

Organochlorine insecticide residues in raw milk sold in Córdoba, Colombia

Residuos de insecticidas organoclorados presentes en leche cruda comercializada en el departamento de Córdoba, Colombia

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Abstract

In this investigation organochlorine pesticide residues in raw milk from Dairy herds in Cordoba were determined. During the extraction procedure it was used a column of diatomaceous earth as eluting system and a mixture of n-hexane-acetone-ethyl acetate (4:2:1), followed by 5% methanol in hexane. For the determination we used a gas Chromatograph Perkin Elmer, Autosystem XL with electron capture detector, splitless injection mode, a capillary column Rtx-5 30m, 0.25 mm id and 0.25 μ m film thickness. The recovery rates for certain pesticides were between 88.5 and 96%, the detection limits were defined between 0.01 and 0.04 ng/g, with relative standard deviations less than 6%. In the 63 samples tested p, p'-DDT, α -HCH, δ -HCH, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide and γ -chlordane were determined, establishing concentrations between 27.1 and 469.6 ng/g. The frequencies of occurrence ranged between 1.6 and 65.1% for heptachlor and p, p'-DDT, respectively. The older population that lives in the sub-regions: Middle Sinú, San Jorge and Savannas were exposed to high health risk associated with the concentration of α -HCH, aldrin and dieldrin in raw milk.

Key words: Cow milk, organochlorine pesticides, pesticide persistence, residues.

Resumen

En el estudio se determinaron residuos de plaguicidas organoclorados en leche cruda proveniente de hatos lecheros del departamento de Córdoba, Colombia. Durante el procedimiento de extracción se utilizó una columna de tierra de diatomeas y como sistema eluyente una mezcla de n-hexano-acetona-acetato de etilo (4:2:1), seguida de metanol al 5% en hexano. Para la determinación se usó un cromatografo de gases Perkin Elmer, Autosystem XL con detector captura de electrones, en modo de inyección 'splitless', una columna capilar Rtx-5 30 m, 0.25 mm di y 0.25 μ m de espesor de película. El porcentaje de recuperación para los plaguicidas determinados se encontró entre 88.5 y 96%, los límites de detección se definieron entre 0.01 y 0.04 ng/g con desviaciones estándar < 6%. En las 63 muestras analizadas se determinaron p,p'-DDT, α -HCH, δ -HCH, aldrín, dieldrín, endrín, heptacloro, heptacloro epóxido y γ -clordano, estableciendo concentraciones entre 27.1 y 469.6 ng/g. Las frecuencias de aparición oscilaron entre 1.6 y 65.1% para heptacloro y p,p'-DDT, respectivamente. La población adulta mayor que habita en las subregiones Sinú Medio, San Jorge y Sabanas se encuentra expuesta a riesgo alto en la salud, asociado con la concentración de α -HCH, aldrín y dieldrín en leche cruda.

Palabras clave: Leche de vaca, persistencia de los plaguicidas, plaguicidas organoclorados, residuos.

Introduction

Pesticides are a group of chemical products used to control pests or to prevent and reduce their damage in crops, landscape and animals. As such, they can be present in foods of daily and frequent consumption (Tadeo, 2008). The health effect of food intake with pesticide residues, transferred through the food chain, has been associated with alterations in the reproductive system. Langer (2003) found a significant relation between the presence of organochlorine insecticides and thyroid gland alterations. Goutner *et al.* (2001) reported residual levels of organochlorine pesticides and PCBs in gull's eggs samples collected in 1997 and 1998, and established a temporal pattern of contamination by the presence of this type of residues in the environment on the Aegean sea.

Gas chromatography is useful to determine pesticides (Fong *et al.*, 1999), however, frequently new variants are found in the extraction, cleaning and injection procedures. Valsamaki *et al.* (2006) developed a chromatography method for multiresidual analysis of 20 organochlorine insecticides and eight PCBs analogs present in the matrix of chicken eggs, which was dispersed in florasil and eluted with in a dichlorometane-hexane (1:1) mix. In the other hand, in Greece Lambropoulou *et al.* (2006) proposed an useful analytic method to determine organochlorine residues in liver samples of different birds by using ultrasound while extraction and sulfuric acid for cleaning.

Hussen *et al.* (2007) developed a selective extraction procedure for multiresidual analysis of organochlorine pesticides in soil from Ethiopia by using pressurized liquid (SPLE). This method make extraction and cleaning simultaneously which results in recovery percentages above 80% for endosulfan, sulfate endosulfan, p,p-DDT and p,p-DDE. Kalyoncu *et al.* (2009) used gas chromatography with electron capture detector to evaluate 18 organochlorine in fish tissue collected in the Konya market, Turkey, finding mainly DDT and HCH residues. Sum of average DDT concentrations varied between 0.0008 and 0.0828 µg/g. The low residual levels were not associated with health risk and food intake.

In Colombia, the use of organochlorine pesticides is restricted and forbidden since the 70's (ICA, 2004). In Córdoba, organochlorine insecticides were heavily used for pest control on cotton, corn, sorghum and plantain (CVS, 2002). Additionally, the development of intensive livestock favors production and commercialization of milk and its derivatives, these foods can be a vehicle for contaminants and residues like organochlorine insecticides (Pardio *et al.* 2003; Waliszewski *et al.* 2003; Zhong *et al.* 2003; Real *et al.* 2005). For the region of study Lans *et al.* (2008) found residual levels of α-HCH, β-HCH, γ-HCH, aldrin y heptachlor epoxide in 0.112 µg/lt, 0.586 µg/lt; 0.112 µg/lt; 0.280 µg/lt and 0.323 µg/lt concentrations, respectively, in water from Ciénaga Grande in the low valley of Sinú river. The aim of this research was to determine organochlorine pesticide residual levels in raw milk samples from commercialized milk in subregions of Córdoba.

Materials and methods

Córdoba is located at the Northwest of Colombia between 7° 22' and 9° 26' N and 76° 30' E. The area of study consisted on ten towns belonging to four subregions: Jorge, Sinú Medio, Sabanas and Costanera (Map 1). Six samplings were done during one year in the wet, dry and transition weather picks in the zone.

Equipment.

For the measurements a gas chromatographer Perkin Elmer, Autosystem XL, equipped with electron capture detector ECD Ni⁶³ serie 61N9060517, a computer with Turbochrom Navigator software for data reading. A GC/MS Thermo Trace Ultra was used to confirm the identification of the pesticides.

Chromatography conditions.

Injector and detector temperatures were 200 °C and 300 °C, respectively. Oven was programmed for an initial temperature of 100 °C for 15 °C/min until 160 °C (6 min), 3 °C/min until 250 °C (10 min). Helium and Nitrogen of high purity was used as carrier gas (12 psi) and make up gas (60 ml/min).

Extraction, cleaning and analytic determination.

Statistical analysis and quality control.

Concentration values are shown as average \pm standard deviation (SD) of the triplicates, normal distribution was evaluated by the Kol-

Results and discussion

The highest levels of average concentration were 469.6 ng/g for α -HCH, 47.17 ng/g for p,p'-DDT and 38.3 ng/g for δ -HCH (Table 1). In contrast, Zapata *et al.* (1996), Prado (1998), Waliszewski *et al.* (2003), Real *et al.* (2005) and Vallejo (1993) in Nicaragua, Mexico and Colombia, respectively, found total DDT and (α + β)-HCH concentrations to be superior to the ones found in this study. Bioavailability of these kind of residues in Córdoba was associated with the pesticide dose use of 50 kg/ha in cotton when the recommendation by

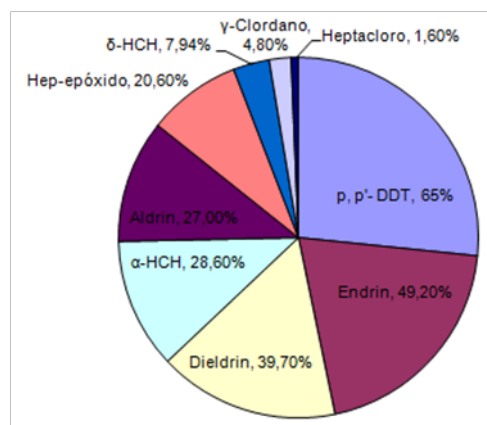


Figure 1. Appearance frequency of organochlorine pesticides in milk samples in regions of Córdoba, Colombia.

the Colombian Institute on Agriculture (ICA) was 2 kg/ha (CVS, 2002). A similar situation was found in Jordania for excessive use of HCH and DDT during the agricultural processes in India (Salem *et al.*, 2009).

Additionally, there were found maximum concentrations of 36.6 ng/g of aldrin, 48.7 ng/g of dieldrin and 47.1 ng/g of endrin (Table 1). The concentrations in the milk samples from the Sinú Medio subregion followed this trend endrin > dieldrin > aldrin and, they were associated with the aldrin metabolism level in soils (Casarett *et al.*, 2008). Similarly, in Colombia, Vallejo (1993) found concentrations of 100 ng/g for aldrin and 40 ng/g for dieldrin. In Mexico, Prado (1998) found concentrations of 250 ng/g (aldrin + dieldrin) and 50 ng/g of endrin.

Maximum concentration of heptachlor in raw milk was 27.1 ng/g, of heptachlor epoxide was 65.3 ng/g and of γ -clordano was 2.6 ng/g (Table 1). In similar studies with this compound Vallejo (1993) found in Colombia higher values (170 ng/g) and in Nicaragua Zapata *et al.* (1996) found 63 ng/g. In Mexico, Prado (1998) found in milk 150 ng/g of heptachlor + heptachlor epoxide, and Real *et al.* (2005) found 90 ng/g for the same mix.

Metabolization level.

For the analyzed samples coming from Sinú Medio and Costanera, the average value of the concentration ratio δ -HCH/ α -HCH was 0.16 and 0.28 respectively which indicates a use close in time of α -HCH that is associated with slow metabolization. Average concentrations

of α -HCH in milk samples taken in Sinú Medio for both periods of study were different ($P > 0.05$), which suggest a recent use of that insecticide in this subregion. These results are contrasting with the findings in Costanera subregion. Concentration ratio of dieldrin/aldrin found in samples from San Jorge (1.55 ng/g), Sinú Medio (1.20 ng/g), and Sabanas (1.19 ng/g) subregions indicate absence of a recent use of aldrin and a medium level of metabolization. No differences were found ($P > 0.05$) between the average concentration of this type of insecticide between periods of study; this suggests a lower use of aldrin in these subregions.

Risk with consumption of organochlorine contaminated milk.

Daily food intake (CDA) proposed by Codex Alimentarius (2005) were adjusted according to the average body weight of an adult person living in the Atlantic Coast of Colombia (Castilla *et al.*, 2010). To qualify the risk associated with consumption of raw and contaminated milk with organochlorine pesticides, the daily possible intake (CDP) was compared with the admissible one (CDA), and it was concluded that for CDP values < 30% of CDA the associated risk is low; whereas for CDP values between 30 and 100% of CDA the risk is medium and, CDP values > 100% the risk is high (Majul *et al.*, 2004) (Table 2).

Risk associated with human health for presence of p,p'-DDT, δ -HCH, heptachlor y heptachlor epoxide residues in milk samples in the subregions studied was considered

Table 1. Organochlorine pesticide concentrations in ng/g in row milk^a from different subregions in Córdoba, Colombia.

Subregion	p.p'- DDT	α -HCH	δ -HCH	Aldrin	Dieldrin	Endrin	Hepta- chlor	Hep.- epoxide	γ - Chlordane
San Jorge	47.2 \pm 29.0	260.2 \pm 112.6	NR	31.4 \pm 6.1	48.7 \pm 24.9	37.6 \pm 12.2	NR	61.7 \pm 18.6	NR
Sinú	36.5 \pm	232.8 \pm	38.2 \pm	33.5 \pm	40.3 \pm	47.1 \pm	27.1 \pm	50.2 \pm	40.8 \pm
Medio	12.2	139.9	5.4	9.2	10.6	19.3	0.5	4.7	11.4
Sabanas	34.3 \pm 7.5	469.6 \pm 7.2	NR	36.6 \pm 14.8	43.5 \pm 11.5	37.9 \pm 10.7	NR	60.1 \pm 12.4	NR
Costanera	37.1 \pm 9.2	122.3 \pm 32.7	34.9 \pm 1.0	NR	30.7 \pm 6.2	37.2 \pm 4.5	NR	NR	NR

a. Milk average density: 1.032 g/ml; Average fat percentage in row milk: 4.0%. * Milk fat base.

Table 2. Health risk by presence of organochlorine pesticides in raw milk samples collected in subregions of Córdoba, Colombia

Pesticide	(CDP/ -adjusted CDA)*100 by region			
	San Jorge	Sinú Medio	Sabanas	Costanera
DDT	11.4 (b)*	8.8 (b)	8.2 (b)	8.9 (b)
α -HCH	156.3 (a)	140.0 (a)	282.4 (a)	73.5 (m)
δ -HCH	nr	23.0 (b)	nr	5.2 (b)
Aldrin	151.0 (a)	161.1 (a)	176.1 (a)	nr
Dieldrin	234.3 (a)	193.8 (a)	209.2 (a)	147.7 (a)
Endrin	90.4 (m)	113.3 (a)	91.2 (m)	89.5 (m)
Heptachlor	nr	2.9 (b)	nr	nr
Heptachlor-epoxide	59.4 (m)	16.1 (b)	57.8 (m)	nr
γ -Chlordane	nr	39.3 (m)	nr	nr

* Risk: (a) high; (m) medium; (b) low; nr: not registered.

low, except for samples of San Jorge region that had heptachlor epoxide. A high risk for presence of α -HCH, aldrin and dieldrin in milk samples from San Jorge, Sinú Medio and Sabana was determined, these results are contrasting to the ones obtained by Castilla *et al.* (2010) for the same analytes. Similarly, Heck *et al.*, (2007) found lower concentrations to the ones obtained in this research and absence of health risk due to their presence in milk samples consumed by children in Rio Grande do Sul in Brazil.

Conclusions

- The organochlorane pesticides p,p'-DDT, α -HCH, δ -HCH, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide and γ -chlordane were found in raw milk samples in the subregions of San Jorge, Sinú Medio, Sabanas and Costanera, in Córdoba, Colombia. Samples taken in Sinú Medio showed a higher variability in contaminants, opposite to what was found in Costanera.
- In the milk samples analyzed there were no detectable analytical signs in: β -HCH, γ -HCH, α -Clordano, p,p'-DDD, endosulfan I, endosulfan sulfate, endrin aldehyde.
- The risk associated with organochlorine pesticide presence in raw milk consumed in different subregions of Córdoba (Colombia), is qualified as high due to the presence of α -HCH, aldrin and dieldrin in sam-

ples from San Jorge, Sinú Medio and Sabanas.

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