07
Myclobutanil	30	1.6	Children	0.329	4.4
			Adults		1.1

ADI: Acceptable Daily Intake, according Codex Alimentarius (FAO/WHO)<sup>3</sup> or ANVISA<sup>2</sup>  
 Estimated intake, according IBGE-POF and the highest residues found  $\text{mg}/\text{kg}$  in this study;  
 bw: body weight - 60kg for adults and 15kg for children

**Table 3.** Pesticide residues in apples (N = 54 Gala and N = 54 Fuji), ADI results and % risk

Pesticides	Reference ADI $\mu\text{g}/\text{Kg}/\text{bw}$	Highest residue found $\text{mg}/\text{Kg}$		Population	Estimated ADI $\mu\text{g}/\text{Kg}/\text{bw}$		% Estimated Risk	
		Gala	Fuji		Gala	Fuji	Gala	Fuji
Cypermethrin	50		8.16	Children	3.54		7.10	
				Adults	0.88		1.8	
Chlorotalonil	30	0.48	0.27	Children	0.36	0.12	1.20	0.40
				Adults	0.09	0.03	0.30	0.10
Dicofol	2			Children		0.01		0.40
				Adults		0.002		0.10
Deltamethrin	10	0.06		Children	0.03		0.30	
				Adults	0.01		0.07	
Difenoconazole	600	0.63		Children	0.03		0.05	
				Adults	0.01		0.01	
Dieldrin	0,1	0.01		Children	0.004		4.30	
				Adults	0.001		1.10	
Folpete	100	0.83		Children	0.15	1.35	0.10	1.40
				Adults	0.04	0.35	0.04	0.030
Procymidone	100	0.19		Children		0.08		0.08
				Adults		0.02		0.02