

## PERSISTENT ORGANOCHLORINE PESTICIDES IN BOVINE MEAT AND MILK FROM VERACRUZ (MEXICO)

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### Abstract

This monitoring study of 170 samples of cow's milk and 165 meat samples collected from the central region of Veracruz state was conducted to determine the contamination levels of organochlorine pesticides. The results obtained for the mean value of total HCH was 0.094 mg/kg in milk samples and 0.728 mg/kg in meat samples, this level is higher than the FAO/WHO tolerance level. The mean total DDT was 0.159 mg/kg in milk samples and 2.545 mg/kg in meat samples which is above the FAO/WHO tolerance level. These results confirmed that bovine meat and milk products in Mexico presented organochlorine pesticide residues owing to their use in sanitary actions, indicating human exposure through these food products.

### Introduction

According to a recent report Mexico is the leading DDT user in Latin America. In 1993-1994 period, Mexico has used approximately 3000 tons of DDT per year in anti-malaria campagne <sup>1)</sup>. Organochlorines such as HCH and DDT are being used in sanitary actions against vector-born diseases in agriculture and livestock <sup>2)</sup>. Because of these pesticides are highly persistent and strongly lipophilic, they are primarily stored in fat-rich tissues and subsequently translocated and excreted through milk fat, and accumulate in fat-rich meat and dairy products, exposing consumers of dairy products to significant levels of contamination <sup>3)</sup>. Therefore, animal fatty foods have become the prime sources of human dietary exposure to organochlorine pesticides, since these products play a central role in human diet <sup>4)</sup>. Since the evidence of organochlorine hormone-disruption activity has been reported <sup>5)</sup>, attempts have to be made to ensure that the organochlorine pesticide residues in food commodities are kept well under recommended tolerance levels in order to minimize the human health risk. The present investigation was undertaken to monitor the levels of HCH and isomers, DDT isomers and metabolites, aldrin, heptachlor, heptachlor epoxide,  $\alpha$ -,  $\beta$ - endosulfane, endosulfane sulfate in bovine meat and milk from the central region of Veracruz State in Mexico.

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## Experimental Methods

**Sampling locations and samples.** Raw food samples were collected during 1996. Meat samples (165) were taken randomly from bovine slaughtered in the municipal slaughterhouse of Veracruz and cow's milk samples (170) were collected weekly at random from several farms of the central region of Veracruz state and taken from bulk transporters hauling milk destined for pasteurization. Samples were kept in chemically clean glass bottle, labeled regarding the day and month of sampling and kept frozen at  $-20^{\circ}\text{C}$  until analyzed.

**Chemical analysis.** Before analysis reagents were tested for impurities by gas chromatography. Analytical standards were purchased from Supelco, Inc. The glassware was washed with chromic mixture, rinsed with distilled water and then with distilled acetone and petroleum ether to prevent contamination of analyzed samples and to make it suitable for pesticide residues analysis. The analysis were carried out on a gas liquid chromatograph Varian model 3300 equipped with a  $^{63}\text{Ni}$  electron capture detector and a Varian model 4400 integrator. For pesticide separation according to the US EPA Method 608<sup>6)</sup> a fused silica capillary column 30m x 0.53mm id. and 0.5 mm film was used at the following temperature program:  $140^{\circ}\text{C}$  (for 3 min) to  $250^{\circ}\text{C}$  at  $10^{\circ}\text{C}/\text{min}$ , held 10min. Carrier gas was nitrogen at 6.7 mL/min, and direct sample injection of  $1\mu\text{L}$  was employed. The stored cow's milk samples were left to defrost and then centrifugated at 3000 rpm to separate the fat from milk. The fat layer was removed from the sample and processed according to Waliszewski and Szymczynski method <sup>7)</sup>. All samples were analyzed in duplicate and results represent the arithmetic mean. To determine the quality of the method, the recovery study was performed on ten replicate overspiked samples of uncontaminated cow milk fat.

**Statistical analysis.** Statistical analysis such as frequency, mean, standard deviations and ranges were estimated using Minitab 10.5 for Macintosh. Differences among DDT and metabolites levels according to the place of residence were examined using Oneway analysis of variance at  $P < 0.05$ . The Tukey-Kramer Test was used to determine the difference among group means due to the place of residence (Minitab 10.5 for Macintosh)

## Results and Discussion

The fortification levels, recovery mean values, standard deviations and detection limits are presented in Table 1. The mean values ranged from 94% to 97% of recovery and the standard deviations were below 10 indicating excellent repeatability of this method. Frequency of positive samples, mean and standard deviations and ranges of obtained values are listed in Table 2. Table 2 lists results for cow's milk and meat samples collected in 1996.

**-Hexachlorobenzene (HCB).** HCB residues were detected in 84.3% of milk samples and in 47.0% of meat samples at mean levels of 0.014 mg/kg and 0.077 mg/kg, respectively. HCB is a by-product of some industrial chlorination processes, thus its presence in food products could be due to industrial contamination.

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-*Hexachlorocyclohexane (HCH)*.  $\alpha$ -HCH was detected in 92.0% of milk samples with a mean level of 0.015 mg/kg and in 66.0 % of meat samples with a mean level of 0.132 mg/kg. Of the milk samples analyzed, 63.3% contained  $\beta$ -HCH at a mean level of 0.049 mg/kg and 43.0 % of the meat samples contained this isomer at a mean level of 0.310 mg/kg, exceeding the FAO/WHO tolerance limit of 0.075 mg/kg<sup>8)</sup>. The most important isomer  $\gamma$ -HCH (Lindane) was present in 80.0% of milk samples at a mean level of 0.030 mg/kg and in 70.0 % of meat samples at a mean level of 0.091 mg/kg. The mean value of total HCH was 0.094 mg/kg in milk samples and 0.728 mg/kg in meat samples, this level is higher than the FAO/WHO tolerance level of 0.1 mg/kg<sup>8)</sup>. Lindane has been used in Veracruz as a pesticide of choice in livestock vector control programs and agricultural pests.

-*Aldrin and endosulfane sulfate*. Aldrin was not detected above the detection limit of 0.002 mg/kg in milk and butter samples. Endosulfane sulfate was not detected above the detection limit of 0.003 mg/kg in all samples. These pesticides were not detected in the meat samples.

Table 1. Fortification levels, mean and standar deviation and detection limits (mg/kg on fat basis) from fortification study.

PESTICIDE	FORTIFICATION LEVEL (mg/kg)	AMOUNT RECOVERED (X + DS) (%)	DETECTION LIMIT (mg/kg)
HCB	0.010	95.8 ± 5.4	0.001
$\alpha$ -HCH	0.010	96.9 ± 7.0	0.001
$\beta$ -HCH	0.020	91.0 ± 8.9	0.002
$\gamma$ -HCH	0.020	99.1 ± 9.9	0.002
Aldrin	0.020	90.1 ± 7.2	0.002
Heptachlor	0.020	90.8 ± 7.8	0.002
Heptachlor epoxide	0.020	91.4 ± 6.9	0.002
p,p'-DDE	0.020	96.9 ± 5.1	0.002
o,p'-DDT	0.040	97.1 ± 5.0	0.003
p,p'-DDD	0.030	94.3 ± 5.9	0.003
p,p'-DDT	0.030	95.7 ± 4.9	0.003
$\alpha$ -Endosulfane	0.030	132.8 ± 9.1	0.003
$\beta$ -Endosulfane	0.030	71.3 ± 9.6	0.003
Endosulfane sulfate	0.030	94.3 ± 5.9	0.003

-*Heptachlor, heptachlorepoide,  $\alpha$  and  $\beta$ -endosulfane*. Heptachlor was detected in 54.0% of milk samples at a mean level of 0.023 mg/kg, whereas heptachlor epoxide was present in 5.0% of milk samples at mean levels of 0.001 mg/kg. The presence of these pesticides indicate their use in agricultural practices. Regarding endosulfane isomers,  $\alpha$ -endosulfane was detected in 30.0% of the milk samples at mean levels of 0.008 mg/kg.  $\beta$ -endosulfane

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was detected in 20.3% of milk samples at a mean level of 0.005 mg/kg. These pesticides were not detected in the meat samples.

*-DDT and metabolites.* Concerning the DDT, among pesticide residues identified, the frequency of pp'-DDE was 98.7% of analyzed milk samples and 100.0% of meat samples, with mean values of 0.044 mg/kg and 0.078 mg/kg, respectively. The frequency of pp'-DDT was 83.7% of milk samples and 40.0% of meat samples, with mean levels of 0.087 mg/kg and 1.571 mg/kg, respectively. The mean total DDT was 0.159 mg/kg in milk samples and 2.545 mg/kg in meat samples which is above the FAO/WHO tolerance level of 1.0 mg/kg<sup>8)</sup>. This contamination could be assumed to antimalaria sanitary actions carry out through out Veracruz state.

The results obtained in other monitoring studies of organochlorine pesticides in cow's milk and meat in comparison with the results obtained from this monitoring survey are presented in Table 3. In relation to organochlorine pesticides residues in cow's milk, the total HCH levels in Mexico and total DDT levels are comparable. On the other side, organochlorine levels detected in meat samples are higher to those found in other countries. The results from this survey confirmed that milk and meat can be contaminated by organochlorine pesticides owing to their use in sanitary actions. This study showed again the need to carry out further monitoring studies in order to improve food safety, since these compounds represent a potential risk to human health.

Table 2. Pesticide residues found in cow's milk samples in mg/kg in fat basis.

PESTICIDE	COW'S MILK		BOVINE MEAT	
	FREQUENCY (%)	X + SD	FREQUENCY (%)	X + SD
HCB	84.3	0.014 ± 0.007	47.0	0.077 ± 0.144
α-HCH	92.0	0.015 ± 0.005	66.0	0.132 ± 0.223
β-HCH	63.3	0.049 ± 0.048	43.0	0.310 ± 0.672
γ-HCH	80.0	0.030 ± 0.020	70.0	0.091 ± 0.128
Σ-HCH		0.094 ± 0.064		0.728 ± 0.071
Aldrin	n.d.	n.d.	n.d.	n.d.
Heptachlor	54.0	0.023 ± 0.016	n.d.	n.d.
Heptachlor epoxide	5.0	0.007 ± 0.001	n.d.	n.d.
p,p'-DDE	98.7	0.044 ± 0.023	100.0	0.078 ± 0.071
o,p'-DDT	60.0	0.032 ± 0.016	9.0	0.078 ± 0.261
p,p'-DDD	13.7	0.004 ± 0.008	n.d.	n.d.
p,p'-DDT	83.7	0.087 ± 0.052	40.0	1.571 ± 6.193
Σ-DDT		0.159 ± 0.081		2.545 ± 7.966
α-Endosulfane	30.0	0.008 ± 0.002	n.d.	n.d.
β-Endosulfane	20.3	0.005 ± 0.002	n.d.	n.d.
Endosulfane sulfate	n.d.	n.d.	n.d.	n.d.

n.d. = not detected

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Table 3. Organochlorine pesticide residues (mg/kg on fat basis) in cow's milk and butter samples from different countries.

PESTICIDE	INDIA <sup>9</sup>	ESPAÑA <sup>10</sup>	SLOVACIA <sup>11</sup>	POLONIA <sup>12</sup>	MEXICO	
	COW'S MILK	MEAT	COW'S MILK	MEAT	COW'S MILK	MEAT
HCB	-	0.010	0.004	0.011	0.014	0.077
α-HCH	0.053	0.009	0.005	0.005	0.015	0.132
β-HCH	0.014	0.018	0.006	0.028	0.049	0.310
γ-HCH	0.004	0.014	0.004	0.010	0.030	0.091
Σ-HCH	0.071	0.041	0.015	-	0.094	0.728
p,p'-DDE	-	0.008	0.051	0.114	0.044	0.078
p,p'-DDD	-	-	-	-	0.004	n.d.
p,p'-DDT	-	-	0.362	0.098	0.087	1.571
Σ-DDT	0.150	-	0.413	-	0.159	2.545

n.d.=not detected; 9) Mukherjee & Gopal 1993; 10) Ariño, 1985; 11) Prachar 1995; 12) Sitarska, 1995; \* This study

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