



Polychlorobiphenyls and organochlorine pesticides in conventional and organic brands of milk: Occurrence and dietary intake in the population of the Canary Islands (Spain)

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ABSTRACT

The population of the Spanish archipelago of the Canary Islands has been studied in depth regarding its levels of contamination by organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs). Foodstuffs of animal origin, such as milk, are prominent contributors to the body burden of these contaminants. As this population presents one of the highest milk-intake in Spain and Europe, we evaluated the level of OCs and PCBs in 26 commercially available brands of milk (16 conventional and 10 organic brands) present in the market of these Islands, in order to estimate the relevance of milk as a source of these chemicals for the Canary population. Our findings showed that hexachlorobenzene, trans-chlordane, and PCB153 were present in almost all the samples with independence of the type of milk. For both types of milks, the concentration of OCs was very low, showing organic milks lower levels than conventional ones. As a consequence, the estimated daily intake for OCs was lower than the tolerable daily intake (TDI) established by International Agencies. The levels of PCBs in milk were also found to be very low, but, in this case, the situation was the opposite: there were higher levels of PCBs in organic than in conventional brands of milk. Unexpectedly, levels of dioxin-like PCBs (DL-PCBs) reached values higher than 25 pg WHO-TEQ g⁻¹ fat in percentile 75 for both types of milk indicating the existence of a number of brands of milk highly contaminated by these toxicants. Consequently, the population who consume the most contaminated milk brands could have estimated daily intakes well above the recommended TDI (2 pg WHO-TEQ kg⁻¹ b.w. d⁻¹) established by European Union Authorities. These results are of concern if we consider the well known adverse health effects exerted by dioxin-like compounds.

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1. Introduction

Organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) are a class of persistent chlorinated compounds to which humans are most often non-intentionally exposed. Many sources of these man-made toxicants have been identified and eliminated in last decades; however, their occurrence in our environment is still of major concern. More than 95% of human intake appears to be via the consumption of food (Focant et al., 2003; Darnerud et al., 2006). Due to the high lipophilic nature of these chemicals,

they enter human body along with the food fat. Foodstuffs of animal origin are prominent contributors of the OCs and PCBs intake (Fries, 1995; Focant et al., 2002). In this sense, milk and dairy products account around a 30% of the total dietary intake of these chlorinated contaminants in Western populations (Focant et al., 2002; Bordajandi et al., 2004).

Similarly to other foodstuffs, a maximum residue limit (MRL) for these chemicals has been attributed to milk and dairy products. In addition, a tolerable daily intake (TDI) has been established by International Agencies for OCs and PCBs. Despite these regulations, data regarding both, OCs and PCBs (mainly dioxin-like PCBs, DL-PCBs) are required to estimate human exposure to these contaminants. This issue is especially relevant since toxic equivalent factors (TEFs) have been assigned to a number of DL-PCBs (Van den Berg et al., 2006). Thus, by using TEFs we can estimate human exposure in terms of toxic equivalence to dioxins (TEQs).

Our group has previously evaluated the level of chemical contamination by OCs and PCBs showed by the population of the

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Canary Islands (Spain). Despite the fact that most OCs pesticides were banned in Spain in the late 1970s, and PCBs in the late 1980s, our results showed that people living in the Canary Islands in the late 1990s presented a characteristic pattern of chemical contamination as compared with other Western populations. Thus, while they showed a high degree of contamination by OCs, their levels of contamination by PCBs were very low (Zumbado et al., 2005; Luzardo et al., 2006; Henríquez-Hernández et al., 2011). In fact, such results seemed to indicate the existence of a chronic exposure to OCs that persisted in the late 1990s (Zumbado et al., 2005; Luzardo et al., 2006) and even in the first decade of the current century (Luzardo et al., 2009) indicating the existence of active environmental sources of OCs, while, on the contrary, the exposure to PCBs seemed to be low and depending mainly from dietary sources (Henríquez-Hernández et al., 2011).

As cited previously, milk and dairy products could be an important route of exposure to OCs and PCBs in Europe (Focant et al., 2002; Marin et al., 2011). In this sense, it should be highlighted that the population of the Canary Islands shows the highest intake of milk and dairy products among European and Spanish regions (Serra-Majem et al., 2000a,b). Thus, the daily consumption of milk and dairy products have been estimated in 301 and 90 grams (g) per day respectively in the Canary Islands, compared with the 294 and 56 g d⁻¹ reported in the Basque Country or the 286 and 74 g d⁻¹ reported in Madrid (Serra-Majem, 1999). Furthermore, according to data published by the European Food Safety Authority (EFSA), the mean consumption of milk and dairy products in the European population (257 g d⁻¹) is much lower than in the Canarian population (391 g d⁻¹) (Serra-Majem, 1999).

The present study reports the results obtained from an independent survey of the most of the commercially available brands of milk (16 conventional and 10 organic brands of milk) available in the market of these islands for the occurrence of OCs and PCBs in order to evaluate the potential differences in levels of contamination among organic and non-organic milks and to estimate the milk-related dietary exposure to these chemicals suffered by the people living in this Archipelago.

2. Materials and methods

2.1. Study area

The Canary Islands are located in the Atlantic Ocean, about 100 km away from the nearest point of the North African coast (southwest of Morocco). Geographically, the Islands are part of the African continent; however, from a historical, economic, political and socio-cultural point of view, the Canaries are completely European. Due to its geographical, economic and cultural circumstances, in the Canary Islands, there is a high rate of imports of animal- and vegetable-origin foods from the Spanish mainland and from other countries, mainly from the European Union (EU), but also from Asian or South American countries (where a number of OCs are still in use).

2.2. Sampling

For this study, 16 commercial brands of conventional full-fat milk and 10 brands of organic full-fat milk were randomly collected from high-delivery-rate supermarkets of the Canary Islands. The milk samples were collected between November 2007 and April 2008. Each of the 26 selected brands was sampled monthly during this period of time (six samples for each brand) to obtain a representative estimation for each one and to evaluate potential fluctuations among different batches. The packaging material was Tetra-Brick® in all cases. Tetra-Bricks were gently shaken before

an aliquot of 80–100 mL was taken. The aliquots were then frozen at –20 °C until extraction and analyses procedures. Lipid content values given by the producer (around 3.5% fat) were used to obtain the final lipid-corrected values. Some classical liquid–liquid extractions of fat were performed on randomly selected milks to ensure that producer's lipid content values were accurate. A total of 156 samples were collected and stored at –20 °C until analysis. Samples were analyzed individually and then the results grouped to evaluate average levels and ranges. All collection and handling equipments in contact with milk samples were tested for possible OCs and PCBs contamination. No contaminating materials were identified.

2.3. Analytical procedure

The aliquots of whole fat milk were subjected to solid-phase extraction (SPE), gel permeation chromatography (GPC) cleanup, silica-gel SPE cleanup and analyzed by gas chromatography/mass spectrometry (GC/MS), using appropriate internal standards. The analytes included in this study were the diphenyl-aliphatic pesticides and metabolites (methoxychlor, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, and *o,p'*-DDD); the persistent and bioaccumulative contaminant hexachlorobenzene (HCB); the four isomers of hexachlorocyclohexane (α -, β -, γ -(commonly known as lindane), and δ -HCH); the cyclodienes dieldrin, aldrin, endrin, heptachlor (and *cis*- and *trans*-epoxides) and chlordane (*cis*- and *trans*-isomers); and endosulfan (α - and β -isomers); we also included the measurement of 19 congeners of PCBs (IUPAC congeners #28, 52, 77, 81, 101, 105, 114, 118, 123, 126, 138, 153, 156, 157, 167, 169, 170, 180 and 189). The standard analytes under study were purchased from Dr. Ehrenstorfer (Riedel-de Haën, Sigma-Aldrich Laborchemikalien GmbH, Germany).

The stored milk (–20 °C) was brought to room temperature and homogenized by vortexing vigorously for 5 min prior to aliquoting. 10 μ L of the internal working standard solution (500 ng mL⁻¹ each compound in acetone) was added to 2 mL of the milk sample. Column extraction of OCs was performed following a modification of the method suggested by Dmitrovic and Chan (2002). Briefly, the aliquot of 2 mL of milk was mixed with 2 mL of glacial acetic acid and 2 mL of methanol and vortexed. The mixture was then sonicated for 45 min and applied at 1 mL min⁻¹ flow rate to a Chromabond C18ec cartridge (3 mL/200 mg, Macherey Nagel, Germany) previously pre-washed with hexane and conditioned with 5 mL each of methanol and de-ionized water by using a RapidTrace SPE Workstation (Caliper Life Sciences, MA, USA). To elute the OCs, 6 mL of hexane were applied at a flow rate of 0.5 mL min⁻¹. The hexane fraction was evaporated to dryness using a RapidVap® N2/48 (Labconco, MIS, USA). The residue was weighed to determine the lipid percent (LeDoux, 2011).

In order to achieve the maximum sensitivity in our analysis, two sequential cleanup steps were performed following a modification of the procedure suggested by Griffith and Craun (1974). Briefly, the lipid was dissolved in 2 mL of dichloromethane (DCM), and divided in two 1 mL-aliquots that were then individually purified using GPC with a 100% Fluorinated Divinylbenzene GPC column (50 cm $\times$ 10 mm i.d. EPA 3640a Pesticide Cleanup GPC Jordi column, Sorbtech Technologies, Atlanta, USA), with DCM as the eluting solvent at a flow rate of 1.6 mL min⁻¹. This GPC system was operated using an automated apparatus (GPC-CL1, Cromlab S.L., Barcelona, Spain). The first 22-mL fraction of the elution, containing the lipids, was discharged. The next 14 mL, containing the organohalogenated contaminants, were collected. The two pesticide-containing fractions per sample were combined and evaporated to near dryness leaving a small amount of an oily residue. This residue was dissolved in 1 mL DCM and subjected to new GPC purification, thereby obtaining a new 14-mL

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