CHLORINATED PERSISTENT PESTICIDES IN BLOOD SERUM OF BRAZIL ADULTS – AN OVERVIEW**

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INTRODUCTION

The intensification of agricultural production, industrialization and urbanization in Brazil have led to human exposure to multiple chemicals. In view of these facts, it becomes important to identify at risk - populations of exposure to contaminants such as persistent organochlorine pesticides because of its severe toxic effects for human health and risks to public health. Persistent organochlorines (aldrin, dodecachlor, dieldrin, DDT, endrin, heptachlor, HCH) were included in the POPs list, approved by the Stockholm Convention on Persistent Organic Pollutants (POPs,2001). São Paulo Metropolitan Region (SPMR), Rio de Janeiro and other regions of Brazil, Espírito Santo, São Paulo, Goiás and Bahia, have high urban population and present contaminated sites. Human biomonitoring is a used tool in environmental medicine to assess the level of internal exposure of the general population, groups and individuals to environmental pollutants. Blood donors constitute a group of healthy individuals and researches has shown that adequately represent the population (CERNA et al, 2007).

OBJECTIVES

The studies had as objective to evaluate exposure by persistent organochlorinated residues in adult populations of Brazil. The SPMR study had also as objective to provide subsidies for realization of the First Brazilian Survey of Populations Exposed to Chemical Substances.

METHODOLOGY

Study Population

Biological monitoring was conducted in blood serum for the determination of organochlorine pesticides of blood donors living in SPMR and of non-occupationally populations living in the states of Rio de Janeiro, Espírito Santo, São Paulo, Goiás and Bahia. All procedures complied with the ethical guidelines.

Analytical method

The methods were based on "Hexane extractable chlorinated insecticides in human blood", Dale et al. (1966) with modifications as described in Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples (EPA, 1980). In the SPMR study, external calibration curves, at least 7 levels of concentrations for each pesticide, were used to quantify pesticide residues, within the linear range of detector (Table 1): of 0,01 - 0,4µg/dL for HCB, α-HCH, γ-HCH, δ-HCH; of 0,04 - 1,0µg/dL for β-HCH; of 0,02 - 0,8µg/dL for heptachlor, heptachlor epoxide

(cis e trans), pp'DDE, dieldrin; of 0,03 - 1,6 µg/dL for op'DDE, op'DDD, pp'DDD, op'DDT, pp'DDT and of 0,04 - 1,7µg/dL for dodecachlor.

The identification and quantification were by CG/µECD for organochlorine pesticides and metabolites, totaling 8205 assays in SPMR study (Table 1).

Qualitative and quantitative analysis in the SPMR study:

- Identification and Quantification: GC Agilent 6890; VF-5MS (5% phenyl 95% dimethylsiloxane) fused-silica capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness); Injector temperature: 250°C, Detector: µECD, temperature: 310°C; Oven Temperature programmed for quantification: 60ºC (3min.), 20ºC/min to 200ºC, 3ºC/min, 280ºC, 290ºC (20min); Flow of carrier gas N_2, 1mL/min, Mode and injection volume: splitless, 2µL.

- Confirmation: CG Thermo Scientific Trace GC Ultra; VF-35MS (35% phenyl 65% dimethylsiloxane) fused-silica capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness); Injector temperature: 50°C, Detector: ECD, temperature: 310°C; Oven Temperature programmed for quantification: 60ºC (3min.), 10ºC/min, 220ºC, 3ºC/min., 280ºC; Flow of carrier gas N_2, 1mL/min, Mode and injection volume: splitless, 2µL.

Table 1. Concentrations of persistent organochlorine pesticides in SPMR blood serum (µg/dL)

Organochlorine pesticides	Mean (x)	SD	Median (Md)	Geometric Mean (MG)	Maximum value	P95	LOQ	Adult population not exposed References	
								Turci et al, 2010 (Novafeltria, Pavia, Italia)	Cruz and Lino 2003 (Coimbra, Portugal)
HCB	0.01	0.001	0.01	0.01	0.03	0.01	0.02	**0.03 (Md)**	
α-HCH	0.01	0.001	0.01	0.01	0.03	0.01	0.02	ND (LD=0.02)	**0.76 (mean)**
β-HCH	0.03	0.038	0.02	0.02	**0.45**	**0.07**	**0.04**	**0.05 (Md) 0.12 (máx)**	**0.16 (mean) 0.35 (max)**
γ-HCH	0.01	0.005	0.01	0.01	**0.12**	0.01	**0.02**	**0.01 (Md) 0.01 (max)**	**0.07 (mean) 0.48 (max)**
δ-HCH	0.01	0.014	0.01	0.01	**0.32**	0.01	**0.02**	-	-
Heptachlor	0.02	0.000	0.02	0.02	0.02	0.02	0.04	-	-
Heptachlor epoxide	0.04	0.000	0.04	0.04	0.04	0.04	0.08	ND **(LD=0.005)**	-
Dieldrin	0.02	0.000	0.02	0.02	0.02	0.02	0.04	-	-
o,p' DDE	0.04	0.000	0.04	0.04	0.04	0.04	0.08	**0.04 (max)**	-
p,p' DDE	0.05	0.085	0.02	0.03	**1.17**	**0.12**	**0.08**	**0.03 (Md) 0.20 (max)**	**0.16 (mean)**
o,p' DDT	0.04	0.000	0.04	0.04	0.04	0.04	0.08	**0.01 (Md)**	**1.54 (Md)**
p,p'DDT	0.04	0.004	0.04	0.04	**0.09**	0.04	**0.08**	**0.01 (Md) 0.07 (max)**	**1.88 (mean)**
o,p'DDD	0.04	0.000	0.04	0.04	0.04	0.04	0.08	-	-
p,p' DDD	0.04	0.000	0.04	0.04	0.04	0.04	0.08	ND **(LD=0.005)**	**1.20 (mean)**
Dodecachlor	0.08	0.000	0.08	0.08	0,08	0.08	0.16	-	-

Table 2: Serum concentration of OCPs (µg/dL) on blood donors (N=547) São Paulo SPMR, 2009.

	% > LOQ	Range	Limit of Quantification
HCB	0.18	< LOQ - 0.03	0.02
α-HCH	0.74	< LOQ - 0.03	0.02
β-HCH	10.70	< LOQ - 0.45	0.04
γ-HCH	0.18	< LOQ - 0.12	0.02
δ-HCH	0.37	< LOQ - 0.32	0.02
p,p'-DDE	31.18	< LOQ - 1.17	0.04
p,p'-DDT	0.74	< LOQ - 0.09	0.08

Table 3: Comparison of serum levels of β-HCH and p,p'-DDE (µg/dL) in non-occupationally exposed populations in other regions of Brazil and SPMR

State	β-HCH	p,p'-DDE	Reference
Rio de Janeiro		11.50	Almeida, 1972
Espírito Santo		11.70	Almeida, 1972
São Paulo	<LOQ	2.39	Fernícola and Azevedo, 1982
Goiás		1.00 – 100.00	Lara et al., 1987
Bahia	1.38	0.83	Carvalho, 1991
São Paulo	0.34	1.43	Minelli and Ribeiro, 1996
Rio de Janeiro		<LOQ – 0.44	Paumgartten et al., 1998
Rio de Janeiro	<LOQ	0.51	Mendonça et al., 1999
Rio de Janeiro	<LOQ	0.48	Mendonça et al., 1999
Rio de Janeiro		<LOQ – 1.02	Delgado et al., 2002
São Paulo - SPMR	< LOQ - 0.45	< LOQ - 1.17	2009 Cardeal de Oliveira et al.,2017

RESULTS AND DISCUSSIONS

The adult populations blood sampled showed similar profile levels of persistent pesticides in Brazil (Table 3). In the SPMR, concentrations levels of heptachior, heptachior epoxide, diedrin, o,p'-DDE, o,p'DDT, o,p'-DDD and Mirex were below the LOQ for all sample analyzed (Table 1). Only, β-HCH and p,p'-DDE were found in concentration levels above the limit of quantification, in a significant number of samples. In SPMR, all organochlorine pesticides had median levels lower than LOQs (0.02 to 0.16 µg/dL) (Table 1); β-HCH, and pp'DDE were found with higher frequencies (24% and 70%) and maximum levels of 0,45µg/dL and 1,17µg/dL, respectively (Table 1). After absorption, DDT is slowly metabolized to op' and pp'DDE, DDA and DDD. DDE is stored

in adipose tissue and excreted via the bile, urine and milk (KLAASSEM 2007). The analysis revealed that individuals with history of previous exposure to pesticides (working with pesticides) had p,p'DDE levels twice higher than those with no past exposure reported. No other organochlorines were found. International studies have shown pp'DDE levels in blood serum of exposed and unexposed population (Cruz et al 2003; CHARLIER & Plomteux 2002). However, higher levels of pp'DDE indicate earliest exposure (ZHOU et al 2006). These data are consistent with the values of pp'DDE being significantly higher among those people who had reported occupation with pesticides in the past. In Brazil there are no established benchmarks for organochlorines pesticides in human serum (Brazil 1994).

CONCLUSIONS

The data obtained in these studies represent significant contributions to the knowledge of the levels of organochlorine pesticides in adults of Metropolitan Area of São Paulo and of other regions of Brazil. The results provide integrated actions to health control authorities in order to reduce human exposure to chemical contaminants, to prevent or minimize the risks and viabilize the implementation of the First National Survey of Populations Exposed to Chemical Substances, under general coordination of CGVAM / SVS / MS.

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