

Available online at www.sciencedirect.com



Food Chemistry

Food Chemistry 102 (2007) 288-294

www.elsevier.com/locate/foodchem

Estimation of children exposure to organochlorine compounds through milk in Rio Grande do Sul, Brazil

M.C. Heck ^a, J. Sifuentes dos Santos ^{a,b}, S. Bogusz Junior ^a, I. Costabeber ^{c,*}, T. Emanuelli ^d

^a Post-Graduate Course in Food Science and Technology, Center of Rural Sciences, Federal University of Santa Maria, Camobi, Santa Maria,

RS, CEP 97105-900, Brazil

^b CNPq fellowship, Brazil ^c Department of Morphology, Center of Health Sciences, Federal University of Santa Maria, Camobi, Santa Maria,

RS, CEP 97105-900, Brazil

^d Department of Food Technology and Science, Integrated Center of Development in Laboratory Analysis (NIDAL), Center of Rural Sciences, Federal University of Santa Maria, Camobi, Santa Maria, RS, CEP 97105-900, Brazil

Received 19 January 2006; received in revised form 15 March 2006; accepted 15 May 2006

Abstract

The presence of organochlorine pesticides (α -HCH, lindane, aldrin, HCB, pp'-DDE, op'-DDD, pp'-DDD, and op'-DDT) and PCBs (congeners 10, 28, 52, 138, and 180) were investigated in raw, pasteurized, and UHT milk from Rio Grande do Sul State (Brazil). Considering the toxicity of these compounds and the importance of milk and dairy products for child nutrition, the estimated daily intake (EDI) of these compounds, through milk, by elementary school children of Santa Maria (Rio Grande do Sul, Brazil) was also determined. HCB and pp'-DDE were found in all samples analyzed. pp'-DDE (11.9 ng/g), op'-DDD (7.38 ng/g), lindane (6.09 ng/g), and PCB 180 (5.31 ng/g) were the compounds found at the highest average concentrations. The EDIs for organochlorine pesticides were below the acceptable daily intakes established by FAO/WHO. Furthermore, few samples exceeded the maximum residue limits for the compounds evaluated.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Organochlorine pesticides; Polychlorinated biphenyls; Milk; Daily intake

Corresponding author. Tel.: +55 55 3220 9375; fax: +55 55 3220 8494. *E-mail address:* ijoni@smail.ufsm.br (I. Costabeber).

1. Introduction

Organochlorine pesticides have been extensively used in tropical countries in malaria control programmes and against livestock ectoparasites and agricultural pests (Waliszewski et al., 1997). PCBs are organochlorine compounds with different degrees and positions of chlorination, which determine their persistence and toxicity (Ross, 2004). Nonortho-chlorine-substituted PCBs (coplanar PCBs) are approximate isostereomers of 2,3,7,8-tetrachlorodibenzo*p*-dioxin (TCDD) and are the most toxic members of all 209 PCB congeners (Safe, 1990).

The main reasons for environmental contamination by these compounds are their great production, uncontrolled

Abbreviations: ADI, acceptable daily intake; aldrin, 1,2,3,4,10,10'-hexachloro – 1,4,4',5,8,8'-hexahydro – exo-1,4-endo-5,8-dimethano – naphthalene; pp'-DDD, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; op'-DDD, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; pp'-DDE, 1,1-dichloro-2,2-bis(*p*-chlorophenyl)-2-(*p*-chlorophenyl)ethane; pp'-DDE, 1,1-dichloro-2,2-bis(*p*-chlorophenyl))-ethane; µECD'-micro electron capture detector; EDI, estimated daily intake; HCB, hexachlorobenzene; α-HCH, α-hexachlorocyclohexane; lindane, γ-hexachlorocyclohexane; LOD, limit of detection; LOQ, limit of quantification; MRL, maximum residue level; PCBs, polychlorinated biphenyls; PCB 10, 2,6 dichlorobiphenyl; PCB 28, 2,4,4' trichlorobiphenyl; PCB 52, 2,2',5,5' tetrachlorobiphenyl; PCB 138, 2,2',3,4,4',5 hexachlorobiphenyl; PCB 180, 2,2',3,4,4',5,5' hepta chlorobiphenyl.

use, inadequate discharge, and persistence in the environment (Ross, 2004). Organochlorine compounds are lipophilic and are hardly metabolized. Hence, environmental exposure of living organisms to these compounds results in their accumulation and persistence in fat tissues (Falandysz et al., 2004). Moreover, organochlorine compounds undergo biomagnification through the food chain (Angulo, Martinez, & Jodral, 1999; Borga, Gabrielsen, & Skaare, 2001). Since man is the last link in the food chain, he will consume the highest levels of these compounds. Food, particularly dairy products, meat and fish. has been identified as the primary immediate intake route of organochlorine pesticides and PCB congeners for the general population (Johansen, Muir, Asmund, & Riget, 2004; Schecter, Cramer, Boggess, Stanley, & Olson, 1997).

Organochlorine pesticides and PCBs have been shown to elicit a wide range of toxic and biochemical effects in both laboratory animals and wildlife (Fox, Kennedy, Norstrom, & Wigfield, 1988; Safe, 1990). They pose a serious risk to health, especially for infants, since their enzymatic and metabolic systems are not fully active. It is already known that PCBs cause deficits in different aspects of animal cognition (WHO, 1993). These data indicate that PCBs are neurobehavioral toxicants and raise the question of whether environmental levels of PCBs may affect cognitive development of children. Significant relationships between prenatal PCB exposure and decrements in neurological tests and cognitive development of humans have been observed (Huisman et al., 1995; Patandin et al., 1999; Stewart, Reihman, Lonky, Darvill, & Pagano, 2003). Furthermore, some epidemiological studies suggest that postnatal exposure, even to environmental background levels of PCBs, could have a negative effect on the neurodevelopment of children (Vreugdenhil, Slijper, Mulder, & Weisglas-Kuperus, 2002; Walkowiak et al., 2001).

Milk-producing animals, such as cows, accumulate residues of these pesticides through contaminated feed, grass/hay, and inhaled air. Bovine milk has been used as an indicator of the persistence of chemical environmental contaminants (Losada et al., 1996). In the southern region of Brazil, few studies have been carried out to determine milk contamination by organochlorine pesticides (Costabeber, Trindade, & Fries, 2000) and no study has evaluated contamination by PCBs. Considering the toxicity of organochlorine compounds and the importance of milk and dairy products for human nutrition, especially for children, the aim of this work was to determine the level of individual PCB congeners and organochlorine pesticides in raw, pasteurized, and ultra high temperature (UHT) milk of frequent intake in the State of Rio Grande do Sul (Brazil). The estimated daily intake of these compounds through milk, by elementary school children from Santa Maria city (Rio Grande do Sul, Brazil) was also determined.

2. Materials and methods

2.1. Materials

All glassware used was previously washed, following the method of Angulo, Costabeber, Gallego, Serrano, and Jodral (1996), with distilled water, rinsed with hexane and acetone, alternately, and dried at 150 °C, to assure chemical cleanliness.

Hexane, petroleum ether for chromatography, and 60/ 100 mesh pesticide reagent grade Florisil were obtained from Mallinckrodt Backer (Kentucky, USA). Florisil was previously activated at 150 °C/12 h and deactivated by adding 2% Milli-Q water before use. Standard organochlorine pesticides (α -HCH, lindane, aldrin, HCB, pp'-DDE, op'-DDD, pp'-DDD, and op'-DDT) were obtained from Ultra Scientific (North Kingstown, RI, USA) and standard PCBs (numbers 10, 28, 52, 138, and 180) were obtained from Supelco Inc. (Bellefonte, PA, USA). All other reagents used were of analytical reagent grade.

2.2. Samples

A total of 41 samples of raw (18 samples), pasteurized (13 samples), and UHT (10 samples) cow milk from Rio Grande do Sul State (Brazil, Fig. 1) were evaluated for the organochlorine pesticides and 24 samples (raw = 12, pasteurized = 8, UHT = 4) for polychlorinated biphenyls. Raw milk samples were collected at random from farms of different cities in Rio Grande do Sul State, while pasteurized and UHT samples were bought at ordinary commercial establishments. Samples were kept frozen at -20 °C prior to analysis.



Fig. 1. Layout of sampling location. Milk samples were obtained from Rio Grande do Sul State, in southern Brazil.

2.3. Analysis of organochlorine pesticides and PCBs

Fat samples were extracted and purified, following the method described by Sandmeyer (1992) with some modifications: 250 ml of milk were centrifuged during 15 min, at 4 °C at 17,300g; milk fat was removed and mixed with 25 g of anhydrous sodium sulfate and 100 ml of petroleum ether. Liquid was filtered through anhydrous sodium sulfate and evaporated under vacuum. The purified fat residue was transferred to a glass vial and kept at -20 °C prior to purification of compounds.

Compounds were purified by the method of Martinez, Angulo, Pozo, and Jodral (1997). Briefly, 1 g of fat sample was mixed with 3 ml of *n*-hexane. The sample was applied to a chromatographic column containing 15 g of florisil and anhydrous sodium sulfate, and eluted with 100 ml of *n*-hexane to extract organochlorine pesticides and PCB congeners. The eluate was filtered through anhydrous sodium sulfate, evaporated to drvness in a rotary evaporator, dissolved in 1 ml of n-hexane, and used for organochlorine pesticide and PCB congener determinations by gas chromatography with an Agilent 6890A model gas chromatograph equipped with a ⁶³Ni microelectron capture detector (µECD). An HP-5 fused silica (cross-linked 5% phenyl methyl siloxane gum) column (30 m length, 0.25 mm internal diameter, 0.25 µm film thickness) was used. The carrier gas was nitrogen (1.5 ml/min). Oven temperature was set at 50 °C, increased at 40 °C/min up to 170 °C, increased at 2 °C/ min up to 180 °C and held 1 min, increased at 5 °C/min up to 200 °C and held 1 min, increased at 1 °C/min up to 210 °C and finally increased at 25 °C/min up to 250 °C and held for 3 min. Injector and detector temperatures were 225 °C and 300 °C, respectively. All samples were analyzed in duplicate and results represent the arithmetic means. To determine the quality of the method, a recovery study was performed on ten replicates of milk fat samples overspiked with organochlorine pesticides and PCBs. Mean recoveries ranged from 72.0 to 121% for organochlorine pesticides and 97.4-105 % for PCBs, and the coefficient of variation was below 10%, indicating an excellent repeatability for the method. Limits of detection and quantification were determined using the average blank values method (Table 1).

2.4. Estimated daily intake

The daily intake of milk by children, the type of milk, and the body weight of children from the first grade of elementary school from Santa Maria city (Rio Grande do Sul State) were surveyed using a questionnaire of food consumption frequency. The questionnaire was delivered in public and private schools of Santa Maria, to a total of 517 children. Estimates of dietary exposure to PCBs and organochlorine pesticides were calculated from the amount of analyte found in milk and the daily milk consumption by children.

Table 1		
Detection and	quantification l	limits

Compound	Limit of detection (ng/g)	Limit of quantification (ng/g)
НСВ	0.20	0.6
α-HCH	0.10	0.4
Lindane	0.10	0.3
Aldrin	0.06	0.2
pp'-DDE	0.40	1.2
op'–DDD	0.07	0.2
pp'-DDD	0.06	0.2
op'-DDT	0.05	0.2
PCB no. 10	0.20	0.3
PCB no. 28	0.20	0.3
PCB no. 52	0.20	0.3
PCB no. 138	0.50	0.6
PCB no. 180	0.50	0.6

2.5. Statistical analysis

Data were analyzed using the Statistica[®] 6.0 software package. The effects of sample type on the levels of organochlorine pesticides and PCB congeners were evaluated by one-way analysis of variance (ANOVA), followed by Duncan's test when appropriate. Differences were considered to be significant when $P \leq 0.05$.

3. Results

Table 2 shows the mean, range, and incidence of organochlorine residues in milk. Concentration is reported as ng/g on a fat basis. A sample was considered positive when residue level was \geq LOQ. All bovine milk samples investigated were positive for at least one compound. pp'-DDE (11.9 ng/g) was the major contributor to the \sum DDT that amounted to 20.1 ng/g fat. op'-DDD (7.38 ng/g) and

Table 2

Mean, range, and incidence of organochlorine pesticides and PCBs in milk samples from Rio Grande do Sul State, Brazil

Compound	Mean (ng/g fat)	Range (ng/g fat)	Incidence (%)
НСВ	2.76	0.28-7.22	100
α-HCH	2.54	<loq -="" 40.9<="" td=""><td>90.2</td></loq>	90.2
Lindane	6.09	<loq 68.7<="" td="" –=""><td>95.1</td></loq>	95.1
Aldrin	3.13	<loq 42.6<="" td="" –=""><td>92.7</td></loq>	92.7
pp'-DDE	11.9	2.26 - 42.5	100
op'–DDD	7.38	<loq -="" 38.2<="" td=""><td>95.1</td></loq>	95.1
pp'-DDD	0.76	<loq 1.84<="" td="" –=""><td>64.1</td></loq>	64.1
op'–DDT	0.95	<loq 2.92<="" td="" –=""><td>75.6</td></loq>	75.6
∑DDT	20.1	2.26 - 72.9	100
PCB no. 10	0.78	<loq 5.60<="" td="" –=""><td>50.0</td></loq>	50.0
PCB no. 28	0.26	<loq 2.27<="" td="" –=""><td>33.3</td></loq>	33.3
PCB no. 52	0.95	<loq 4.88<="" td="" –=""><td>45.8</td></loq>	45.8
PCB no. 138	0.05	<loq 1.02<="" td="" –=""><td>8.3</td></loq>	8.3
PCB no. 180	5.31	<loq 45.5<="" td="" –=""><td>62.5</td></loq>	62.5
∑PCB	7.34	<loq -="" 50.6<="" td=""><td>91.6</td></loq>	91.6

 \sum DDT = pp'-DDE + op'-DDD + pp'-DDD + op'-DDT.

 \sum PCB was calculated by the sum of all congeners evaluated.

N = 41 for residues of organochlorine pesticides and N = 24 for residues of PCBs.

LOQ = Limit of quantification.

lindane (6.09 ng/g) were also found at relatively high concentrations when compared to the other organochlorine compounds. PCB 180 (5.31 ng/g) was the major contributor to the \sum PCB that amounted to 7.34 ng/g fat. Lindane (95.1%), op'-DDD (95.1%), pp'-DDE (100%), and HCB (100%) were the most frequent pesticides found in bovine milk. Among polychlorinated biphenyls, the highest frequency was 62.5% for PCB 180.

The mean concentrations of organochlorine pesticides and PCB congeners in raw, pasteurized and UHT milk samples are summarized in Tables 3 and 4. One-way ANOVA revealed that op'-DDD and \sum DDT levels were significantly higher in raw milk than in pasteurized and UHT milk, while pp'-DDD was significantly higher in UHT than in raw milk (Table 3). In raw milk, the organochlorine pesticides found at the highest concentration were pp'-DDE (15.9 ng/g), op'-DDD (13.0 ng/g), and lindane (7.47 ng/g fat). pp'-DDE (8.19 ng/g) was also the compound found at the highest concentration in pasteurized milk. In UHT milk, pp'-DDE (9.06 ng/g) was found at the highest concentration, followed by lindane (7.73 ng/g fat).

Concerning polychlorinated biphenyls (Table 4), the levels of PCB 10 and \sum PCB were significantly higher in pasteurized milk when than in raw and UHT milk. PCB 180 was found at the highest concentration in raw (2.50 ng/g fat) and pasteurized milk (11.7 ng/g fat), while, in UHT

milk, PCBs 52 and 180 (1.02 and 1.00 ng/g fat) were the compounds found at the highest concentrations.

The average milk consumption by elementary school children from Santa Maria city (Rio Grande do Sul, Brazil) has been evaluated recently by Heck et al. (2002). Raw milk was consumed by 26.6% of surveyed children at an average of 303 ml/day. Pasteurized and UHT milk were consumed by 33.8 and 55.6% of surveyed children, respectively. Average consumptions were 363 ml/day for pasteurized and 425 ml/day for UHT. The average child weight was 26.35 kg.

Based on these data from Heck et al. (2002), we calculated the estimated daily intake (EDI) of the compounds by children from elementary school. These results are summarized in Table 5. Maximum acceptable daily intakes (ADIs) established by FAO (1993) are included for comparison purposes. It was observed that no EDI exceeded the corresponding ADI value. EDI for the sum of all compounds was higher for raw milk (18.5 ng/kg/day) than for pasteurized (14.1 ng/kg/day) or UHT milk (14.6 ng/kg/ day). Analyzing milk contribution for the maximum acceptable daily intake of these compounds, it was observed that the EDIs corresponded to 0.015-0.047% of the ADI for lindane, 0.5-1.9% for aldrin and 0.022-0.130% for \sum DDT. ADI values for HCB, α -HCH, and \sum PCB are not established.

Table 3

Mean organochlorine pesticide residues (ng/g fat) in raw, pasteurized, and UHT milk samples from Rio Grande do Sul State, Brazil

Compound	Raw milk $(n = 18)$	Pasteurized milk $(n = 13)$	UHT milk $(n = 10)$
НСВ	$2.59 \pm 1.55 \ (0.46 - 7.22)$	$2.52 \pm 1.61 \; (0.28 - 5.81)$	$3.38 \pm 1.44 \; (0.85 - 5.15)$
α-HCH	$4.17 \pm 9.46 \ (< LOQ - 40.9)$	$1.35 \pm 1.87 \; (< LOQ - 6.01)$	$1.14 \pm 2.70 \ (0.71 - 1.53)$
Lindane	$7.47 \pm 15.76 \; ({<}\text{LOQ} - 68.7)$	$2.92 \pm 4.91 \ (\leq LOQ - 17.93)$	$7.73 \pm 15.2 \; (0.37 - 50.3)$
Aldrin	$5.69 \pm 11.7 \ (< LOQ - 42.6)$	$1.21 \pm 0.68 \; (0.67 – 3.27)$	1.02 ± 0.42 (0.22–1.62)
pp'-DDE	15.9 ± 12.3 (2.71–42.5)	$8.19 \pm 10.6 \; (2.26 - 41.5)$	9.06 ± 6.17 (2.64–21.1)
op'-DDD	$13.0 \pm 13.5^{a} \ (\leq LOQ - 38.2)$	$2.89 \pm 1.53^{\mathrm{b}} (\leq \mathrm{LOQ} - 5.67)$	$3.17 \pm 2.52^{\rm b}$ (<loq 9.20)<="" td="" –=""></loq>
pp'-DDD	$0.51 \pm 0.56^{\mathrm{b}} \ (\leq \mathrm{LOQ} - 1.37)$	$0.80 \pm 0.54^{a,b} \ (\leq LOQ - 1.38)$	$1.19 \pm 0.54^{a} \ (\leq LOQ - 1.84)$
op'-DDT	$0.83 \pm 1.18 \; (\leq LOQ - 2.92)$	$0.97 \pm 0.95 \; ({\leq} LOQ - 2.45)$	$1.13 \pm 0.88 \; (\leq \text{LOQ} - 2.71)$
∑DDT	30.1 ± 21.0^{a} (4.47–72.9)	$11.4 \pm 11.1^{\rm b} \ (\leq \rm LOQ - 47.55)$	$14.4 \pm 5.88^{\mathrm{b}} \ (6.35 - 26.7)$

Results are presented as means \pm standard deviation (range).

Values < LOQ were assumed as equal to zero in the statistical analysis.

 \sum DDT = pp'-DDE + op'-DDD + pp'-DDD + op'-DDT.

Values within the same line that have no common superscript are significantly different (p < 0.05).

LOQ = Limit of quantification.

Table 4				
Mean PCB residues (ng/g fat) in ra	w, pasteurized, and U	HT milk samples from	Rio Grande do Sul	State, Brazil

Compound	Raw milk $(n = 12)$	Pasteurized milk $(n = 8)$	UHT milk $(n = 4)$
PCB no. 10	$0.10 \pm 0.19^{\mathrm{b}} \ (< \mathrm{LOQ} - 0.47)$	$1.97 \pm 1.89^{\mathrm{a}} \ (< \mathrm{LOQ} - 5.60)$	$0.42 \pm 0.60^{\mathrm{b}} \ (< \mathrm{LOQ} - 1.27)$
PCB no. 28	$0.32 \pm 0.66 \ (< LOQ - 2.27)$	$0.29 \pm 0.41 \ (< LOQ - 1.01)$	<loq< td=""></loq<>
PCB no. 52	$0.59 \pm 1.29 \ (\leq \text{LOQ} - 4.52)$	$1.43 \pm 2.09 \ (\leq \text{LOQ} - 4.88)$	$1.02 \pm 0.90 \ (\leq \text{LOQ} - 2.19)$
PCB no. 138	<loq< td=""><td>0.14 ± 0.36 (<loq -="" 1.02)<="" td=""><td><loq< td=""></loq<></td></loq></td></loq<>	0.14 ± 0.36 (<loq -="" 1.02)<="" td=""><td><loq< td=""></loq<></td></loq>	<loq< td=""></loq<>
PCB no. 180	2.50 ± 3.72 (<loq 11.3)<="" td="" –=""><td>11.7 ± 15.1 (<loq 45.5)<="" td="" –=""><td>$1.00 \pm 2.01 \ (< LOQ - 4.03)$</td></loq></td></loq>	11.7 ± 15.1 (<loq 45.5)<="" td="" –=""><td>$1.00 \pm 2.01 \ (< LOQ - 4.03)$</td></loq>	$1.00 \pm 2.01 \ (< LOQ - 4.03)$
∑PCB	3.52 ± 3.62^{b} (<loq 11.3)<="" td="" –=""><td>$15.5 \pm 15.61^{\mathrm{a}} (3.03 - 50.6)$</td><td>$2.45 \pm 2.93^{b}$ (<loq -="" 6.65)<="" td=""></loq></td></loq>	$15.5 \pm 15.61^{\mathrm{a}} (3.03 - 50.6)$	2.45 ± 2.93^{b} (<loq -="" 6.65)<="" td=""></loq>

Results are presented as mean \pm standard deviation (range).

Values <LOQ were assumed as equal to zero in the statistical analysis.

 \sum PCB was calculated by the sum of all congeners evaluated.

Values within the same line that have no common superscript are significantly different (p < 0.05).

LOQ = Limit of quantification.

Aldrin ∑DDT

 $\overline{\Sigma}$ PCB

All compounds

Estimated daily intake (EDI) from milk and acceptable daily intake (ADI) for organochlorine pesticides and PCBs				
Compound	EDI (ng/kg) ^a			
	Raw milk	Pasteurized milk	UHT milk	
НСВ	0.89	1.04	1.63	
α-HCH	1.44	0.56	0.55	
Lindane	2.57	1.21	3.74	

0.50

4.36

641

14.1

Table 5

 \sum DDT = pp'-DDE + op'-DDD + pp'-DDD + op'-DDT.

 \sum PCB was calculated by the sum of all congeners evaluated.

1.96

1.21

10.4

18 5

NE = Not established.

^a Calculated based on the average milk consumption by children of the elementary school from Santa Maria city (Rio Grande do Sul, Brazil), previously reported by Heck et al. (2002).

 b^{b} Values established by FAO (1993).

^c Including dieldrin.

4. Discussion

Maximum residue levels (MRL) of pesticides allowed in milk in Brazil are established by Normative Instruction number 42, December 20 (Brasil, 1999). Six milk samples exceeded the MRL of α -HCH (4 ng/g fat), five exceeded the MRL of lindane (10 ng/g fat), three exceeded MRL of aldrin (6 ng/g fat), and four exceeded the MRL of \sum DDT (50 ng/g fat). There is no the MRL for PCBs in milk, in Brazil, but according to Bester et al. (2001), in the European Community, they are allowed up to 200 ng/g fat in animal food products. No sample analyzed in the present study exceeded this limit.

Few studies have investigated organochlorine pesticide residues and no study has evaluated PCB levels in milk samples from Brazil. Almeida and Barreto (1971) analyzed pasteurized milk from São Paulo, Brazil. They found higher levels for α -HCH (20 ng/g fat) and lindane (11 ng/ g fat). Costabeber et al. (2000) evaluated organochlorine pesticides in UHT milk from Santa Maria, Rio Grande do Sul State (Brazil). They found higher lindane levels (10 ng/g fat) and lower HCB levels (1 ng/g) than those of the present study. In the present study, in addition to α -HCH, lindane, and HCB, we also analyzed compounds that have not been previously evaluated in Brazilian milk (aldrin, pp'-DDE, op'-DDD, pp'-DDD, op'-DDT, and some PCB congeners). Despite the relatively small sample size for PCB assay (n = 4-12), results are important because this is the first paper describing background concentrations of PCBs in milk from Rio Grande do Sul, Brazil. Besides, the number of samples evaluated in the present study was higher than that of the only other paper that has evaluated PCB levels in a dairy product (butter) in Brazil (n = 4; Kalantzi et al., 2001). Considering that the economy of Rio Grande do Sul is based on agriculture and cattle raising for meat and milk production, surveys on the content of persistent organic pollutants in animal food products of this region are of great importance. Persistent

organic pollutants concentrate in dairy fats (Losada et al., 1996). Thus, their contents in dairy products reflect the regional environmental contamination and may be of great value for scientific and public health knowledge.

0.49

6.98

1.18

14.6

ADI^b (ng/kg)

NE NE 8000

100^c

NE

NE

20,000

Average contents of lindane, α-HCH and HCB found in the present study are similar to those found by Storelli, Storelli, and Marcotrigiano (2001) in cow milk from two agricultural areas of Apulia in Southern Italy (5.01, 1.28, and 6.49 ng/g fat, respectively). However, Frank, Braun, Sirons, Rasper, and Ward (1985) found lower HCB levels in raw milk samples from Canadá (0.67 ng/g fat) than those found in the present study. In Spain, Losada et al. (1996) found α -HCH at an average of 2.8 ng/g wet weight, lindane at 2.2 ng/g and aldrin at 3.7 ng/g wet weight. Although these results are not presented as ng/g fat, considering a milk fat content of around 3%, it is possible to conclude that these values are markedly higher than those found in the present study. $\sum DDT$ was observed at an average of 159 ng/g fat in Mexico, with pp'-DDT (87 ng/ g fat) as the major contributor (Waliszewski et al., 1997). Kannan, Tanabe, Ramesh, Subramanina, and Tatsukawa (1992) evaluated milk from India and found levels of \sum DDT, PCBs, and lindane (110, 49, and 160 ng/g fat, respectively) above those found in the present study, while the levels of HCB and aldrin (1.5 and 1.5 ng/g fat) were lower than those found in the present study. In Greece, Mallatou, Pappas, Kondyli, and Albanis (1997) found lindane and α -HCH at lower frequencies (13.1% and 5.3% of samples) than in the present study. The mean concentration of HCB (3.35 ng/g fat) found in Egyptian milk was similar to the levels found in this study, while α -HCH and lindane levels (7.42 and 9.60 ng/g fat) were higher and \sum DDT level (7.67 ng/g fat) was lower than those found in the present study (Aman & Bluthgen, 1997).

 Σ PCB found in the present study is similar to that previously reported in British milk for the sum of PCBs 28, 52, 153, 138, and 180 (4.61 ng/g fat; Sewart & Jones, 1996). However, PCB content found by Storelli et al. (2001) in Italian milk (50.6 ng/g fat) was markedly higher than that found in the present study for the \sum PCB. Aman and Bluthgen (1997) also found higher levels of PCB congener numbers 138, 28, and 52 (2.07, 5.37, and 10.9 ng/g fat, respectively), but lower levels of PCB 180 (3.16 ng/g fat) in milk from Egypt when compared to the present study. Data on PCB levels in milk from the United States in 1973–1974 revealed lower levels (mean concentration= 1.91 ng/g fat, range 0.32–4.99; WHO, 1993) than those of the present study. Similarly, European milk also had lower levels when compared to the present study: PCB levels in the range 0.09–0.14 ng/g fat in the Federal Republic of Germany (1982–1986), 0.034–0.144 ng/g in Switzerland (1987), 0.10–0.13 ng/g in Denmark (1981–1982), and 0.06– 0.33 ng/g in the Netherlands (1975–1977) (WHO, 1993).

The effect of heat treatment on organochlorine content of milk has previously been investigated. Some studies found no change in organochlorine content of milk due to heat treatment (Molochnikov, Mochalov, Davydova, & Serevrennikova, 1970; Van Renterghem, 1976), while others found degradation after milk pasteurization or sterilization (Abou Arab, 1999; Martinez, 1994). Accordingly, we found higher levels of op'-DDD and \sum DDT in raw milk than in pasteurized or UHT milk. However, our results are probably related to differences in environmental contamination among distinct regions of Rio Grande do Sul State, since samples were collected from different locations. This proposal is reinforced by the fact that we found higher levels of other organochlorine compounds (pp'-DDD, PCB 10, and \sum PCB) in UHT and/or pasteurized milk than in raw milk samples.

According to Kannan et al. (1992), the contributions of dairy products to the average dietary intake of α -HCH, DDT, aldrin + dieldrin, and PCB by Indians were 70%, 87%, 87%, and 31%, respectively. In this work, the dietary intake of aldrin + dieldrin exceeded the ADI recommended by FAO/WHO (WHO, 1988). Mallatou et al. (1997) determined the EDI of lindane from milk in Greece at 0.025 µg/ day and for α -HCH at 0.110 µg/day. The EDIs of lindane and α -HCH found by Mallatou et al. (1997) were similar to the EDIs found in the present study for child intake from milk.

Results of the present study indicated that few samples exceeded the maximum residue limits for the organochlorine compounds evaluated and that child dietary intake of organochlorine compounds through milk consumption corresponded to a small portion of the ADI established by FAO/WHO (WHO, 1988). Hence, there is no indication of important health risks associated with milk consumption in Southern Brazil.

Acknowledgements

This work was supported by FAPERGS and CNPq. I. Costabeber was the recipient of a Newly Doctor Fellowship (CNPq) and T. Emanuelli was the recipient of a CNPq Research Fellowship (proc.550691/02-2).

References

- Abou Arab, A. A. K. (1999). Effects of processing and storage of dairy products on lindane residues and metabolites. *Food Chemistry*, 64, 467–473.
- Almeida, M. E., & Barreto, H. H. C. (1971). Resíduos de pesticidas clorados em leite consumido em São Paulo. *Revista do Instituto Adolfo Lutz*, 31, 13–20.
- Aman, I. M., & Bluthgen, A. (1997). Occurrence of residues of organochlorine pesticides and polychlorinated biphenyls in milk and dairy products from Egypt. *Milchwissenschaft-Milk Science International*, 52, 394–399.
- Angulo, R., Costabeber, I., Gallego, M. C., Serrano, S., & Jodral, M. (1996). Cleanup destillation: critical points in the organochlorine residue analysis (p. 59). ST European Pesticide Residue Workshop. Alkmaar, Netherlands.
- Angulo, R., Martinez, P., & Jodral, M. L. (1999). PCB congeners transferred by human milk, with an estimate of their daily intake. *Food* and Chemical Toxicology, 37, 11081–11088.
- Bester, K., De Vols, P., Le Guern, L., Harbeck, S., Hendrickx, F., Kramer, G. N., et al. (2001). Preparation and certification of a reference material on PCBs in pig fat and its application in quality control in monitoring laboratories during de belgian "PCB-crisis". *Chemosphere*, 44, 529–537.
- Borga, K., Gabrielsen, G. W., & Skaare, J. U. (2001). Biomagnification of organochlorines along a Barents Sea food chain. *Environmental Pollution*, 113, 187–198.
- Brasil. 1999. Ministério da Agricultura Pecuária e Abastecimento. Instrução normativa número 42 de 20/12/1999.
- Costabeber, I., Trindade, R., & Fries, L. M. (2000). Residuos de DDE, HCB, heptaclor epóxido y lindano en leche UHT comercializada en Santa María, RS. *ILE – Industrias Lacteas Españolas*, 259, 42–47.
- Falandysz, J., Wyrzykowska, B., Warzocha, J., Barska, I., Garbacik-Wesolowska, A., & Szefer, P. (2004). Organochlorine pesticides and PCBs in perch Perca fluviatilis from the Odra/Oder river estuary, Baltic sea. *Food Chemistry*, 87, 17–23.
- FAO, 1993. Status of Codex Maximum Residues Limits for pesticides in food and animal feed. Codex Committee Alimentarius on Pesticide Residues, 25th Session, Havana, Cuba, April 19–26, Codex Alimentarius Commission, World Health Organizations, Geneva, Switzerland. Evaluation of certain food additives and contaminants. 41st Report of the Joint FAO/WHO Experts Committee of Food Additives.
- Fox, G. A., Kennedy, S. W., Norstrom, R. J., & Wigfield, D. C. (1988). Porphyria in herring gulls: a biochemical response to chemical contamination of Great Lakes food chains. *Environmental Toxicology* and Chemistry, 7, 831–839.
- Frank, R., Braun, H. E., Sirons, G. H., Rasper, J., & Ward, G. G. (1985). Organochlorine and organophosphorus insecticides and industrial pollutants in the milk supplies of Ontario – 1983. *Journal of Food Protection, 48*, 499–504.
- Heck, M. C., Rossato, S., Santos, J. S., Bogusz Júnior, S., Costabeber, I., & Emanuelli, T. (2002). Fatores que influenciam o consumo de leite por crianças da 1^a série do ensino fundamental do município de Santa Maria (RS). Nutrire Journal of the Brazilian Society of Food Nutrition, 24, 21–32.
- Huisman, M., Koopman-Esseboom, V., Fidler, M., Hadders-Algra, C., Van Der Paauw, L., Tunistra, L., et al. (1995). Perinatal exposure to polychlorinated biphenyls and dioxins and its effect on neonatal neurological development. *Early Human Development*, 41, 111–127.
- Johansen, P., Muir, D., Asmund, G., & Riget, F. (2004). Human exposure to contaminants in the traditional Greenland diet. *Science of the Total Environment*, 331, 189–206.
- Kalantzi, O. I., Alcock, R. E., Johnston, P. A., Santillo, D., Stringer, R. L., Thomas, G. O., et al. (2001). The global distribution of PCBs and

organochlorine pesticides in butter. *Environmental Science and Technology*, 35, 1013–1018.

- Kannan, K., Tanabe, S., Ramesh, A., Subramanina, A., & Tatsukawa, R. (1992). Persistent organochlorine residues in foodstuffs from India and their implications on human dietary exposure. *Journal of Agricultural* and Food Chemistry, 40, 518–524.
- Losada, A., Fernández, N., Diez, M. J., Terán, M. T., García, J. J., & Sierra, M. (1996). Organochlorine pesticide residues in bovine milk from León (Spain). *The Science of the Total Environment*, 181, 133–135.
- Mallatou, H., Pappas, C. P., Kondyli, E., & Albanis, T. A. (1997). Pesticide residues in milk and cheeses from Greece. *The Science of Total Environment*, 196, 111–117.
- Martinez, M.P. (1994). Niveles de pesticidas organoclorados y bifenilos policiorados en leches naturales y pasteurizadas. Estudio experimental del efecto de la temperatura sobre estos compuestos. [Thesis]. Facultad de Veterinaria, Universidad de Córdoba (Spain) (p. 485) Available from: Central Library of Universidad de Córdoba.
- Martinez, M. P., Angulo, R., Pozo, R., & Jodral, M. (1997). Organochlorine pesticides in pasteurized milk and associated health risks. *Food and Chemical Toxicology*, 35, 621–624.
- Molochnikov, V. V., Mochalov, V. I., Davydova, I. R., & Serevrennikova, V. A. (1970). Excretion of chloro-organic pesticides with milk (review of the literature). *Veterinariia*, 1, 29–32.
- Patandin, S., Lanting, C., Mulder, P., Boersma, E., Sauer, P., & Weisglas-Kuperus, N. (1999). Effects of environmental exposure to polychlorinated biphenyls and dioxins on cognitive abilities in Dutch children at 42 months of age. *Journal of Pediatrics*, 134, 229–232.
- Ross, G. (2004). The public health implications of polychlorinated biphenyls (PCBs) in the environment. *Ecotoxicology and Environmental Safety*, 59, 275–291.
- Safe, S. (1990). Polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and related compounds: environmental and mechanistic considerations which support the development of toxic equivalency factors (TEFs). *Critical Reviews in Toxicology*, 51, 51–88.

- Sandmeyer, U. (1992). Determinación rápida de pesticidas clorados en leche, mediante cromatografía de exclusión molecular. *Revista Española de Lechería*, 3, 56–58.
- Schecter, A., Cramer, P., Boggess, K., Stanley, J., & Olson, J. R. (1997). Levels of dioxins, dibenzofurans, PCB and DDE congeners in pooled food samples collected in 1995 at supermarkets across the United States. *Chemosphere*, 34, 1437–1447.
- Sewart, A., & Jones, K. C. (1996). A survey of PCB congeners U.K. cows milk. *Chemosphere*, 32, 2481–2492.
- Stewart, P. W., Reihman, J., Lonky, E. I., Darvill, T. J., & Pagano, J. (2003). Cognitive development in preschool chidren prenatally exposed to PCBs and MeHg. *Neurotoxicology and Teratology*, 25, 11–22.
- Storelli, M. M., Storelli, A., & Marcotrigiano, G. O. (2001). Polychlorinated biphenyls, hexachlorobenzene and organochlorine pesticide residues in milk from Apulia. *Italian Journal of Food Science*, 13, 113–117.
- Van Renterghem, R. (1976). Linfluence des procedes des technologiques de preparation du latí de conssomation sur la teneur en pesticides organochlorés. Le Lait, 56, 537–545.
- Vreugdenhil, H. J. I., Slijper, F. M. E., Mulder, P. G. H., & Weisglas-Kuperus, N. (2002). Effects of perinatal exposure to PCBs and dioxins on play behavior in Dutch children at school age. *Environmental Health Perspective*, 110, A593–A598.
- Waliszewski, S. M., Pardío, V. T., Waliszewski, K. N., Chantiri, J. N., Aguirre, A. A., Infanzón, R. M., et al. (1997). Organochlorine pesticide residues in cow's milk and butter in Mexico. *The Science of the Total Environment*, 208, 127–132.
- Walkowiak, J., Weiner, A. A., Fastabend, A., Heinzow, B., Kramer, U., Schmidt, E., et al. (2001). Environmental exposure to polychlorinated biphenyls and quality of the home environment: effects on psychodevelopment in early childhood. *The Lancet*, 358, 1602–1607.
- WHO (1988). Assessment of health risks in infants associated with exposure to PCBs, PCDDs and PCDFs in breast milk. Environmental Health Series. N. 29. Geneva: Wiley.
- WHO (1993). Polychlorinated byphenyls and terphenyls. Environmental Health Criteria N. 140. Geneva: World Health Organization.