ORGANOCHLORINE PESTICIDES LEVELS AND ASSOCIATED FACTORS IN THE POPULATION OF THE METROPOLITAN REGION OF SÃO PAULO - BRAZIL*

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INTRODUCTION

The former worldwide use of organochlorine pesticides is a Public Health concern given that the presence of high levels of these compounds in humans can lead to serious health problems.

OBJECTIVES

The study had as objective to evaluate exposure to persistent organochlorinated pesticide residues in the adult population from the Metropolitan Region of São Paulo (MRSP) and provide subsidies for realization of the First Brazilian Survey of Populations Exposed to Chemical Substances.

This research aimed to evaluate 15 organochlorine pesticides in the serum of 547 blood donors and to investigate factors associated with the levels of these compounds.

MATERIAL and METHODS

Study group:

Blood donors (N = 547) aged 18 to 65 from nine blood donation centers in the Metropolitan Region of Sao Paulo (MRSP)

Analytical method:

Hexachlorobenzene (HCB), hexachlorocyclohexane (HCH): α, β, γ and δ isomers, dieldrin, heptachlor, heptachlor epoxide, dodecachlor, o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE and p,p'-DDE were determined by gas chromatography with μ-eletron capture detection, according Dale (1966) and EPA Manual(1981), with modifications.

The mean recoveries at the limit of quantification level were in the range of 62 - 116% and the relative standard deviation for five replicate samples was 1.8 - 18.4%.

The limit of quantification (LOQ) was 0.02µg/dL for HCB, α-HCH, γ-HCH, and δ-HCH; 0.04µg/dL for β-HCH, heptachlor, dieldrin, and p,p'-DDE; 0.08µg/dL for heptachlor epoxide, o,p'-DDE, o,p'-DDT, p,p'-DDT, o,p'-DDD, and p,p'-DDD; and 0.16µg/dL for dodecachlor.

Qualitative and quantitative analysis

	Column	**Instrument**	**Chromatographic conditions**
Identification and Quantification	**VF-5MS** (5% phenyl 95% dimethylsiloxane) fused-silica capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness)	GC Agilent 6890	**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); **Carrier gas** N_2, Flow of 1mL/min, **Mode and injection volume**: splitless, 2µL.
Confirmation	**VF-35MS** (35% phenyl 65% dimethylsiloxane) fused-silica capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness	CG Thermo Scientific Trace GC Ultra	**Injector** temperature: 250°C, **Detector: ECD**, temperature: 310°C, **Oven** Temperature programmed for quantification: 60ºC (3min.), 10ºC/min, 220ºC, 3ºC/min., 280ºC; **Carrier gas** N_2, Flow of 1mL/min, **Mode and injection volume:** splitless, 2µL.

RESULTS AND DISCUSSION

The concentrations of the pesticide residues of heptachior, heptachior epoxide, diedrin, o,p'-DDE, o,p'DDT, o,p'-DDD and Dodecachlor were below the LOQ for all sample analyzed and are not reported on **table 1.** All other compounds are shown on **table 1.**

Table 1 – Serum concentrations of organochlorine compounds (μg/dL) on a group of blood donors from MRSP.

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

LOQ = limit of qualification

Only pesticide residues of β-HCH and p,p'-DDE were found in concentration levels above the limit of quantification, in a significant number of samples.

The mean β-HCH concentration was 0.028 μg/dL and mean p,p'-DDE concentration was 0.045 μg/dL, **figures 1 and 2**

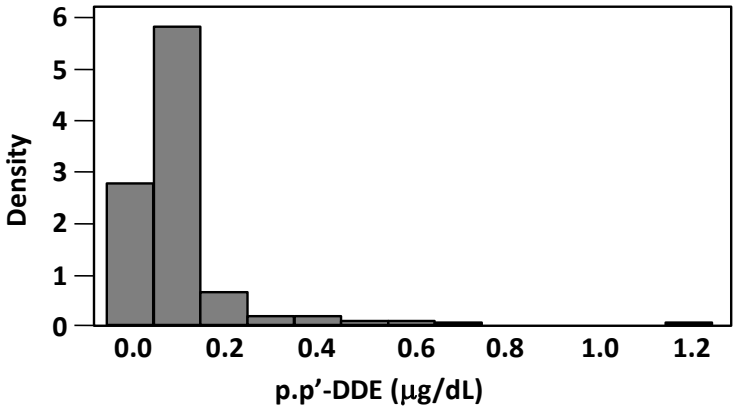

Figure 1– Distribution of samples above the LOQ for p,p'-DDE residues

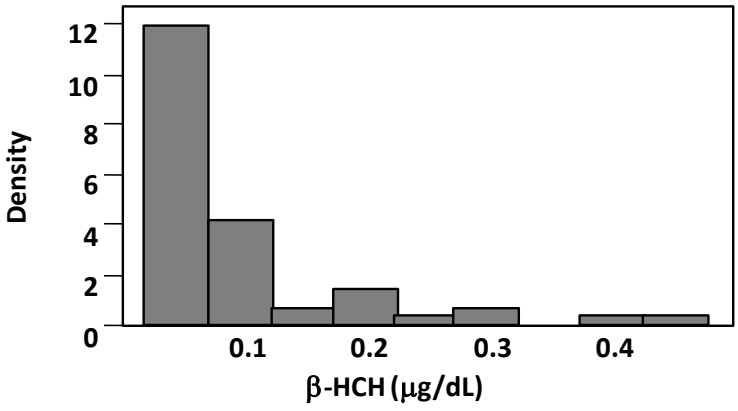

Figure 2 – Distribution of samples above the LOQ for β-HCH residues

Table 2 – Multiple regression linear for p,p'-DDE residues results in serum of blood donors

Variables	Exp (β)	p-value
Gender: Male (ref= female)	0.78	0.018
Color: non white	1.27	0.020
Worked with pesticides: Yes	1.78	0.005
Alcohol intake: yes	0.75	0.024
Water source (ref= piped)		0.019
Bottled	0.99	0.995
Alternative	2.03	0.008

Higher concentration levels of β-HCH residues were mainly associated with past occupational exposure and diet, while p,p'-DDE residues concentration levels were strongly associated with past exposure to pesticides and water sources. Gender had an important association with both compounds, females having higher residues concentration levels than males.

Table 3 – Multiple regression linear for β-HCH results in serum of blood donors

Variables	Exp (β)	p-value
Gender: Male (ref= female)	0.80	0.001
Previous contact with pesticides: Yes	1.29	0.004
Worked as a pesticide applicator in public health campaigns: Yes	2.27	0.001
Worked in capacitors or transformers companies: Yes	3.06	<0.001
Worked in chlorinated solvents industry: Yes	1.39	0.049
Income in minimum wages (ref= 1)		0.009
1 to 3	0.73	0.004
3 to 5	1.46	0.009
5 to10	0.95	0.772
Seafood consumption up to twice per week (ref = never)	1.18	0.020
Meat consumption (ref= never)		0.003
Up to twice per week	1.73	0.005
More than twice per week	0.99	0.943
Frequent beer consumption (ref= rarely)	0.32	0.001

CONCLUSION

The data obtained represent significant contribution to the knowledge of organochlorine pesticides residues levels in adults of Metropolitan Area of São Paulo.

References

1. Brasil, Ministério do Trabalho. Secretaria de Segurança e Saúde no Trabalho. Portaria nº 24 (NR-7), de 29/12/1994, D.O.U. de 30/12/94, Seção 1: 21278-280.
2. CETESB. Companhia de Tecnologia de Saneamento Ambiental - Relação de áreas contaminadas do Estado de São Paulo. Update in December 2012. http://www.cetesb.sp.gov.br/areas-contaminadas/relacoes-de-areas-contaminadas/15-publicacoes.
3. CERNÁ M, SPĚVÁCKOVÁ V, BATÁRIOVÁ A, ET AL. Human biomonitoring system in the Czech Republic. Int J Hyg Environ Health. 2007; 210(3-4):495-9
4. CHARLIER JC, PLOMTEUX GJ. Determination of organochlorine pesticide residues in the blood of healthy individuals. Clin Chem Lab Med. 2002; 40 (4): 361-364.
5. CRUZ S, LINO C, SILVEIRA MI. Evaluation of organochlorine pesticide residues in human serum from an urban and two rural populations in Portugal. The Science of the Total Environment 2003; 317:23-35.
6. DALE, W.E., CURLEY, A. and CUETO, C., Hexane extractable chlorinated insecticides in human blood. Life Sciences, 5:47, 1966. In Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples, Environmental and Protection Agency, 5A, (3), (a), rev. 1979. Manual of Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples, 2nd revision. 1981. Available at https://nepis.epa.gov/Exe/ZyNET.exe/ nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=30000EN6.TXT
7. KLAASSEM CD EDITOR. Casarett and Doull's Toxicology The Basic Science of Poisons, New York, 17th Ed., Mac Graw Hill Medical, 2007.
8. POPs - Persistent Organic Pollutants, 2001: Text of the Convention of POPs, Stockholm, Sweden,.22 May 2001. http://chmpps.int/The Convention/Overview/TextotheConvention/tabid./2232/Default.aspx.
9. TURCI R. ET AL. A simple and fast method for the determination of selected organohalogenated compounds in serum samples from the general population. Toxicology Letters, 192 (2010) 66-71.
10. ZHOU R, ZHU L, YANG K, CHEN Y. Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. Journal of Hazardous Materials A. 2006; 137: 68-75.
11. DO NASCIMENTO, F.P., KUNO, R., LEMES, V.R.R., NAKANO, V. E., ROCHA S. B., CARDEAL DE OLIVEIRA, M. C. KIMURA, I.A., GOUVEIA N. Organochlorine pesticides levels and associated factors in a group of blood donors in São Paulo. Environmental Monitoring and Assessment 2017 Aug; 189(8): 380

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