

# Organochlorine pesticides residues in marketed tomato, Mérida-Venezuela.



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## Abstract.

In order to maintain a high production yield is necessary the use of pesticides as a conventional agricultural practice. Governments and international organizations have regulated the use of pesticides, setting maximum levels for pesticide residues (MRLs) in foods, but the incorrect application of chemicals may leave harmful residue above MRLs, which involve possible environmental and public health risk. This study determined the presence of organochlorine pesticide residues in tomatoes sold in different local marketing (municipal markets, supermarkets, and other retail stores) of the Libertador Municipality in Mérida city, Venezuela. The results reveal the presence of DDT in the majority of tomato samples analyzed, although the use of these organochlorine pesticide are banned in this country.

## INTRODUCTION

The presence of chemicals residue in food are gaining increasing importance, due to the lack of government inspections and awareness of the agricultural producer and consumer about this matter. As a consequence, food consumers are face to face with food products which could have high residue levels of pesticides. Considering the Venezuela case, the monitoring of pesticides in foods is limited and poorly implemented, despite being a country with an extensive agricultural production. The tomato crop is an important food in the Venezuelan diet, nevertheless there are not enough data concerning their pesticide content. Therefore, the aim of this investigation is to determine organochlorine pesticides residues in tomato samples randomly purchased from different local marketing channels of the Libertador's Municipality in Mérida city, Venezuela. The use of organochlorine pesticides (OCPs) has been banned in more developed countries as they constitute an important group of dangerous organic contaminants due to their low biodegradability and persistence. The analysis was carried out by gas chromatography with electron capture detector (ECD). The extraction of the samples was realized by liquid-liquid extraction and cleanup by column chromatography. All tomato samples showed organochlorine pesticide residues.

## EXPERIMENTAL METHODOLOGY

### Reagents, solvents and standard reference.

Ethyl acetate (Mallinckrodt, HPLC chroma, 99.9%), anhydrous sodium sulfate (Riedel de Haen, 99%), sodium chloride (Riedel de Haen, 99.5%). Organochlorine mixture, Dr. Ehrenstorfer, 1000 mg / 1 mL mix in hexane, containing: Alpha-HCH, beta-HCH, gamma-HCH, delta-HCH, heptachlor, aldrin, heptachlor-epoxide, alpha-endosulfan, dieldrin, endrin, beta-endosulfan, DDE, DDD, endrin aldehyde, endosulfan sulfate, DDT, and methoxychlor.

### Sampling and Extraction procedure.

The tomato samples were taken in the major shops and markets in the Libertador Municipality of Mérida State, which the highest influx of consumers. We sampled approximately 200 g of tomato in a total of 8 shops. Each tomato sample was washed and homogenized, and 20 g of sample was mixed with 50 mL of ethyl acetate and 0.4 g NaCl. The mixture is left stirring for 30 min. Subsequently, is filtered, and dried with sodium sulfate anhydride. The extract is evaporated to 1 mL at 40 °C in a rotating evaporator and then passed through a column containing neutral alumina and eluted with 20 ml hexane, evaporated again to 2 mL and analyzed by gas chromatography.



### Method validation.

The determination was made in a Varian 3800 Gas chromatograph, with a WCOT Capillary column (CP-Sil 8 CB, 30m, 0.25 mm ID), equipped with <sup>63</sup>Ni electron capture detector and 1079 injector in splitless mode. Working conditions are present in table 1. Quantification of organochlorine pesticides was performed from calibration curves, constructed with external standards at different concentration levels (0.003 to 0.025 mg/Kg) for each pesticide analyzed under identical operating conditions. The figure 2 shows a chromatogram of the OCPs mixture studied. All pesticides analyzed show correlation coefficients exceeding 0.99 in the concentration range studied (see Table 2). The accuracy was evaluated considering the recovery percentage of OCPs made in tomato without pesticide residues at two levels of concentration (0.005 and 0.025 mg/Kg). The recovery percentages for each concentration level of OCPs studied are between 60 and 107 % for most of the pesticides under study. The detection and quantification limits obtained for each of the pesticides studied are shown in Table 2. The detection limits are between 0.003 and 0.005 mg/Kg, whereas the quantification limits are between 0.005 and 0.007 mg /Kg.

## RESULTS

All tomato samples tested showed some type of pesticide compounds. The pesticide found more frequently in tomato samples analyzed is DDT followed by the gamma-HCH, Aldrin and endosulfan sulfate. The ratio of these pesticides is shown in Figure 1. The concentration of certain pesticides for each sample are shown in Table 3. This table shows that the values of HCH and Aldrin exceed limits for pesticide residues in foods by the European Union in two of the sampled studied. Several samples have pesticide residues unknown.

## CONCLUSIONS

OCPs presence in tomato marketed in Mérida reveals the application of these banned pesticides in crops. DDT is present in the 83% of the tomato samples analyzed. Aldrin and HCHs are present above the MRLs in some of the samples studied. DDE and DDD are not present in the tomato samples studied revealing recent application of DDT.



Table 1. Chromatographic conditions.

Injector	200 °C
Detector	300 °C
column temperature	80 °C (1 min), 150 °C to 20 °C / min (1 min), 200 °C to 2 °C / min (5 min) 280 °C to 20 °C / min (5 min)
Gas carrier	Helium, linear flow of 1 mL / min
Injection volume	1 µL

Table 2. Parameters obtained from the calibration curve, limit of detection and quantification (mg/Kg) for each of the OCPs analyzed..

No.	Pesticide	tr	Range	Equation	r <sup>2</sup>	LOD	LOQ
1	α-HCH	12.53	0,003-0,025	y = 2721.9 x - 8061.4	0.996	0,001	0,002
2	γ-HCH	14.33	0,003-0,025	y = 2518.4 x - 8291.9	0.993	0,002	0,003
3	Δ-HCH	16.84	0,003-0,025	y = 2234.4 x - 16244	0.993	0,005	0,007
4	Heptachlor	18.17	0,003-0,025	y = 3055.4 x - 7254.7	0.992	0,001	0,002
5	Aldrin	20.45	0,003-0,025	y = 2968.8 x - 5268.7	0.991	0,001	0,002
6	Heptachlor-epoxide	23.46	0,003-0,025	y = 2693.4 x + 4646.6	0.991	0,001	0,003
7	Endosulfan I	26.10	0,003-0,025	y = 2576.1 x + 1158	0.993	0,001	0,002
8	Endrin	29.84	0,003-0,025	y = 2230.2 x + 5187.4	0.991	0,003	0,007
9	Endosulfan II	31.13	0,003-0,025	y = 2246 x + 3768.3	0.980	0,001	0,002
10	4,4'-DDD	31.97	0,003-0,025	y = 1548.6 x + 2320.5	0.995	0,002	0,005
11	Endrin aldehyde	32.51	0,003-0,025	y = 1702.4 x - 6393.6	0.995	0,003	0,004
12	Endosulfan Sulfate	34.87	0,003-0,025	y = 1527.7 x + 7069.1	0.975	0,001	0,004
13	p,p' DDT	35.35	0,003-0,025	y = 1584.7 x - 6111.3	0.963	0,001	0,004

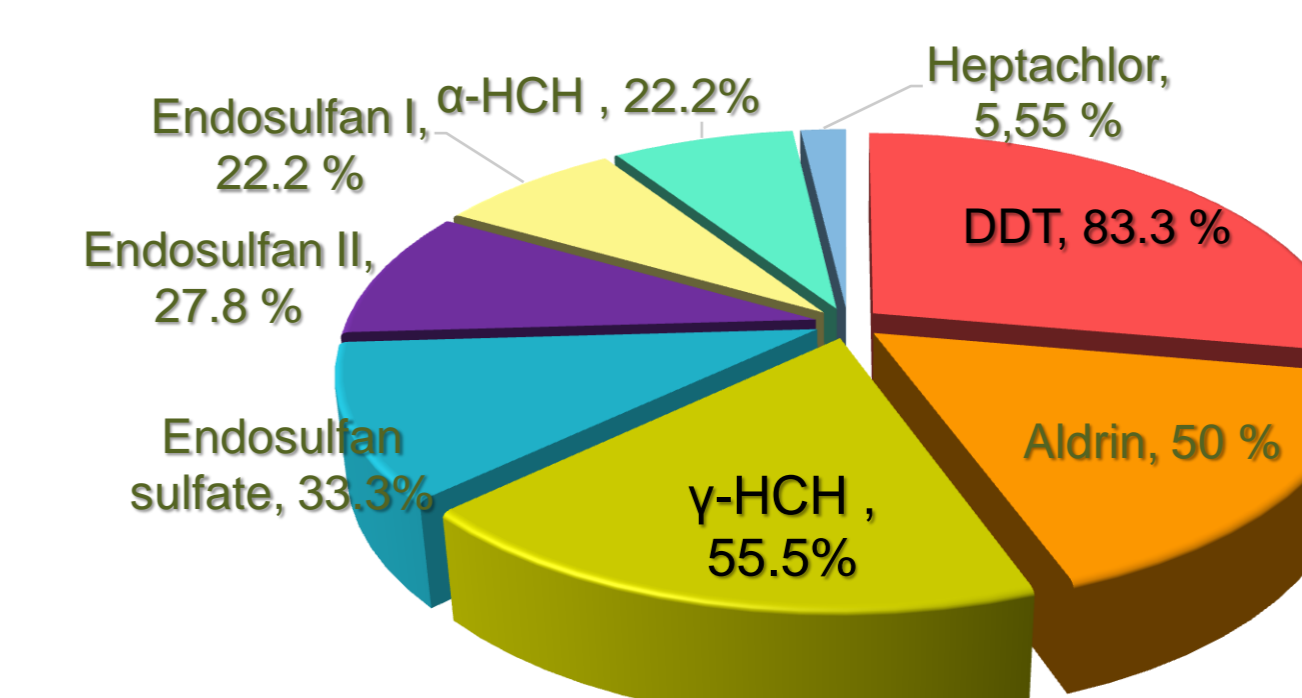


Figure 1. Proportion pesticides found in samples of commercial tomato analyzed.

Table 3. Concentration of organochlorine pesticides (mg/kg) identified in tomato acquired at different shops.

Pesticide/ Markets	Aldrin	DDT	Endosulfan	HCH	γ-HCH
A	-	0.006	-	0.012	-
B	0.015	0.009	0.004	0.002	0.012
C	0.005	0.008	0.009	0.003	-
D	0.005	0.018	0.001	0.006	-
E	0.002	0.024	-	0.038	-
F	0.001	0.016	-	-	0.005
G	0.002	0.015	0.055	-	0.004
H	0.002	0.010	0.022	0.008	0.014

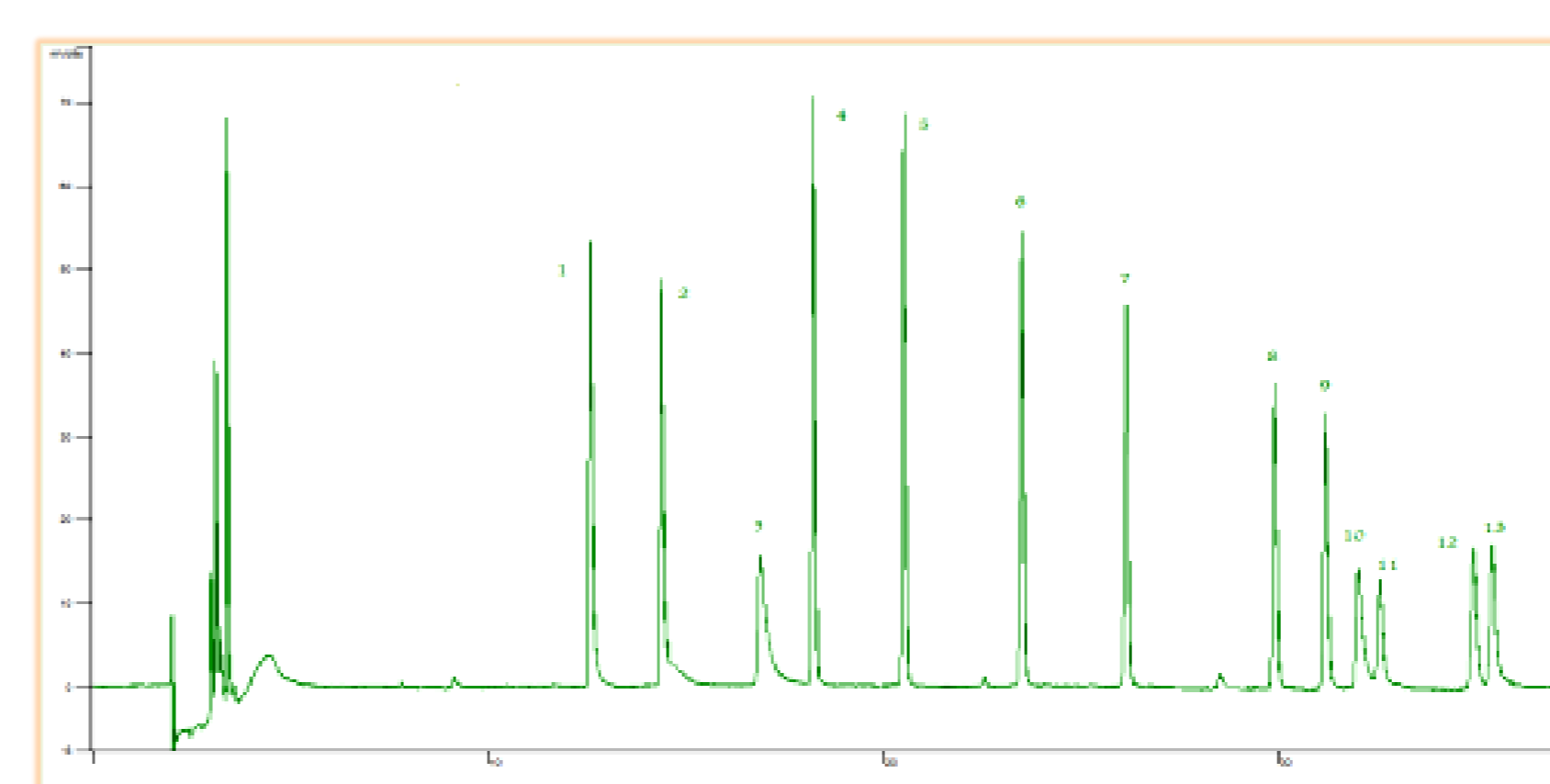


Figure 2. Chromatogram of a mixture of OCPs.

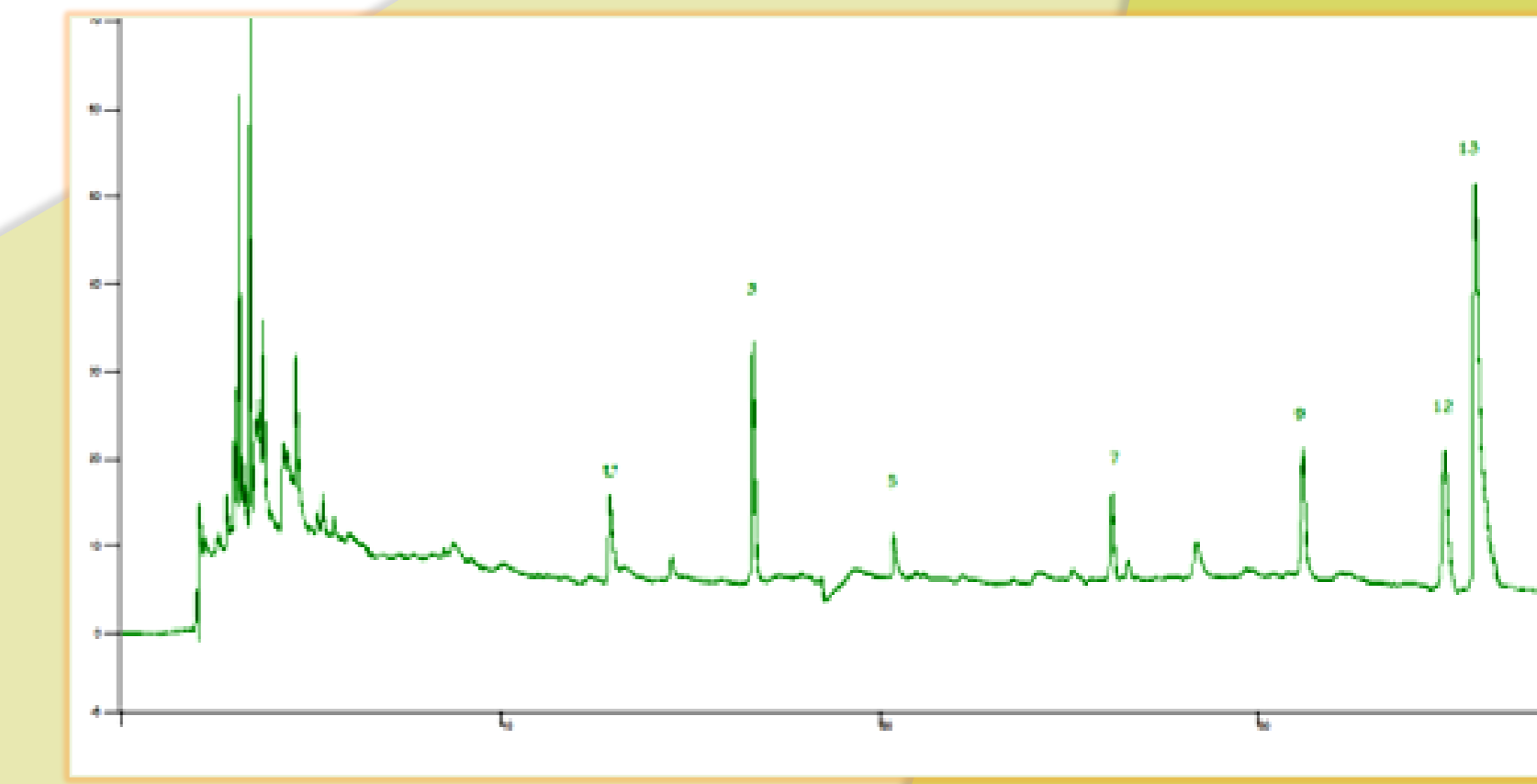


Figure 3. Chromatogram of samples taken at the market tomato C.