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Estimated daily intake of organochlorine pesticides from dairy products in Brazil

Joice Sifuentes Dos Santos [a, b], Thiago Guilherme Schwanz [c], Andreia Niederauer Coelho [c], Marla Cristina Heck-Marques [c], Marisa Marroni Mexia [a], Tatiana Emanuelli [d], Ijoni Costabeber [e, *]

[a] Master Science Program on Milk Science and Technology, University North of Paraná, Londrina, PR CEP 86041-140, Brazil
[b] Master Science Program on Health and Production of Ruminants, University North of Paraná, Londrina, PR CEP 86041-140, Brazil
[c] Graduate Course in Food Science and Technology, Center of Rural 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
[e] Department of Morphology, Center of Health Sciences, Federal University of Santa Maria, Camobi, Santa Maria, RS CEP 97105-900, Brazil

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Chemical compounds studied in this article:
HCB (PubChem CID 8370)
α-HCH (PubChem CID 727*)
Lindane (PubChem CID 727*)
Aldrin (PubChem CID 12310947)
p,p′-DDE (PubChem CID 3035)
o,p′-DDD (PubChem CID 4211)
p,p′-DDD (PubChem CID 6294)
o,p′-DDT (PubChem CID 13089)
*α-HCH and lindane (γ-HCH) are isomers, but considered as synonyms in PubChem list.

ABSTRACT

The estimated daily intake (EDI) of organochlorine (OC) pesticides (HCB, α-HCH, lindane, aldrin, p,p′-DDE, p,p′-DDD, and o,p′-DDT) through consumption of dairy products from Rio Grande do Sul State (Brazil) was investigated. Fluid milk and cheese had similar ΣOC levels (26.04 and 26.14 ng g^{-1} fat, respectively), whereas milk powder had lower levels (2.23 ng g^{-1} fat). OC levels in UHT milk exhibited a declining trend over time (ΣOC = 27.70 ng g^{-1} fat in 2000 vs. 1.50 ng g^{-1} fat in 2009/2010). The EDI of OC pesticides was remarkably higher for children (8.266 ng kg^{-1} day^{-1}) than for adolescents, adults, and the elderly (ranging from 0.393 ng kg^{-1} day^{-1} to 0.614 ng kg^{-1} day^{-1}). The average EDIs for OC pesticides were below the acceptable daily intakes (ADI), with the exception of aldrin, which greatly exceeded the ADI for children. In addition, some samples (8.8%) exceeded the maximum residue limit for the compounds evaluated.

1. Introduction

Organochlorine (OC) pesticides were introduced in the 1940s and widely used in agriculture and pest control until government restrictions or bans on their use were introduced in the 1970s and 1980s. Due to their chemical stability, however, they persist in the environment.

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

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OC compounds are lipophilic and poorly metabolised. Hence, environmental exposure of living organisms to these compounds results in their accumulation and persistence in fat tissues. Foods, particularly animal-based foods, are the most important source of human exposure for many persistent organic compounds (Alcock, Sweetman, Juan, & Jones, 2000), including OCs.

Milk and dairy products play a central role in human nutrition, especially for vulnerable groups, such as infants, school-age children and the elderly. Bovine milk may contain high levels of pesticide residues as a result of their concentration in the tissues following exposure during cattle dipping or through the consumption of contaminated feedstuffs or water (Kampire, Kiremire, Nyanzi, & Kishimba, 2011). Thus, milk is one of the most important foodstuffs where OCs are continuously monitored (Storelli, Storelli, & Marcotrigiano, 2001).

Among OC pesticides, dichlorodiphenyltrichloroethane (DDT) is the most studied. Commercial DDT is a mixture of several closely related compounds. Among DDT isomers, the major component is the p,p′ isomer (77%), but the o,p′ isomer is also present at significant amounts (15%). Dichlorodiphenylethane (DDE) and dichlorodiphenyldichloroethane (DDD) are the major metabolites and breakdown products of DDT in the environment. The term "total DDT" refers to the sum of all DDT-related compounds (p,p′-DDT, o,p′-DDT, DDE, and DDD). The degradation of DDT involves HCl elimination to produce DDE and/or reductive dechlorination to produce DDD (WHO, 1979). Despite its carcinogenic potential, DDT is still allowed for indoor application to control vector-borne diseases, such as malaria (WHO, 2007) and leishmaniasis in endemic regions in the Amazon (Azeredo et al., 2008). In the United States, DDT is still registered for emergency health purposes to control mosquitoes that carry malaria and yellow fever (Fisher, Walker, & Powell, 2003).

The toxicity of OCs, as well as their ubiquity, persistence and tendency to accumulate in body tissues indicate a risk for human health due to low but chronic exposure. Epidemiological studies reviewed by Toft, Hagmar, Giwercman, and Bonde (2004) suggest reproductive abnormalities in human populations exposed to high concentrations of DDE, including reduced semen quality and testicular cancer in males, menstrual cycle abnormalities and spontaneous abortions in females, prolonged waiting time to pregnancy, reduced birth weight of offspring, skewed sex ratio, and altered age of sexual development. The International Agency for Research on Cancer (IARC) classified the compounds DDT, HCB and HCH as possibly carcinogenic to humans (group 2B) (IARC, 2006), whereas aldrin is not classifiable as to its carcinogenicity to humans (group 3).

Dietary exposure to a given chemical is estimated by multiplying its level in the food by the amount of food consumed per kg of body weight (IPCS, 2009). In Brazil, few studies have investigated the dietary intake of OC compounds (Heck, Santos, Bogusz Junior, Costabeber, & Emanuelli, 2007; Mello, 1999). The aim of the present work was to estimate the dietary intake of OCs that results from the consumption of milk and dairy products, comparing novel data on fluid milk and milk powder contamination with previously published data on the contamination of milk (Heck et al., 2007) and cheese (Santos, Xavier, Ries, Costabeber, & Emanuelli, 2006) collected from the same region.

2. Material and methods

2.1. Sampling

A total of 113 samples were used: 56 samples were comprised of fluid milk (pasteurised, UHT and raw milk), 39 of milk powder and 18 of cheese of different brands. The samples were collected at random from ordinary commercial establishments in Santa Maria, Brazil between 2000 and 2010. Fluid milk samples were collected in 2000 (41 samples, Heck et al., 2007) and 2009/2010 (15 samples, unpublished data), cheese samples in 2004 (Santos et al., 2006), and milk powder samples in 2008/2009 (39 samples, unpublished data). All products were produced in the Rio Grande do Sul State, Southern Brazil. The samples were kept at −20 °C prior to the analysis.

2.2. Materials

All glassware used in the study was previously washed with distilled water, following the method of Angulo, Costabeber, Gallego, Serrano, and Jodral (1996), rinsed three times 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 (Paris, KI USA). Florisil was previously activated at 150 °C for 12 h and deactivated by adding 2% Milli-Q water before use. Standards of hexachlorobenzene (HCB), α-hexachlorocyclohexane (α-HCH), γ-hexachlorocyclohexane (lindane), 1,2,3,4,10,10′-hexachloro−1,4,4′,5,8,8′-hexahydro−exo-1,4-endo-5,8-dimethano−naphthalene (aldrin), 1,1-dichloro-2,2-bis(*p*-chlorophenyl) ethylene (p,p′-DDE), 1,1-dichloro-2-(*o*-chlorophenyl)−2-(*p*-chlorophenyl)ethane (o,p′-DDD), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (p,p′-DDD), and 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl)-ethane (o,p′-DDT) were obtained from Ultra Scientific (North Kingstown, RI, USA). All other reagents used were of analytical reagent grade.

2.3. Analysis of organochlorine pesticides

The extraction and clean-up of milk samples followed the method described by Heck et al. (2007), whereas that of cheese samples was conducted according to Santos et al. (2006). For milk powder, 55 g of sample was dissolved in 110 mL of distilled water, homogenised, and centrifuged for 30 min at 4 °C and 17,300 × *g*. Then, the milk fat was removed and mixed with 30 g of anhydrous sodium sulphate and 80 mL of petroleum ether. The liquid was filtered through anhydrous sodium sulphate and evaporated under a vacuum. The purified fat residue was transferred to a glass vial and kept at −20 °C until purification of the compounds.

OCs were purified using the method described by Martinez, Angulo, Pozo, and Jodral (1997), using florisil as the stationary phase component and n-hexane as the mobile phase. Separation and quantification was achieved by gas chromatography with an Agilent 6890A model gas chromatograph equipped with a ^{63}Ni micro-electron 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 operating conditions were as follows: the injector was set at 250 °C, the detector was set at 350 °C, the oven temperature was held at 110 °C for 5 min, then increased to 280 °C at 14 °C min^{-1} and held for 2 min. The carrier gas was nitrogen at a column flow rate of 1.6 mL min^{-1}. All samples were analysed in duplicate. A mixture of OCs was used for calibration and recovery evaluation.

The mean recoveries ranged from 72.0 to 120.6%, and the coefficient of variation was below 10%, indicating an excellent repeatability for the method.

The limits of detection (LOD) and of quantification (LOQ) were evaluated using the average blank values method. The LOD and LOQ of HCB, α-HCH, lindane, aldrin, p,p′-DDE, o,p′-DDD, p,p′-DDD, and o,p′-DDT were 0.2 and 0.6; 0.1 and 0.4; 0.1 and 0.3; 0.06 and 0.2; 0.4